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PHILIP W. WEST & KENNETH D. REISZNER

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A passive dosimeter-type personal monitor for vinyl chloride has undergone extensive field testing. Collaborative studies by a number of laboratories confirm the accuracy, reliability, convenience and general acceptability of personal monitors utilizing gas permeation for sample collection and quantification. Data are generated as timeweighted averages and response is linear from 5 ppb to 50 ppm. The monitors which weigh only 35 g are unaffected by variations in environmental conditions.

Field tests of a permeation-type personal monitor for vinyl chloride

PHILIP W. WEST, Ph.D, D.Sc. and KENNETH D. REISZNER, Ph.D.
Environmental Sciences Institute, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

introduction

The analytic process begins with a need, whether real or imagined. The analysis itself may involve a number of steps including sampling, sample stabilization, preparation, concentration, separations and finally, the desired determination or measurement. The analytic process also involves data processing and, very possibly, validation. Unfortunately, measurement is often considered to be synonymous with analysis and much of the emphasis in the past has been on the measurement step under the assumption that this was the most critical part of the analysis. In reality, however, sampling is often the most difficult and subject to the most error. For industrial hygiene studies the sampling of the workplace atmosphere is of utmost importance. It is especially important that a convenient, reliable method for personal monitoring be used so that valid information be provided for the protection of the individual and for the extension of factual knowledge required in the evaluation of hazards.

In a general sense, sampling can be classified as either active or passive. The sampling of atmospheres has most generally been accomplished by means of some mechanical or active process, such as the use of a pump for pulling the sample through some metering device and a collection medium such as an adsorber or absorber. Although such active sampling techniques are standard, they do present certain difficulties. The use of motors, pumps, power sources and collectors when incorporated into personal monitoring devices tend to present a cumbersome and often unreliable sampling mechanism. Such mechanical devices tend to break down or wear out and they are relatively expensive. The recent introduction of passive sampling by means of permeation offers a simple, reliable, convenient and low-cost alternative.

OSHA regulations are based primarily on NIOSH recommendations. For gaseous hazards such as vinyl chloride, the collection and stabilization by charcoal tubes has been specified. No specifications have been promulgated regarding motors, pumps, metering devices or other components that would normally be considered integral parts of personal monitors. Thus the collection of samples by means of permeation should be considered valid provided the quantification is accurate and falls within specified confidence limits. The device for the personal monitoring of vinyl chloride employs charcoal as recommended by NIOSH. The measurement step, likewise, is the same as that already in use whereby the collected sample on charcoal can be eluted using carbon disulfide and the amount determined by conventional gas chromatography. Also, the personal monitor meets requirements because laboratory and field tests show accuracies achieved with permeation are well within specified limits.

Because the unique and critical feature of the permeation device for vinyl chloride is the permeation process itself, a brief summary describing the process is presented.

The terms permeation and diffusion are familiar. Although there are similarities between permeation and diffusion, there are subtle but at times important differences. Basically, diffusion represents the passage of molecules through holes in a discrete barrier whereby turbulence is minimized. Beyond the barrier or draft shield a stagnant air layer provides a means for mass transfer to a collecting medium with quantification of the transport following Fick's Law of Diffusion:

$$N = -DA(dc/dx)$$

where,

N = rate of diffusive transport, moles/sec
D = diffusivity of contaminant, cm^2/sec
A = area of diffusion path, cm^2
x = length of diffusion path, cm
c = concentration of contaminant, $moles/cm^3$

The Walden "GasBadge" utilizes the diffusion principle.(1)

For permeation, a barrier to ambient atmospheres is also involved but its function is to serve in the direct quantification of contaminant species. In this case there are no holes in the barrier. Instead, a polymeric membrane is utilized and gaseous contaminants contact the membrane and dissolve, permeate and thus are transported through the membrane to a collection and stabilization medium such as charcoal. The permeation constant, k, for the membrane used and for a given contaminant permits the determination of the time-weighted-average concentration for the contaminants,

$$C = wk/t$$

where,

C = concentration, ppm
w = weight of contaminant, μg
t = exposure time, hrs

The permeation constant is first determined by calibration using appropriate contaminant concentrations in an exposure chamber. The first use of permeation for sample collection was for the determination of sulfur dioxide in ambient air.(2) Its use in personal monitoring for vinyl chloride exposures has been described recently(3) and a commercially produced dosimeter, the MINIMONITOR, is now available (REAL Inc., Box 3341, Baton Rouge, LA 70821).

Consideration of mathematic expressions relating to diffusion and permeation fails to disclose effects that might result from non-ideal parameters. For personal monitors, for example, what is the effect of movement relating the atmosphere being sampled to the collecting interface? What is the effect of humidity? Of temperature? Do particulates or various coexisting gases have effects? In our studies, both in the laboratory and in the field, the permeation approach has proven to be the method of choice. Air movement, or lack of it, was of no significance nor were changes in humidity nor was the coexistance of various gaseous or particulate species. Permeation rates were known to vary according to temperature but this problem was negated by use of special membranes having properties that were altered but little by varying temperatures. For example, the vinyl chloride monitor exhibited essentially no temperature dependence over the range of zero to 40°C.

experimental

permeation device

The permeation-type personal monitor used for the evaluation studies was the same as that described previously(3) with only minor modifications (Figure 1). It consisted of a hollowed out aluminum plate which served as a reservoir for activated charcoal, a silicone permeable membrane for quantification of gas collection, and a front grid which protected the membrane from physical abuse.

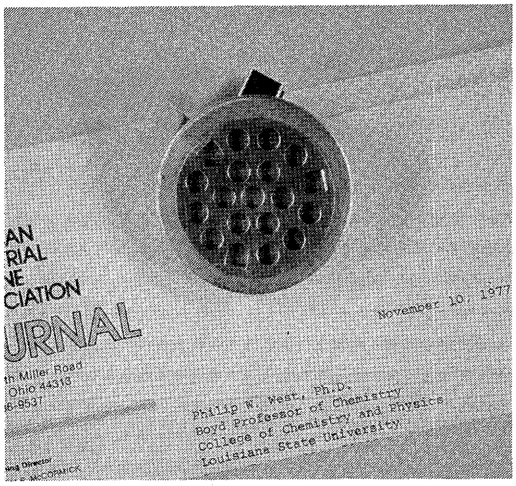

Figure 1 — Permeation personal monitor.

TABLE I

Preliminary Field Evaluation (4hr. TWA)

		Vinyl Chloride, ppm	
Sample	Conventional Monitor	ASTM Monitor	Permeation Monitor
	(ppm VCl)	(ppm VCl)	(ppm VCl)
1	1.00	1.00	1.19
2	0.10	0.12	0.19
3	0.12	0.14	0.10
4	0.12	0.13	0.17
5	0.34	0.37	0.51
6	0.04	0.05	0.07
7	< 0.02	< 0.02	< 0.02

TABLE II

Contributed Field Data, USA

	Vinyl Chloride, ppm		
	Permeation Device		
Temp. °C (°F) % Humidity	No. 2	No. 4	Sipin Pump Sampler
29 (84)/80	0.11		0.08
26 (78)/87		0.11	0.15
24 (76)/91	0.09		0.12
29 (85)/74	0.44		0.47
31 (87)/67	0.32		0.35
24 (76)/71*		0.32	0.33
24 (76)/71*	0.29		0.36
23 (73)/73*	1.28		1.80

*7 hr. exposure in fixed location (VCM Lab.). PD adjacent to sampler carbon tube.

Calibration of the monitors was done by the cooperating laboratories in accordance with their respective preferences. Permeation tubes and standard gas mixtures were used, the choice being a matter of company practice. The activated charcoal used for the sample adsorption in each case was similar to that used in the pump-charcoal tube monitors used for comparison. The analytic finish in all cases was by means of standard gas chromatography following sample desorption using carbon disulfide. Calibration, therefore, consisted of exposing the monitors in a standard gas atmosphere containing vinyl chloride and determining the weight of material collected over the exposure period,

$$k = ct/w$$

where,

k = device permeation constant
c = known concentration of vinyl chloride
t = time of exposure
w = weight of vinyl chloride adsorbed

validation

A test program was organized to determine the characteristics of a badge-type personal monitor for vinyl chloride. The original laboratory studies were backed up with field studies. Both the laboratory and field work have now been extended by independent investigations carried out in a number of plants and laboratories in the United Kingdom, as well as in Canada and the United States. The findings are presented here without identifying the cooperating individuals and laboratories. The data presented were contributed as a means of furthering the protection of colleagues throughout the world who might be exposed to potentially hazardous concentrations of toxic materials such as vinyl chloride.

A local manufacturer of vinyl chloride contributed data from a preliminary field evaluation (Table I) in which ASTM and conventional pump monitors were compared with permeation-type monitors. The results were obviously good. Further studies were made under differing conditions of temperature and humidity. As shown in Table II, values obtained on days with temperatures ranging from 22.8 to 30.6°C and humidities of 67 to 91% gave excellent agreement and confirmed laboratory findings that there was essentially no temperature effect over a range of zero to 40°C nor any due to humidity over the range of 100% to less than 10%. An additional set of data presented in Table III simply confirms those given in Table I. The two studies were made at different times and under somewhat different conditions.

A second company located in the Gulf Coast area submitted the data shown in Table IV. Again, the results confirm the reliability of the permeation approach for sample collection. It is of interest to note that all data presented in the four tables were generated in a very complex industrial region where a wide variety of organic and inorganic manufacturing or processing operations were always in progress.

Collaborative studies conducted in the United Kingdom were initiated by the committee on vinyl chloride and were performed in a number

TABLE III

Vinyl Chloride Personal Monitor Data

	Vinyl Chloride (ppm)		
Sample	Conventional Monitor	Permeation Monitor	Monitor Number
2	0.83	0.98	2
3	0.10	0.17	3
5	0.05	0.16	2
6	0.10	0.15	3
7	0.07	0.12; 0.11	2; 5
8	0.07	0.05; 0.08	3; 4
9	0.50	0.51; 0.49	2; 5
10	0.41	0.42; 0.48	3; 4
11	0.02	<0.05; <0.05	2; 3
12	0.88	0.92; 0.97	4; 5

Note: Sample 1 gave the following results: 6.9 ppm by conventional and 8.9 ppm by permeation monitor (monitor no. 1) and Sample 4 gave 3.6 ppm by conventional and 5.1 ppm by permeation monitor (monitor no. 1). Due to the difference in the results, they are not included in the Table (difference may be due to a calibraton error).

TABLE IV

Contributed Data, USA - No. 2

			Vinyl Chloride, ppm		
			Permeation[3] Device		
Date	Ambient Temp. °C (°F)	Relative Humidity, %	No. 2	No. 4	Pump Sampler
6/16/76[1]	28 (83)	86	1.31		1.07
6/1	28 (83)	86		0.12	0.12
6/17	-	73	0.12		0.23
6/21	32 (90)	82		0.59	0.34
6/21	32 (90)	82	0.97		0.50
6/24	29 (85)	70	0.40		0.49
6/25	31 (88)	60		0.95	0.38
6/28	-	-		0.84	0.82
6/28	-	-	0.18		0.16
6/29	27 (80)	73	0.27		0.30
6/29	.	-		1.40	1.75
6/30	-	-		0.41	0.33
6/30	-	-	0.63		0.65
7/1	30 (86)	61	0.10		0.05
7/1	-	-		0.11	0.06
7/2[2]	-	-	0.16		0.11
7/2	-	-		0.90	0.90
7/6	-	-	0.17		0.08
7/6	-	-		1.18	0.23
7/7	29 (84)	80	0.11		0.08
7/7	29 (84)	80		0.11	0.08
7/8	26 (78)	87		0.11	0.15
7/8	26 (78)	87	0.15		0.19
7/9	24 (76)	91	0.09	0.09	0.12
7/12	-	-		0.25	0.25
7/12	-	-	0.23		0.48
7/13	28 (83)	72	0.47		0.53
7/14	29 (85)	74	0.44		0.47
7/14	29 (85)	74		0.99	0.86
7/15	31 (87)	67	0.32		0.35
7/15	31 (87)	67		0.36	0.35
7/16	-	-	0.09		0.10
7/16	-	-		1.01	0.86

7/19	-	-		0.35	0.69
7/20*	-	-	0.11		0.12
7/20*	-	-		0.13	0.12
7/26*	24 (76)	71		0.32	0.33
7/26*	24 (76)	71	0.29		0.36
7/27*	23 (73)	73	1.28		1.80

(1) PD placed on one side of collar, pump on other.

(2) PD placed adjacent to pump on same side of collar.

(3) Monitors were calibrated at LSU.

*7 hr exposure in fixed location (VMC Lab.). PD adjacent to sampler carbon tube.

TABLE V

Contributed Data, United Kingdom

VCM present, ppm v/v	VCM concentration found—ppm v/v			
	A	B	C	D
1.5	1.4	1.4	1.3	1.5
1.9	2.1	2.2	2.1	2.1
3.7	3.4	3.2	3.6	3.3
3.9	3.9	4.0	4.1	3.8
3.9	4.0	3.9	4.0	3.7
4.0	3.9	3.8	3.7	3.9
5.7	5.7	5.8	5.9	5.3
7.5	7.8	7.8	7.6	7.6
13.9	14.3	14.1	13.2	13.1

of laboratories. The results presented in Table V give replicate values obtained using four permeation devices. As a matter of interest, a sample calibration graph submitted by the U. K. committee is shown in Figure 2, (also see Table VI). Of special significance are the conclusions and recommendations which are quoted as follows:

conclusions

"Convention would require the laboratory work recorded here to precede plant trials. The results from the plant trials have already been acknowledged to be encouraging; the calibration series now completed further justifies the faith inspired by the badges from the outset. A fair spread of time/concentration combinations has been covered, without revealing any weakness likely to arise in the conditions met in personal monitoring.

We feel curiosity, rather than concern, that the permeation constant, K, found here may differ from those established elsewhere.

recommendations

The Louisiana badge and the Century Systems programed thermal desorber have undergone independent evaluation, with favourable results. There is no reason to be apprehensive about using the two together, but a limited series of laboratory trials should be run when the Automatic Injection valve becomes available for the P-D. This system promises to be the best and most economic for future personal and similar monitoring."

discussions and conclusions

The validation studies contributed by impartial industrial laboratories have confirmed the accuracy and reliability of the permeation approach for personal monitoring. The permeation-type monitors showed a small positive bias in the field studies which did not

TABLE VI

Plant Trials, United Kingdom

Date	Pump VCM, ppm	Permeation VCM, ppm
5/4/76	2.96	3.78
5/6	2.16	2.25
5/7	2.32	2.33
5/8	2.44	2.90
5/9	pump broke	8.40
5/10	2.72	3.11
5/10	8.36	10.91
5/11	8.21	10.11
5/11	2.11	2.59
5/12	3.48	3.77
5/12	5.85	11.00
5/13	4.92	5.14
5/13	1.48	2.27
5/14	16.7	21.0
5/14	16.3	15.8
5/17	5.97	7.54
5/18	8.74	9.84
5/18	6.99	7.36
5/18	4.54	4.76
6/22	14.4	12.1
6/22	4.1	3.9
6/23	16.4	19.4
6/23	pump broke	7.50
6/25	6.2	6.5
6/25	12.4	14.5
6/28	8.5	9.1

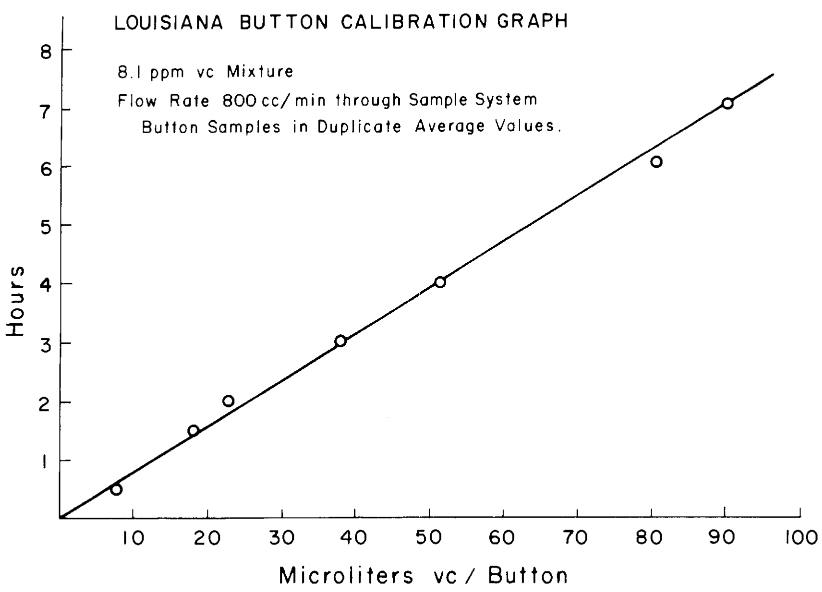

Figure 2 — Louisiana button calibration graph.

appear in laboratory evaluations. The only explanation proposed for the lower results obtained in the field with pump-type monitors was the possibility that battery driven motors were used and battery fatigue might have caused smaller than expected samples to result.

There were no failures nor malfunctions reported in the use of the permeation-type monitors. This was in contrast to the experiences reported with the conventional monitors. The latter were beset with pump failures as well as occasional motor and battery problems.

In addition to the low cost and reliability of the permeation approach, the great advantage of convenience made the permeation-type monitors completely acceptable to the wearers as contrasted to the objectionable discomfort reported by personnel forced to wear conventional equipment.

A final matter of interest is that of cost. The permeation approach makes it possible to provide monitors which are essentially indestructible and which cost less than $50 each.

acknowledgements

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