Designation: D 6246 – 02

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 and for wind speeds less than 0.5 m/s. Such sampling periods and wind speeds are the most common in the indoor workplace setting. Given a suitable exposure chamber, the practice can be extended to cover sampler use for other sampling periods and conditions. The aim is to provide a concise set of experiments for classifying samplers primarily in accordance with a single sampler accuracy figure. Accuracy is defined (3.2.1) in this standard so as to take into account both imprecision and uncorrected bias. 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 when the sampler is used in the field. Futhermore, the accuracy accounts for the effects of diffusive loss of analyte on 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.

1.2 This practice is an extension of previous research on diffusive samplers (**1-14**)[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, the costs of sampler evaluation are reduced.

1.3 Knowledge gained from similar analytes expedites 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. The test for diffusive analyte loss can be omitted if the effect is found negligible for a given sampler or analyte series.

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 *Symmetric Accuracy Range A*—the fractional range, symmetric about the true concentration *c*, within which 95 %

[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.

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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.

of sampler measurements are to be found (**14-19**). In terms of the bias Δ relative to true concentrations and the total relative standard deviation *RSD*, the accuracy range A is closely approximated (**19**) by:

$$A = \begin{cases} 1.960 \times [\Delta^2 + RSD^2]^{1/2}, |\Delta| < RSD / 1.645 \\ |\Delta| + 1.645 \times RSD, otherwise \end{cases} \quad (1)$$

3.2.1.1 *Discussion*—In the case that bias is corrected, leaving only an uncorrectable residual bias due to uncertainty in the correction, 95 %-confidence limits on *A* play the role of the expanded uncertainty in (**20**). As described in (**14**), such an interpretation is an extension of (**20**) for measurement, as in occupational hygiene, of concentrations which are neither spatially nor temporally constant. Rather than continually re-evaluating a method through estimate replicates, the accuracy provides confidence intervals bracketing (true) concentrations at greater than a given probability (95 %) for a fixed confidence (95 %) in the initial sampler evaluation. Such intervals with double confidence levels (in both measurement and evaluation) are related to a branch of statistics known as the theory of tolerance intervals.

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	=	symmetric accuracy range as defined in terms of bias and imprecision
$\hat{A}$	=	estimated symmetric accuracy range A
$A_{95\,\%}$	=	95 % confidence limit on the symmetric accuracy range 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 in accordance with 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
$t_{0.95}(\upsilon)$	=	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 reference 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 near conditions of intended sampler use (T_0, h_0, v_0, and c_0). Testing is required at the concentration c_0 of intended use, as well as at concentrations reduced at least to $c_0/2$. Furthermore, the sampler bias and the inter-sampler standard deviation are measured. Finally, the effect of diffusion of material out of the sampler is measured. Pressure effects result in correctable bias and are not evaluated in this practice (4.6).

4.1.2 Using four samplers for each of five experimental runs (the minimum possible), the sensitivities α_T, α_h, α_v, and α_c(relative to the chamber reference concentration and target environmental parameters) to changes in T, h, v, and c are measured, following the sampler manufacturer's instructions regarding p- and T- corrections (if any). These experiments also give a value for the estimated sampler bias Δ relative to the chamber reference concentration (defined for the target conditions). Two further runs describing time-effects (4.2.5) from diffusive loss of analyte are also carried out. The chamber reference concentration must be traceable to primary standards of mass and volume.

4.1.3 Error in the estimates of the sensitivities α_T, α_h, α_v, and α_c will exist on account of inter-sampler relative standard deviation RSD_s and an inter-run chamber standard deviation RSD_{run}. The latter results in part from uncertainty in the reference concentration. RSD_s is obtained by pooling the variance estimates from each run and therefore is estimated with $7 \times 3 = 21$ degrees of freedom (or 15 degrees of freedom

if the reverse diffusion experiment is omitted (1.3)). 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 sensitivities α and RSD_s, are estimated is presented in the Annex A1.

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 %.

4.1.3.1 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.

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 is generally only significant in the case that an analyte is 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 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:

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

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:

$$\Delta\mu_{95\,\%} = \Delta c - s \times t_{0.95}(\upsilon)/Sqrt[n] \quad (3)$$

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 %,

$$(s/c)\times t_{0.95}(\upsilon)/Sqrt[n] = 3.3\ \%. \quad (4)$$

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. 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 (mL/s) 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.

NOTE 3—With diffusion through air, the concentration expressed as ppm is independent of the pressure during sampling, unlike the mass concentration (mg/mL).

4.6.2 If the sampling rate is more complicated than with diffusion through air alone or through a semi-permeable membrane alone, justification for the given correction formula shall be made available by the sampler manufacturer.

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. Therefore, experiments are done with wind parallel with the sampler face.

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 candidate samplers 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 *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 up to 0.5 m/s must be attainable as face velocities across the sampler face as representative of the local conditions when the sampler is used as a personal sampler.

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

6.2.3 *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.

6.2.4 *Pressure*—Atmospheric pressure in the chamber must be constant to 1 % within any run.

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 4—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 Obtain pressure correction formula justification (4.6) from the sampler manufacturer as necessary.

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

8.3 Through five runs with four samplers each, complete the experiments at non-fluctuating concentration (Runs 1–5 of Annex A1 (which also includes the wind speed, *v*, effect)).

8.4 Eight samplers shall also be simultaneously exposed (Runs 6–7 of Annex A1) 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 8.3 if necessary for quantification, as long as the time-weighted average over sampling periods of intended use is not exceeded.

8.5 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).

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

8.7 Storage stability tests are not given here, although (**3,12**) or EN 838 may provide guidance as to their future development.

8.8 Shelf-lifetime tests are not given here, although (**3**) or EN 838 may provide guidance as to their future development.

9. Sampler Performance Classification

9.1 Data from the experiments described above allow a simple classification of candidate diffusive samplers. Aside from evidence that sampler capacity is not exceeded, 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:

$$RSD^2 = RSD^2_t + RSD^2_s + \alpha^2_T RSD^2_T + \alpha^2_h RSD^2_h + \alpha^2_V RSD^2_V + \alpha^2_c RSD_c{}^2 \quad (5)$$

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 relative sensitivity 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:

$$\sigma_T = 5°C \text{ about } T_0 = 25°\text{C} \quad (6)$$
$$\sigma_h = 5 \text{ mm Hg about } h_0 = 10 \text{ mm Hg}$$
$$\sigma_v = 0.125 \text{ m/s about } v_0 = 0.25 \text{ m/s}$$
$$RSD_c = 30\ \%$$

For example, $\sigma_T = 5°$C corresponds to sampler use (95 % of the time) between 15 and 35°C. Similarly, $\sigma_v = 0.125$ m/s covers the wind speeds (<0.5m/s) observed at a frequency greater than 95 % in a recent study covering a wide range of indoor workplaces (**21**).

NOTE 5—If the respective variabilities are expected to be less than the nominal values given by Eq 6, then the calculated sampler accuracy range is a conservative estimate. Alternatively, if a manufacturer explicitly states that a sampler is to be used over a narrow environmental range, the accuracy range 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 *Accuracy Range Confidence Limit*:

For computing the confidence limit $A_{95\,\%}$, an algorithm similar to an approximation developed by Satterthwaite (**22-23**) for confidence limits on linear combinations of independent variance estimates has been found accurate and simple to implement. Namely, an estimate $\hat{A}$ [Hats, as here, refer to estimates.] is approximated in terms of a chi-square random variable $\chi_\upsilon{}^2$ for the two cases in Eq. 1 by:

$$\hat{A} / A \approx \begin{cases} \sqrt{\chi^2_\upsilon / \upsilon}, & |bias| < RSD / 1.645 \\ \chi^2_\upsilon / \upsilon, & otherwise \end{cases} \quad (7)$$

The effective number of degrees of freedom υ is determined by forcing the variance of $\chi_\upsilon{}^2$ to reproduce the estimated variance of $\hat{A}^2$ or $\hat{A}$ in their respective cases:

$$\upsilon = \begin{cases} 2A^4 / var[\hat{A}^2], & |bias| < RSD / 1.645 \\ 2A^2 / var[\hat{A}], & otherwise \end{cases} \quad (8)$$

Calculation of var[$\hat{A}^2$] or var[$\hat{A}$] is straightforward, using any math program which can handle the calculation of matrix inverses. More details are given in (**14**), but are invisible to the user of a computer program available as Research Report D22–XXXX for this Practice, as illustrated in Annex A1.

The confidence limit $A_{95\,\%}$ is then easily found using a table of chi-square quantiles $\chi^2_{0.05,\,\upsilon}$:

$$A_{95\,\%} = \hat{A} \times \begin{cases} \sqrt{\upsilon / \chi^2_{0.05,\,\upsilon}}, & |bias| < RSD / 1.645 \\ \upsilon / \chi^2_{0.05,\,\upsilon}, & otherwise \end{cases} \quad (9)$$

10.3 *Expanded Uncertainty*:

Another application of the symmetric accuracy range *A* is for specifying confidence intervals on an unknown concentration *X*. Suppose the likelihood that $|A_{95\,\%}| > 100\ \%$ is negligible. Then at 95 % confidence in the method evaluation,

$$\frac{\hat{\hat{X}}}{1 + A_{95\,\%}} < X < \frac{\hat{\hat{X}}}{1 - A_{95\,\%}}, \quad (10)$$

for greater than 95 % of the estimates $\hat{\hat{X}}$. Such double-confidence intervals are the counterpart to GUM's expanded uncertainty (coverage factor together with combined uncertainty) in the case of negligible *bias* (acknowledging that, though important, known *bias*, aside from its own uncertainty

as accounted for here, does not contribute to *uncertainty* in a concentration estimate since biased estimates may be corrected).

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 in accordance with specific accuracy criteria. Alternatively, the NIOSH accuracy criterion (**14-18**) presents a pass/fail requirement that acceptable sampling methods have better than 25 % symmetric accuracy range at the 95 % (evaluation) confidence level and that uncorrected bias is less than 10 %. The accuracy range 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 bias (Δ) and sensitivities (α) determined from the experimental data.

11.4 Overall symmetric accuracy range of the sampler.

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

11.6 Statement that the manufacturer's stated 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 the sampler provides a direct reading or requires laboratory analysis.

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

NOTE 6—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; uncertainty; vapors; workplace atmospheres

ANNEX

(Mandatory Information)

A1. WORKED EXAMPLE: PROGRAM FOR DIFFUSIVE SAMPLER ACCURACY RANGE CALCULATION

A1.1 Table A1.1 and corresponding data analysis by means of a computer program's input/output form (Table A1.2) illustrate the experiments and calculations described in the practice. The computer program is available from ASTM International as Research Report D22–XXXX for this Practice.

TABLE A1.1 Experimental Design with Seven Runs for Covering a Range of Environmental Conditions

Run	*Temperature*	Humidity	*Windspeed*	*Concentration*
1	target	high	target	target
2	target	low	target	target
3	target	low	target	low
4	target	target	high	low
5	high	low	target	target
6 degassed pulse				
7 non-degassed pulse				

TABLE A1.2 Diffusive Sampler Performance: Test Results and Accuracy Analysis

Chamber Conditions and Four (4) Candidate Sampler Replicates/Run:

Input:

Run 1	Conditions	Replicates (ppm)
temperature (°C) =	25	139.2
humidity (mm Hg) =	19.40	138.2
wind speed (m/s) =	0.11	138.6
true concentration (ppm) =	123	145
Run 2	Conditions	Replicates (ppm)
temperature (°C) =	25.1	108.3
humidity (mm Hg) =	3.60	110
wind speed (m/s) =	0.11	110.7
true concentration (ppm) =	101.1	112.8
Run 3	Conditions	Replicates (ppm)
temperature (°C) =	25.1	14.2
humidity (mm Hg) =	3.60	15.3
wind speed (m/s) =	0.11	12.9
true concentration (ppm) =	12.7	14.6
Run 4	Conditions	Replicates (ppm)
temperature (°C) =	26.7	14.9
humidity (mm Hg) =	11.90	14.6
wind speed (m/s) =	0.5	15.3
true concentration (ppm) =	11.5	15
Run 5	Conditions	Replicates (ppm)
temperature (°C) =	39	109
humidity (mm Hg) =	2.50	109.2
wind speed (m/s) =	0.11	107.1
true concentration (ppm) =	91.3	105
Run 6		Replicates (ppm)
Half–hour pulse		139
degassing: 7.5 h		140
		140
true concentration (ppm) =	135	140
Run 7		Replicates (ppm)
Half–hour pulse		144
degassing: 0.0 h		145
		138
true concentration (ppm) =	135	139

Application Conc. (ppm) = 50 *RSDrun* = 0.008693183

Output:
Performance Test Accuracy Summary

Accuracy Range = 28.65 %
95 % Accuracy Range Confidence Limit = 31.03 %

Bias = 18.12 %
Relative Standard Deviation = 6.40 % *RSDs* = 2.86 %

Percent Accuracy Range Dependencies on:

Sampler:	*Percent Effect*
bias	88.90 %
inter-sampler variation	2.21 %
reverse diffusion	0.03 %
Environment:	
temperature variation	2.61 %
humidity variation	0.84 %
wind variation	5.33 %
concentration variation	0.07 %

REFERENCES

(**1**) Brown, R.H., Charlton, J., and Saunders, K.J., "The Development of an Improved Diffusive Sampler," *Am. Ind. Hyg. Assoc. J.*, Vol 42, 1981, pp. 865-869.

(**2**) Bartley, D.L., Doemeny, L.J., and Taylor, D.J., "Diffusive Monitoring of Fluctuating Concentrations," *Am. Ind. Hyg. Assoc. J.*, Vol 44, 1983, pp. 241-247.

(**3**) Cassinelli, M.E., Hull, R.D, Crable, J.V., and Teass, A.W., "Protocol for the Evaluation of Passive Monitors," *in Diffusive Sampling*, Royal Society of Chemistry, London, England, 1987, pp. 190-202.

(**4**) Kennedy, E.R., and Hull, R.D., "Performance of the DuPont Pro-Tek^{R} Formaldehyde Badge and the 3M Formaldehyde Monitor," *Am. Ind. Hyg. Assoc. J.*, Vol 47, 1987, pp. 94-105.

(**5**) van den Hoed, N., and Halmans, M.T.H., "Sampling and Thermal Desorption of Tube-Type Diffusive Samplers: Selection and Performance of Adsorbents," *Am. Ind. Hyg. Assoc. J.*, Vol 48, 1987, pp. 364-373.

(**6**) Bartley, D.L., Woebkenberg, M.L., and Posner, J.C., "Performance of Thick-sorbent Diffusive Samplers," *Ann. Occup. Hyg*., Vol 32, 1988, pp. 333-343.

(**7**) Underhill, D.W., and Feigley, C.F., "Boundary Layer Effect in Diffusive Monitoring," *Anal. Chem*., Vol 63, 1991, pp. 1011-1013.

(**8**) van den Hoed, N., and van Asselen, O.L.J., "A Computer Model for Calculating Effective Uptake Rates of Tube-Type Diffusive Air Samples," *Ann. Occup. Hyg*., Vol 35, 1991, pp. 273-285.

(**9**) Guild, L.V., Myrmel, K.H., Myers, G., and Dietrich, D.F., "Bi-Level Passive Monitor Validation: A Reliable Way of Assuring Sampling Accuracy for a Larger Number of Related Chemical Hazards," *Appl. Occup. Environ. Hyg*., Vol 7, 1992, pp. 310-317.

(**10**) Nordstrand, E., and Kristensson, J., "A Computer Program for Simulating the Performance of Thick Bed Diffusive Samplers," *Am. Ind. Hyg. Assoc. J*., Vol 55, 1994, pp. 935-941.

(**11**) Nordstrand, E.," A Computer Program for Simulating the Performance of Thick Bed Diffusive Samplers-Predicted and Experimental Sample Loss Due to Reversible Adsorption," *J. Chrom*., Vol 709, 1995, p. 283.

(**12**) OSHA, "Development of a Protocol for Laboratory Testing of Diffusive Samplers," OSHA Salt Lake Technical Center Report, 1996.

(**13**) Harper, M., and Guild, L.V., "Experience in the Use of the NIOSH Diffusive Sampler Evaluation Protocol," *Am. Ind. Hyg. Assoc. J*., Vol 57, 1996, pp. 1115-1123.

(**14**) Bartley, D.L., and Irwin, K.C., "Accuracy in Measurements using Diffusive Samplers," Proceedings of the International Conference on Diffusive Sampling, Montpellier, France, 2002.

(**15**) Busch, K.A., "SCP Statistical Protocol," in: *Documentation of the NIOSH Validation Tests*, Taylor, D.G., Kupel, R.E., and Bryant, J.M., eds., Pub. No. 77-185, DHEW (NIOSH), Cincinnati, 1977.

(**16**) Gunderson, E.C., and Anderson, C.C., "Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances," (NIOSH) Publication No. 80-133, Department of Health and Human Services, Cincinnati, 1980.

(**17**) NIOSH *Manual of Analytical Methods*, 4th Ed., Eller, P.M., ed., U.S. DHHS Publication No. 94-113, Cincinnati, 1994.

(**18**) Kennedy, E.R., Fischbach, T.J., Song, R., Eller, P.M., and Shulman, S.A., "Guidance for Air Sampling and Analytical Method Development and Evaluation," DHHS (NIOSH) Publication No. 95-117, Cincinnati, 1995.

(**19**) Bartley, D.L., "Definition and Assessment of Sampling and Analytical Accuracy," *Annals of Occupational Hygiene*, Vol 45, 2001, pp. 357-364.

(**20**) *Guide to the Expression of Uncertainty in Measurement*, International Organization for Standardization, Geneva, 1993.

(**21**) Baldwin, P.E.J., and Maynard, A.D., "A Survey of Wind Speeds in Indoor Workplaces," *Ann. Occup. Hyg*, 1998.

(**22**) Smith, H.F., "The Problem of Comparing the Results of Two Experiments with Unequal Errors," *Journal of the Council of Scientific and Industrial Research*, Vol 9, 1936, pp. 211-212.

(**23**) Satterthwaite, F.E., "An Approximate Distribution of Estimates of Variance Components," *Biometrics*, Vol 2, 1946, pp. 110-114.