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Monitoring methodology for gaseous hazards

Passive monitors and portable instruments

by Mary L Woebkenberg, MS [1]

WOEBKENBERG ML. Monitoring methodology for gaseous hazards: Passive monitors and portable instruments. *Scand j work environ health* 9 (1983) 223—229. Reliable sampling and analytical procedures for monitoring workplace hazards must be developed and evaluated. In the present communication three studies involving the evaluation and development of personal monitoring techniques were presented. The first study described an evaluation of three passive monitors for organic solvent vapors. Toluene, trichloroethylene, n-hexane, acetone, methylene chloride, and vinyl chloride, each at three concentrations, as well as effects of temperature, humidity, linear adsorption capacity, variable concentration, complex solvent mixture, and storage time, were addressed. The results indicated that under specified conditions passive monitors are viable monitoring methods. The second study was an evaluation of two carbon monoxide dosimeters. Instrument accuracy, precision, and performance under a variety of experimental conditions were examined. Sufficient samples were taken to show that the Energetics Science series 9000 dosimeter was within ± 25 % of the true value 95 % of the time. The General Electric model 15ECS1CO2 did not meet this same criterion. The third study describes the development of a unique sampling method for nitrogen dioxide using Poroplastic® film impregnated with the absorbing liquid and a spacing material which allows for airflow and distribution to the absorber. The overall method, evaluated over the concentration range of 0.9 to 19 μg/l in 36-l samples, had an average bias of 7 % with a coefficient of variation of 10 %.

Key terms: carbon monoxide, diffusion, nitrogen dioxide, organic vapors, permeation, personal monitoring.

Among the responsibilities of the National Institute for Occupational Safety and Health (NIOSH) is the task of providing accurate sampling and analytical methodologies for monitoring worker exposure to concentrations of hazardous substances in the workplace. To accomplish this task, the Institute has an active research program in the development and evaluation of personal monitoring methods. The results of three recently completed studies are presented in this report.

[1] Division of Physical Sciences and Engineering, National Institute for Occupational Safety and Health, Cincinnati, Ohio, United States.

Reprint requests to: Ms ML Woebkenberg, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226, USA.

Passive organic vapor monitors

The first study (2) involved an extensive laboratory evaluation of three commercially available passive organic vapor monitors: the 3M company's Organic Vapor Monitor, the Abcor (now National Mine Service) Gasbadge, and the REAL Inc MiniMonitor. The first two are diffusion controlled devices, while the MiniMonitor is permeation controlled. This study had the following four main goals: (i) to conduct specific tests on the monitors, (ii) to evaluate performance characteristics of the passive monitors, (iii) to recommend a set of quality control standards, and (iv) to provide recommendations of the best techniques for use of the passive monitors.

All experiments were conducted in a dynamic, partially recirculating exposure chamber with a total internal volume of

3 m^3 (fig 1). The nominal test conditions were exposure time 7 h, temperature 25 °C, relative humidity 80 %, and face velocity 0.51 m/s. The monitors were exposed to each of six compounds, individually, at three concentrations. The compounds studied included toluene, trichloroethylene, n-hexane, acetone, methylene chloride, and vinyl chloride. The precision and accuracy of the monitors were determined, as well as the effects of temperature, humidity, variable concentration, complex solvent mixture, and storage time.

Table 1 presents data from the complex solvent mixture experiment, which illustrated that, for stably adsorbed compounds such as toluene, the passive monitors accurately measured the challenge concentration, while the same was not true for highly volatile compounds. In fact the data suggest the presence of preferential adsorption due to competition for adsorptive sites between the compounds. The presence of dissimilar compounds at varied concentrations may affect individual monitor capacity and therefore cause displacement of specific compounds. The differences in the design of the individual monitors, type of charcoal utilized, quality control, type of adsorption pad, particle size of the charcoal, the surface area and amount of charcoal, and

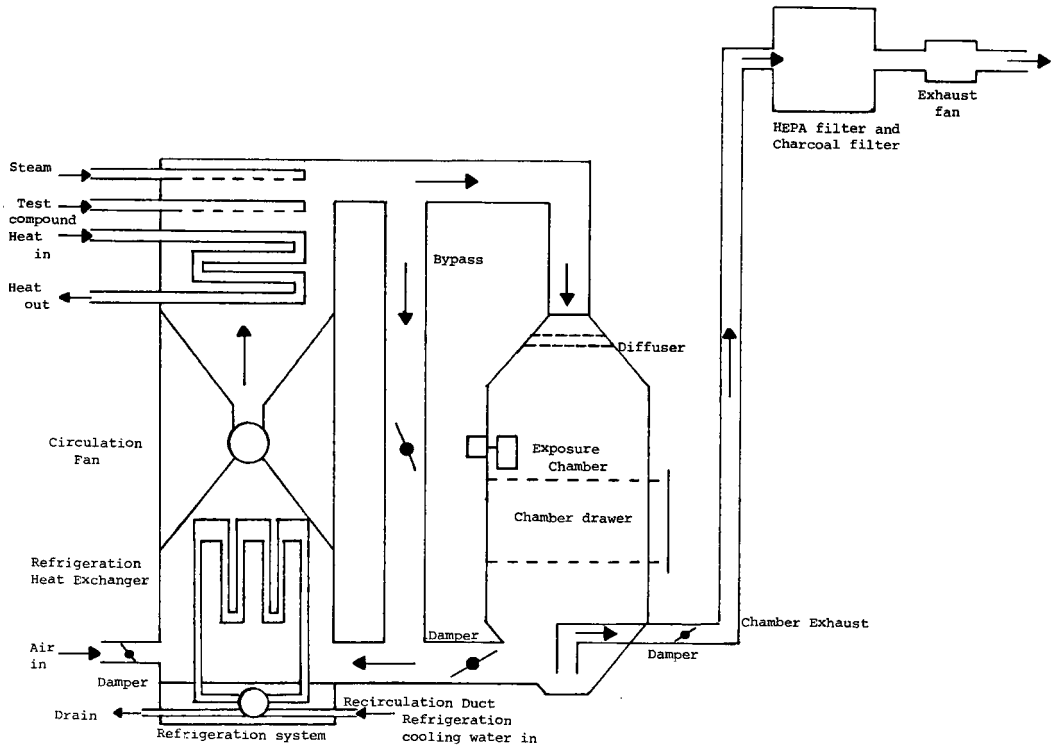

Fig 1. Schematic representation of the exposure chamber system.

Table 1. Complex organic mixture exposure.

Compound and true concentration	3M 3500 Organic Vapor Monitor		Gasbadge		MiniMonitor	
	Mean	SD	Mean	SD	Mean	SD
Hexane (20 ppm)	20.5	0.39	6.82	1.01	17.5	0.79
Acetone (10 ppm)	10.2	0.47	2.28	0.09	None detected	
Methylene chloride (10 ppm)	1.40	0.12	None detected		11.3	0.62
Trichloroethylene (25 ppm)	27.0	0.63	14.4	2.83	27.7	2.25
Toluene (50 ppm)	54.8	1.60	58.2	2.02	54.2	5.90

membrane or draft shield create a unique performance for each monitor with respect to the compounds tested. The passive monitoring of compounds with a low boiling point is best accomplished with multiple, short-term samples.

The exposure interval effect on monitor loading and the monitor-indicated concentration was studied with toluene, trichloroethylene, and vinyl chloride in separate experiments at two different concentrations each. In each experiment, one of each brand of monitor was removed from the exposure chamber at 0.5, 1, 2, 3, 4, 5 and 6 h. Six of each type of monitor were removed after the full 7 h. Fig 2 and 3 show representative results of a trend toward a decrease in the rate of analyte collection with increasing exposure interval.

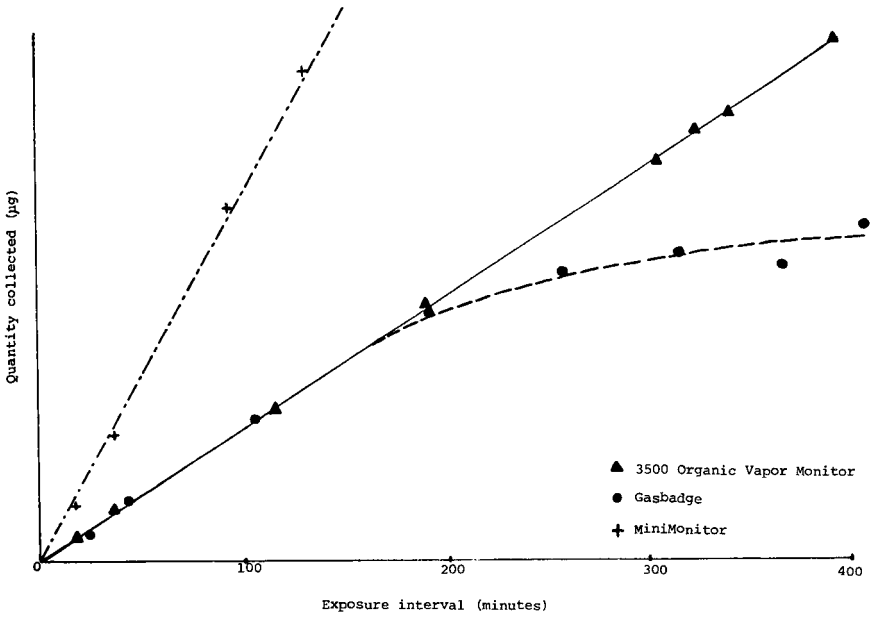

Fig 2. Exposure interval effect on the passive monitor collection of toluene at high concentrations.

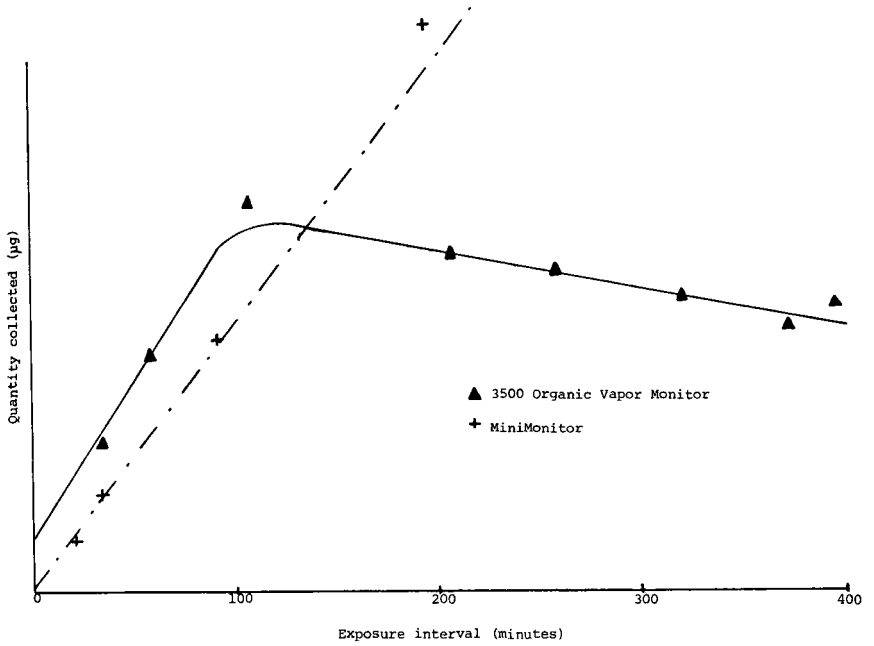

Fig 3. Exposure interval effect on the passive monitor collection of vinyl chloride at high concentrations.

Some studied variables had predictable effects upon the passive monitor-indicated concentrations. High relative humidity, for instance, resulted in a reduced monitor-indicated concentration since activated charcoal adsorption capacity is lowered at high humidity, and the collection elements in all of these monitors are activated charcoal. Temperature did not seem to have a great effect on the monitor results although its actual influence may have been masked by the effects of humidity. Corrections for temperature, as directed by the manufacturers, did increase any error in the monitor-indicated concentrations. There was no consistent effect associated with sample storage, although it must be noted that only toluene and trichloroethylene were used in this particular experiment.

To demonstrate the effects of variable concentrations, a set of four experiments, each involving a different concentration variation through a series of step functions, was conducted. The data, in table 2, indicate that the two diffusional monitors gave higher results than either the permeation device or the charcoal tubes. Besides the reasons for differing monitor performance shown in table 1, these higher results may also be due hysteresis effects.

Taken collectively, the results from this study indicate that under specified conditions passive organic vapor monitors can be viable alternatives to traditional sampling methodologies. The overall precision of the passive monitors, as represented by their average coefficients of variation, is $\overline{CV}_{3M} = 3.2$ % for N = 126,

Table 2. Effect of variable concentration for toluene.

True concentration (ppm)		3M 3500 Organic Vapor Monitor		Gasbadge		MiniMonitor	
Consecutive samples [a]	Single samples [b]	Mean	SD	Mean	SD	Mean	SD
90.6	92.2	114	3.2	107	6.4	91.3	8.46
51.0	51.7	60.7	0.90	61.3	2.73	51.7	3.24
59.7	65.6	74.5	1.88	77.5	3.49	62.5	6.67
83.4	83.8	94.2	4.65	97.8	2.15	86.1	6.36

[a] Concentration calculated using full-period, consecutive charcoal tube samples.
[b] Concentration calculated using a single, full-period charcoal tube sample.

Table 3. Accuracy and precision of the carbon monoxide monitors.

Exposure conditions			Monitor results			
Challenge concentration (ppm)	Relative humidity (%)	Time (min)	General electric (ppm)		Energetics science (ppm)	
			Mean	SD	Mean	SD
25	30	60	33.2	3.42	24.3	0.58
25	30	360	18.0	1.00	23.3	0.96
25	80	60	35.0	5.80	22.0	1.00
25	80	360	18.6	1.14	24.7	1.16
50	30	60	66.8	11.6	46.0	4.58
50	30	360	39.2	3.53	51.5	1.67
50	80	60	66.6	10.0	44.7	4.16
50	80	360	38.8	3.27	51.7	5.44
100	30	60	151.6	26.6	108.3	0.58
100	30	360	157.6	29.0	106.0	10.4
100	80	60	133.0	23.5	96.3	2.52
100	80	360	78.6	6.46	105.3	3.51

$\overline{CV}_{Gasbadge} = 10.1$ % for N = 108, and $\overline{CV}_{MiniMonitor} = 10.4$ % for N = 120. Marketing and use of the passive monitors should be accompanied by the development, performance, and documentation of a simple, standardized quality control exposure and analysis protocol specific for a given passive monitor. Such a procedure could alert the manufacturer to possible problems prior to marketing a given lot of passive monitors and could increase user confidence in the monitor.

Generic recommendations for the use of passive monitors must include strict adherence to the manufacturer's instructions for use, thorough recordkeeping including exposure time, ambient information (temperature, relative humidity and pressure), and other pertinent information such as potential interferences or co-adsorbants, and both a laboratory (if possible) and field pretest of the devices to ascertain that the passive monitors sample accurately in a specific situation.

Carbon monoxide monitors

Two personal monitors for carbon monoxide, the General Electric model 15ECS1C02 and the Energetics Science Inc series 9000, were evaluated in the laboratory and the field to judge their performance in measuring exposures to carbon monoxide (3). These two devices are active samplers requiring a mechanical air mover, such as a personal sampling pump, for sample collection. Both monitors are electrochemical sensors in which current, generated in proportion to the influent carbon monoxide concentration, is stored by the monitor until a readout (in parts per million-hours) is obtained on the appropriate readout device.

In the laboratory tests five General Electric and four Energetic Science carbon monoxide monitors were exposed, in a series of experiments, to three concentrations of carbon monoxide (0.5, 1 and 2 times the permissable exposure limit of 50 ppm of the Occupational Safety and Health Administration), at two levels of relative humidity (< 30 % & > 80 %) for two time periods (1 & 6 h). The precision and accuracy of the instrument response were determined from these data. To determine the extent, if any, of the zero drift, the carbon monoxide monitors were calibrated and zeroed in accordance with the manufacturer's instructions, connected to a sampling manifold, and allowed to sample zero air for 6 h. Table 3 summarizes the results of the precision and accuracy tests, while fig 4 presents the zero-drift and rise-time information.

Field studies were conducted for 5 d at toll booths outside the Queens Midtown Tunnel, New York City. This tunnel serves 80,000 vehicles, gasoline and diesel-powered, per day. An ecolyzer, series 2000, was used to obtain full-shift, real-time carbon monoxide data which was

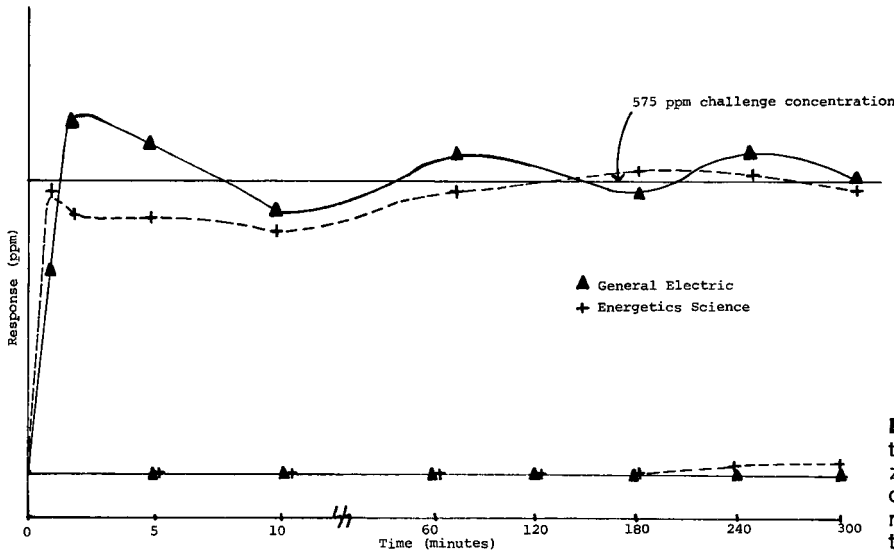

Fig 4. Results of the rise-time and zero-drift studies of the carbon monoxide monitors.

integrated over the full sampling time and compared to the time-weighted average response of the carbon monoxide monitors. These data are summarized in table 4.

The combined overall statistical summary for the laboratory and field studies is given for the carbon monoxide monitors in table 5.

The General Electric monitor has a built-in pump and was mechanically reliable throughout the study, while the Energetics Science unit requires the use of an auxiliary sampling pump and suffered down-time, primarily due to battery failure during the course of the study. Energetics Science has since replaced the type of battery used in the monitor. The carbon monoxide monitors, with their direct-readout capabilities, proved themselves to be accurate sampling techniques worthy of use as industrial hygiene tools.

Table 4. Carbon monoxide field exposure results.

Ecolyzer series 2000 (time-weighted average, ppm)	General Electric (mean, ppm) (N = 4)	Energetics Science (mean, ppm) (N = 3)
40	36	..
48	54.4	..
38	41.2	..
24	..	24
44	36.4	39
28	29.3	32

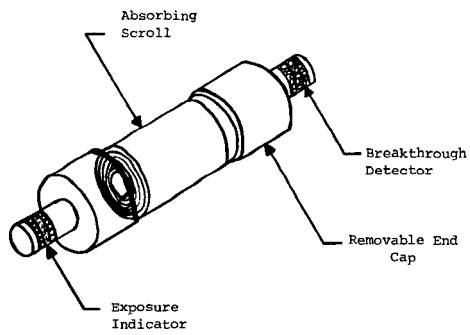

Fig 5. Poroplastic sorbent tube, nitrogen dioxide monitor.

Nitrogen dioxide sampler

A unique sampler for nitrogen dioxide was developed under contract to NIOSH by the Moleculon Research Corporation. The heart of the sampler is Poroplastic®, an ultramicroporous polymer based on cellulose triacetate with an open cell structure having pore dimensions in the range of 2—20 nm. Seventy to over ninety percent of the Poroplastic material can be loaded with virtually any liquid of choice. Poroplastic, which can be formed in powders, beads, rods, and films, was in film form for this work.

The sampler, shown in fig 5, consists of a center cylindrical glass section, 6 cm long (with an inner diameter of 1.5 cm), which houses the scroll-configured sampling section, and two removable glass end sections. The glass end sections contain plugs of Poroplastic chips impregnated with a buffered acid solution of a noncarcinogenic benzidine derivative. These small chips are initially honey-colored, but upon exposure to nitrogen dioxide they turn green and finally black so that the chips in the influent end of the tube indicate collection of nitrogen dioxide, while those in the effluent end indicate breakthrough. The scroll-configured sampling section is composed of Poroplastic film (impregnated with a 60 % triethanolamine solution) which is layered with a spun-woven polypropylene spacer material and scrolled to a prescribed tension around a solid core. The purpose of the interleaving material is to improve gasflow coefficients, increase dwell time, and increase gas-liquid contact area. The solid core prevents channeling.

In actual practice, this sampler would be used for personal monitoring and would require the collection of a 36- to 60-l sample with a personal sampling pump at a known flow rate between 60 and 120 ml/min. After the sampling, the device is returned to the laboratory where elution with nitrite-free water is followed by reaction with a sulfanilic acid color solution and colorimetric analysis at 550 nm.

Once this sampling system was assembled, a series of tests were conducted to evaluate its performance (1). The testing protocol addressed the capacity, desorption efficiency, precision, and

Table 5. Overall statistical results of laboratory and field studies for the carbon monoxide monitoring.

	Total number of observations	Relative standard deviation [a]	Mean square error (ppm) [b]	Mean coefficient of variation [c]
General Electric	61	0.098	0.109	0.161
Energetics Science	40	0.113	0.110	0.091

[a] Measure of precision.
[b] Measure of accuracy.
[c] Measure of single unit repeatability.

Table 6. Results of the testing of the poroplastic nitrogen dioxide monitor.

Parameter tested	Result
Overall bias	7.0 %
Overall coefficient of variation	10.0 %
Desorption efficiency	
16-μl loading	98.0 %
162-μl loading	110.0 %
322-μl loading	106.0 %
Storage stability (postsampling)	
After 7 d	No change
After 14 d	No change
Shelf-life stability (presampling)	
Prepared 7 d prior	No change
Prepared 14 d prior	— 10.0 %
Recommended sample size	36—60 l
Recommended sampling rate	60—120 ml/min
Temperature	
0 ± 1.5°C	No effect
40 ± 1.0°C	No effect
Relative humidity	
10 ± 2 %	No effect
90 ± 3 %	No effect
Monitor capacity for nitrogen dioxide	1,680 μl

accuracy under ambient conditions and extremes of temperature and humidity, storage stability, and shelf-life stability. Table 6 summarizes both the effects of the various parameters on sampling and the results of the evaluation.

The capacity of the sampler was found to be 1,680 μl of nitrogen dioxide, while the desorption efficiency averaged 105 % over three loadings (16, 162 & 322 μl). There was no statistically significant sample loss after 14 d of storage, but the shelf-life of the sampler (prior to use) was limited. Samplers stored for 14 d prior to use showed a 10 % decline in performance. At ambient temperature, the sampling and analytical overall bias was 7.0 % with a corresponding coefficient of variation of 10 %. Extremes of temperature had no effect on the samplers, while high humidity slightly increased the variability of sampler results.

The main objective of this program was to demonstrate a technology that could be used as an effective replacement for free-liquid impingers. To this end, the program was successful. The technique can now be expanded and should prove extremely useful for a wide range of hazardous air contaminants.

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