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A simple method for the determination of desorption efficiencies of organic compounds collected on the 3M 3500 Organic Vapor Monitor has been devel ped. The technique involves the introduction of the organic compound, in the liquid state, onto a piece of filter paper placed between the elutriation cap and the diffusion plate of the organic vapor monitor. This is accomplished by direct injection of the organic compound through the center elutriation port of the monitor cap. The port is closed and the organic compound is given sufficient time to vaporize and consequently be adsorbed by the charcoal sorbent. The filter paper is removed and analyzed as a separate sample to assure complete transfer of the organic compound. All samples are desorbed by a suitable s lv nt and analyzed by gas chromatography. Desorption efficiencies for methyl chloroform, benzene, heptane, acetone, dioxane, isobutanol and ethyl acetate are determined. A comparison with results by the phase equilibrium method is made.

Determination of desorption efficiencies in the 3M 3500 Organic Vapor Monitor

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introduction

For a quantitative determination of the amount of contaminant collected on any sorbent, it is necessary to know how much of the adsorbate is eluted out. The ratio of the measured weight recovered by the desorbing solvent to the known weight of contaminant added to the adsorbent is defined as the desorption efficiency or recovery coefficient

One procedure for determining recovery coefficients from charcoal tubes involves direct injection of a known amount of the liquid compound into the activated charcoal using a microliter syringe [1] After overnight standing, the sample is eluted with an appropriate solvent and analyzed by gas chromatography. Especially for polar compounds, the results from this method are often inconsistent.[2] In addition, direct spiking of liquid does not correspond to actual field sampling of vapor from the atmosphere. Liquid spiking may be a source of error, since the compound is localized in a small area of the sorbent rather than being uniformly distributed throughout the sorbent.

In activated charcoal sorbent, the spaces, called pores, between the individual microcrystallites may be further classified as:

a) micropores, with effective radii of less than 18-20 Angstroms, comprising a minimum of 95% of the total surface area;

b) mesopores, also called transitional pores, where capillary condensation takes place; with effective radii of roughly 20-1000 Angstroms which make up not more than 5% of the total surface area; and

c) macropores with effective radii of more than 1000 Angstroms which are too big to be filled by capillary condensation.[3]

The ratio in which the different classes of pores are present in a specific type of activated charcoal dictates its suitability for specific purposes. Microporous activated carbons are most effective for adsorption of small concentrations of gases and vapors On the other hand, mesoporous carbons are better used to recover industrial solvent vapors. The pore size distribution determines the adsorption desorption processes involved and also the resulting efficiencies Micropores may be suitable for efficient adsorption of vapors but consequent desorption from them is difficult since there may be no room for a displacing agent to enter [4]

Consider a model picture of the microcrystallites of activated charcoal [5] During a vapor spike, schematically shown in Figure 1a, we can imagine the molecules first entering the macropores, then the mesopores and finally the micropores where some interactions with the walls tend to increase retention and decrease recovery by a solvent. However, a liquid spike would be concentrated in spots and tend to wet the walls of the mesopores. Imagine now that we have menisci as in Figure 1b which exhibit some surface tension It has been verified experimentally that the vapor pressure of solvents in capillaries of a few microns radius are lowered 10-80 times more than what the Kelvin Equation predicts.[6] The Kelvin Equation relates the normal vapor pressure of a liquid (assuming a flat surface) to that observed over the curved surface of the liquid given its spherical surface radius. A decrease in vapor pressure makes it harder for the liquid to vaporize and occupy the micropores The liquid would tend to stay in the mesopores where wall effects are small and the energy of adsorption is less. Consequent elution would then result in higher recoveries

With these possible deficiencies of liquid spiking in mind, the vapor-state spiking technique for the 3M 3500 Organic Vapor Monitor was developed

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Figure 1a — Concept of molecules in activated charcoal pores



Figure 1b — Meniscei formation by molecules in activated charcoal pores

experimental

gas chromatography

A Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector and an automatic sampler, Model 7672A, was used. The columns were 15% Carbowax 20M on 80–100 mesh Supelcoport, 1.8 m × 6.4 mm o.d. glass (6 ft. × 1/4 in.); 15% Carbowax 20M on 80–100 mesh Chromosorb W, 2.3 m × 3.2 mm o.d. stainless steel (7 1/2 ft. × 1/8 in.); 10% SP-2100 on 80–100 mesh Supelcoport, 3.0 m × 3.2 mm o.d. stainless steel (10 ft. × 1/8 in.); 0.1% SP-1000 on 80–100 mesh Carbopack C, 1.8 m × 3.2 mm o.d. stainless steel (6 ft. × 1/8 in.) and Chromosorb 101, 100–120 mesh, 0.9 m × 6.4 mm o.d. glass (3 ft. × 1/4 in.).

Samples to be analyzed were contained in 1 ml glass vials sealed with Teflon-lined septum caps.

procedure

For the vapor-state spiking technique, Whatman #4 filter paper, 1.6 cm in diameter, was placed between the elutriation cap and the diffusion plate in each 3M 3500 Organic Vapor Monitor. The elutriation caps were snapped on and a known quantity of the organic solvent under study was injected onto the paper through the center elutriation port. The port was closed and the system was allowed to stand at room temperature for 16-24 hours before elution to give sufficient time for total transfer of the organic compound from the filter paper to the sorbent.

Gaseous compounds, *i.e.*, ethyl chloride, were studied by inserting a rubber septum into the center elutriation port and injecting the known quantity of gas through the septum with a gastight syringe. In this case, the filter paper was eliminated. The system was allowed to stand at room temperature overnight prior to elution.

Another alternative for gas spikes was to cover the 3M 3500 *Organic Vapor Monitor* with a cylindrical glass dome equipped with an injection port and a Teflon-lined septum, as in Figure 2. To insure against leakage, Parafilm® was wrapped around the glass at contact points with the monitor. The known amount of gas was then injected through the septum into the air above the monitor. After standing 16-24 hours, the dome, barrier film and the barrier film holder of the monitor were removed. The elutriation cap was then snapped into place and both ports closed.

A measured volume (1.5 ml) of eluent was added to each monitor through the center port using an automatic dispenser. The port was resealed and the sample was allowed to elutriate for one-half hour with occasional gentle agitation. After decanting the eluate from the monitor into glass vials, analysis by gas chromatography was performed on each sample. The filter paper of each sample was separately analysed.

Standards were prepared by spiking an equivalent amount of the organic compound into sealed glass vials containing 1.5 ml of the appropriate eluent using the same injection

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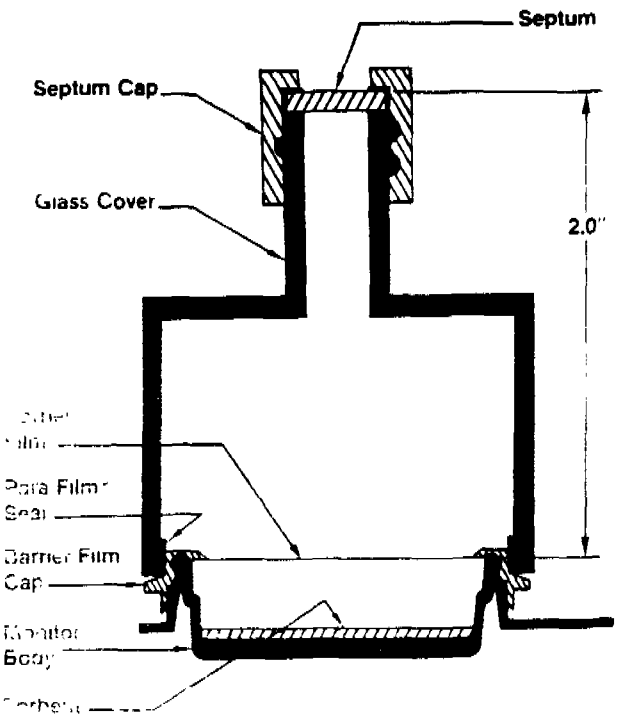


Figure 2 — Cylindrical glass dome for gas spiking

syringe. The punctured seals were replaced by new ones and the standards prepared were kept in the refrigerator at 5–6°. Before analysis, they were allowed to come to room temperature.

A parallel experiment using the Phase Equilibrium method was run simultaneously.[7] Working solutions of organic compounds diluted with the appropriate solvent were prepared. The charcoal sorbent in some monitors was removed and 1.5 ml of the working solution were added through the sampler port of the elutriation cap. These were used as the standards. An equal aliquot was added to another set of monitors which still contained the charcoal sorbent.

Both sets of monitors for each organic compound under investigation were allowed to elutriate for one-half hour at room temperature, decanted into glass vials, sealed, and analyzed by gas chromatography.

results and discussion

The sampling rates of the 3M 3500 Organic Vapor Monitor for acetone, benzene, dioxane, ethyl acetate, ethyl chloride, heptane, isobutanol, methyl chloroform and methyl ethyl ketone are listed in Table I. The Threshold Limit Value - Time-Weighted-Average (TLV-TWA) concentration for each compound was taken from the ACGIH handbook.[8] The amount spiked was the number of milligrams expected in a monitor which samples a concentration of one-half TLV-TWA for four hours except when it was beyond the capacity of the monitor. For those cases, 75% of the capacity was used.

Considering benzene with a sampling rate of 35.5 cc/min and a TLV-TWA of 30 mg/m³, we expect 0.1 mg adsorbed by the monitor at one-half TLV-TWA for four hours (mg = 35.5 cc/min × 60 min/hr × 4 hrs × 30 mg/m³ × 1/2 × 1 m³/10⁶ cc).

A comparison of desorption efficiencies obtained by the vapor-state spike and by the Phase Equilibrium method is shown in Table II. The results of five determinations per experiment are given with standard deviations. There is close agreement between the two methods except for the results of isobutanol and ethyl chloride. Both of these were eluted with methylene chloride while the rest were desorbed with carbon disulfide.

Table III lists some physical constants for methylene chloride, isobutanol and ethyl chloride. When two atoms with different electronegativities are bonded together, the bonding electrons spend a greater time near the atom of higher electronegativity, so that there is a net positive charge at the other atom and the molecule takes on a polar character. The dielectric constant and dipole moment are measures of polarity, the higher the value, the more polar is the compound. The measured diffusion coefficients for methylene chloride and isobutanol are listed while that for ethyl chloride is a theoretical value from the Hirschfelder Equation.[9]

TABLE I
Compound Guide for Determination of Desorption Efficiencies in the 3M 3500 Organic Vapor Monitor

Compound	OVM Sampling Rate cc/min	TLV-TWA[8] PPM	TLV-TWA[8] mg/m³	Spiked Amount* mg
Acetone	40.1	(1000)	(2400)	2.2
Benzene	35.5	10	30	0.1
Dioxane	34.5	(50)	(180)	0.8
Ethyl Acetate	34.5	400	1400	5.8
Ethyl Chloride	38.8	1000	2600	0.2
Heptane	28.9	400	1600	5.6
Isobutanol	35.9	50	150	0.6
Methyl Chloroform	30.9	350	1900	7.0
Methyl Ethyl Ketone	36.3	200	590	2.6

*Amount sampled by the monitor at a concentration of 1/2 TLV-TWA for four hours except when it is beyond the capacity of the monitor. For those cases, the amount spiked is 75% of the capacity.

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The molecular radius of the compounds were predicted from atomic volumes.[10] From our concept of the activated charcoal surface with the different pore structures, we can imagine that with the presence of both methylene chloride and isobutanol in the Phase Equilibrium method, there results a competition between the two compounds as they travel into the pores. The greater mobility of the smaller molecule, in this case, methylene chloride, also results in faster diffusion into the micropores.

Another contributing factor is the higher concentration of methylene chloride, present as the solvent, which allows for more collision and interaction with the surface than the isobutanol, permitting deep penetration into the finer pores. There exists, therefore, a higher concentration of isobutanol in the mesopores which have lower energies of adsorption. Upon decantation and analysis of the resulting solution, high isobutanol recoveries are obtained.

Using vapor-state spiking, there is no competitor with isobutanol for the active sites on the charcoal surface, so the molecules are free to seek even the fine pores which have higher energies of adsorption.

We have observed that a 30 minute interval was sufficient to transfer all the spiked isobutanol from the filter paper to the charcoal. For an experiment, several monitors were spiked with isobutanol and allowed to stand for 0.5, 1.0, 4.0 and 24 hours prior to elution and analysis. Even at 30 minutes, no trace of isobutanol was found on the filter paper. Table IV shows that a longer adsorption time can cause lower recoveries for isobutanol.

More molecules are adsorbed in the micropores, thus desorption is difficult. Since analysis of samples does not immediately follow the field sampling, it is therefore recommended that the method used for determination of desorption efficiencies be designed to duplicate actual use situations as closely as possible.

The effect of time was also studied for the Phase Equilibrium method using ethyl chloride. Aliquots of a prepared solution of ethyl chloride in methylene chloride were added to several organic vapor monitors and were analyzed at different time intervals. the results in Table V show a change in the adsorption desorption process within 24 hours, giving an average desorption efficiency of 1.02 ± 0.01.

TABLE II
Comparison of Desorption Efficiencies

Compound	Desorption Efficiencies	
	Vapor Spike	Phase Equilibrium
Acetone	0.93 ± 0.03	0.94 ± 0.01
Benzene	0.99 ± 0.01	0.99 ± 0.01
Dioxane	0.92 ± 0.03	0.88 ± 0.02
Ethyl Acetate	0.98 ± 0.03	0.98 ± 0.01
Ethyl Chloride	0.81 ± 0.03	1.01 ± 0.01
Heptane	1.04 ± 0.03	1.03 ± 0.01
Isobutanol	0.90 ± 0.02	1.04 ± 0.01
Methyl Chloroform	1.02 ± 0.02	1.02 ± 0.01

These data also demonstrated that the 3M 3500 Organic Vapor Monitor does not leak and that the monitor materials are inert both chemically and physically. The efficient seal of the organic vapor monitor was further verified by a test wherein monitors with the elutriation caps on were exposed to a chamber saturated with xylene vapors for two hours. A control sample without a cap was used and this collected about 59 mg of xylene while the capped ones only showed trace amounts.

The results from an investigation of concentration effects on desorption efficiencies by both vapor-state spiking and Phase Equilibrium methods are summarized in Table VI. The concentrations chosen were all less than the suggested spiked amount of 2.6 mg MEK/1.5 ml carbon disulfide (see Table I).

The unpaired t statistical evaluation of the data showed no significant differences between the desorption efficiencies of concentration Levels II and III for both methods.[11] At a confidence level of 95%, the test statistic t values for the vapor-state spiking method and for the Phase Equilibrium method were 0.24 and −0.89, respectively. Desorption efficiency values at concentration Level I were significantly different from the pooled results of concentration Levels II and III for both methods. At low concentrations, the walls of the pores in the sorbent strongly hold onto the molecules of the compound and the eluent cannot completely sever all bonds formed, thus creating a case of irreversible adsorption.

A comparison between a vapor-state spike and a directly injected liquid spike onto the charcoal sorbent of the 3M

TABLE III
Physical Constants[12,13]

	Methylene Chloride	Isobutanol	Ethyl Chloride
Molecular Formula	CH_2Cl_2	$C_4H_{10}O$	C_2H_5Cl
Molecular Weight	84.94	74.12	64.52
Boiling Point	39.75 °C	108 °C	12.3 °C
Dielectric Constant	1.0065 (gas) 9.08 (liq.)	15.8 (liq.)	1.0132 (gas)
Dipole Moment	1.60 debyes	1.64 debyes	2.05 debyes
Diffusion Coefficient	0.1037 cm²/sec	0.0880 cm²/sec	0.1134 cm²/sec
Molecular Radius	4.754 Å	5.637 Å	4.856 Å

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TABLE IV
Effect of Time on Vapor State Spiking of Isobutanol

Adsorption Time (hrs)	Desorption Efficiency
0 5	0 97
1 0	0 99
4 0	0 98
24 0	0 91

TABLE V
Effect of Time on Phase Equilibrium Method for Ethyl Chloride

Adsorption Time (hrs)	Desorption Efficiency
0 5	1 02
1 0	1 01
2 0	1 01
3 0	1 03
5 0	1 01
6 0	1 02
7 0	1 02
24 0	1 01
Average	1 02 ± 0 01

3500 Organic Vapor Monitor was made and the results are listed in Table VII. No difference in the desorption efficiencies of MEK by both methods was seen when overnight adsorption was utilized (test statistic t was −0 973 at α 0 05). The effect of different adsorption time intervals was studied. Results are given in Table VIII. It was noted that complete transfer of the compound from the filter paper to the sorbent was accomplished within 30 minutes prior to elution.

No significant change was observed even after 24 hours adsorption time by the vapor-state spike method. On the other hand, a slight decrease in desorption efficiency was observed using the direct liquid spike method.

summary

The efficiency of elution recovery processes can be affected by many variables, including sample introduction, adsorption, desorption time, chemical structures and concentration. Much of the variability can be explained by differences in the mechanisms of filling and emptying the pores of specific shape and size. Since the filling of pores of the sorbent in the 3M 3500 Organic Vapor Monitor in an actual field sampling of vapors from the atmosphere runs parallel to that in the vapor-state spiking method, more reliable desorption efficiencies by this latter method is expected.

Although it was shown that no differences were found between the vapor-state spiking method and the direct liquid spiking method for the determination of the MEK desorption efficiency, other factors like concentrations, the length of time of adsorption and chemical structure may make

TABLE VI
Effect of Concentration on Desorption Efficiency of MEK

Concentration (μg/mL)	Vapor-State Spiking Technique	Phase Equilibrium Technique
Level I		
80 54	0 70	0 94
	0 69	0 87
	0 69	0 92
	0 68	0 86
	0 70	0 85
Average	0 69 ± 0 01	0 89 ± 0 04
Level II		
805 4	0 90	0 91
	0 89	0 95
	0 90	0 93
Average	0 90 ± 0 01	0 93 ± 0 02
Level III		
1610 8	0 87	1 02
	0 90	0 93
	0 92	0 95
	0 89	0 93
	0 89	0 93
Average	0 89 ± 0 02	0 95 ± 0 04

G C Column	15% Carbowax 20M on 80 100 mesh Supelcoport 1 8 m × 6 4 mm o d glass (6 ft × 1/4 in)
Temperature	Isothermal 60 °C
Carrier Gas	Helium 30 3 mL min
MEK Retention Time	1 25 minutes

TABLE VII
Comparison of Desorption Efficiencies of MEK

Vapor Spike		Liquid Spike	
0 92		0 91	
0 92		0 92	
0 89		0 92	
0 91		0 92	
0 92		0 92	
Average	0 91 ± 0.01	Average	0 92 ± 0.004

TABLE VIII
Effect of Time on Desorption Efficiency of MEK

Adsorption Time (hrs)	Desorption Efficiency	
	Vapor State Spike Method	Liquid Spike Method
0 5	0 91	0.94
1 0	0 90	0 92
4 0	0.92	0.91
24.0	0.90	0.91

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greater differences. In our experiment, we used the suggested spiked amount for MEK representing an exposure of one-half TLV-TWA for four hours. Measuring lower concentrations in the field may produce 5-29% differences depending on whether the determination of the desorption efficiency of MEK is doen by the vapor-state spike or the Phase Equilibrium techniques. The differences seem to be more pronounced with polar compounds. The results of the two techniques agreed when less polar to nonpolar compounds were studied

The time of adsorption to achieve equilibrium of the adsorbed molecules with the structural atoms of the surface of the sorbent affects the vapor-state spiking method more than the Phase Equilibrium technique.

The vapor-state spiking technique used to determine 3M published values is therefore recommended for the determination of desorption efficiencies using the 3M 3500 Organic Vapor Monitor.

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