Designation: D 6246 – 01

Standard Practice for Evaluating the Performance of Diffusive Samplers[1]

This standard is issued under the fixed designation D 6246; 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 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. Futhermore, 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. Futhermore, 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 Atmospheres[3]

D 4597 Practice for Sampling Workplace Atmospheres to Collect Organic Gases or Vapor with Activated Charcoal Diffusive Samplers[3]

D 4598 Practice for Sampling Workplace Atmospheres to Collect Gases or Vapor with Liquid Sorbent Diffusional Samplers[4]

D 4599 Practice for Measuring the Concentration of Toxic Gases or Vapors Using Length-of-Stain Dosimeters[3]

2.2 *International Standards:*

CEN EN 838 European Standard, Workplace atmospheres - Diffusive samplers for the determination of gases or vapours - Requirements and test methods[5]

MDHS 27 Protocol for assessing the performance of a diffusive sampler, Health and Safety Laboratory, United Kingdom[6]

MDHS 80 Volatile organic compounds in air, Health and Safety Laboratory, United Kingdom[6]

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

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

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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.

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 imprecision *RSD* simply by:

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

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)
$\hat{RSD}_{\mathrm{s}}$ = 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
$t_{0.95}(\upsilon)$ = value which, at probability 95 %, exceeds random variables distributed according to the studentized t-distribution with υ 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
υ = degrees of freedom in determining RSD_{s}
υ_{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:

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

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

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 at 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 5×3 = 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 $\Delta_t(>0)$ represent one-half the bias between estimates from a 0.5-h pulse at the end versus the beginning of the sampling period, relative to the mean of the estimates. Assume, conservatively (see, for example, (**6**)), that the bias in the estimates of 0.5-h pulse occurring at random within (for example, an 8–h sampling period ranges uniformly between $-\Delta_t$ and $+\Delta_t$. Then the variance RSD_t^2 associated with sampling a 0.5–h pulse at random within the sampling period is as follows:

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

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:

$$\Delta\mu_{95\,\%} = \Delta c - s \times t_{0.95}(\upsilon)/Sqrt[n] \qquad (4)$$

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

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

$$(s/c)\times t_{0.95}(\upsilon)/Sqrt[n] = 3.3\,\%. \qquad (5)$$

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.

4.5.2 In the case of thermal desorption, the efficiency must be > 95 %. (MDHS 80)

4.6 *Atmospheric Pressure*:

4.6.1 Most diffusive sampler manufacturers provide a formula for correcting for the difference between atmospheric pressure at points of sampler application and calibration. Unlike the case with temperature, where sorbent properties may be temperature-dependent, the formula is simple. For diffusion through air, the sampling rate is inversely proportional to the pressure, whereas if the sampling rate is determined by a semi-permeable membrane rather than air, the rate is independent of pressure. The difference is because of the differing expansion coefficients of the media comprised of the scattering molecules.

4.6.2 If the correction formula for a given sampler type is suspected of error, then a simple experiment using eight samplers at a pressure shifted from the experiments of (4.1) will determine the effect. The result will be reported (11.9) as the correctable bias which would be expected under a 15 % shift in the atmospheric pressure.

4.7 *Wind Direction*:

4.7.1 For use in personal sampling, the wind direction is expected to generally have an insignificant effect on concentration estimates, since the air flow near the body will be usually across the face of the sampler. However, as a precaution, for each sampler type a single set of experiments is recommended comparing estimates with wind parallel versus into the sampler face (using, for example, eight samplers for each direction). Concentration estimates should agree within 15 %. Because the effect is sampler specific, the wind velocity tests need only be performed once for each sampler type.

5. Significance and Use

5.1 Gas or vapor sampling is often accomplished by actively pumping air through a collection medium such as activated charcoal. Problems associated with a pump–inconvenience, inaccuracy, and expense–are inextricable from this type of sampling. The alternative covered by this practice is to use diffusion for moving the compound of interest onto the collection medium. This approach to sampling is attractive because of the convenience of use and low total monitoring cost.

5.2 However, previous studies have found significant problems with the accuracy of some samplers. Therefore, although diffusive samplers may provide a plethora of data, inaccuracies and misuse of diffusive samplers may yet affect research studies. Furthermore, worker protections may be based on faulty assumptions. The aim of this practice is to counter the uncertainties in diffusive sampling through achieving a broadly accepted set of performance tests and acceptance criteria for proving the efficacy of any given diffusive sampler intended for use.

6. Apparatus

6.1 *Exposure Chamber Specifications*:

6.1.1 *Chamber Capacity*—The chamber must be capable of exposing 25 samplers at a time with less than 5 % depletion of test analyte by the samplers at the lowest air flow.

6.1.2 *Exposure Time*—The chamber must be capable of maintaining conditions for up to 12 h.

6.1.3 *Analyte Generation*—Equipment must be provided for the measured delivery of gases, or the vaporization and measured dilution in a mixing chamber of controlled amounts of mixtures of test analytes, liquid over normal room temperature ranges.

6.1.4 *Reference Concentration Measurement*—Provision must be made for monitoring of the analyte concentration from at least five locations within the chamber.

6.1.5 *Construction Materials*—The chamber interior and all parts exposed to the test analytes must be corrosion-resistant and fireproof. Polypropylene is a likely candidate for this purpose.

6.1.6 *Size*—The chamber must be containable within a walk-in hood of dimensions–2 × 2 × 3m.

6.1.7 *Monitoring Equipment to be Included with the Chamber*—Monitors for measuring the environmental conditions listed in 6.2 must be included with the chamber.

6.2 *Controlled Environmental Conditions*:

6.2.1 *Air Flow*—Air flows equal to 0.05 and 0.5 m/s must be attainable as face velocities across and normal to the sampler face as representative of the local conditions when the sampler is used as a personal sampler.

6.2.2 *Dynamic Concentration Shift*—It must be possible to reduce the test concentration to < 5 % of the starting concentration at any sampler exposure position (that is, controlling dead air) within 1 min.

6.2.3 *Humidity Variation*—Relative humidity equal to 25 ± 5 %, 50 ± 5 %, and 80 ± 5 % must be attainable at 20°C.

6.2.4 *Temperature*—Temperatures equal to 10 ± 3°C, 20 ± 3°C, and 30 ± 3°C must be attainable and maintainable. If the chamber is manufactured of stainless steel, then insulation of the chamber or conditioning of the air entering the walk-in hood may be necessary.

6.2.5 *Pressure*—Atmospheric pressure in the chamber must be constant to 1 % within any run and must be settable within a range of 95 % and 105 % of ambient atmospheric pressure.

6.3 *Inter-run Variability*—The chamber must be characterized as to inter-run variability RSD_{run} through one of several possible experimental designs. One possibility is through analysis of variance of data from 16 runs with four samplers each at fixed environmental conditions in the chamber. Experiment on a similar chamber (**12**) indicated that $RSD_{run} < 3\ \%$ is attainable.

NOTE 3—The exposure chamber's specifications listed in 6.1 and 6.2 are sufficient for evaluating sampler performance in this practice, but do not exclude other chamber types which may also suffice.

7. Reagents and Materials

7.1 A wide variety of (analytical grade) reagents are candidates for testing the various types of diffusive samplers.

7.2 Sample desorption (analytical grade) reagents may also be required.

7.3 Alternatively, thermal desorption, if used for sample extraction, would obviate the necessity of desorption reagents.

8. Procedure

8.1 At the initial characterization of a sampler type, conduct the wind velocity experiments (eight samplers (plus necessary blanks)) for determining the effect of wind speed, *v*, parallel to the sampler face and also wind perpendicular to the face (4.1, 4.7).

8.2 Verify pressure correction (4.6) as necessary.

8.3 Following initial characterization, select (for each analyte to be tested) 28 samplers for testing.

8.4 Through four runs with four samplers each, complete the experiments (4.1 and Appendix X1 (which also includes the wind speed, *v*, effect)).

8.5 Eight samplers shall be simultaneously exposed for one-half hour at 80 % (or greater) relative humidity prior to or during the exposure. Four of the samplers shall be analyzed immediately and four held in a non-stagnant sampling environment at zero analyte concentration for the remainder (for example, 7.5 h) of the recommended sampling period prior to analysis. The average analyte mass found for samplers analyzed immediately shall be compared to the average quantity found from samplers held at zero concentration. The magnitude of any decrease (% loss relative to the mean mass) shall be taken as twice the bias (that is, $2 \times \Delta_t$) due to reverse diffusion as described in 4.2. Note that the concentration of the pulse can be elevated above that of 8.4 if necessary for quantification, as long as the time-weighted average over sampling periods of intended use is not exceeded.

8.6 Using eight samplers, confirm the manufacturer's claimed limits on the sampler capacity (4.3) in the presence of manufacturer-stated interfering compounds (including water vapor).

8.7 Measure (**12**) desorption efficiency.

8.8 Storage stability may be measured as in (**3,12**) or EN 838.

8.9 Shelf-lifetime may be measured as in (**3**) or EN 838.

9. Sampler Performance Classification

9.1 Data from the experiments described above allow a simple classification of candidate diffusive samplers. Aside from evidence that the manufacturer's stated sampler capacity (4.3, 8.6) and wind direction effects (4.7, 8.1) are not excessive, samplers are to be characterized by their overall accuracy in view of environmental variability.

9.2 For evaluating the accuracy function, *A* (Eq 1), the estimated total imprecision, $\hat{RSD}$, is given by propagation of errors in terms of its independent components as follows:

$$RSD^2 = RSD_t^2 + RSD_s^2 + \alpha_T^2 RSD_T^2 + \alpha_h^2 RSD_h^2 + \alpha_V^2 RSD_V^2 + \alpha_c^2 RSD_c^2 \tag{6}$$

where RSD_T, RSD_h, RSD_V, and RSD_c represent the relative (inter-day) standard deviations of the temperature, humidity, wind speed, and concentration expected in the workplace, and the sampler parameters $\{\alpha\}$ are described in (4.1.2).

9.3 In order to assess the accuracy of a diffusive sampler as applied in a specific workplace, these environmental variabilities would require characterization. However, sampler classification is obtained here by adopting nominal values for these four quantities. Namely, the following values are adopted:

$$\begin{aligned}\sigma_T &= 5°C \text{ about } T_0 = 25°C \\ \sigma_h &= 5 \text{ mm Hg about } h_0 = 10 \text{ mm Hg} \\ \sigma_v &= 0.25 \text{ m/s about } v_0 = 0.5 \text{ m/s} \\ RSD_c &= 30\ \%\end{aligned} \tag{7}$$

For example, $\sigma_T = 5°C$ corresponds to sampler use (95 % of the time) between 15 and 35°C. Similarly, $\sigma_v = 0.25$ m/s covers wind speeds as observed in most indoor workplaces (**18**).

NOTE 4—If the respective variabilities are expected to be less than the nominal values given by Eq 7, then the calculated sampler accuracy is a conservative estimate. Alternatively, if a manufacturer explicitly states that a sampler is to be used over a narrow environmental range, the accuracy can and should be computed correspondingly.

10. Accuracy

10.1 This practice provides an estimate of the accuracy of a candidate diffusive sampler under evaluation. Because the evaluation is not perfect, the accuracy estimate itself may be biased or imprecise. The uncertainty in the estimated accuracy is therefore characterized here in terms of a conservative 95 % confidence level on the accuracy.

10.2 *Precision Confidence Limit*:

The confidence limit on the total relative standard deviation *RSD* is approximated as follows. First, the probability distribution of $\hat{RSD}$ is approximated as chi-square by way of Satterthwaite's approximation (**19-20**):

$$\upsilon_{eff}\frac{\hat{RSD}^2}{RSD^2} = \chi^2 \tag{8}$$

where υ_{eff} is an effective number of degrees of freedom determined so that the variance of the left side of Eq 8 is equal to $2\,\upsilon_{eff}$, the variance of the right-hand side. This approximation then establishes a confidence limit $\hat{RSD}_{95\,\%}$ on *RSD* given by:

$$\hat{RSD}_{95\,\%} = \hat{RSD} \,/ \sqrt{\chi^2_{0.05}(\upsilon_{eff}) / \upsilon_{eff}} \tag{9}$$

10.3 *Accuracy Confidence Limit*—The confidence limit $A_{95\,\%}$ on the Busch probabilistic accuracy (3.2.1) is then given by:

$$A_{95\,\%} = 1.960 \times RSD_{95\,\%} \tag{10}$$

11. Report

11.1 Several alternatives exist for using the results of the experimental evaluations described here. For example, EN 838 on diffusive sampler requirements suggests *classifying* the samplers according to specific accuracy criteria. Alternatively, the NIOSH accuracy criterion (**14-17**) presents a pass/fail requirement that acceptable sampling methods have better than 25 % accuracy at the 95 % (evaluation) confidence level and that uncorrected bias is less than 10 %. The accuracy itself may, in fact, be defined in alternative manners. Here it is suggested simply that sufficient information is presented that a large number of such performance criteria suited for specific application can be easily implemented. Therefore, as a minimum, the following should appear in the report of the sampler evaluation.

11.2 Analytes used for sampler test.

11.3 A listing of the model parameters (α) determined from the experimental data.

11.4 Overall accuracy of the sampler.

11.5 Ninety-five percent confidence limit on the sampler overall accuracy.

11.6 Statement that the manufacturer's claimed sampler capacity was or was not exceeded in the case of single-analyte tests and also in the presence of listed interfering compounds at stated concentrations.

11.7 Statement as to whether sampler provides a means of detecting sorbent capacity overload.

11.8 Statement as to whether the sampler provides a direct reading or requires laboratory analysis.

11.9 Statement as to whether the uncorrected bias is less than 10 %.

11.10 Statement as to whether wind direction effects exceed 15 %.

NOTE 5—Samplers tested to this protocol shall be preferred in use over samplers tested to a lower level of evaluation (for example, calculated uptake rates).

NOTE 6—Samplers tested to a protocol considered an equal or greater level of evaluation (for example, EN 838 or Cassinelli et al., 1987) do not require re-testing to be considered as having met the requirements of this protocol.

NOTE 7—Samplers used outside the ranges of environmental conditions chosen either for the tests or for intended application (9.3) in this protocol do not provide results of assured accuracy. For example, the practice does not address sampling in an environment with a correlated combination of high temperature, high humidity, and high concentration with interference.

12. Keywords

12.1 accuracy; air monitoring; bias; concentration; diffusive; evaluation; gases; passive; performance; precision; sampling and analysis; samplers; tests; vapors; workplace atmospheres

APPENDIX

(Nonmandatory Information)

X1. WORKED EXAMPLE: PROGRAM FOR DIFFUSIVE SAMPLER ACCURACY CALCULATION

X1.1 Table X1.1 and Table X1.2 and Fig. X1.1 illustrate the experiments and calculations described in the practice as implemented using the calculational program Mathematica. The programs may be translated from Mathematica as desired. The optional experimental design in Table X1.1 was used (**12**) in exposing four samplers per run to toluene vapor for completing 8.3 and 8.4 (including a wind speed effect).

TABLE X1.1 Experimental Design with Six Runs for Covering a Range of Environmental Conditions

Run	*T* (°C)	h (mm Hg)	*v* (m/s)	*c* (mg/m^3)
1	25	2.75	0.1	738.7
2	25	16.0	0.1	771.1
3	25	1.30	1.9	755.9
4	40	27.6	0.1	73.14
5	25	16.9	0.1	658.6
6	25	16.9	0.1	738.7

NOTE 1—Runs 1 to 5 were conducted over sampling periods equal to 2 h, whereas Run 6 was over a short (0.5 h) period prior to closing the sampler. The values in the column, *c* (mg/m^3), averages of active sampling results, are used as reference concentrations. Results from Run 6 were compared to reference concentrations, rather than to pulses at the start of sampling, as recommended in 4.2 and 8.5.

TABLE X1.2 Concentration Estimates (mg/m^3) from Four Samplers at Each Environmental Condition Using the Experimental Design of Table X1.1

Run	Diffusive Sampler-Estimated Concentrations (mg/m^3)			
1	829.6	865.0	865.0	850.2
2	862.9	890.6	847.4	836.6
3	948.7	935.0	947.9	917.7
4	84.99	80.67	77.67	83.96
5	725.8	716.6	738.3	695.5
6	834.0	791.9	797.1	791.1

X1.2 The concentration estimates in Table X1.2 were obtained from the four diffusive samplers in each run using the manufacturer's recommended sampling rate (m^3/s) and sampling period (s) to convert sampled mass (mg) to concentration (mg/m^3):

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(* The following give the above concentration estimates expressed relative to reference
concentrations c: *)


c[[1]]={1.123,1.171,1.171,1.151};
c[[2]]={1.119,1.155,1.099,1.085};
c[[3]]={1.255,1.237,1.254,1.214};
c[[4]]={1.162,1.103,1.062,1.148};
c[[5]]={1.102,1.088,1.121,1.056};
c[[6]]={1.129,1.072,1.079,1.071};

(* Computation of Inter-sampler Variability: *)

Do[var[[j]]=Variance[Log[c[[j]]]],{j,1,4}]

RSDs=Sqrt[Mean[var]];

Print["RSDs = ";RSDs]

RSDs = 0.0258

nu=18 (* degrees of freedom in RSDs: *);

______________________________________________

(* Accuracy Computation: *)

(* The following are the means of the estimates from the first five runs above: *)

del={1.154,1.115,1.240,1.119,1.092}-1.;

(* Central environmental conditions for model: *)

T0=25 (* temperature (°C) *);
H0=10 (* humidity (mm Hg) *);
V0=0.50  (* wind speed (m/s) *);
Crel0=1.0 (* concentrations relative to the target concentration *);

(* The test conditions [12], expressed as
{1, (T-T0)/T0, (H-H0)/H0, (V-V0)/V0, (C-Crel0)/Crel0},
are represented for the first five above runs by: *)
```

FIG. X1.1 Computer Program for Evaluating Performance Test Data

```
beta={   {1, (25-T0)/T0, (2.75-H0)/H0, (0.1-V0)/V0, (1.0-Crel0)/Crel0},
         {1, (25-T0)/T0, (16.0-H0)/H0, (0.1-V0)/V0, (1.0-Crel0)/Crel0},
         {1, (25-T0)/T0, (1.30-H0)/H0, (1.9-V0)/V0, (1.0-Crel0)/Crel0},
         {1, (40-T0)/T0, (27.6-H0)/H0, (0.1-V0)/V0, (1.0-Crel0)/Crel0},
         {1, (25-T0)/T0, (16.9-H0)/H0, (0.1-V0)/V0, (0.1-Crel0)/Crel0},   };

(* Mean relative concentration from pulse run (the 6-th run above): *)

delt=1.088;

betainv=Inverse[beta];

alpha=betainv.del;

(* alpha[[1]] is the bias at the central environmental conditions. *)

(* Modeled concentration estimate relative to the true (reference) concentration: *)

Cmodel[T_,H_,V_,Crel_]:=1.00+alpha[[1]]+
         alpha[[2]]*(T/T0-1)+alpha[[3]]*(H/H0-1)+
         alpha[[4]]*(V/V0-1)+alpha[[5]]*(Crel/Crel0-1)

(* Bias from pulse experiment: *)

BIASt=delt/Cmodel[25.,16.9,.1,1.]-1;

(* Assumed environmental uncertainties: *)

RSDT=5./T0;
RSDH=5./H0;
RSDV=.25/V0;
RSDC=.30;

(* Total imprecision: *)

RSD=Sqrt[BIASt^2/3+RSDs^2+
         alpha[[2]]^2*RSDT^2+alpha[[3]]^2*RSDH^2+
         alpha[[4]]^2*RSDV^2+alpha[[5]]^2*RSDC^2];

(* Computation of confidence limit on RSD: *)

(* Assumed inter-run variability (obtained from two 9-run experiments on toluene and methylene
chloride [7]): *)

RSDrun=0.035;
```

FIG. X1.1 Computer Program for Evaluating Performance Test Data *(continued)*

```
(* Covariance matrix for the model parameters: *)

cov=betainv.Transpose[betainv]*(RSDrun^2+RSDs^2/4);

der=(-2/3)*BIASt*(BIASt+1)^2/delt;

DvarDalpha={
            der,
            der*(25/T0-1)      + 2*alpha[[2]]*RSDT^2,
            der*(16.9/H0-1)   + 2*alpha[[3]]*RSDH^2,
            der*(0.1/V0-1)     + 2*alpha[[4]]*RSDV^2,
            der*(1.0/Crel0-1) + 2*alpha[[5]]*RSDC^2
            };

varVAR=2*RSDs^4/nu + DvarDalpha.cov.DvarDalpha+
            BIASt^2*RSDs^2/9;

nuEff=2*RSD^4/varVAR;

RSD95=RSD/Sqrt[chisq[nuEff,0.05]/nuEff];

A95=1.96*RSD95;

(* Output: *)

Print["alpha = ",alpha];
Print["RSD = ",RSD];
Print["nuEff = ",nuEff]
Print["RSD95 = ",RSD95,"A95 = ",A95];

(* alpha-subscripts: bias, T, H, V, C:  *)

alpha = {0.150458, 0.0681572, -0.0309434, 0.0223648, 0.0213501}

(* Note:  The indicated 15 % bias resulted from the low pressure (652 mm Hg) of the
evaluation experiment relative to the calibration pressure.  This bias can be eliminated
by a simple pressure correction. *)

RSD = 0.0376              nuEff = 5.8

RSD95 = 7.3 %

The 95 % confidence limit on the sampler accuracy = 14 %.
```

FIG. X1.1 Computer Program for Evaluating Performance Test Data *(continued)*

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