

Tentative Laboratory Performance Specifications

Testing Protocol

and Evaluation Criteria for Passive Samplers

3M 001469

Purpose

The purpose of this work is to define performance specifications and to recommend testing protocols for passive samplers used in determining personal time weighted average (TWA) exposures. Additionally, evaluation criteria for passive samplers and their associated analytical finish have been developed.

Background

Technical information concerning capabilities and limitations is supplied to the user with some passive samplers, while other samplers are furnished with little or no technical information. Even with samplers for which technical information is made available, it is often difficult to determine which sampler is best for a given application because different types of experiments may have been conducted in evaluating the different devices. In some cases, information necessary to conduct successful field surveys is not supplied by the manufacturer (e.g., monitor capacity in multicomponent or humid atmospheres). The intent in developing and making available the attached performance specifications is: for passive monitor suppliers to realize the parameters and the ranges of these parameters over which their sampling devices must operate in order to be acceptable sampling media; to make potential users of passive monitors aware of the critical parameters and limitations associated with these devices; and to alert testing and evaluating laboratories to the necessary areas of consideration for passive monitors. The attached testing protocol provides a recommended experimental

scheme by which suppliers, independent laboratories, and users may evaluate passive monitors to determine their performance characteristics with respect to standard evaluation criteria. The attached evaluation criteria are an adaptation of the sampling and analytical methods validation criteria developed in 1974 for the joint NIOSH/OSHA Standards Completion Program (1). These evaluation criteria are pertinent to passive sampling, unlike the previous criteria which were primarily intended for active (pumped) sampling systems, and did not address some of the factors significant to diffusional or permeation sampling (1,2). Since the two sampling systems, passive and active, function by different mechanisms and therefore have different capabilities and limitations, different performance specifications and evaluation criteria are required.

Passive Samplers

Passive samplers rely on molecular diffusion across a quiescent zone or permeation through a membrane as the means of mass transport of the analyte to the sorbent. Personal passive monitors utilizing each of these mechanisms for the rate limiting diffusive step were reported in the literature in 1973. Palmes and Gunnison (3) devised an open-end tube with a quiescent zone across which the analyte diffused to the sorbent, while Reiszner and West (4) employed a permeable membrane into which the analyte must dissolve, diffuse through, and then out of the other side in order to reach the sorbent. Passive monitors currently on the market employ one of these two principles, diffusion across a quiescent zone or permeation through a membrane, as the rate limiting step.

The mathematics initially used to describe samplers using diffusion across a quiescent zone were limited to the integrated form of Fick's First Law of Diffusion (3):

$$J = (DA/L)(C_0 - C) \quad (1)$$

Where: J = diffusive flux

D = diffusion coefficient of the analyte in air

A = cross-sectional area of the diffusion zone

L = length of the diffusion zone

C_0 = ambient concentration of the analyte

C = analyte concentration at the sorbent surface

If the analyte concentration at the sorbent surface (C) is assumed to be zero (since the sorbent captures the analyte) and all of the analyte that enters the monitor is collected (J = quantity collected, Q) for some exposure time (t), then the first equation conveniently reduces to:

$$Q = (DA/L) C_0 t \quad (2)$$

The DA/L term is the sampling rate and can be calculated from the diffusion constant of the analyte in air (D) and the geometry of the monitor (A and L). While this term does define the sampling rate, it is probable that

draft shields or other mechanisms may inhibit the mass flow somewhat and make the calculated sampling rate only an approximation. Also, the diffusion coefficient is typically an experimentally determined value and as such has some error associated with it and therefore may cause the calculated sampling rate to be different from the actual sampling rate. For this reason, sampling rates for passive monitors must be verified in the laboratory.

Additionally, an assumption was made in using Fick's First Law ($C=0$) that may not necessarily be true. For solid sorbents, the analyte concentration at the sorbent face during sampling will actually be some equilibrium vapor concentration (C_e) of the analyte above the sorbent (i.e. $C = C_e$ instead of zero). After substituting C_e for C and rearranging, equation 1 becomes:

$$J = (DA/L) C_0 - (DA/L) C_e \quad (3)$$

Consequently, when the equilibrium vapor concentration (C_e) of the analyte at the sorbent surface is very low, i.e. the sorbent has a very high affinity for the analyte, the C_e term drops out and equation 3 can be made equal to equation 2. The reverse diffusion term $[-(DA/L)C_e]$ becomes significant for a weakly retained species particularly for the following cases: when the analyte is competing for sorbent sites (e.g. coadsorption of other species, including water vapor); when a high peak exposure is followed for a significant sampling time by no or very low analyte exposure; and when

long storage times occur between exposure and analysis (5, 6). Laboratory verification is necessary to confirm that a passive monitor does not operate under these "reverse diffusion" conditions. For passive monitors incorporating irreversible sorption (the analyte is reacted with the sorbent) the sorbent acts as an efficient collector of the analyte and equation 2 instead of equation 3 applies.

As was already mentioned, passive monitoring may also be accomplished using a permeable membrane as the rate limiting step (4, 7). The flow of a vapor through a membrane can be expressed as:

$$J = DA (C_0 - C_1)/S \quad (4)$$

Where: J = diffusive flux

D = solubility of the analyte in the membrane

A = cross-sectional area of the membrane

C_0 = concentration of the analyte on the exposed side
of the membrane

C_1 = concentration of the analyte on the sorbent side
of the membrane

S = membrane thickness

If the sorbent is an efficient collector of the analyte then $C_1 = 0$ and C_0 is due to the atmospheric concentration of the analyte.

Consequently, the quantity of analyte collected (Q) over an exposure time (t) is:

$$Q = kC_0 t \quad (5)$$

where k is a constant (sampling rate) dependent on properties of the analyte and membrane and the dimensions of the membrane (4, 7).

Note that the sampling rate term of equation 2, providing the length of the diffusion zone (L) does not change during sampling, can be set equal to some constant (k) and the resulting expression is the same as that describing permeation sampling (equation 5). Thus for empirically determined sampling rates, equation 5 may be used for either permeation or quiescent zone diffusion controlled passive samplers.

There are several factors that affect the sampling rate, and subsequently the precision and accuracy of determinations made following diffusional or permeation sampling. Additionally, the nature of the sorbent and the analytical finish used will add some imprecision to the sampling and analysis regimen. Those factors that affect the amount of analyte collected and consequently the determined air concentration will be discussed in the following sections.

General Considerations

Several factors will affect the performance of passive samplers. These include; the sampling rate and its related parameters (linearity, response time, and reverse diffusion), ambient conditions during sampling (face velocity, temperature, humidity, and pressure), and direct sampling interferences (coadsorption, etc.). There are also several factors which must be known for all sampling and analytical methods regardless of whether diffusion, permeation, or a mechanical pump is used to effect the analyte/sorbent contact. These include the analytical range (as determined from the sensitivity and capacity), precision, accuracy, analytical interferences, and stability (including shelf-life before sampling and stability of the analyte on the sorbent after sampling).

The performance specifications, recommended experimental protocol and evaluation criteria are summarized in the following table. Following the table, the individual specifications, experiments, and criteria are discussed.

<u>Performance Specification</u>	<u>Experimental Protocol</u>	<u>Evaluation Criterion</u>
1. <u>Analytical Recovery</u>		
For monitors utilizing desorption, analytical recoveries should be complete and precise	Spike and analyse monitors at each of 4 concentration levels (0.1, 0.5, 1.0 & 2.0 X PEL)*	The means of the recovery for each of the 3 higher levels must be $\geq 75\%$ and the $\overline{CV}_1$ must be $\leq 0.1^{**}$
2. <u>Sampling Rate and Capacity</u>		
Sampling rate should be empirically verified and the maximum recommended sampling time (MRST) determined.	Expose monitors for varying times (80% R.H., 100 fpm, 2 X PEL) prior to analysis. Plot quantity determined vs. time exposed.	The sampling rate (slope of the plot) must be constant over the MRST.
3. <u>Stability During Exposure</u>		
Reverse diffusion should not be significant	Expose monitors at 80% R.H., 100 fpm and 2 X PEL for 50% of MRST, remove and analyze some monitors, analyze others after exposure at 80% R.H., 100 fpm and zero analyte for remainder of MRST.	The different between the means of the two sets of monitors must not exceed 10% at the 95% confidence level

<u>Performance Specifications</u>	<u>Experimental Protocol</u>	<u>Evaluation Criteria</u>
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4. Storage Stability

Monitors should be stable for a reasonable amount of time between exposure and analysis

Expose 3 sets of monitors at 80% R.H., 100 fpm, 1XPEL and 1X MRST and analyze one set on day after exposure, one set after 14 days storage at room temperature and one set after 15 days refrigerated storage

The difference between the means of monitors analyzed on days 1 and 14 or days 1 and 15 must not exceed 10% at the 95% confidence level

5. Performance Factors

The following factors (over the ranges shown) should not affect the quantity of analyte determined

Use 16 run fractional factorial to determine significant factors and interactions

Any factor that causes a statistically significant difference in the recovery at the 95% confidence level must be defined.

<u>Performance Specifications</u>	<u>Experimental Protocol</u>	<u>Evaluation Criteria</u>
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<u>Factor</u>	<u>Range</u>
concentration	0.1-2XPEL
exposure time	0.1-1XMRST
face velocity	20-300fpm
humidity	10-80%RH
interferrent	0-1XPEL
orientation	parallel-perpendicular (to air flow in chamber)

6. Temperature Effects

Variation in quantity determined with exposure temperature should be defined.	Expose monitors to the same analyte concentration and at 10, 25 and 40°C while maintaining a constant (+5% absolute humidity.)	The temperature affect must be defined and correction factors provided if needed
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7. Precision and

Accuracy

Monitors should be precise and accurate over the intended sampling ranges.	Expose monitors at 80% R.H., 100 fpm and 1 X MRST at 0.1, 0.5, 1.0 and 2.0 X PEL. Analyze monitors.	$\overline{CV_T}$ must be acceptable.
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* 2 X PEL = two times the Occupational Safety and Health, Permissible Exposure Limit.

** See Appendix A - Statistical Methodology

1. Analytical Recovery

- a. Performance Specification: For monitors utilizing desorption, analytical recoveries should be complete and precise.
- b. Experimentation: Spike at least six monitors at each of four concentration levels (0.1, 0.5, 1.0 and 2.0 X PEL). Allow at least twelve hours for equilibration then desorb and analyze the monitors.
- c. Evaluation Criterion: The means of the recoveries for 0.5, 1.0 and 2.0 X PEL must not be statistically different (at the 95% confidence level), must be greater than 75% and the $\overline{CV}_1$ must be ≤ 0.1 .
- d. Before investigating the factors affecting analyte collection, it is necessary to verify that the analytical methodology used is accurately determining the quantity of material collected. A means for accomplishing this is by spiking the sorbent material with a suitable solvent containing dissolved quantities of analyte representative of exposures at 0.1, 0.5, 1.0, and 2.0 X PEL, allowing the analyte and sorbent to equilibrate, desorbing and analyzing the sample. Spiking is normally done by pipetting an analyte containing solvent (preferably $<10 \mu\text{L}$) directly onto the sorbent. This method of spiking has been shown to be the most

comparable to dynamic sampling (8). In calculating the quantity of analyte necessary for spiking, a sampling time of 8 hours for TWA measurements or 15 minutes for ceiling exposure measurements should be used. If previous experimentation has shown that an eight hour exposure time is unrealistic because of monitor capacity, this time must be adjusted accordingly but should not be less than one hour for TWA measurements. The sampling rate used in calculating the quantity to spike should be known from previous experimentation or furnished by the monitor manufacturer.

2. Sampling Rate and Capacity

- a. Performance Specification: The sampling rate should be empirically verified and the maximum recommended sampling time (MRST) determined.
- b. Experimentation: Expose monitors for varying times (eg. 1, 2, 4, 6, 8, 10 and 12 hours for TWA samplers and 5, 10, 15, 20, 25 and 30 minutes for ceiling samplers) at 80% R.H., 100 fpm face velocity and 2 X PEL. Analyze at least two monitors for each time period. Plot the quantity of analyte determined versus the time exposed. The capacity (at 2 X PEL and 80% R.H.) is defined as the point at which a 5% deviation in linearity (using goodness of fit statistics) is determined. The MRST is defined as 0.67 times the capacity for single substance monitors and 0.33 times the capacity for multiple substance monitors.

- c. Evaluation Criterion: The sampling rate (slope of the above described plot) must be constant over the MRST. Also, the capacity in units of time at 80% R.H. and 2 X PEL must be defined.
- d. Although sampling rates may be calculated as previously discussed, it is necessary to verify the actual sampling rate in the laboratory. This laboratory verification is necessary for several reasons; the calculated sampling rate has some error associated with it (particularly in the diffusion coefficient), some assumptions were made in developing the sampling rate equation which may not always be true, the use of draft shields or other mechanisms to prevent face velocity effects may alter the sampling rate somewhat and the diffusion coefficient or solubility in the permeable membrane may not be known.

The actual analyte capacity of the monitor may depend on the concentration of analyte in the atmosphere being sampled as well as the presence of other gases or vapors that exhibit an affinity for the sorbent. A concentration level of 2 X PEL was chosen since the monitor capacity is generally lower for high exposure concentrations than low exposure concentrations. Consequently, the capacity at low exposure concentrations will be at least (and may actually be greater than) the capacity determined at 2 X PEL. Since relative humidity levels may vary considerably between exposure sites and the

water vapor may compete with the sorbent for sorbent sites, the "worst case" (i.e. high humidity level) was chosen for investigation. Also, since any of several different substances may compete with the analyte for sorbent sites and reduce the actual capacity, a safety factor was included. This is applied by defining the MRST as two-thirds of the capacity. For multiple substance monitors a safety factor of two-thirds may not be sufficient (9), consequently a factor of one-third is used. The MRST is defined in units of time (hours or minutes) for an exposure concentration of 2 X PEL and a relative humidity level of 80%. In several instances the actual monitor capacity will likely be greater than that defined in this manner however, an MRST as described will give the industrial hygienist a valuable, easy to work with reference.

3. Stability During Exposure:

- a. Performance Specification: Reverse diffusion should not be significant.
- b. Experimentation: Expose at least 20 monitors at 2 X PEL, 80% R.H., and 100 fpm for 50% of the MRST. Remove and analyze 50% of the monitors and expose the others for the remainder of the MRST (no analyte but at 80% R.H., and 100 fpm). Remove and analyze these remaining monitors.

- c. Evaluation Criterion: The difference between the means of the two sets of monitors must not exceed 10% at the 95% confidence level.
 - d. As was previously discussed, reverse diffusion may be significant for weakly retained species. This experiment provides a means of checking to determine if reverse diffusion is occurring for a particular sampling system.
4. Storage Stability:
- a. Performance Specification: Monitors should be stable for a reasonable time period between exposure and analysis.
 - b. Experimentation: Expose three sets of at least 10 monitors per set at 80% R.H., 100 fpm, 1 X PEL and 1 X MRST. Analyze one set of monitors on the day following exposure, one set after 14 days storage at room temperature (~25 °C) and one set after 14 days refrigerated storage (~5 °C).
 - c. Evaluation Criterion: The difference between the means of monitors analyzed within one day of exposure and monitors analyzed after two weeks storage following exposure (for either room temperature or refrigerated storage) must not exceed 10% at the 95% confidence level.

- d. Since there is invariably a lag time between exposure and analysis of sampling devices, the stability of the exposed monitors during this waiting period must be determined. The monitors are tested with both room temperature storage and refrigerated storage. Storage at room temperature is preferred since it eliminates problems that may result in trying to maintain samples at decreased temperatures during shipment to the laboratory. Provision is made in the protocol to examine refrigerated sample storage if recoveries are inadequate following room temperature storage.

5. Performance Factors

- a. Performance Specification: The following factors (over the ranges shown) should not affect the quantity of analyte determined.

<u>Factor</u>	<u>Range</u>
concentration	0.1 - 2 X PEL
exposure time	0.1 - 1 X MRST
face velocity	20 - 300 fpm
humidity	10 - 80% R.H.
interferent	0 - 1 X PEL
orientation	parallel - perpendicular (to air flow in chamber)

- b. Experimentation: Use a 16 run fractional factorial experimental design to determine significant factors and two factor interactions. Use at least 4 monitors per run.
- c. Evaluation Criterion: The operational (functional) range for any factor that causes a statistically significant difference in the recovery (at the 95% confidence level) must be defined.
- d. Ambient conditions during exposure should have minimal effects on results determined with passive monitors. Specifically, there are desired ranges for factors affecting the sampling rate over which the monitors should properly function. These factors and their desired operational ranges are analyte concentration (0.1 - 2 X PEL), exposure time (0.1 - 1 X MRST), face velocity (20 - 300 fpm), temperature (10-40 °C) and interferences (relative humidity, 10-80% R.H. and chemical or analytical, 0 - 2 X PEL). These factors may all be evaluated using a fractional factorial experimental design with a significance level of 0.95 (10).

Knowledge of the analyte concentration range and the exposure time range over which a monitor properly functions is necessary for the industrial hygienist conducting the sampling. Face velocities may vary significantly in the workplace and may lead to undersampling

(at low face velocities starvation may occur) or to oversampling (at high face velocities turbulence may occur in the quiescent zone). The range of 20-300 fpm should effectively bracket the range of face velocities encountered in a typical workplace. Convection induced currents alone have minimum velocities of 10 to 20 fpm (11) and when combined with other causes of air movement (heating and cooling, ventilation, and personnel and equipment movement) most likely result in minimum face velocities of greater than 20 fpm. The velocity of air striking a worker in an indoor facility is very likely less than 300 fpm. This corresponds to the face velocity created by briskly walking (3.5 miles/hour) in still air. For routine outdoor use, the monitors should be investigated at face velocities of up to 1800 fpm (20 miles/hour).

There are two principal types of interferences that may cause problems in sampling and analysis with passive monitors. These are competition of the analyte with another substance for the sorbent (coadsorption) and substances that react with the sorbent or react during analysis to give an erroneous measurement (chemical interference). Moisture (humidity) is a potential coadsorbent which may change daily and will certainly be different for different processes and facilities. It must be investigated over the range where it will most likely be encountered (10-80%.)

In addition to moisture, other gasses or vapors may be present during sampling and compete for the sorbent in adsorption type monitors. For this case, a material should be chosen which is known to have some degree of affinity for the sorbent which will likely be present during sampling. This material should be investigated at concentrations of 0 and 1 times the PEL to determine if it causes an erroneous measurement. For absorption type monitors, a suspected analytical interference should be chosen as something that would likely be present during sampling and investigated at a concentration range of 0 to 1 times the PEL.

If the 16 run fractional factorial provides insufficient data to determine the useful (operational) range of significant factors, then these factors must be further investigated to determine this useful range. If more than one factor requires further investigation then a second quarter replicate (16 run fractional factorial) is probably the most efficient experimental scheme and should be used.

6. Temperature Effects

- a. Performance Specification: The variation in quantity of analyte determined with exposure temperature should be defined.

- b. Experimentation: Expose at least 10 monitors at each of 3 temperature levels (10, 25, and 40 °C) at 1 X PEL, 100 fpm, and 1 X MRST while maintaining a constant ($\pm 5\%$) absolute humidity.
- c. Evaluation Criterion: The temperature effect must be defined and a correction factor provided if needed.
- d. Temperatures will vary in workplace environments and the diffusion coefficient (for quiescent zone sampling) varies proportionately to temperature raised to the 1.5 power. However, the gaseous volume also varies with temperature such that the concentration on a mole per unit volume basis varies inversely with temperature (12, 13). Consequently, the quantity of material sampled varies as a function of temperature to the 0.5 power. This may be perturbed depending on the effect of temperature on the material used for draft shields and on the sorbent/analyte affinity. For permeation type monitors, temperature effects are due to the nature of the permeable membrane and may be quite large or small depending on the material used (4).

7. Precision and Accuracy

- a. Performance Specification: Monitors should be precise and accurate over the desired sampling range.

- b. Experimentation: Expose monitors (at least 6 per concentration level) to 0.1, 0.5, 1.0 and 2.0 X PEL, 100 fpm, 80% RH and 1 X MRST. Analyze the monitors and calculate the $\overline{CV_T}$.
- c. Evaluation Criterion: CV_T for 0.5, 1.0 and 2.0 X PEL (for six samplers at each concentration level) must be less than or equal to 0.105 for a non-biased system. The critical $\overline{CV_T}$ for a biased system is taken from Figure 1. Bias is determined as the difference between the average of the values obtained for the independent methods and the values obtained with the passive monitors.
- d. The precision and accuracy of the sampling and analytical method (over the range of 0.1 to 2.0 times the PEL) must be defined and should be such that the determined concentration will be within +25% of the true value 95% of the time. The 0.1 concentration level is included in the experimentation in order to obtain some degree of confidence in measurements taken at this level. It is not included as a requirement in the evaluation criterion since the criterion is concerned primarily with the precision near the standard.

Use of the Specifications, Protocol and Criteria

Reference values are determined as the average of two independent methods. Analyte concentration in the chamber determined by these two mechanisms must agree within at least 5%. The independent methods should be NIOSH Class B or better methods (if they exist), a calibrated instrument with demonstrated accuracy and stability of calibration, or the calculated chamber concentration. If permeation tubes or certified gas cylinders are used, the permeation rate of the tube or the cylinder concentration should be verified on a routine, periodic basis.

In many cases four concentration levels are utilized in the experimentation, however, successful completion of only the three higher levels are necessary to meet the evaluation criteria. The protocol/criteria were established in this manner so that monitors which perform satisfactorily at these low levels ($0.1 \times \text{PEL}$) will be evaluated and consequently usable with some degree of confidence at these concentration levels. Monitors which do not perform satisfactorily at these low levels but are acceptable at the other three levels (0.5 , 1.0 and $2.0 \times \text{PEL}$) should be also be considered evaluated and consequently usable for the indicated concentration levels.

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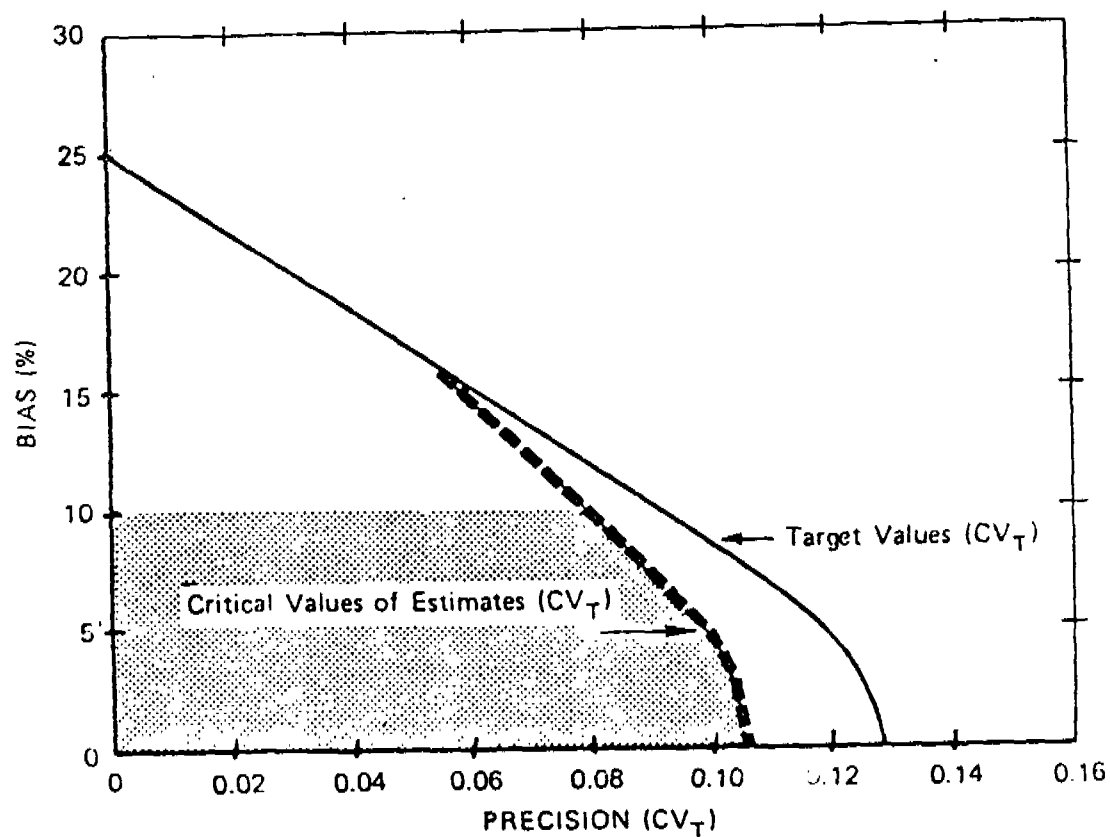


FIGURE 1. COMBINATIONS OF CV_T AND BIAS WHICH YIELD NET ERRORS (Sampling and Analysis) OF 25% OR LESS AT LEAST 95% OF THE TIME

The critical estimates curve shown is for three sets of six samples. This curve will be slightly different for larger sample sizes.

Appendix Mathematics and Statistics Used in Evaluation

The statistics used are essentially those described in references 1 and 2 adapted for passive monitors. These statistics are based on the assumption that the total sampling and analytical error should be less than 25% for at least 95% of the samples analyzed at levels of 0.5 - 2.0 times the PEL. In order to meet this accuracy requirement the experimentally determined total coefficient of variation ($\overline{CV}_T$) must be less than 0.105 for an unbiased method (1). For a biased method, the critical $\overline{CV}_T$ is reduced according to the graph in Figure 1.

Definitions:

Mean = $\bar{x}$ = arithmetic average
 n = number of observations

$$\text{standard deviation} = s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

$$\text{Coefficient of variation} = CV = s/\bar{x}$$

CV_1 = CV of the 6 spiked samples at each concentration level.

CV_2 = CV of the 6 generated samples at each concentration level.

$$\text{Pooled coefficient of variation} = \overline{CV} = \sqrt{\frac{\sum_{i=1}^3 f_i (CV_i)^2}{f}}$$

where: f_i = degrees of freedom ($n-1$) at each concentration level
 CV_i = CV of the observations at the i th concentration level
 i = index for the three concentration levels
 $f = \sum_{i=1}^3 f_i$

$\overline{CV}_1$ = pooled CV based on the spiked samples at 0.5, 1.0 and 2.0 X PEL (6 samples at each level)

$\overline{CV}_2$ = pooled CV based on the generated samples at 0.5, 1.0 and 2.0 X PEL (6 samples at each level)

$\overline{CV}_T$ = pooled CV for sampling and analysis and desorption efficiency *

$$\overline{CV}_T = \sqrt{(\overline{CV}_2)^2 + 0.1667 (\overline{CV}_1)^2}$$

Grubbs test (1,2) should be used to determine if an observation should be rejected as an outlier and Bartlett's test for homogeneity of CV's (1,2) should be applied to determine the feasibility of pooling the CV's. Chi-squared must be less than 9.21 to pass Bartlett's test at the 1% significance level (1,2).

*Note that an assumed pump error of 5% is not used in these calculations since pumps are not used with passive monitors and sampling error will be a part of $\overline{CV}_2$