Technical Report: Design Rationale, Validation Scheme, and Test Results - Organic Vapor Monitor

RATIONALE - Increased Requirements for Monitoring

Recent increased use of Diffusive (personal) Monitors by industrial hygienists is attributable to their efficiency versus other samplers in acquiring statistical data to demonstrate an employer's degree of compliance with Exposure Limits (ELs).

BACKGROUND – Validation Parameters of NIOSH, EC, ANSI, & ASTM Protocols

To verify the performance of Diffusive Samplers, NIOSH drafted a Validation Protocol which served as a prototype for more advanced protocols developed by the European Community (EC), the American National Standards Institute (ANSI), and the American Society for Testing and Materials (ASTM). While differing in their statistical approach, the protocols all answer essentially the same performance questions using a common set of Evaluation Parameters as follows.

(1) Verify % Recovery from Sampler; (2) Verify Sampling (Uptake) Rate

3. **Verify Effect of Environmental Factors on Accuracy**

Air Velocity/Orientation; (b) Temperature; (c) Humidity; (e) Interfering Substances

Determine Loss (if any) of Analyte from Sampler (Reverse Diffusion or Decomposition)

(a) During Sampling; (b) During Storage or Transport to Lab

This Protocol utilizes statistical parameters employed in the Draft ANSI Protocol dated 2-1-98.

(1) METHOD for % RECOVERY or De-Sorption Efficiency

Back Method **– Place charcoal wafer from a Sampler into a glass vial containing a measured volume of analytical solvent spiked with a known quantity of Analyte and close the vial with an inert closure. Similarly treat a control containing an identical quantity of Analyte and solvent with no charcoal. After agitation for 3 hours, analyze the samples via gas chromatography. Perform in triplicate at three concentration levels.**

Forward Method **– Place one charcoal wafer from a Sampler into a glass vial fitted with a gas-tight septum valve. Spike the Wafer through the septum valve with a known quantity of Analyte using a microsyringe. Close the valve and allow to equilibrate for 15 minutes. Then, open the valve and add a measured volume of analytical solvent. Similarly treat a control containing an identical quantity of Analyte and solvent with no charcoal. After agitation for 3 hours, analyze the samples via gas chromatography. Perform in triplicate at three concentration levels.**

Determination of De-Sorption Efficiency **- Calculate De-Sorption Efficiency (DE) as follows.**

$$\text{De-Sorption Efficiency (DE)} = \frac{\text{[Analyte Found (µg), charcoal]}}{\text{[Analyte Found (µg), control]}}$$

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(2) METHOD for UPTAKE (SAMPLING) RATE Verification

Uptake (Sampling) Rate of an Analyte by a Diffusive Sampler is determined only by the sampler's geometry and the diffusion co-efficient of the Analyte. In practice, the measured Uptake Rate may be affected by Environmental Parameters, Evaporative Losses, or Decomposition, so it is prudent to verify this parameter by calibrating the sampler in exposures to known contaminant levels near the EL. The Uptake Rate, calculated from the *quantity of Analyte collected per unit of Exposure,* is expressed as the *Sampling Rate* (in *ml/minute*) of air required to collect the same quantity of Analyte by active sampling.

Generate Analyte levels using a commercial Exposure Chamber (See Appendix) incorporating inert inner surfaces and utilizing a humidity-controlled Flow Generator, Analyte Vaporizer, Temperature Controller, and Reference Ports for active sampling. Estimate Analyte Concentration from the Analyte Delivery Rate/Air Flow generated by the system using the following equation:

$$\text{ANALYTE LEVEL } (22^{o}C) = \frac{\text{(Analyte Delivery Rate in } \mu g/hr) \times (24.2\ \mu l/\mu mole)}{\text{(Air Flow in } l/hr) \times \text{(Molecular Wt in } \mu g/\mu mole)}$$

Confirm Analyte Concentrations by Active Sampling using the same media (charcoal), sampling interval (time), and analytical method (Gas Chromatography) used for the Diffusive Samplers under test.

Place 4-6 Samplers in each of 4-8 separate Exposure Tests which bracket the range of 0.5-2.0 times the Exposure Limit and which include the shortest and longest Recommended Sampling Time (RST).

In conjunction with each Exposure Test, analyze the Active and Diffusive Samplers using the same analytical process. Determine the Uptake (sampling) Rate as follows:

$$\text{UPTAKE RATE } (ml/min) = \frac{[1000]\,[M]\,[R]}{[DE]\,[MW]\,[C]\,[T]}$$

M = Ave. Mass Analyte found per Diffusive Sampler (μ *g*)

R = Ideal Gas Constant = 24.2 L / MOLE @ 22°C

DE = De-Sorption Efficiency (fraction)

MW = Molecular Weight of Analyte (*g/mole*)

C = Ave. Analyte Concentration determined by Active Sampling (*ppm*)

T = Time of Exposure/Sampling (*min*)

Compare the Uptake Rates determined at short and long sampling times and at low and high Analyte concentrations to determine the effects of varying concentrations and times. Use the average of all acceptable Exposure Tests to compute the Mean Uptake Rate.

Uptake Rates for Analytes not subjected to Exposure tests may be estimated by an interpolation method which uses the molecular volume along with experimental Sampling Rates determined for chemically analogous Analytes. (See Appendix)

(3) METHOD for ENVIRONMENTAL EFFECTS – Air Velocity, Orientation, Temperature

Air Velocity, Orientation, and Temperature effects on Diffusive Samplers have previously been shown to be attributable mainly to physical factors and relatively independent of the particular Analyte being sampled. Accordingly, it has become customary to conduct these tests using a few "representative" Analytes and to interpret the results as generally applicable to the particular sampler regardless of the Analyte being sampled. This approach has been recognized as valid by the ANSI and ASTM protocols.

Select the extreme, minimum and maximum, conditions over which Air Velocity, Orientation, and Temperature will be varied, typically as follows:

Air Velocity – 15, 100, & 150 cm/sec

Temperature - 10°C, 25°C, and 40°C

Orientation –

Face Normal to Air Flow

Sampler Face Tangential to Air Flow

Generate Exposure Tests as described under Part (2) in which 4-6 Samplers are placed in each of two Exposure Tests performed at identical Exposure Levels of Analyte near the Exposure Limit but at the extremes of the environmental parameter values to be studied.

Normalize results for Analyte concentration differences between Exposure Tests and compare the extreme conditions (e.g. results for 15 *cm/sec* vs 150 *cm/sec* and results for 10^{o}C vs 40^{o}C) to determine the significance of environmental effects. If a significant effect is observed, perform an additional test at a value of environmental parameter in between the extreme conditions and estimate the trend.

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(3e) METHOD for ENVIRONMENTAL FACTOR EFFECTS – Potentially Interfering Substances

Activated carbon (charcoal) has been shown to sample and retain more than 200 organic chemicals, the ability to analyze one Analyte in the presence of many others is much more *dependent upon the nature of the analytical method used* than upon the nature of the sampler. When gas chromatography is used to analyze samples collected on charcoal, the issues are essentially the same whether active sampling (charcoal tubes) or passive (diffusive) sampling is employed.

To minimize the effects of potentially Interfering Substances with respect to the AT541 and AT546 Monitors, Assay Technology has chosen a gas chromatography method which is an extension of OSHA Method #7 utilizing a high-resolution separation on dual capillary gas chromatography columns (60 m x 0.32 mm) in which the identity and quantity of each analyte determined on each chromatography column is compared before a result is reported. (see Appendix)

Determine chromatography retention parameters for each contaminant which may be present in the environments in which sampling will take place to determine if any contaminants may co-elute with the Analyte of interest on the chromatography columns specified in the analytical method. Perform analysis of each Analyte tested separately from each injected sample on two chromatography columns, separately calibrated. The quantitative analysis of Analyte on separate columns should agree within $\pm$10% if other substances present do not interfere. A lack of interference is demonstrated if the Analyte can be analyzed independently on two chromatography columns with agreement within $\pm$10%.

(3c)METHOD for ENVIRONMENTAL FACTOR EFFECTS – Humidity

Since the effects of variation of relative humidity on results obtained in Diffusive Sampling have been shown to be interactive with sample capacity effects, humidity effects have been included together with tests for detecting Evaporative Loss of Analyte (also known as Reverse Diffusion) which normally occurs when the Sampler's "capacity" for a particular analyte is exceeded.

Select the extreme, minimum and maximum, conditions over which Humidity will be varied, typically 20RH & 80%RH. Generate Exposure Tests as described under Part (2) in which 4-6 Samplers are placed in each of two Exposure Tests performed at identical Exposure Levels of Analyte near the Exposure Limit but at the extremes of Humidity to be tested.

Normalize results for Analyte concentration differences between Exposure Tests and compare the extreme conditions (e.g. results for 20%RH vs 80% RH) to determine the significance of environmental effects. If a significant effect is observed, perform an additional test at a value of environmental parameter in between the extreme conditions and estimate the trend.

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(4) METHOD for REVERSE DIFFUSION EFFECTS - Losses of Analyte from Sampler

In this test, a group of Samplers exposed at or near the Exposure Limit for a short period of time (e.g., 1-2 hours) is split into two sub-groups, one of which is analyzed immediately, while a second sub-group is left to sample for a longer duration (e.g. 4-8 hours) in an environment with zero exposure to Analyte.

To the extent that Sampler is susceptible to Evaporative Loss (Reverse Diffusion) due to its having exceeded its capacity for a volatile Analyte, the second sub-group which has been exposed to "zero air" for a long period of time will contain less Analyte than the first sub-group which was analyzed immediately after the actual exposure.

To pass the Reverse Diffusion challenge, the average quantity of Analyte recovered from the "challenge" samples exposed at the PEL must not be more than 10% less than the average quantity recovered from controls when experimental error has been taken into account.

DESIGN CONSIDERATIONS – Avoiding Loss of VVOCs (Very Volatile Organic Compounds)

Air sampling methods for VVOCs (e.g. methylene chloride, butadiene, vinyl chloride, methyl bromide, propylene oxide, vinyl acetate, etc.) have often been revised with an eye toward improvements which would minimize evaporative losses leading to underestimation of exposures. Improvements have often focused on increasing the mass of carbon in the sampling train. Thus, jumbo tubes and multi-tube sampling trains have proven popular for air sampling of very volatile contaminants.

While increasing the quantity of charcoal media used has become popular, an equally valid approach would be to hold the quantity of charcoal media constant while decreasing the volume of air sampled. In practice, the goal of *increasing the ratio of charcoal mass to sample volume is achieved either by increasing charcoal mass or by decreasing the air volume sampled.*

The approach of increasing the mass of charcoal media has disadvantages, namely, that extra solvent is required to analyze larger quantities of charcoal, and extra tests are required to analyze the second stage of a multi-stage sampler. With modern instrumentation, analytical sensitivity is not a problem; thus, *a sample of equal quality can be collected on a small charcoal mass by reducing the sampling rate so as not to exceed the capacity of activated carbon for very volatile analytes.*

This can be understood mathematically as follows.

Sample Capacity Ratio (CR) = ***(QTY Charcoal) / (Sampling Rate)***

To maximize the Sample Capacity Ratio (CR), *one would like to collect as little analyte as possible* per gram of charcoal consistent with preserving the lab's ability to detect exposures as low as 1% of the PEL.

Assuming the lab's ability to detect 0.2 microgram per sampler using current technology, and assuming sampling times of 8 hours (PEL) and 15 minutes (STEL), one can calculate from the following equation the Detection Limit, in ppm, which could be achieved at substantially lowered Sampling Rates as follows.

$$[\text{Detectable Conc}_{\text{typical}} ppm] = \frac{[\text{Detectable Mass}_{\text{typical}} \mu g][24.2\ L./mole][1000\ mL/L]}{[\text{MolWt}_{\text{typical}}\ g/mole][\text{Sampling Time}_{\text{typical}}\ min][\text{SampRate}\ (mL/min)]}$$

= [0.2 μ *g*][24.2 μ *L/μ mole*][1000 *mL/L*]} / {[100 μ *g/μ mole*] [480 *min*][8 *ml/min*]} = 0.01 *ppm*

= [0.2 μ *g*][24.2 μ *L/μ mole*][1000 *mL/L*]} / {[100 μ *g/μ mole*] [15 *min*][8 *ml/min*]} = 0.4 *ppm*

SAMPLE CAPACITY of the ChemDisk™ Monitor

Beginning with a fine-pore, coconut charcoal of high surface area with an adsorption isotherm facilitating adsorption of small molecules, Assay Technology has developed a process for manufacturing charcoal wafers having very low levels of background impurities. The "cleaned" charcoal wafer combined with advanced GC and HPLC instruments which can detect low analyte levels made it possible to utilize lowered Sampling Rates *(70-90% lower than traditional monitors)* in combination with a substantial charcoal reservoir (ca. 190 mg) to produce a Diffusive (personal) Monitor for volatile organics having the highest available Sample Capacity Ratio (CR) as follows.

Monitor No	Sampling Rate (a)	Capacity Ratio (b)	Typical Applications (c)
Monitor 541 High Sampling Rate	6-14 *ml/min*	14-32 *mg* charcoal per *ml/min* of Sampling Rate	15-min STEL Monitoring; 8-hr TWA Monitoring if PEL < 5 ppm
Monitor 546 High Sample Capacity	1.5-3.5 *ml/min*	55-130 *mg* charcoal per *ml/min* of Sampling Rate	8-hr TWA Monitoring if PEL > 5 ppm especially if b.p. < 80❍ C
Traditional OV Monitor	20-40 *ml/min*	3-5 *mg* charcoal per *ml/min* of Sampling Rate	1-4 hr TWA Monitoring for VOCs 8-hr TWA for VOCs if b.p. > 80❍ C

a. **Sampling Rate (SR) proportional to diffusion co-efficient for each analyte.**

b. **Capacity Ratio = (Qty of Charcoal) / (Sampling Rate).**
c. **These are "typical" applications ... for specific recommendations for each Analyte, see Lab Request Form.**

SAMPLE CAPACITY Limitations in the Sampling of VVOCs

It has been demonstrated that activated carbon has a specific capacity for adsorption which varies with each compound, and when this capacity is exceeded, there is a tendency for the compound to evaporate from the charcoal (known as "break through" in the case of a respirator cartridge or sampling train). The following Table, listing a number of VOC and VVOCs, indicates the quantity of Analyte (contaminant) which will be collected by different air sampling methods in comparison to the capacity of charcoal (estimated by the PACS method).

SAMPLE CAPACITY LIMITATIONS in the Sampling of VOCs by Several Methods

				Predicted Activated	Capacity of Carbon (a)	Qty of	Analyte @10ppm	Found on for 8 hour	Sampler
Name Of VVOC	b.p.	CAS No	Mol Wt	@10ppm (50%RH)	@10 ppm (75%RH)	AT 541 Sampler	AT 546 Sampler	3M 3500 Sampler	Charcoal Tube/Pump @25ml/min
	oC		g/mole	μ g/100mg	μ g/100 mg	*μ g/100 mg*	*μ g/100 mg*	*μ g/100 mg*	*μ g/100 mg*
Ethylene Oxide	11	75-21-8	44.05	5	1	***42***	***11***	***349***	***218***
Chloromethane	-24	19961-13-8	50.49	13	4	***52***	13	***401***	***250***
Bromomethane	4	74-83-9	94.94	92	22	93	23	***770***	***471***
Vinyl Chloride	-13	75-01-4	62.50	203	48	44	11	***506***	***310***
Propylene Oxide	34	75-56-9	58.08	918	288	37	9	***434***	288
Dichloromethane	40	75-09-2	84.93	1,731	654	49	12	***638***	421
Butadiene	4	106-99-0	54.09	1,740	717	81	20	459	268
Diethyl ether	35	60-29-7	74.12	3,740	1,900	71	18	541	368
1,1-Dichloroethylene	30	75-35-4	96.94	5,809	2,700	62	15	729	481
Chloroform	61	67-66-3	119.38	10,224	4,940	100	25	793	592
1-Bromopropane	71	106-94-5	123.00	8,000(est)	5,000(est)	72	18	976	610
Vinyl Acetate	72	108-05-4	86.09	8,560	5,200(est)	86	21	611	427
n-Hexane	69	110-54-3	86.18	11,158	9,260	59	15	547	427
Cyclohexane	81	110-82-7	84.16	9,151	6,800	70	18	541	417

If *Qty on Sampler* significantly exceeds capacity (50%RH), quantity is printed in bold, italics. (e.g., *349*)

(a) Activated Carbon adsorption parameters taken from "VOC Adsoption", PACS, Coraopolis, PA