

Seventy-eight pairs of side-by-side charcoal tube and 3M Brand "passive vapor monitor samples were taken in the field and analyzed for 22 organic chemicals including trichloroethylene, benzene, toluene, MEK, m-, p-, and o-xylenes, isopropanol, and several C5 through C8 alkanes. Sixty-four pairs were personal and fourteen pairs were area samples. Linear regression analyses were performed for ten chemicals detected over a sufficiently large range of concentrations. Satisfactory correlation ($r = 0.90$ and slopes not significantly different from 1.0) was found between monitors and tubes for n-hexane, methylcyclopentane, toluene, 2-methylpentane, 3-methylpentane, n-heptane, n-pentane, and isopentane. Tube and monitor results differed for methylcyclohexane and n-octane. Paired t tests were performed on the remainder of the chemicals, and no consistent significant differences (5% level) in the means were found.

Field comparison of charcoal tubes and passive vapor monitors with mixed organic vapors

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Introduction

Several brands of charcoal-adsorption passive vapor monitors have been marketed recently. These monitors hold much attraction for measuring workplace vapor exposures because they are lightweight, require no power, pump, or tubing, and are not likely to interfere with workers' movements.

The operating principles of these monitors have been described, and their advantages and limitations have been compared to those of charcoal tube/pump monitoring systems.¹⁻⁴ The performance of passive monitors has been evaluated for various chemicals under various conditions.⁵⁻⁷

However, field studies of the performance of passive monitors in assaying mixed organic vapors are lacking, although an extensive field comparison of passive monitors and charcoal tubes is planned.^{8,9}

Procedures

Seventy-eight sets of simultaneous charcoal tube and 3M Brand #3500 organic vapor monitor samples were collected and analyzed for 22 organic chemicals as part of a survey of tire manufacturing facilities. The chemicals, listed in Table I, were selected for analysis on the basis of their presence in materials used in tire manufacture.

Samples were collected during regular work shifts in two plants during two 2-day periods in July and August, 1979. Sixty-four sets were personal samples and 14 were area samples.

The sampling periods varied from three to five hours. Charcoal tubes were usually changed during the sampling period to reduce the possibility of overloading; the monitors were not. Thus, with few exceptions, each pair of results consists of the concentration from a single monitor and the time-weighted average concentration from two charcoal tubes.

Chemical analysis

After exposure to the solvent vapors, the organic vapor monitors and charcoal tubes were capped and stored at -7°C until time of analysis. Monitors were analyzed in accordance with the manufacturer's instructions, using a Perkin-Elmer gas chromatograph (Model Sigma 1) equipped with a flame ionization detector. Concentration data were calculated with a Perkin-Elmer Sigma 10 data system. The desorption efficiency for each solvent was determined by our laboratory using the method recommended by the 3M Company.¹⁰ Concentrations were calculated in accordance with manufacturer's instructions.¹¹ The diffusion factors or "sampling rates" (analogous to diffusion coefficients) used are listed in Table I for each chemical. Charcoal tubes were desorbed in the standard manner and analyzed under the same procedures as the monitors.

Results

Ten of the chemicals were detected over a sufficiently wide range of concentrations in one or both plants to permit a linear regression analysis of passive monitor and charcoal tube sampling results. Slopes, intercepts, correlation coefficients and 95% confidence intervals for prediction of individual values¹² are given in Table II, separately for the two surveys and for the combined data from both groups. Charcoal tubes were (X) values and monitors were (Y) values; that is, charcoal tube sample results were considered to reflect "true" concentrations, as a basis for comparison.

The second column in Table II indicates the range of concentrations found in the samples. Columns 3 and 4 are the slope and Y-intercept of the linear regression line, which indicates how well the two methods agree. A slope of 1.0 and a Y-intercept of zero indicate close overall agreement. The correlation coefficient (column 5) reflects the degree of

TABLE I
Chemicals Analyzed and Sampling Rates

Chemical	Sampling Rates (mL min) ^a
Isopentane	29.8
n-Pentane	29.8
2,2-Dimethylbutane	28.2
3-Methylpentane	28.2
2-Methylpentane	28.2
n-Hexane	28.2
Cyclopentane	28.2
Methylcyclopentane	28.2
n-Heptane	27.7
Cyclohexane	28.2
Methylcyclohexane	27.2
n-Octane	21.8
1,1,1-Trichloroethane	28.1
Methyl ethyl ketone	31.2
Isopropanol	35.9
Benzene	33.0
Trichloroethylene	28.0
Toluene	30.4
Ethylene dichloride	32.1
p-Xylene	23.7
m-Xylene	25.6
o-Xylene	25.7

^aReference #6

departure of data-pairs from the regression line. An *r* value of 1.00 indicates near perfect correlation, and lower *r* values indicate poorer correlation. The last two columns are the predicted 95% confidence limits of an individual passive monitor sample, given some "true" concentration of X as indicated by charcoal tube samples. The predictions were made for concentrations at the top of the data range observed.

The other twelve chemicals were detected in comparatively few samples or mostly at low concentrations (less than 1 ppm), so no linear regression analyses were performed. Instead, the paired *t*-test⁽¹¹⁾ was used to determine if the monitor and tube sample means were statistically different at the 0.05 probability level, assuming normal distribution. No consistent difference in means was demonstrated except for *n*-octane.

discussion

The data in Table II show two trends. In Group No. 1, for every chemical except *n*-heptane the passive monitors show higher vapor concentrations than the charcoal tubes, as indicated by linear regression slopes greater than 1.0. In three cases (toluene, *n*-octane and methylecyclohexane) the slopes were significantly different at the 95% confidence level from the ideal slope of 1.0. The observation of higher concentrations from passive monitors than from charcoal tubes is not unique. In one report,⁽¹²⁾ acrylonitrile was monitored with 18 GasbadgesTM and charcoal tubes side-by-side; the badges averaged 2.73 ppm and the tubes 2.14 ppm, a mean difference of 25 percent.

The second trend was that Y-intercepts for nearly all chemicals in all groups were very close to zero (less than 1 ppm), and were in the main negative. Although a slight negative intercept is of little importance in monitoring substances with relatively large TLVs, it may indicate a detec-

tion threshold or lack of sensitivity in the passive monitors at very low concentrations. Such a condition, if confirmed, should be considered in making decisions on the use of passive monitors for detection of substances with TLVs in the 1 ppm range or lower.

Correlation coefficients (*r*) for several of the substances were 0.94 or higher. The 95 percent prediction limits on individual passive monitor sample concentrations are shown in Table II for given chemical concentrations. The predicted monitor concentrations are generally within ± 25 percent of the reference concentrations, in Group No. 2 and the combined data, but vary widely in Group No. 1 because of the high slope values. This predictability would be much improved by use of the regression curve to "calibrate" the monitors. However, it is presumed that the curve will not be known *a priori*. If the slopes for any chemical had consistently varied from 1.0 appreciably in both groups (as with *n*-octane and methylecyclohexane), an inaccurate "sampling rate" for diffusion published by the passive monitor manufacturer might be responsible.

For the statistical analysis, charcoal tube sampling results were presumed to reflect the true concentrations, and be subject to much less variation than the passive monitors. This is by no means a certainty. However, statistical analyses where both methods are subject to error are rather complicated⁽¹³⁾ and the method used here is considered to be satisfactory for this purpose.⁽¹⁴⁾

sources of error

Several possible sources of errors in the results of this study are discussed below.

1. The "sampling rates" used with the monitors may be imprecise. These sampling rates are analogous to diffusion coefficients. Published sampling rates were used where available; the others were estimated on the basis of chemical similarity. Use of too low a sampling rate would increase the slope (*b*) of the regression line in inverse proportion to the sampling rate error, but would not affect the correlation coefficient. This result was observed with methylecyclohexane, raising the possibility that the estimated "sampling rate" used (27.2 mL min) was too low. Use of too high a sampling rate would tend to depress slopes in inverse proportion to the error. This type of systematic error could account for regression line slopes tending to be consistently greater than 1.0.
2. There may have been interference from unknown chemicals. Many small unidentified peaks were present in some of the chromatograms. Such interference would have affected tubes and monitors similarly.
3. On-site temperature and pressure departures from 298°K and 760 mm were not corrected. They were presumed to affect monitors and tubes equally except for the temperature correction⁽¹⁵⁾ to the sampling rate $(T^\circ K / 298)^\frac{1}{2}$. This could cause differences in monitor results ranging from -3 to +5 percent, as

TABLE II
Comparison of Results of Simultaneous Sampling by
Passive Monitors and Charcoal Tubes

Chemical	Range of Data (ppm)	Linear Regression		Correlation Coefficient (r)	95% Prediction Interval for Passive Monitor Sample at True Concentration X	
		Slope & 95% C.L.	Y Intercept (ppm)		X (ppm)	Monitor Sample (ppm)
Group No. 1 (30 sample pairs)						
n-Hexane	0-37	1.02 ± 0.12	0.50	0.96	40	33.8 to 46.6
Methylcyclopentane	0-17	1.11 ± 0.13	0.72	0.96	20	18.3 to 24.6
Toluene	0-18	1.31 ± 0.12	0.36	0.97	20	23.2 to 28.6
n-Octane	0-10	1.41 ± 0.15	0.01	0.96	10	12.0 to 16.2
2-Methylpentane	0-18	1.10 ± 0.15	0.50	0.94	20	17.7 to 25.5
3-Methylpentane	0-30	1.13 ± 0.16	0.61	0.94	30	27.0 to 39.5
n-Heptane	0-7	0.94 ± 0.13	0.31	0.94	10	7.3 to 10.9
Methylcyclohexane	0-7	1.33 ± 0.30	0.04	0.86	10	9.7 to 16.9
n-Pentane	0-6	1.29 ± 0.47	0.01	0.73	10	7.9 to 17.9
Isopentane	0-13	1.12 ± 0.68	0.92	0.54	10	3.4 to 20.9
Group No. 2 (48 sample pairs)						
n-Hexane	0-27	0.91 ± 0.10	-0.11	0.94	25	17.9 to 27.6
Methylcyclopentane	0-20	0.99 ± 0.11	0.26	0.94	20	16.1 to 22.9
Toluene	0-20	0.97 ± 0.10	0.16	0.97	20	16.6 to 22.4
2-Methylpentane	0-16*	0.92 ± 0.07	0.04	0.97	20	16.2 to 20.6
3-Methylpentane	0-30	0.91 ± 0.05	-0.02	0.98	30	24.6 to 30.0
n-Heptane	0-25*	1.09 ± 0.13	-0.56	0.93	25	22.2 to 31.0
Methylcyclohexane	0-20	1.39 ± 0.13	0.15	0.96	20	24.3 to 31.0
n-Pentane	0-30*	0.93 ± 0.07	-0.05	0.97	30	24.1 to 31.3
Isopentane	0-40**	1.06 ± 0.03	-0.17	0.99	40	40.4 to 44.2
Combined Data (78 sample pairs)						
n-Hexane	0-37	0.97 ± 0.07	-0.26	0.95	40	33.5 to 43.9
Methylcyclopentane	0-20	1.03 ± 0.08	0.38	0.95	20	17.6 to 23.6
Toluene	0-20	1.09 ± 0.08	0.06	0.95	20	19.0 to 24.6
2-Methylpentane	0-18	0.99 ± 0.07	0.09	0.95	20	17.1 to 22.5
3-Methylpentane	0-30	1.01 ± 0.06	0.15	0.97	30	26.4 to 33.8
n-Heptane	0-25	1.07 ± 0.10	0.53	0.93	25	22.7 to 29.7
Methylcyclohexane	0-20	1.38 ± 0.11	0.12	0.94	20	24.4 to 30.6
n-Pentane	0-30	0.92 ± 0.07	0.15	0.95	30	24.3 to 31.3
Isopentane	0-40	1.06 ± 0.08	0.31	0.94	40	37.2 to 47.9

*Only 21 pairs < 1 ppm

**Only 15 pairs < 1 ppm

the temperatures at sampling sites were judged to range from 5 °C below to 10 °C above 25 °C.

4. Overloading of tubes and monitors could cause errors. Charcoal tubes sampled from 90 to 190 liters of air, averaging 130 liters, at 1 L/min. Only two charcoal tubes showed concentrations over 100 ppm total organic vapors assayed (120 ppm and 150 ppm). These two tubes indicated 28 and 45 ppm total vapor respectively in their back charcoal sections. For other tubes, the total collected in the back section was less than 25 percent of that in the front section. Each monitor was exposed as long as both tubes in a set. Any significant overloading of monitors would result in regression line slopes substantially below 1.0. This did not occur.
5. The back section of a tube was analyzed whenever the chromatogram of the front section showed rather high peaks. In essence, the backs were analyzed if total organic vapors assayed exceeded about 50 ppm, which occurred in roughly half the samples. It is possible that a portion of vapors collected in the

tubes was missed in analyzing samples from areas with low vapor concentrations. This would tend to increase regression line slopes slightly and give substantially positive Y intercepts. The latter did not occur.

6. Tubes were analyzed 12 weeks after sampling, and monitors 17 weeks. All were kept at -7 °C in the interim. This delay may have resulted in loss of collected vapors. One could speculate that migration of vapors to the back sections of charcoal tubes during storage might account for some loss in tubes whose back sections were not assayed. Losses in the monitors might be less as the vapors would have no alternate sink. Such migration would tend to increase regression line slopes slightly.

It is the judgment of the authors that the potential errors did not significantly affect the results.

significance of findings

Since observed concentrations of substances were generally far below TLVs and permissible exposure limits (PELs), no

conclusions can be drawn from these data regarding correlation of monitors and tubes at concentrations approaching TLVs, without assuming linearity beyond the observed data.

However, since one of the anticipated values of the passive monitor is in routine monitoring, it is important to demonstrate that they can reliably measure low exposures as well as high ones. The results of this study indicate that the passive monitor reliably assayed low concentrations of mixed vapors of 20 of the chemicals mentioned equally as well as charcoal tubes, under the conditions encountered. Charcoal tube and passive monitor results differed significantly for methyleyclohexane and n-octane.

The tendency toward negative Y-intercepts (Table II) may indicate a sub-ppm detection threshold in the monitors for some chemicals. More such comparative studies are needed to build a body of literature on which to establish the applications and limitations of the passive monitor.

Research support

This research was supported by United Rubber Workers Union, Firestone Tire and Rubber Co., The General Tire and Rubber Co., Goodyear Tire and Rubber Co., and Uniroyal, Inc.

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