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An evaluation of benzene in the presence of gasoline by active and passive sampling methods

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This research project examined the capability of both the active and passive methods to evaluate the amount of benzene vapor in an environment composed of a complex mixture of competing organic vapors (gasoline). Activated charcoal tubes and three brands of passive organic vapor monitors (3M 3520, SKC Solid Sorbent Badge, and MSA Vaporgard™) were exposed to four concentration levels of benzene in the presence of gasoline, and all results were evaluated against the NIOSH acceptance criteria for sampling and analytical methods. Each type of sampler was then compared to each of the other tested samplers to determine the overall similarity of the results as determined by the different devices. The samplers were also subjected to a benzene environment without gasoline to establish baseline response criteria for comparative purposes. The test results indicated that three of the four methods examined met the NIOSH criteria (ACT, 3M, and SKC). The fourth method (MSA) failed due to significant benzene levels found in the blanks for this method. Only the SKC badges and the ACTs were shown to have statistically equivalent responses. Exposure to the complex mixture of organic vapors had an adverse effect on the overall system accuracies of each of the tested samplers. **Spielman, C.R.; Blehm, K.D.; Buchan, R.M.; Hager, R.N.**: An evaluation of benzene in the presence of gasoline by active and passive sampling methods. *Appl. Ind. Hyg. 2*:66-70; 1987.

Introduction

It has been nearly ten years since the introduction of a commercial passive organic vapor monitor.(1) Numerous studies have been conducted to determine the ability of these passive organic vapor monitors (POVM) to accurately and precisely estimate airborne vapor concentrations under a wide variety of environmental conditions.(2-8) Several of these studies attempted to compare the POVM response to that of the activated charcoal tube (ACT) and pump method of sampling. For the most part, these investigations had centered on the response of these systems in single-component or simple, multicomponent vapor environments. None of the published laboratory evaluations had subjected POVMs and ACTs to a highly complex mixture of vapors to determine how well they respond. This is important as many industrial situations routinely expose personnel to this type of environment. Additionally, some studies had erred in assuming that the ACT results represented the true airborne vapor concentration. The ACT data were then used as a benchmark for the POVM results with the possible assumption that the passive systems were not as accurate as the active method.(2-8) The implication of these comparisons may have been a reluctance by industrial hygienists to use POVMs in favor of the standard pump and tube method.

The purpose of this research project was to investigate the ability of both POVMs and ACTs to accurately and precisely assess benzene vapor concentration as a part of a complex mixture of organic vapors known collectively as gasoline. Two hypotheses were tested:

1. The benzene concentrations yielded by each organic vapor sampling device would be within ± 25% of the true benzene concentration given a 95% confidence level.
2. When exposed to identical challenge environments, each type of passive organic vapor monitor and activated charcoal tube would provide an indication of the benzene concentration that was not significantly different than that provided by any of the other tested organic vapor sampling devices.

Methods

Three brands of POVMs were chosen for testing as well as the standard ACT and pump. The 3M 3520 Organic Vapor Monitor™ (OVM), the SKC Solid Sorbent Badge 530 Series with Anasorb CA capsules, and the MSA Vaporgard™ Organic Vapor Dosimeter were each chosen because they shared the following traits with the ACT: each has a backup section to detect breakthrough, each utilizes activated carbon as the col-

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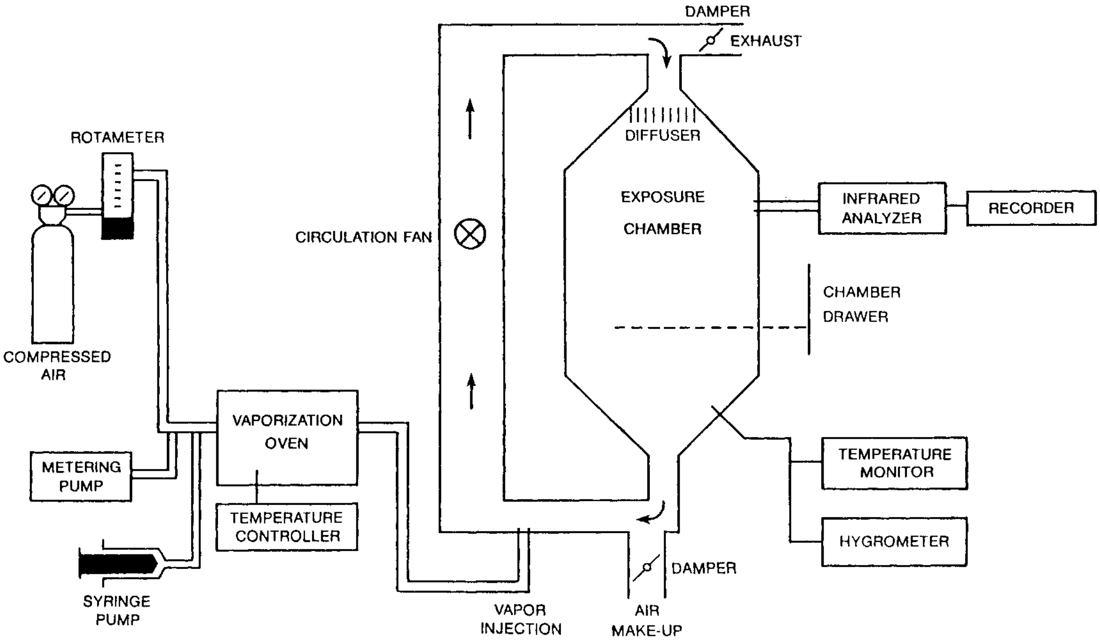

Figure 1—Dynamic exposure chamber (schematic).

lection medium, and each is analyzed by solvent desorption of the charcoal and injection of the solute/solvent into a gas chromatograph.(9) Gillian Model 113 HS constant flow air pumps were used in conjunction with SKC Model 224-26-04 variable rate flow controllers to draw air at a constant rate through the ACTs. Benzene sampling rates for the POVMs were taken directly from the manufacturers' instructions. Flow rates for the ACTs were set and calibrated by the bubble burette method.

Six sets of samplers, each set consisting of one of each of the POVMs and one ACT, were placed in a dynamic exposure chamber and exposed to the following target concentrations of benzene: 3, 15, 30, and 60 milligrams per cubic meter of air. Gasoline concentrations for each of these runs was approximately 250 mg/m^3. One additional trial exposing six sets of samplers to a benzene-only environment was run as a means of observing the effect the complex gasoline environment had on the outcome.

A motorized syringe was used to inject a benzene/gasoline mixture into the exposure chamber as shown in Figure 1. As benzene is a normal constituent of gasoline, the first benzene concentration was achieved by injecting unadulterated, unleaded gasoline into the vaporizer and chamber until the target concentration was attained. The subsequent benzene target values were attained by adding appropriate amounts of benzene to the gasoline, thoroughly mixing it, and injecting the mixture into the chamber until the next benzene target was reached. The objective was to increase benzene concentrations while maintaining a relatively stable overall gasoline concentration.

The concentrations of benzene and gasoline vapors were monitored independent of the samplers by means of both gas chromatography and infrared spectrophotometry. Five milliliters of chamber air was removed via a gas-tight syringe and injected into a gas chromatograph to determine benzene concentrations. The volume of the syringe was determined using a volume displacement (bubble burette) method. A calibration curve was derived for the gas chromatograph by injection of known quantities of benzene in the desorption solvent. A Miran 1A infrared analyzer and strip chart recorder were used to maintain a constant, real-time record of the gasoline concentration by monitoring the predominant alkane constituents. Since the gasoline and benzene were injected simultaneously into the chamber, it was reasonable to assume that the benzene concentration would be a direct function of the gasoline concentration. The chamber benzene concentrations determined by the gas chromatograph were plotted as a function of the Miran derived gasoline concentrations and resulted in a linear relationship having a correlation coefficient of 0.96 or better for each of the four benzene in gasoline runs.

Each of the exposure runs was allowed to proceed for four hours. The temperature inside the chamber was maintained between 23° and 27°C, relative humidity was continuously monitored and ranged from 15 to 25 percent, and the velocity of the air passing by the POVMs averaged 50 feet per minute in order to avoid starvation effects.

After each exposure run, the POVMs and ACTs were removed and capped or sealed to avoid any further contamination. The samplers were stored overnight and analyzed the next day by standard gas chromatographic techniques. The front and back sorbent sections of each device were desorbed separately using carbon disulfide for at least 30 minutes and not longer than 90 minutes prior to analysis. A four microliter aliquot was then injected using standard solvent flush techniques into a Hewlett-Packard 7610-A High Efficiency Gas Chromatograph equipped with a 10% TCEP column. The column was operated isothermally at 85°C. The analysis of the sample results was aided by the use of a Hewlett-Packard 21 MX computer and 2645A terminal. All results were corrected for desorption efficiencies and benzene contamination in the carbon disulfide.

The laboratory results were used to determine the precision, bias, and accuracy of the POVM and ACT systems. The precision of measurement is represented by the coefficient of variation which indicates the degree to which a group of values agree with the mean of

TABLE I

Summary of benzene-in-gasoline results

	Trial 1	Trial 2	Trial 3	Trial 4	Pooled MCV	Pooled $\bar{b}$	Pooled OSA
Chamber conc. (mg/m^3)							
Benzene (mean)*	3.0	15.2	27.7	60.2			
Gasoline (mean)*	180	250	270	330			
Charcoal tubes							
Mean* benzene conc. (mg/m^3)	3.1	13.8	22.5**	61.6**			
CV (%)	6.2	8.8	6.1	5.3	6.8	−5.7	19
3M 3520 OVM™							
Mean benzene conc. (mg/m^3)	3.2	16.0	26.3	71.0			
CV (%)	8.2	6.1	7.3	3.8	6.6	+6.2	19
SKC solid sorbent badge							
Mean* benzene conc. (mg/m^3)	2.8	14.5	22.7	57.5			
CV (%)	12.0	6.0	5.2	2.9	7.5	−8.4	23
MSA Vaporgard™							
Mean* benzene conc. (mg/m^3)	0.25	16.5	26.9	96.6			
CV (%)	160.0	12.0	11.0	8.8	83	+6.3	170
Relative humidity (%)	25	15	20	20			
Temperature (°C)	25	25	25	25			

mg/m^3 = milligrams per cubic meter
CV = coefficient of variation
MCV = mean coefficient of variation
$\bar{b}$ = mean bias
OSA = overall system accuracy
* = geometric mean value
**Only five charcoal tubes included in this result; all others the result of six samples.

these values. Bias is a measure of accuracy which represents the percent difference between a measured value and the true value. The overall system accuracy (OSA) is a measure of the total error of the sampling and analytical method due to bias and precision. The OSA indicates the error range which will include at least 95 percent of the data. The OSA was calculated by the following equation:

$$\mathrm{OSA} = b + 2(\mathrm{MCV})$$

where:
OSA = overall system accuracy (%)
b = absolute value of the mean bias (%)
MCV = mean coefficient of variation (%)

The overall system accuracy must be less than or equal to 25 percent in order to meet the NIOSH acceptability criteria.(10)

Two series of statistical analyses were required to determine the degree to which each of the devices were in agreement. First, the mean concentration determined by each device was compared to all other samplers within each of the concentration ranges by using Duncan's multiple range test. Secondly, a two-way analysis of variance was performed to determine if the sampling devices were in agreement over the entire range of concentrations used. This comparison was the more powerful of the two analyses as it utilized all the available data whereas the multiple range test primarily identified those concentrations where differences did exist. All statistical analyses were performed at a significance level of 0.05.

Results and discussion

Table I provides a summary of the results of the four benzene-in-gasoline trials. The charcoal tube method, as well as the 3M OVM and the SKC badge passive systems, met the NIOSH acceptability criteria. The MSA Vaporgard did not meet these criteria. Table II presents the results of the Duncan's multiple range tests and the contrasting two-way analysis of variance. Only the ACTs and the SKC passive samplers were found to be significantly in agreement relative to their concentration determinations. Neither the 3M nor the MSA systems agreed with any of the other sampling methods.

The ACTs performed consistently at each of the four tested concentration levels. The coefficients of variation (CV) at each level ranged from 5.3 to 8.8 percent, indicating a high degree of precision. The OSA was found to be 19 percent. The bias determined for three of the exposure levels were fairly consistent; however, the trial bias at a concentration of 27.7 mg/m^3 was substantially above those of the other three. The overall bias was found to be negative, indicating that the ACT and pump method tended to underestimate the benzene concentration in a complex environment. However, it is important to note that two of the gasoline trials did result in slight overestimations.

The OSA calculated for the 3M 3520 OVMs was identical to that found for the ACTs. The OVMs tended to have a slightly smaller CV, thus a better precision than the ACTs. In fact, these devices had the best overall precision of any of the tested systems. The biases noted for each of the first three benzene levels were very consistent; however, a large increase was detected at the highest concentration. The overall bias was found to be slightly positive meaning the OVMs tended to overestimate the benzene concentration.

The SKC Solid Sorbent Badges had a relatively high degree of variability at the lowest benzene exposure level which improved substantially for each succeeding trial. The bias determined at each of the concentration levels was generally equivalent to, or slightly bet-

TABLE II

Summary of Duncan's multiple range test and contrasts

		Sampling method ACT	Sampling method 3M	Sampling method SKC	Sampling method MSA
Benzene Exposure Level (mg/m^3)	3.0	MSA	MSA, SKC	MSA, 3M	ACT, SKC, 3M
	15.2	3M, MSA	ACT	MSA	ACT, MSA
	27.7	3M, MSA	ACT, SKC	3M, MSA	ACT, SKC
	60.2	3M, MSA	SKC, ACT, MSA	MSA, 3M	SKC. ACT, 3M
	Pooled	3M, MSA	ACT, SKC, MSA	3M, MSA	SKC, ACT, 3M

ACT—Activated Charcoal Tubes
3M—3M 3520 Organic Vapor Monitors™
SKC—SKC Solid Sorbent Badge 530 Series with Anasorb CA Capsules
MSA—MSA Vaporgard™ Organic Vapor Dosimeters

The notations ACT, 3M, SKC, and MSA under the column headings indicate that the sampler's mean value is significantly different from the column heading's mean at an $\alpha = 0.05$.

ter than, the ACT or the 3M OVM values. As with these other two systems, the bias of one trial was substantially above the remaining three. The SKC badge had an overall negative bias which was slightly more pronounced than the ACTs. The slight increases in variability and bias resulted in an OSA which was four percentage points higher than the OVMs and ACTs but still within the NIOSH acceptability guidelines.

The MSA Vaporgard sampler exhibited the highest variability of any of the devices tested. The coefficients of variation ranged from 8.8 percent to 160 percent. The CVs were particularly poor at the lowest concentrations. The overall bias was quite deceiving as it was only −6.3 percent, which was between the values for the ACT and SKC samplers. However, the biases encountered also had broad variations ranging from −92 percent to +61 percent. These erratic values tend to cancel one another out in the mean bias calculation. In reality, it was not certain what the true bias was at any given concentration level.

The primary cause of these poor results was believed to stem from the exceptionally high background levels of benzene found on several of the Vaporgard blanks. Benzene quantities ranging from 0.052-0.15 mg per blank accounted for values of 6 percent to 100 percent of the total benzene detected in the exposed badges. This highly variable quantity of benzene already existing within the charcoal strips of the badges had a most noticeable effect on the overall results. Not only was benzene found on the blanks, but a large number of other materials were also discovered. At least 13 distinct compounds were detected by the gas chromatographic analysis. Other than benzene, no effort was made to identify these contaminants. It was postulated that the possible source of this contamination was the off-gassing of volatile components of the plastics used to house and transport the badges. This hypothesis was not confirmed by this study.

The results of the benzene-only trial are recorded on Table III. The purpose of this trial was to expose the samplers to a single-component (benzene) environment in order to evaluate the effect produced by the complex gasoline environment. Due to the lack of adequate instrumentation to continuously monitor the benzene concentration in the chamber, hexane was mixed in with the benzene in a 1:4 ratio as a tracer substance for the Miran 1A. The resultant environment was a binary mixture of vapors with the benzene fraction predominating. Only one benzene concentration level was tested, and the average chamber concentration was approximately 85 mg/m³.

Each of the four sampling devices demonstrated system accuracies which fell within the NIOSH criteria. Coefficients of variation were quite small and in all cases were less than half of the mean CVs found in the gasoline trials. The system accuracies noted in the "benzene-only" trial were substantially lower than those found in the complex mixture exposures for each of the devices evaluated.

It was quite interesting to contrast the conclusions which could be reached by utilizing the two types of statistical analysis. Even though the ACT, SKC, and 3M OVMs were shown to be acceptable by NIOSH criteria, only the ACT and SKC methods were statistically similar. The primary differences between the response of the ACTs, the SKCs, and the 3M OVMs were their biases. The ACTs and SKCs tended to be negatively biased while the OVMs were positively biased.

TABLE III

Summary of benzene-only results

	Sampling method			
	ACT	**3M**	**SKC**	**MSA**
Chamber				
Mean* concentration (mg/m³)	84.6	84.6	84.6	84.6
Air volume				
Sampled (liters)	9.4-10.7	8.52	4.27	8.42
Mean* sampler conc. (mg/m³)	92.3	81.4	90.2	93.8
Standard deviation	2.81	2.59	2.57	6.03
Coefficient of variation (%)	3.0	3.2	2.8	6.4
Bias (%)	9.1	− 3.8	6.6	11.0
Accuracy (%)	15	10	12	24

mg/m³ — milligrams benzene per cubic meter of air
* — Geometric mean value

Previous studies have assumed that the ACT results were the true measure of the airborne contaminant concentration or otherwise compared the results of the POVMs being tested to the ACT data. This investigation clearly demonstrated that three sampling methods meeting NIOSH acceptability criteria can be shown to be not equivalent when compared directly to one another. Concluding that one method of sampling is inaccurate or imprecise based on its comparison to another may lead to incorrect interpretations.

Conclusions

The analysis of the results of this study led to the following conclusions:

1. The activated charcoal tube and air pump, the 3M 3520 OVM, and the SKC Solid Sorbent Badge methods of organic vapor sampling met NIOSH acceptability criteria for the conditions studied.
2. The activated charcoal tube and pump and the SKC passive monitor systems were found to be statistically equivalent for the overall range of concentrations studied. The 3M and MSA passive systems were not statistically equivalent with any of the other samplers studied.
3. Passive organic vapor samplers performed as well as the active sampling method, provided a high degree of quality control in reference to their diffusional rates and background contamination is maintained.
4. The presence of a complex mixture of organic vapors may adversely affect the overall accuracy of measurement of a single component of that mixture.
5. The use of statistical methods which compare one sampling method directly to another may not determine the true acceptability of either of the examined methods.

Recommendations

POVMs were shown to perform within NIOSH acceptance criteria under conditions of this study, provided adequate quality control attention is given during the manufacturing process. Industrial hygienists are cautioned to suspect decreased accuracy and precision for adsorption techniques when sampling complex mixtures or under conditions of high humidity. Direct comparison of one adsorption technique to another (assuming one technique is a benchmark) can lead to false conclusions regarding precision and accuracy. An independent method of sampling and/or analysis must be used in comparative trials. Future research should explore sampler response relative to complex mixtures in a variety of environmental conditions.

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