Accuracy in Measurements using Diffusive Samplers

David L. Bartley
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
4676 Columbia Parkway R-3
Cincinnati, Ohio 45226, United States
phone: 1-513-841-4277 fax: 1-513-841-4500 dbartley@cdc.gov

Katherine C. Irwin
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025
phone: 1-650-859-5648 fax: 1-650-859-4291 katherine.irwin@sri.com

Performance tests for evaluating diffusive samplers have been set up so as to permit the evaluation of a large number of sampler/analytes. Experimentation has been minimized by omitting re-evaluation of the exposure chamber at each sampler evaluation. Furthermore, a single figure of merit, the *symmetric-range accuracy*, is obtained for each sampler/analyte by combining measured sampler environmental sensitivity with a set of nominal environmental characteristics selected with the expected application in mind. The result is a means of deciding sampler suitability by selecting a value for acceptable accuracy. Also, confidence intervals containing measurand concentrations at probability > 95% may be obtained at given confidence (e.g., 95%) in the performance evaluation. A pilot test of the performance protocol is described.

Key words: precision, systematic deviation, reverse diffusion, influence parameters, confidence, tolerance

1. Introduction

Because of their convenience relative to methods employing personal sampling pumps, diffusive samplers have found widespread industrial-hygiene use within the United States' private sector. Similar application within compliance and research agencies is also expected, although in this case the uncertainty in measurement must be carefully documented. Previous evaluation protocols [1-4] for measuring and documenting sampler accuracy were developed essentially from the point of view of sampler design and, as such, are expensive to implement in a production-mode assessment. In order to evaluate a large number of sampler/analytes, the National Institute for Occupational Safety and Health (NIOSH) has developed a streamlined evaluation protocol, which has now been published as parallel standards by the American Society for Testing and Materials (ASTM) [5] and the International Organization for Standardization (ISO) [6].

For documenting measurement uncertainty, the *ISO Guide to the Expression of Uncertainty in Measurement* (GUM) [7] is heavily relied upon. GUM is extended [8] as necessary 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, confidence intervals are specified 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.

As diffusive sampler behavior may depend in part on the environment itself (e.g., on the ambient temperature), true confidence intervals may depend on the environment of application. This protocol sidesteps this problem by adopting specific parameters characterizing nominal environmental variations. The result, together with experimental data on candidate samplers, is a single accuracy value for each sampler/analyte. Therefore, a simple comparison among the samplers is possible. It must be kept in mind, of course, that specific applications may deviate widely from the assumed environmental characterization and would therefore require special consideration.

Another ingredient of this test protocol is the adoption of minimal testing. If only a single sampler were being tested for sampling a single analyte, linear regression on a large number of sampler results under different environmental conditions would be carried out. This would give the needed environmental sensitivities as well as the inter-sampler variability. The residual error in the regression would characterize uncertainty in the exposure chamber itself. Here, however, it is assumed that the chamber is sufficiently characterized that the inter-run uncertainty is known accurately, so that environmental sensitivity can be directly measured using data from a number of experiments equal to the number of parameters to be estimated, i.e., without regression on a large number of data points.

2. Uncertainty characterization

Establishment of confidence intervals mentioned above is simplified through the use of a specific accuracy function of imprecision and bias relative to reference ("true") concentrations C. The accuracy function has been in use for many years by NIOSH [9-11] for evaluating measurement methods. Define the *symmetric-range accuracy*, referred to henceforth as simply the *accuracy* A, as the fractional range, symmetric about the true concentration (*e.g.,* C), within which 95% of measurements are expected to fall. The accuracy A is, therefore, an increasing function $A[bias, RSD]$ of the magnitude of *bias* and the true relative standard deviation RSD, defined in terms of a mean estimate c and the estimate's standard deviation σ as:

$$\begin{aligned} bias &\equiv (c - C)/C \\ RSD &\equiv \sigma/C \end{aligned}, \tag{1}$$

both approximated here as independent of the reference concentration C. Note that in the original ASTM and ISO protocols, it was assumed that sampler bias (due, for example, to inaccurate specification of the sampling rate by the sampler manufacturer) is negligible. Here we propose to use the accuracy function A to account for the effect of *bias* so as to encourage accuracy in stating sampling rates.

A related issue is the pressure-dependence of the sampling rate. This dependence arises, because a change of pressure relates directly to a change in the air's molecular number density and therefore the distance analyte molecules travel before scattering. However, the atmospheric pressure at any one site varies little, and so it is assumed that calibration from one site relative to another is simple enough that this dependence can be corrected effectively. The ASTM/ISO protocols have a simple check for this correction.

The accuracy $A[bias, RSD]$ may be computed from its implicit definition given above. More useful, however, is the following accurate approximation [8], which is simple enough for computing with a hand-held calculator:

$$A = \begin{cases} 1.960 \times [bias^2 + RSD^2]^{1/2}, & |bias| < RSD/1.645 \\ |bias| + 1.645 \times RSD, & otherwise \end{cases}. \tag{2}$$

One application of the symmetric-range accuracy A is the adoption by NIOSH of an accuracy criterion for evaluating methods, recommending that the confidence limit $A_{95\%}$ on the accuracy at confidence level = 95% is less than 25%. For computing the confidence limit $A_{95\%}$, an algorithm similar to an approximation developed by Satterthwaite [12] for confidence limits on linear combinations of independent variance estimates has been found accurate, exhibits negligible effect from the discontinuity in eqn. (2), and is simple to implement. Namely, an estimate $\hat{A}$ [Hats, as here, refer to estimates.] is approximated in terms of a chi-square random variable χ^2_υ for the two cases in eqn. (2) by:

$$\hat{A}/A \approx \begin{cases} \sqrt{\chi_\upsilon^2/\upsilon} & , |bias| < RSD/1.645 \\ \chi_\upsilon^2/\upsilon & , otherwise \end{cases} . \tag{3}$$

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

$$\upsilon = \begin{cases} 2A^4/\mathrm{var}[\hat{A}^2] & , |bias| < RSD/1.645 \\ 2A^2/\mathrm{var}[\hat{A}] & , otherwise \end{cases} . \tag{4}$$

Calculation of $\mathrm{var}[\hat{A}^2]$ or $\mathrm{var}[\hat{A}]$ is straightforward, using any math program which can handle the calculation of matrix inverses, but is left to Appendix A for those readers who need to omit some of the math at this point.

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

$$A_{95\%} = \hat{A} \times \begin{cases} \sqrt{\upsilon/\chi_{0.05,\upsilon}^2} & , |bias| < RSD/1.645 \\ \upsilon/\chi_{0.05,\upsilon}^2 & , otherwise \end{cases} . \tag{5}$$

Another application of the symmetric-range accuracy 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,

$$\frac{\hat{X}}{1 + A_{95\%}} < X < \frac{\hat{X}}{1 - A_{95\%}}, \tag{6}$$

for greater than 95% of the estimates $\hat{X}$. 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).

3. Computing *RSD*

Several assumptions are made about the approximate intended sampler application so as to arrive at a single figure of merit for any candidate sampler. These involve, first of all, characteristics of the environment, including the possibility that the sampling rate may be somewhat sensitive to the concentration sampled (as the diffusion path may lengthen as sorbent is consumed). Secondly, because of reverse diffusion, the amount of analyte sampled over an extended sampling period (e.g., 8 hours) may depend on the time-dependence of the analyte concentration as well as its time-weighted average alone. Finally, inter-sampler variability (due, for example to sampler dimension and analytical variation) may be significant.

assumed nominal sampler application

Research [13-21] into diffusive sampler performance has uncovered possible effects of the ambient temperature, humidity, and wind speed on sampling rate. Together with variation of the analyte concentration, the following values are adopted as representative variance σ_i^2 (where i identifies an environmental variable):

σ_T = 5° C about T_0 = 25° C (temperature)
σ_h = 5 mm Hg about h_0 = 10 mm Hg (humidity)
σ_v = 0.125 m/s about v_0 = 0.25 m/s (wind speed)
RSD_C = 30%. (concentration variation) (7)

For example, σ_T = 5° C corresponds to sampler use (95 % of the time) roughly between 15° C and 35° C. Similarly, σ_V = 0.125 m/s covers the wind speeds (0 to 0.5 m/s) observed in most indoor workplaces [22].

reverse diffusion

In addition to these sensitivities, the effects of *reverse diffusion* must be accounted. Suppose that analyte may evaporate from the sorbent. If the evaporation is significant, then concentration estimates may depend on the time dependence of the concentration sampled. As an extreme case, if the analyte appears as an isolated pulse, then more material may be found on the sorbent if the pulse occurs at the end of the sampling period, rather than at the beginning, where evaporation over the entire sampling period is possible.

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 protocol is set up 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. Note that challenging samplers to 0.5-h pulses is similar to tests suggested by NIOSH [1] and CEN [2].

Let $bias_{\mathrm{pulse}}$ (> 0) represent one-half the bias between estimates from a 0.5-hour pulse at the end vs beginning of the sampling period, relative to the mean of the estimates. Assume, conservatively (see for example [17]), that the bias in the estimates of 0.5-hour pulses occurring at random within (e.g.) an 8-hour sampling period ranges uniformly between $-bias_{\mathrm{pulse}}$ and $+bias_{\mathrm{pulse}}$. Then the variance RSD_{pulse}^2 associated with sampling a 0.5-h pulse at random within the sampling period can be shown to equal:

$$RSD_{pulse}^2 = \tfrac{1}{3} bias_{pulse}^2 . \tag{8}$$

combined uncertainty

The combined relative uncertainty *RSD* can then be expressed as:

$$RSD^2 = RSD_{method}^2 + \sum_{i=2}^{5} \alpha_i^2 \sigma_i^2 + RSD_{pulse}^2, \tag{9}$$

where α_i represents the sensitivity (See Appendix A.) to the i-th environmental variable (eqn. 7), and RSD_{method} represents sampler or analytical variability.

4. Experimental

In order to implement the evaluation protocols, a chamber was designed and constructed for exposing a number of samplers to the various gases or vapors of interest. The chamber is capable of challenging samplers to the potential problems posed by diffusive sampling described above. Environmental parameters, which may be varied include: temperature, pressure, humidity, and wind speed. A pilot sampler evaluation was then undertaken [23] to suggest ways the performance protocol and perhaps chamber could be improved.

inter-run variability

A series of experiments for characterizing the chamber was completed first, prior to evaluating the performance of any diffusive samplers. To this end, seven runs were carried out using a mixture of benzene, toluene, o-xylene, ethylbenzene, and mesitylene with constant generation parameters corresponding to fixed concentrations (neglecting variation in the generation system). In each run, seven active samples (Anasorb CSC) were taken at various points in the chamber.

A result of this experiment is that the active samplers in the mean agreed well with the concentrations as calculated from the generation parameters. Specifically, a mean bias equal to –2.5% was found (active sampler estimates relative to the calculated concentration). The agreement appears to be close enough that the mean concentration as measured by the seven active samplers may be taken as the reference concentration, with the understanding that a run would be voided if for some reason the reference and calculated concentrations differ significantly (e.g., > 5%, as in [3]).

Adopting this point of view, the inter-run variability may be estimated from the variability in the active samplers. Pooling the relative standard deviations of all the active samplers together, an estimate of the relative standard deviation RSD_{run} expected in the average of seven active sampler results per run can be made. It is found that $RSD_{\mathrm{run}} = 2.3\%/\mathrm{Sqrt}[7]$ at the 99% confidence level.

environmental sensitivity, bias, reverse diffusion, and method variability

A series of runs was then carried out with several sampler types to measure sampler *bias*, reverse diffusion, inter-sampler variability, and sensitivities to the environmental parameters. The same mixture of organic compounds listed above was used for testing the following samplers: 3M 3500, SKC 575, and Assay Technology (AT) 541. Four samplers of each type were tested in each of five runs, varying the air speed, pressure, temperature, relative humidity, and concentration level.

A further run with eight samplers of each type was then carried out for estimating the response to 0.5-hour pulses of a mixture of dichloromethane, trichloroethylene, o-xylene, and toluene. All eight samplers were exposed identically for 0.5 hours. Four were immediately capped, whereas the remaining four were permitted to de-gas in lab air for 7.5 hours.

For estimating the concentration of o-xylene or toluene then, the data permitted estimation of sampler *bias* (i.e., the sampling rate) relative to the reference concentrations (measured as the mean of seven active samplers), sensitivities to temperature, humidity, wind speed and concentration, imprecision from extreme time-dependence effects, and method variability with $7 \times 3 = 21$ degrees of freedom. The other compounds in the mixture provided a test of the effect of impurities. All estimates were corrected for deviation of temperature and pressure from that of the sampler calibration.

results

Some of the results of the pilot study are shown in Table 1. Without re-calibration, all but one of the sampler/analyte pairs have the 95%-confidence limit $A_{95\%}$ on the accuracy < 25% and thus would satisfy the NIOSH accuracy criterion. The one failure is easily improved by adjusting the advertised sampling rate as shown in Table 1, where correction factors were selected to reduce *bias* to zero.

Also shown in Table 1 are the contributions (in the form of variances as in eqn. (9)) to the accuracy *A*. The most significant components were $bias^2$, method variability, and the effect of wind speed.

Table 1. Components (variances and $bias^2$) of accuracy (in $\%^2$). Also shown are the symmetric-range accuracy (in %), and 95%-confidence limit $A_{95\%}$ (in %), together with their improvement through correcting the vendor-supplied sampling rates.

source →	*bias*	T	humidity	wind speed	conc	pulse	method	Accuracy	$A_{95\%}$
SKC 575									
o-xylene	327.4	9.7	3.1	19.9	0.2	0.1	8.5	29%	31%
					with 0.847 correction factor:			11%	14%
toluene	65.8	3.3	0.2	17.7	0	0.7	14.1	18%	21%
					with 0.925 correction factor:			11%	15%
3M 3500									
o-xylene	11.3	1.4	0.4	19.0	0	0.3	14.9	13%	18%
					with 0.967 correction factor:			12%	15%
toluene	0.5	0	0.7	23.8	0	0.4	14.8	12%	18%
					with 1.007 correction factor:			12%	18%
AT 541									
o-xylene	11.8	0.8	0	9.2	2.4	0	18.1	13%	17%
					with 0.967 correction factor:			11%	15%
toluene	24.1	0.7	0.7	3.4	2.0	0.0	15.4	13%	16%
					with 1.052 correction factor:			9%	13%

Some of the results of the reverse diffusion test are given under the heading, *pulse*, in Table 1, indicating a negligible effect when estimating o-xylene or toluene concentrations with these samplers. Other results are presented in Table 2, showing a significant effect in the sampling of dichloromethane, selected because of its volatility.

Table 2. Reverse diffusion effect: $|bias_{\text{pulse}}|$ (%).

Sampler	dichloromethane	o-xylene	toluene
3M 3500	5.7%	1.0%	1.0%
SKC 575	2.8%	0.7%	1.4%
AT 541	4.5%	0.3%	0%

5. Conclusions

The purpose of this research was to test and improve a new performance protocol and an exposure chamber for evaluating diffusive samplers of gases and vapors. For instance, the generally small effect of reverse diffusion mentioned above suggests a further streamlining of the tests. A central point of the protocol is to simplify testing so as to make a program of sampler evaluation affordable. Furthermore, a single figure of merit for each sampler/analyte pair is obtained, simplifying decisions as to the suitability of a given candidate sampler.

This work will establish a solid footing for those diffusive sampling methods which are accurate. Furthermore, difficulties with some sampler/analytes will be detected and perhaps easily corrected. Eventually, this type of sampler will be useable in both the private and public sector as a reliable means of assessing the workplace environment.

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Appendix A—Calculation of $\mathrm{var}[\hat{A}^2]$ or $\mathrm{var}[\hat{A}]$

The following model is adopted for analyzing the evaluation experiment data consisting of the 4-sampler mean estimates $\hat{c}_j$ taken in the j-th run (j = 1, … , 5) at reference concentration Cj at relative deviations β_{ji} (i = 2, … , 5) of the environmental parameters around central values. Relative deviations $\hat{\delta}_j$ are given by:

$$\hat{\delta}_j \equiv (\hat{c}_j - C_j)/C_j = bias + \sum_{i=2}^{5} \alpha_i \beta_{ji} + \hat{\varepsilon}_j, \tag{A.1}$$

where α_i are sensitivity parameters.

The random variable $\hat{\varepsilon}_j$ is assumed to be normally distributed about 0 with variance σ^2:

$$\sigma^2 = RSD_{run}^2 + \tfrac{1}{4} RSD_{method}^2, \tag{A.2}$$

reflecting the inter-run variability RSD_{run}^2 and the variability in the mean of four samplers with inter-sampler relative standard deviation RSD_{method}, estimated with υ (e.g., 21) degrees of freedom.

Adopting the convention $\alpha_1 = bias$ and $\beta_{j1} = 1$, eqn. (A.1) is neatly expressed as a vector equation:

$$\hat{\delta} = \beta \cdot \alpha + \hat{\varepsilon}. \tag{A.3}$$

Then given estimates $\hat{\delta}$, the parameters $\boldsymbol{\alpha}$ may be estimated by computing the inverse of the matrix $\boldsymbol{\beta}$:

$$\hat{\alpha} = \beta^{-1} \cdot \hat{\delta}. \tag{A.4}$$

As $\hat{A}$ is a function of $\hat{\alpha}$, the covariance matrix $\mathrm{cov}[\hat{\alpha}]$ is needed for computing variances:

$$\mathrm{cov}[\hat{\alpha}]_{ij} = \sum_{k,l} \frac{\partial \hat{\alpha}_i}{\partial \delta_k} \mathrm{cov}[\hat{\delta}]_{kl} \frac{\partial \hat{\alpha}_j}{\partial \delta_l}. \tag{A.5}$$

Since $\mathrm{cov}[\hat{\delta}]$ is diagonal with elements σ^2, $\mathrm{cov}[\hat{\alpha}]$ can be expressed via the matrix equation:

$$\mathrm{cov}[\hat{\alpha}] = \sigma^2 \beta^{-1} \cdot \beta^{-1T}. \tag{A.6}$$

Finally, $\mathrm{var}[\hat{A}^2]$ and $\mathrm{var}[\hat{A}]$ for use in eqn. (4) are obtained from eqns. (2) and (9) by computing variances of functions $f[\hat{\alpha}]$ as:

$$\mathrm{var}[f[\hat{\alpha}]] = \frac{\partial f[\hat{\alpha}]}{\partial \hat{\alpha}} \cdot \mathrm{cov}[\hat{\alpha}] \cdot \frac{\partial f[\hat{\alpha}]}{\partial \hat{\alpha}}. \tag{A.7}$$