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Workplace atmospheres — Protocol for evaluating the performance of diffusive samplers

Air des lieux de travail — Protocole pour l'évaluation de la performance des dispositifs de prélèvement par diffusion

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16107 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

This second edition cancels and replaces the first edition (ISO 16107:1999), which has been technically revised.

Introduction

Gas or vapor sampling is often accomplished by actively pumping air through a collection medium such as activated charcoal. Problems associated with a pump, such as inconvenience, inaccuracy and expense, are inextricable from this type of sampling. The alternative covered by this International Standard 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.

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 protection may be based on faulty assumptions. The aim of this International Standard 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.

This International Standard is intended specifically for the large-scale evaluation of many diffusive sampler/analyte pairs of practical application and is complementary to EN 838. An affordable, experimental evaluation determines a single performance value indicating how a sampler performs in a typical situation. A sampler can thereby be quickly judged as to acceptability. Additionally, sufficient data are obtained to predict performance in many atypical situations. For example, although sampling may normally be done at room temperature, a particular need may call for use in extreme cold. In such a case, the single performance value would be superseded by the particular needs.

Workplace atmospheres — Protocol for evaluating the performance of diffusive samplers

1 Scope

This International Standard specifies methods for evaluation of sampler performance in terms of workplace conditions: wind speed, humidity, temperature, atmospheric pressure, and analyte variation. The concise set of experiments specified aims to minimize cost to the user. The evaluation is limited to conditions commonly encountered in personal sampling in the indoor workplace setting, namely wind speeds of up to 0,5 m/s and for sampling periods typically from 2 h to 8 h.

Static or area sampling, unlike personal sampling where movement of the subject is significant, may sometimes be subject to sampling-rate reduction due to stagnation at very low wind speeds. This International Standard therefore does not apply to wind speeds of less than 0,1 m/s relative to static samplers. Samplers are also tested for compliance with the manufacturer's stated limits on capacity, possibly in the presence of interfering compounds. Given a suitable exposure chamber, the sampler evaluation protocol can be extended to cover sampler use for other sampling periods and conditions.

This International Standard indicates how to measure diffusive sampler uncertainty for characterizing concentration estimates obtained subsequent to the evaluation. It is impractical continually to re-evaluate diffusive sampler performance under various environmental conditions prevailing during application.

NOTE 1 In this International Standard, the confidence level for the initial method evaluation becomes an integral part of the measurement uncertainty. This approach slightly broadens the statistical protocols given in ISO Guide 98:1995. Furthermore, the possibility of sampler errors related to correctible sampler bias is addressed.

NOTE 2 This International Standard is an extension of previous research on diffusive samplers (References [1] to [17] inclusive and EN 838).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 838, *Workplace atmospheres — Diffusive samplers for the determination of gases and vapours — Requirements and test methods*

ISO Guide 98:1995, *Guide to the expression of uncertainty in measurement*. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 838 and ISO Guide 98:1995 and the following apply.

3.1
symmetric accuracy range

A

fractional range about the measurand concentration, c, within which 95 % of sampler measurements are found

NOTE See References [18] to [21] inclusive.

If the modulus of the bias is small, i.e. $|\Delta| < R/1{,}645$, the symmetric accuracy range, A, can be shown to be closely approximated (Reference [21]) by Equation (1):

$$A = 1{,}960 \times \sqrt{\Delta^2 + R^2} \tag{1}$$

where

Δ is the bias, expressed relative to true concentrations;

R is the overall true relative standard deviation, expressed relative to true concentrations.

Otherwise

$$A = |\Delta| + 1{,}645 \times R \tag{2}$$

If the bias is corrected, the expected value of Δ^2 in Equation (1) becomes equal to the variance of the bias correction, reflecting an uncorrectable residual bias due to uncertainty in the correction. Then if the bias uncertainty is under control, the low bias modulus model of Equation (1) indicates the proportionality of A to the root mean squared combined uncertainty components.

4 Symbols and abbreviated terms

A	symmetric accuracy range (3.1) in terms of bias and precision
A_{est}	estimated symmetric accuracy range, A
$A_{95\,\%}$	95 % confidence level on the symmetric accuracy range, A
c	true or reference analyte concentration, in milligrams per cubic metre, or parts per million as a ratio of analyte to air molecules, per instructions of the sampler manufacturer
c_{est}	mean of (four) concentration estimates (including pressure and temperature corrections), in milligrams per cubic metre or parts per million as a ratio of analyte to air molecules, per instructions of the sampler manufacturer
h	humidity, partial pressure of water vapor, in kilopascals
n	number of diffusive samplers tested for measuring sampler capacity
p	(atmospheric) pressure
R	overall true relative standard deviation of concentration estimates (dependent on assumed environmental variability), expressed as a percentage relative to a “true” concentration as estimated by reference sampling

R_{est}	estimated true relative standard deviation, expressed as a percentage
R_{run}	true relative standard deviation characterizing inter-run chamber variability, expressed as a percentage
R_{s}	intersampler component of the true relative standard deviation, expressed as a percentage
$R_{\mathrm{s\ est}}$	estimated intersampler true relative standard deviation, R_{s}, expressed as a percentage
R_t	pulse-induced true relative standard deviation, expressed as a percentage
$R_{95\ \%}$	95 % confidence limit on the true relative standard deviation, expressed as a percentage
s	estimated standard deviation characterizing intersampler variation
$t_{0,95}(v)$	value which, at the 95 % probability level, exceeds random variables distributed according to the Student t-distribution with v degrees of freedom
T	temperature, in degrees Celsius
u	ambient wind speed, in metres per second
α_x	concentration estimate dependence on environmental variable, x (T, h, u, or c)
Δ	bias relative to concentration, c
Δ_{est}	estimated bias, Δ
Δ_t	bias associated with concentration pulse
$\Delta_{95\ \%}$	95 % confidence limit on the bias, Δ
v	degrees of freedom in determining R_{s}
v_{eff}	effective number of degrees of freedom in determining R
σ_c	assumed concentration variability
σ_h	assumed humidity variability
σ_T	assumed temperature variability
σ_u	assumed ambient wind speed variability

5 Summary of test protocol

5.1 Factors affecting performance

5.1.1 Diffusive sampling may first of all suffer from error in the sampling rate as stated by the manufacturer of the sampler. As diffusive samplers are usually used without recalibration, this error implies a bias or systematic error in all concentration estimates made. As the bias may be in one direction, such error cannot be minimized by averaging several measurements. If the error is correctible it is not strictly part of the sampler uncertainty.

5.1.2 Aside from bias, several sources of random error exist. Some of these errors are associated with the sampler itself. For example, the sampler's dimensional tolerance may be low, leading to variation in the sampling rate, sampler to sampler. The sampler may become overloaded or may not follow concentration changes adequately.

5.1.3 Other errors relate to a non-constant environment which may affect the sampling rate. Potentially significant environmental *influence quantities* include temperature, humidity, wind speed, and atmospheric pressure. To predict the effect of any such parameter, an experiment on the sampler type may be carried out. Moreover, the variation expected of the parameter requires estimation. So as to result in a single performance measure, typical ranges of these environmental parameters are specified in this International Standard.

5.2 "Accuracy" as providing a single performance value linking to measurement uncertainty

5.2.1 A sampler presented by a manufacturer for evaluation may be found to exhibit both imprecision and bias. In the language of ISO Guide 98:1995, imprecision and bias together relate to the "accuracy" of a sampler, rather than "uncertainty". Accuracy refers to the closeness between measured values and measurand (in this case the concentration to be measured), whereas uncertainty refers to what is known about the measurand on the basis of the measurement. In other words, the manufacturer could recommend use of information about the bias for correction of the measured values. This International Standard provides means of judging a sampler as recommended for use by a manufacturer.

5.2.2 A useful statistical measure exists which summarizes the overall effect of both random variation and bias. This function has come to be known as the symmetric accuracy range, A (3.1).

5.2.3 The definition directly implies that A increases with both random error and bias magnitude. Therefore A is one particular quantification of accuracy as defined in ISO Guide 98:1995. The greater the disparity between measured values and measurand, the larger the value of A.

NOTE A is not the only way of quantifying accuracy. For example, the selection of 95 % as coverage level is arbitrary. Furthermore, other functions consistent with the qualitative idea of accuracy as described in ISO Guide 98:1995 are possible.

5.2.4 A indicates quantitatively how far off measurements would generally be if further correction of the sampler were not made. A further advantage of A is that a direct link to the uncertainty described in ISO Guide 98:1995 is obtained in the case that bias is minimized, e.g. through results of the evaluation.

5.2.5 Moreover, a measurement element not covered extensively within ISO Guide 98:1995 is dealt with explicitly. Namely, diffusive samplers are generally used as obtained from the manufacturer without re-evaluation at each use. Therefore, uncertainty in a measured value must account for confidence in the [single] evaluation itself as well as variation and possible residual bias at the point of use.

5.2.6 The result of approaching uncertainty from the point of view of accuracy results in an "expanded uncertainty" (in the language of ISO Guide 98:1995) proportional via a "coverage factor" to the root mean squared *combined uncertainty components* comprised of bias uncertainty, the effects of sampler variation, and influence quantities described above. The coverage factor is determined by the confidence required [e.g., 95 %] in the sampler evaluation and the coverage [also 95 %]. The final result is a value of expanded uncertainty with specific [tolerance or predictive] meaning, namely, in providing the 95 % coverage range about the [true] measurand at 95 % confidence in the evaluation.

5.3 Bias, intersampler variability and the effects of environmental uncertainty

5.3.1 This International Standard 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); ambient wind speed, u, across the sampler face [see (5.7) regarding wind direction]; and concentration, c. An experiment is carried out which provides information about the dependencies of the concentration estimates on these variables near conditions of intended sampler use (T_0, h_0, u_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 intersampler 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 International Standard (5.8).

5.3.2 Using four samplers for each of five experimental runs (the minimum possible), the dependencies α_T, α_h, α_u, and α_c (relative to the chamber reference concentration and target environmental parameters) on changes in T, h, u, and c are measured, following the sampler manufacturer's instructions regarding pressure and temperature 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-dependent effects (5.4.5) from diffusive loss of analyte are also carried out. The chamber reference concentration must be traceable to primary standards of mass and volume.

5.3.3 Error in the estimates of the dependencies α_T, α_h, α_u, and α_c will exist on account of the intersampler component of the true relative standard deviation R_s and an inter-run chamber true relative standard deviation, R_run. The latter results in part from uncertainty in the reference concentration. R_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). So as to avoid re-measurement at each sampler/analyte evaluation, R_run is obtained by a separate characterization of the chamber with several runs at (for example) fixed environmental conditions. An example in which the dependencies α and R_s are estimated is presented in Annex A.

NOTE It is up to the user as to how traceability is established. In Reference [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 (Reference [12]) on the accuracy of such reference measurements using sorbent tubes indicates that a true relative standard deviation of the order of 2 % can be achieved for the individual measurements. Alternatively, Reference [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 shall agree within 10 %.

5.3.4 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, i.e. 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 five runs with $5 \times 3 = 15$ degrees of freedom in the estimate of R_s.

5.4 Reverse diffusion

5.4.1 A potential problem with diffusive samplers is presented by the possibility of reverse diffusion (sometimes denoted as “back-diffusion” or “off-gassing”) of the analyte. Reverse diffusion is generally only significant in the case that an analyte is only weakly bound to the sorbent (Reference [6]). Therefore, inaccuracy associated with these effects may usually be minimized through proper sorbent selection.

5.4.2 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 h to 12 h) for sample loss, possibly resulting in a low estimate relative to a pulse at the end.

5.4.3 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 analyte only then. This could imply a positive bias in the concentration estimates obtained from a day's sampling. For simplicity, however, this International Standard is designed to assess performance of samplers for use in a concentration fluctuating in a stationary manner, 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.

5.4.4 Challenging samplers to 0,5 h pulses is similar to the tests of NIOSH (Reference [3]) and EN 838.

5.4.5 Let Δ_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, Reference [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, R_t^2, associated with sampling a 0,5 h pulse at random within the sampling period is given by Equation (3):

$$R_t^2 = \frac{1}{3}\Delta_t^2 \tag{3}$$

5.5 Capacity — Control of effects from interfering compounds

5.5.1 This International Standard 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 of 30 °C. Additionally, a manufacturer may claim a value of capacity for sampling in the presence of specific interferences at stated concentrations.

5.5.2 For the purposes of this International Standard, capacity is defined as the sampled mass (or equivalently as the concentration for 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.

5.5.3 An example of the test is as follows: eight diffusive and eight active samplers are exposed to the analyte of interest 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 given by Equation (4):

$$\Delta\mu_{95\%} = \Delta c - [s \times t_{0,95}(\nu)/\sqrt{n}] \tag{4}$$

where

Δc is the estimated mean difference between diffusive and active results;

s is the estimated standard deviation characterizing intersampler variation, calculated from the eight diffusive sampler estimates;

n is the number of samplers of each type (in this case, 8);

ν is the number of degrees of freedom ($n - 1 = 7$).

Then $\Delta\mu_{95\,\%}$ shall be greater than −10 % c, where c is the mean concentration estimate from the reference samplers.

EXAMPLE Suppose the diffusive sampler component of the true relative standard deviation, $R_s = 5\ \%$:

$$(s/c) \times t_{0,95}(\nu)/\sqrt{n} = 3.3 \tag{5}$$

Therefore, in this case the mean value of the diffusive results shall be greater than 93,3 % of the reference concentration.

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

5.6 Capacity overload detection

The capability to detect capacity overload (e.g. 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 multianalyte environment. The capability of voiding a sample when interferences become demonstrably problematic may therefore be useful. At present, the efficacy of such breakthrough detection is not evaluated. However, evaluation tests may be developed in the future for this purpose.

5.7 Desorption efficiency

5.7.1 A further control of the effects from interfering compounds is afforded by restricting the permissible desorption efficiency. As in Reference [3], the desorption efficiency, in the case of solvent extraction, shall 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.

5.7.2 In the case of thermal desorption, the efficiency shall be >95 %.

5.8 Atmospheric pressure

5.8.1 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 through a semi-permeable membrane, the rate is independent of pressure. The difference is because of the differing expansion coefficients of the media comprised of the scattering molecules.

5.8.2 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 5.1 will determine the effect. The test report [see Clause 11 h)] should give the correctable bias which would be expected under a 15 % shift in the atmospheric pressure.

5.9 Wind direction

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 usually be across the face of the sampler. Therefore, experiments are done with wind direction parallel to the sampler face.

5.10 Simplifications

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 in Reference [9] is suggested: Following evaluation of a sampler in use at a single homologous series member according to this International Standard, higher relative molecular mass members would receive partial validations considering sampling rate, capacity, analytical recovery and interferences. Similarly, testing for diffusive analyte loss can be omitted if the effect is found negligible for a given sampler or analyte series.

6 Apparatus

6.1 Exposure chamber specifications

6.1.1 Chamber capacity

The chamber shall be capable of exposing at least eight samplers at a time together with required reference samplers with less than 5 % depletion of test analyte by the samplers at the lowest air flow.

6.1.2 Exposure time

The chamber shall be capable of maintaining conditions for up to 12 h.

6.1.3 Analyte generation

Equipment shall be provided for the measured delivery of gases, or the vaporization and measured dilution in a mixing chamber at application concentrations of controlled amounts of mixtures of test analytes in the vapor phase.

6.1.4 Reference concentration measurement

Provision shall be made for simultaneous 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 shall be corrosion resistant and fireproof. Polypropylene is a likely candidate for this purpose, although stainless steel is preferred as it is less likely to act as a significant sink.

6.1.6 Monitoring equipment

Monitors for measuring the environmental conditions listed in 6.2 shall be included with the chamber.

6.2 Controlled environmental conditions

6.2.1 Air flow rate

Air flow rates up to 0,5 m/s shall be attainable as 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) % shall be attainable at 20 °C.

6.2.3 Temperature

Temperatures equal to (10 ± 3) °C, (20 ± 3) °C and (30 ± 3) °C shall be attainable and maintainable. If the chamber is manufactured of stainless steel, then insulation of the chamber or conditioning of the air entering the test chamber may be necessary.

6.2.4 Pressure

Pressure within the chamber shall be constant to 1 % within any run and shall be fixed and maintained within a range of 95 % to 105 % of atmospheric pressure.

6.3 Inter-run variability

The chamber shall be characterized as to inter-run true relative standard deviation, R_{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 (Reference [14]) indicated that $R_{\text{run}} < 3$ % is attainable.

NOTE The exposure chamber's specifications (6.1) and environmental conditions (6.2) are sufficient to ensure effective evaluation of sampler performance in accordance with this International Standard, but do not necessarily exclude other chamber types.

7 Reagents and materials

Unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

Thermal desorption, if used for sample extraction, may obviate the necessity for desorption reagents.

8 Procedure

8.1 Obtain pressure correction formula justification (5.6) 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, 2, 3, 4, and 5 of Annex A, which also includes the effect of wind speed, u).

8.4 Eight samplers shall also be simultaneously exposed (runs 6 and 7 of Annex A) for 30 min at 80 % (or greater) relative humidity prior to or during the exposure. Four of the samplers shall be analysed 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 analysed immediately shall be compared to the average quantity found from samplers held at zero concentration. The magnitude of any decrease (percentage loss relative to the mean mass) shall be taken as twice the bias (i.e. $2\Delta_t$) due to reverse diffusion as described in 5.4. 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 (5.3) in the presence of manufacturer-stated interfering compounds (including water vapor).

8.6 Measure the desorption efficiency (see Reference [12]).

8.7 Storage stability may be measured as in References [3] and [12] or EN 838.

8.8 Shelf-life of the diffusive sampler in the original package shall be as specified by the manufacturer. At the end of the shelf-life, the results obtained in accordance with desorption efficiency tests shall not differ by more than 10 % from the original values.

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 (5.3, 8.6) is not excessive, samplers are to be characterized by their overall accuracy in view of environmental variability.

9.2 For evaluating the symmetric accuracy range, A [Equation (1)], the square of the estimated total true relative standard deviation R_{est} is given by propagation of errors in terms of its independent components by Equation (6):

$$R_{\text{est}}^2 = R_t^2 + R_{\text{s}}^2 + \alpha_T^2 R_T^2 + \alpha_h^2 R_h^2 + \alpha_u^2 R_u^2 + \alpha_c^2 R_c^2 \qquad (6)$$

where R_T, R_h, R_u, and R_c represent the (inter-day) coefficients of variation of the temperature, humidity, wind speed, and concentration expected in the workplace, and the sampler dependencies, α, are as described in 5.3.

9.3 In order to assess the accuracy of a diffusive sampler as applied in a specific workplace, these environmental dependencies require characterization. However, sampler classification is obtained here by adopting nominal values for these four quantities, namely

$$\sigma_T = 5\ °\text{C}\ (T_0 \approx 25\ °\text{C}) \tag{7}$$

$$\sigma_h = 0{,}5\ \text{kPa}\ (h_0 \approx 1{,}0\ \text{kPa}) \tag{8}$$

$$\sigma_u = 0{,}25\ \text{m/s}\ (u_0 \approx 0{,}50\ \text{m/s}) \tag{9}$$

$$R_c = 30\ \% \tag{10}$$

EXAMPLE $\sigma_T = 5$ °C corresponds to sampler use (95 % of the time) between 15 °C and 35 °C. Similarly, $\sigma_u = 0{,}25$ m/s covers wind speeds as observed in most indoor workplaces (Reference [22]).

NOTE If the respective environmental dependencies are expected to be less than the nominal values given by Equations (7) to (10), 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 General

This International Standard 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 by computing a conservative 95 % confidence level on the accuracy.

10.2 Accuracy range confidence limit

For computing the 95 % confidence level on the symmetric accuracy range, $A_{95\ \%}$, an algorithm similar to an approximation developed in References [23] and [24] for confidence limits on linear combinations of independent variance estimates has been found accurate and simple to implement. Namely, random variation in the estimate A_{est} is approximated in terms of a random variable, $\chi^2_{\nu_{\text{eff}}}$, for the cases in Equations (1) and (2) by Equations (11) and (12):

$$A_{\text{est}}/A = \begin{cases} \sqrt{(\chi^2/\nu_{\text{eff}})} & \text{if } |\Delta| < R/1{,}645 \quad (11) \\ \chi^2/\nu_{\text{eff}} & \text{otherwise} \quad (12) \end{cases}$$

The effective number of degrees of freedom ν_{eff} is determined by forcing the variance of $\chi^2_{\nu_{\text{eff}}}$ to reproduce the estimated variance of A^2_{est} or A_{est} in their respective cases:

$$\nu_{\text{eff}} = \begin{cases} 2A^4/\text{var}[\,A^2_{\text{est}}\,] & \text{if } |\Delta| < R/1{,}645 \quad (13) \\ 2A^2/\text{var}[A_{\text{est}}] & \text{otherwise} \quad (14) \end{cases}$$

Calculation of var[A_{est}^2] or var[A_{est}] is straightforward, using any mathematics program which can handle the calculation of matrix inverses. More details are given in Reference [14] and reproduced in Annex B, but are invisible to the user of a computer program available at: http://standards.iso.org/iso/16107.

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

$$A_{95\,\%} = \begin{cases} A_{\text{est}} \times \sqrt{(\nu_{\text{eff}} / \chi^2_{0.05,\nu_{\text{eff}}})} & \text{if } |\Delta| < R/1{,}645 \quad (15) \\ A_{\text{est}} \times (\nu_{\text{eff}} / \chi^2_{0.05,\nu_{\text{eff}}}) & \text{otherwise} \quad (16) \end{cases}$$

10.3 Expanded uncertainty

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

$$\frac{c_{x,\text{est}}}{1 + A_{95\,\%}} < c_x < \frac{c_{x,\text{est}}}{1 - A_{95\,\%}}, \tag{17}$$

for more than 95 % of the estimates, $c_{x,\text{est}}$. Such double-confidence intervals are the counterpart to the expanded uncertainty (coverage factor together with combined uncertainty) of ISO Guide 98:1995 in the case of negligible bias (acknowledging as described in 5.2.1 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 Test report

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 (References [18] to [21] inclusive) presents a pass/fail requirement that acceptable sampling methods have better than 25 % accuracy at the 95 % (evaluation) confidence level and that the uncorrected modulus of the bias is <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 test report of the sampler evaluation:

a) analytes used for sampler test;

b) list of the model parameters determined from the experimental data;

c) overall accuracy of the sampler;

d) 95 % confidence limit on the sampler overall accuracy;

e) 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;

f) statement as to whether the sampler provides a means of detecting breakthrough;

g) statement as to whether the uncorrected modulus of the bias is <10 %;

h) if appropriate, a statement as to the correctable bias determined from a 15 % change in atmospheric pressure, calculated according to manufacturer advice if available.

Samplers tested to this protocol shall be preferred in use over samplers tested to a lower level of evaluation (e.g. calculated uptake rates).

Samplers tested to a protocol considered an equal or greater level of evaluation (e.g. EN 838 or Reference [3]) do not require re-testing to be considered as having met the requirements of this protocol.

NOTE 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, this International Standard does not address sampling in an environment with a correlated combination of high temperature, high humidity and high concentration with interference.

Annex A
(informative)

Worked example — Program for diffusive sampler accuracy range calculation

Table A.1 and corresponding data analysis via an input/output form for a computer program (Table A.2) illustrate the experiments and calculations described in this practice (see: http://standards.iso.org/iso/16107).

Table A.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 A.2 — Diffusive sampler performance: Test results and accuracy analysis for four candidate sampler replicates per run

Input		
Chamber conditions		**Replicates (ppm)**
Run 1: T = 25 °C; h = 2,59 kPa; u = 0,11 m/s		
True concentration (ppm)	123	139,2
		138,2
		138,6
		145
Run 2: T = 25,1 °C; h = 0,48 kPa; u = 0,11 m/s		
True concentration (ppm)	101,1	108,3
		110
		110,7
		112,8
Run 3: T = 25,1 °C; h = 0,48 kPa; u = 0,11 m/s		
True concentration (ppm)	12,7	14,2
		15,3
		12,9
		14,6