

# INTERNATIONAL STANDARD

**ISO**  
**16107**

First edition  
1999-09-15

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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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Reference number  
ISO 16107:1999(E)

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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 3.

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.

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

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## Introduction

Gas or vapour 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 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.

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.

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# Workplace atmospheres — Protocol for evaluating the performance of diffusive samplers

## 1 Scope

1.1 This International Standard covers the evaluation of the performance of diffusive samplers of gases and vapours for use over sampling periods from 4 h to 12 h. Sampling periods of such duration are the most common in workplace sampling. Given a suitable exposure chamber, this International Standard 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.

NOTE Accuracy estimates refer to conditions of sampler use which are normally expected in a workplace setting. These conditions may be characterized by the temperature, atmospheric pressure, humidity and ambient wind speed, none of which may be constant or accurately known. Furthermore, the accuracy accounts for difficulty in the estimation of time-weighted averages of concentrations which may not be constant in time.

In addition to accuracy determination, a method is provided to test the samplers for compliance with the manufacturer's stated limits on capacity, possibly in the presence of interfering compounds. A method is given for classification of samplers according to their capability to detect situations in which sampler capacity may be exceeded.

1.2 This International Standard is an extension of previous research on diffusive samplers [1-17] as well as EN 838. Essential advantages are the estimation of sampler accuracy under actual conditions of use and the reduction in cost of sampler evaluation.

NOTE 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 in [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.

## 2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

EN 838: *Standard on workplace atmospheres — Diffusive samplers for the determination of gases or vapours — Requirements and test methods.*

## 3 Terms and definitions

For the purposes of this International Standard, the terms and definitions given in EN 838 as well as the following apply.

## 3.1

**Busch probabilistic accuracy**

A

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

See [18-21].

NOTE In the case considered here, effects on sampler accuracy from environmental unknowns are all handled as *variances*, leaving negligible uncorrectable bias.

$$A = 1,960 \times CV \quad (1)$$

where  $CV$  is the coefficient of variation (overall relative standard deviation).

**4 Symbols and abbreviated terms**

$A$	Busch probabilistic accuracy as defined in terms of bias and precision
$A_{\text{est}}$	estimated Busch probabilistic accuracy $A$
$A_{95\%}$	95 % confidence level on the Busch probabilistic accuracy $A$
$c$	true or reference analyte concentration, in milligrams per cubic metre
$c_{\text{est}}$	mean of (four) concentration estimates [including ( $p, T$ )-corrections], in milligrams per cubic metre, obtained per instructions of sampler manufacturer
$h$	humidity (expressed as partial pressure)
$n$	number of diffusive samplers tested for measuring sampler capacity
$p$	atmospheric pressure
$CV$	coefficient of variation (overall relative standard deviation) of concentration estimates (dependent on assumed environmental variability), expressed as a percentage
$CV_{\text{est}}$	estimated coefficient of variation, expressed as a percentage
$CV_{\text{run}}$	coefficient of variation characterizing inter-run chamber variability, expressed as a percentage
$CV_{\text{s}}$	intersampler imprecision (relative to the reference concentration), expressed as a percentage
$CV_{\text{s est}}$	estimated intersampler imprecision $CV_{\text{s}}$ , expressed as a percentage
$CV_{\text{t}}$	pulse-induced imprecision, expressed as a percentage
$CV_{95\%}$	95 % confidence limit on the coefficient of variation, expressed as a percentage
$s$	estimated standard deviation characterizing intersampler imprecision
$t_{0,95}(v)$	value which, at probability 95 %, exceeds random variables distributed according to the Studentized $t$ -distribution with $v$ degrees of freedom
$T$	temperature, in degrees Celsius
$v$	ambient wind speed, in metres per second
$\alpha_x$	concentration estimate dependence on environmental variable $x$ ( $T$ , $h$ , $v$ , or $c$ )
$\Delta$	bias relative to concentration $c$

$\Delta_{\text{est}}$	estimated bias $\Delta$
$\Delta_r$	bias associated with concentration pulse
$\Delta_{95\%}$	95 % confidence limit on the bias $\Delta$
$\nu$	degrees of freedom in determining $CV_s$
$\nu_{\text{eff}}$	effective number of degrees of freedom in determining $CV$
$\sigma_c$	assumed concentration variability
$\sigma_h$	assumed humidity variability
$\sigma_T$	assumed temperature variability
$\sigma_v$	assumed ambient wind speed variability

## 5 Summary of test protocol

### 5.1 Bias, intersampler variability and the effects of environmental uncertainty

**5.1.1** This International Standard gives a procedure for assessing the effects of variability in the following workplace parameters: temperature  $T$ , humidity  $h$  (expressed in terms of the water vapour partial pressure to minimize interaction with the temperature), the ambient wind speed  $v$  across the sampler face (see 5.7 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, intersampler variability, 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 (5.6).

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

$$c_{\text{est}}/c = 1 + \Delta + \alpha_T \cdot (T/T_0 - 1) + \alpha_h \cdot (h/h_0 - 1) + \alpha_v \cdot (v/v_0 - 1) + \alpha_c \cdot (c/c_0 - 1) \quad (2)$$

omitting error terms. The concentration  $c$  is the chamber "reference concentration" and shall be traceable to primary standards of mass and volume. Estimates of the model parameters  $\Delta$ ,  $\alpha_T$ ,  $\alpha_h$ ,  $\alpha_v$  and  $\alpha_c$  are obtained from an experiment consisting of five runs, varying  $T$ ,  $h$ ,  $v$  and  $c$ , with four diffusive samplers each. The parameter  $\Delta$  characterizes sampler bias at the intermediate conditions ( $T_0$ ,  $h_0$ ,  $v_0$ ,  $c_0$ ). Error in equation (2) will exist on account of intersampler imprecision (characterized by  $CV_s$ ) together with an inter-run chamber variability ( $CV_{\text{run}}$ ) resulting in part from uncertainty in the reference concentration.  $CV_s$  is obtained by pooling the variance estimates from each run, together with a further run describing time effects (5.2.5), and therefore is estimated with  $6 \times 3 = 18$  degrees of freedom. To avoid re-measurement at each sampler/analyte evaluation,  $CV_{\text{run}}$  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  $CV_s$  are estimated is presented in annex A.

**NOTE** 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 shall agree within 10 %.

**5.1.3** 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  $CV_s$ .

## 5.2 Reverse diffusion

**5.2.1** 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.

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

**5.2.3** 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 International Standard is designed for assessing performance of samplers for use in a stationarily fluctuating concentration, 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.

**5.2.4** Challenging samplers to 0,5-h pulses is similar to tests suggested by NIOSH [3] and CEN (EN 838).

**5.2.5** Let  $\Delta_t$  represent the corrected bias in estimating a 0,5-h pulse at the end of the sampling period relative to a known concentration  $c$ , where  $\Delta$  is the uncorrected bias in sampling over the sampling period of intended application (e.g. 8 h). For pulses occurring at other times, assume conservatively (see e.g. [6]) that the bias  $\Delta_t$  is proportional to the interval from the centre of the sampling period to the time the pulse occurs. Then the variance  $CV_t^2$  associated with sampling a 0,5-h pulse at random within the sampling period is:

$$CV_t^2 = \Delta_t^2/3. \quad (3)$$

## 5.3 Capacity — Control of effects from interfering compounds

**5.3.1** 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 equal to 30 °C. Additionally, a manufacturer may claim a value of capacity for sampling in the presence of specific interferences at stated concentrations.

**5.3.2** For the purposes of this International Standard, capacity is defined 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.

**5.3.3** An example of the test is as follows: eight diffusive and eight active samplers are exposed to the analyte of concern under the stated environmental conditions. Suppose the individual diffusive sampler inaccuracy estimate is  $s$ . 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:

$$\Delta\mu_{95\%} = \Delta c - s \cdot t_{0,95}(v)/\sqrt{[v]}; \quad (4)$$

where  $\Delta c$  is the estimated mean difference between diffusive and active results,  $n = 8$ , and  $v = n - 1 = 7$ . 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 coefficient of variation  $CV_s = 5\%$ ,

$$(s/c) \cdot t_{0,95}(v) / \sqrt{[v]} = 3,3 \% \quad (5)$$

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.

## 5.4 Capacity overload detection

The capability of *detecting* 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.

## 5.5 Desorption efficiency

**5.5.1** 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, 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.

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

## 5.6 Atmospheric pressure

**5.6.1** 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 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.

**5.6.2** 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 5.1 will determine the effect. The result will be reported [1 h] as the correctable bias which would be expected under a 15 % shift in the atmospheric pressure.

## 5.7 Wind direction

**5.7.1** 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 usually be 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 vs. wind into the sampler face (using e.g. 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.

# 6 Apparatus

## 6.1 Exposure chamber specifications

### 6.1.1 Chamber capacity

The chamber shall 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 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 vapourization and measured dilution in a mixing chamber at application concentrations of controlled amounts of mixtures of test analytes, liquid over normal room temperature ranges.

### 6.1.4 Reference concentration measurement

Provision shall 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 shall be corrosion-resistant and fireproof. Polypropylene is a likely candidate for this purpose.

### 6.1.6 Dimensions

The chamber shall be containable within a walk-in hood.

### 6.1.7 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 flowrate

Air flowrates equal to 0,05 m/s and 0,5 m/s shall 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 shall be possible to reduce the test concentration to < 5 % of the starting concentration at any sampler exposure position (i.e. controlling dead air) within 1 min.

### 6.2.3 Humidity variation

Relative humidity equal to  $(25 \pm 5)$  %,  $(50 \pm 5)$  % and  $(80 \pm 5)$  % shall be attainable at 20 °C.

### 6.2.4 Temperature

Temperatures equal to  $(10 \pm 3)$  °C,  $(20 \pm 3)$  °C and  $(30 \pm 3)$  °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 walk-in hood may be necessary.

### 6.2.5 Pressure

Atmospheric pressure in the chamber shall be constant to 1 % within any run and shall be settable within a range of 95 % to 105 % of atmospheric pressure.

## 6.3 Inter-run variability

The chamber shall be characterized as to inter-run variability  $CV_{run}$  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  $CV_{run} < 3$  % is attainable.

NOTE 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

A wide variety of (analytical grade) reagents are candidates for testing the various types of diffusive samplers. Sample desorption (analytical grade) reagents may also be required.

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 wind velocity experiments [eight samplers (plus necessary blanks)] for determining the effect of wind speed  $v$  parallel to the sampler face and also wind speed perpendicular to the face (5.1, 5.7).

**8.2** Verify pressure correction (5.6) 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 [5.1 and annex A (which also includes the wind speed  $v$  effect)].

**8.5** Using four samplers, determine estimates from sampling a 0,5-h exposure to a concentration, followed by immediate closure of the samplers (5.2 and annex A). 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 (5.3) in the presence of manufacturer-stated interfering compounds (including water vapour).

**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 (5.3, 8.6) and wind direction effects (5.7, 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  $A$  [equation (1)], the estimated total imprecision  $CV_{\text{est}}$  is given by propagation of errors in terms of its independent components by:

$$CV^2 = CV_t^2 + CV_s^2 + \alpha_T^2 CV_T^2 + \alpha_h^2 CV_h^2 + \alpha_v^2 CV_v^2 + \alpha_c^2 CV_c^2 \quad (6)$$

where  $CV_T$ ,  $CV_h$ ,  $CV_v$  and  $CV_c$  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 as described in 5.1.2.

**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:

$$\sigma_T = 5 \text{ }^\circ\text{C about } T_0 = 25 \text{ }^\circ\text{C} \quad (7)$$

$$\sigma_h = 5 \text{ mmHg about } h_0 = 10 \text{ mmHg}$$

$$\sigma_v = 0,25 \text{ m/s about } v_0 = 0,50 \text{ m/s}$$

$$CV_c = 30 \text{ \%}.$$

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

NOTE If the respective variabilities are expected to be less than the nominal values given by equation (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 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 Precision confidence limit

The confidence limit on the coefficient of variation (total relative standard deviation)  $CV$  is approximated as follows. First the probability distribution of  $CV_{\text{est}}$  is approximated as  $\chi^2$  via Satterthwaite's approximation [23, 24]:

$$v_{\text{eff}} CV_{\text{est}}^2 / CV^2 = \chi^2 \quad (8)$$

where  $v_{\text{eff}}$  is an effective number of degrees of freedom determined so that the variance of the left side of equation (8) is equal to  $2v_{\text{eff}}$ , the variance of the right-hand side. This approximation then establishes a confidence limit  $CV_{95 \text{ \%}}$  on  $CV$  given by:

$$CV_{95 \text{ \%}} = CV_{\text{est}} / \sqrt{\left[ \chi_{0,05}^2 (v_{\text{eff}}) / v_{\text{eff}} \right]} \quad (9)$$

### 10.3 Accuracy confidence limit

The confidence limit  $A_{95 \text{ \%}}$  on the Busch probabilistic accuracy (3.1) is then given by

$$A_{95 \text{ \%}} = 1,960 \times CV_{95 \text{ \%}} \quad (10)$$

## 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 [19-21] 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 test report of the sampler evaluation:

- a) analytes used for sampler test;
- b) list of the model parameters  $\{\alpha\}$  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 sampler provides a means of detecting breakthrough;
- g) statement as to whether the sampler provides a direct reading or requires laboratory analysis;
- h) statement as to whether the uncorrected |bias| is less than 10 %;
- i) statement as to whether wind direction effects exceed 15 %.

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 [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, the practice does not address sampling in an environment with a correlated combination of high temperature, high humidity and high concentration with interference.

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## Annex A (informative)

### Worked example — Computer program for diffusive sampler accuracy calculation

NOTE Within the following computer program, the decimal point is denoted as “.” to distinguish from “,” which separates elements of arrays.

This annex illustrates the experiments and calculations described in the practice as implemented using the calculational program Mathematica™. The programs given below may be translated from Mathematica as desired. The following (optional) experimental design was used [12] in exposing four samplers per run to toluene vapour for completing 8.3 and 8.4:

Run	$T$ °C	$h$ mmHg	$v$ m/s	$c$ mg/m <sup>3</sup>
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

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 last column,  $c$  (mg/m<sup>3</sup>), averages of active sampling results, are used as reference concentrations.

The following concentration estimates were obtained from the four diffusive samplers in each run using the manufacturer's recommended sampling rate (m<sup>3</sup>/s) and sampling period (s) to convert sampled mass (mg) to concentration (mg/m<sup>3</sup>):

Run	Diffusive sampler-estimated concentrations			
	mg/m <sup>3</sup>			
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

(\* 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 Intersampler Variability, where RSD, in percent, is the coefficient of variation: \*)

```
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 (mmHg) *);
```

```
V0=0.50 (* wind speed (m/s) *);
```

```
Crel0=1.0 (* concentrations relative to the target concentration *);
```

(\* The test conditions [12], expressed as  $\{1, (T-T_0)/T_0, (H-H_0)/H_0, (V-V_0)/V_0, (C-C_{rel0})/C_{rel0}\}$ , are represented for the first five above runs by: \*)

```
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. \*)

(\* Modelled concentration estimate relative to the true (reference) concentration: \*)

$$C_{model}[T\_ , H\_ , V\_ , Crel\_ ] = 1.00 + \alpha[[1]] +$$

$$\alpha[[2]] * (T/T0 - 1) + \alpha[[3]] * (H/H0 - 1) +$$

$$\alpha[[4]] * (V/V0 - 1) + \alpha[[5]] * (Crel/Crel0 - 1)$$

(\* Bias from pulse experiment: \*)

$$BIAS_t = \text{delt} / C_{model}[25., 16.9., 1., 1.] - 1;$$

(\* Assumed environmental uncertainties: \*)

$$RSD_T = 5. / T0;$$

$$RSD_H = 5. / H0;$$

$$RSD_V = .25 / V0;$$

$$RSD_C = .30;$$

(\* Total imprecision: \*)

$$RSD = \text{Sqrt}[BIAS_t^2 / 3 + RSD_s^2 +$$

$$\alpha[[2]]^2 * RSD_T^2 + \alpha[[3]]^2 * RSD_H^2 +$$

$$\alpha[[4]]^2 * RSD_V^2 + \alpha[[5]]^2 * RSD_C^2];$$

(\* Computation of confidence limit on RSD: \*)

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

$$RSD_{run} = 0.035;$$

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

$$cov = \text{betainv} . \text{Transpose}[\text{betainv}] * (RSD_{run}^2 + RSD_s^2 / 4);$$

$$der = (-2/3) * BIAS_t * (BIAS_t + 1)^2 / \text{delt};$$

$$DvarDalpha = \{$$

$$der,$$

$$der * (25/T0 - 1) + 2 * \alpha[[2]] * RSD_T^2,$$

$$der * (16.9/H0 - 1) + 2 * \alpha[[3]] * RSD_H^2,$$

$$der * (0.1/V0 - 1) + 2 * \alpha[[4]] * RSD_V^2,$$

$$der * (1.0/Crel0 - 1) + 2 * \alpha[[5]] * RSD_C^2$$

$$\};$$

$$varVAR = 2 * RSD_s^4 / nu + DvarDalpha . cov . DvarDalpha +$$

$$BIAS_t^2 * RSD_s^2 / 9;$$

$$nuEff = 2 * RSD^4 / varVAR;$$

$$RSD_{95} = RSD / \text{Sqrt}[\text{chisq}[nuEff, 0.05] / nuEff];$$