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Evaluation of the Standard NIOSH Type Charcoal Tube Sampling Method for Organic Vapors in Air

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The standard charcoal tube method as developed by NIOSH offered an improved method for sampling organic airborne contaminants. The method was validated for over 200 organic compounds. The protocol used, however, had several shortcomings. These shortcomings included dry air dilution, small dose levels (0.5-1.0× OSHA standard for 5-53 minutes), and lack of verification of test gas mixtures by on-line instrumentation calibrated with certified mixed gas cylinders. An improved protocol recently developed has been used to test a number of the more common organic airborne contaminants. When this procedure was used, 14 of the 22 compounds failed to meet NIOSH accuracy requirements (≤±25% over the range of 0.5 to 2.0× OSHA standard at the 95% confidence level). This work suggests that workers in the industrial hygiene field should consider the charcoal tube method only as an independent method and not as a primary standard for air monitoring.

Introduction

In 1970, workers at the Bureau of Occupational Safety and Health (BOSH), now the National Institute of Occupational Safety and Health (NIOSH), introduced a method for sampling organic airborne contaminants using a glass tube packed with activated charcoal.(1) This method resulted in an integrated exposure sample. Later, two researchers reported on a modified tube sampling method that was evaluated using 14 common organic vapors.(2) Other investigators verified the use of charcoal tubes for sampling a variety of organic vapors in air and suggested modifications to the method.(3-5)

In 1974, workers at NIOSH[D] reported on a comprehensive study of charcoal tube sampling.(6) That same year validation tests on 245 compounds were published.(7)

Up to this time there were no reported studies in which the charcoal tube method was checked for overall accuracy, including precision and bias, using certified organic vapor/air gas mixtures in conjunction with calibrated on-line instrumentation.

Melcher *et al.*(8) and Shotwell *et al.*(9) cautioned the industrial hygiene community on long-term (8-hour) sampling of organic vapors with solid sorbents. The authors suggested criteria to be used in judging methods and emphasized the need for establishing sampling guidelines that were both *precise* and *accurate*.

With the introduction of passive personal samplers (badges), a number of studies were undertaken to compare these new methods with the "standard" NIOSH charcoal tube sampling method.(10-15) Those involved in these tests generally assumed that the charcoal tube method (NIOSH P&CAM 127) was the "reference method" and that it gave the true concentration of all organic vapors under both laboratory or field sampling conditions since validation tests had been documented for various compounds. Close inspection of the validation test data for charcoal tube sampling of 243 organic compounds reveals three shortcomings in the protocol. First, although breakthrough was clearly established, the contaminant tested was mixed with dry (8% RH) air. This level of relative humidity is significantly different from most field exposure conditions where relative humidity averages 50% or greater. Second, exposure levels were tested at 0.5×, 1.0×, and 2.0× the OSHA standard with the correct concentrations in ppm or mg/m^3. However, the exposure times ranged from as low as 5 minutes in some tests to a high of 53 minutes in other tests. These conditions represent levels as low as 0.005× the dose level in ppm-hours for an 8-hour exposure. For example, in the validation test data for toluene (NIOSH Method S343), charcoal tubes were exposed for 10 minutes at 150, 300, and 600 ppm at flow rates of 200 cm^3/min. These rates represent 25, 50, and 200 ppm-hours doses, which are 0.016 to 0.063 times the OSHA 8-hour TWA dose (2400 ppm-hours). Third, the validation tests presented no data on the performance of charcoal tubes when used to determine a known vapor concentration verified by on-line instrumentation calibrated with certified mixed gas cylinders.

This paper reports on a study in which standard NIOSH-type charcoal tubes were used as an independent check on the concentration in dynamic exposure chambers which were continuously monitored with an on-line gas chromatograph and/or an infrared analyzer, each calibrated daily with mixed gas cylinders certified (±2%) by the supplier. Tests were conducted for 6 hours at 80% relative humidity to simulate the worst conditions for industrial TWA monitoring and were part of an ongoing program to establish reliable sampling rate data for Du Pont's GBB organic vapor monitoring badges.

[D]A division of the Centers for Disease Control, Department of Health and Human Services.

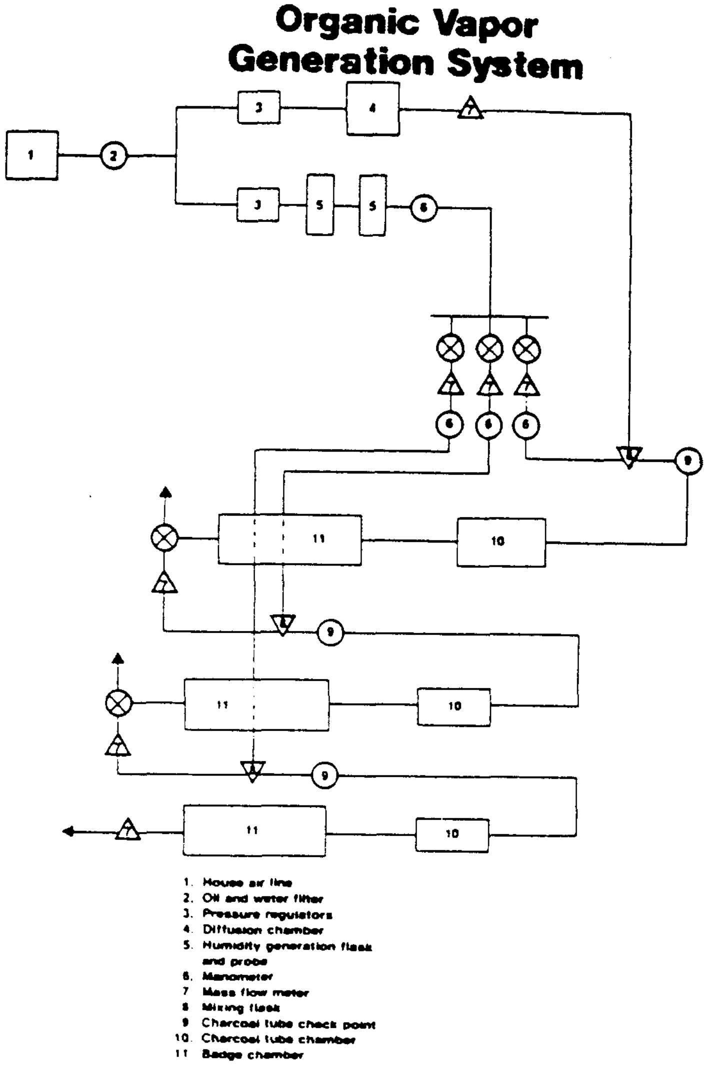

Figure 1 — Schematic of laboratory apparatus.

Experimental

The laboratory test apparatus and test protocol used are described in a separate manuscript.[16]

The controlled test atmosphere system used was designed to accommodate both the Du Pont GAA or GBB organic vapor passive dosimeters and six charcoal tubes in the same environment. The system was also designed to produce three simultaneously generated vapor concentrations: 1/2, 1 and 2 times the permissible exposure limit, as recommended by NIOSH but for 6-hour duration at 80% relative humidity.

The entire system was constructed of glass, Teflon® fluorocarbon resin and stainless steel, to minimize effects from the contamination of other materials.

Two airstreams flow into the system (Figure 1). One stream was passed over a heated flask of water to generate humidified air which was monitored continuously with YSI Model 91HC electronic hydrometer and Model 9102 dual humidity probe. The relative humidity was maintained at 80% to simulate worst case conditions, since water is known to compete very strongly for active sites on charcoal.

The second air stream was passed through a Freeland type diffusion chamber in which the organic vapors were generated from diffusion tubes. The rate at which the organic vapor was introduced into the system was calculated by dividing the total weight loss from the tube by the length of time that it was in the diffusion chamber.

There were three passive dosimeter chambers, each followed by a charcoal tube sampling manifold, in series, in system (Figures 2 and 3). Both the humidified and contaminant airstreams were mixed previous to passing through the first charcoal tube manifold and badge chamber. As the flow exited the first badge chamber, half the flow was exhausted into the hood and the remaining half was introduced into a mixing flask and diluted with an equal volume of humidified air, thus halving the concentration. This contaminant flow was then introduced into the sampling chamber and the dilution process repeated before introduction into the last chamber. In this manner three different concentrations could be produced by serial dilution.

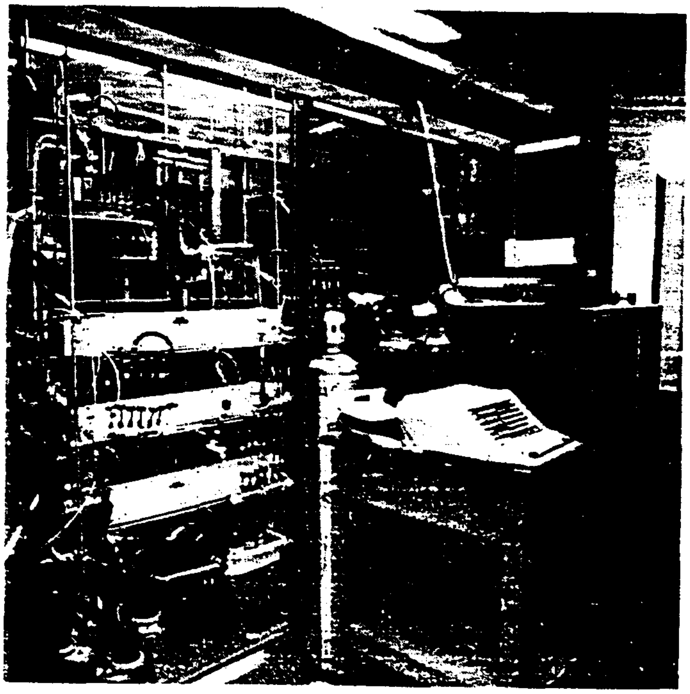

Figure 2 — Photo of laboratory validation setup.

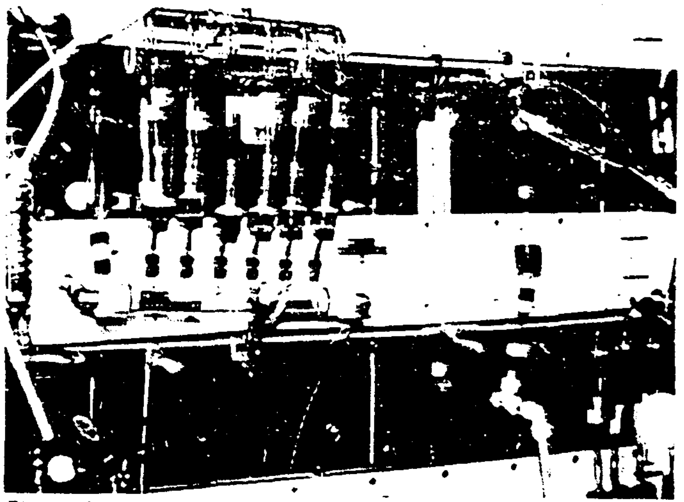

Figure 3 — Closeup photo of charcoal tube sampling manifold.

Measuring, as well as balancing flows and leak testing, was accompanied by the use of Kurz Model 565-6 flow meters calibrated with a soap bubble buret. Six charcoal tubes were connected to each sampling manifold as shown in Figure 4.

Badge chamber and charcoal tube manifold concentrations were monitored hourly by an on-line gas chromatograph, Hewlett-Packard Model 5880A, equipped with a flame ionization detector and an automatic gas sampling valve. The gas chromatograph was calibrated before and after each test with a certified (±2%) mixed gas cylinder (Scott Environmental Technology, Inc.) with a concentration close to that generated for the exposure test. Samples at other points in the system were taken with gas syringes and analyzed on the same gas chromatograph. The "known" exposure concentration during the duration of the test period was determined from the average of the gas chromatograph readings, as well as from the weight loss of the diffusion tubes. The test period was generally 6 hours. These agreed within 5% on most tests.

Charcoal tube flow rates were controlled at 50 cubic centimeters per minute (cm^3/min) with the use of critical orifices. Critical orifices were calibrated weekly.

Charcoal tube desorption efficiencies were determined at three levels as close as possible to the anticipated exposure concentrations. The phase equilibrium method was used in all charcoal tube desorption tests.(18) Known quantities of each compound of interest were added to the desorbing solvent and refrigerated for 1 hour. Refrigeration limits solvent lost due to evaporation caused by the heat produced from the exothermic adsorption reaction. Usually, carbon disulfide was used to desorb the charcoal, although in some cases the addition of 5-10% isopropanol increased recovery. Six passive dosimeters and charcoal tubes were desorbed at each of the three concentrations that were tested in the system. No desorption efficiency was accepted unless greater than 75%, and the sample coefficient of variation did not exceed 7%. The charcoal tubes used were SKC type 226-38 from Lot 120. All desorbed samples were analyzed on a gas chromatograph equipped with a flame ionization detector and automatic liquid sampler. The chromatographic conditions used for each organic compound are summarized in Table 1. The weight in nanograms of contaminant found on the front (100 mg) and back section (50 mg) of the tube was corrected using the experimentally determined desorption

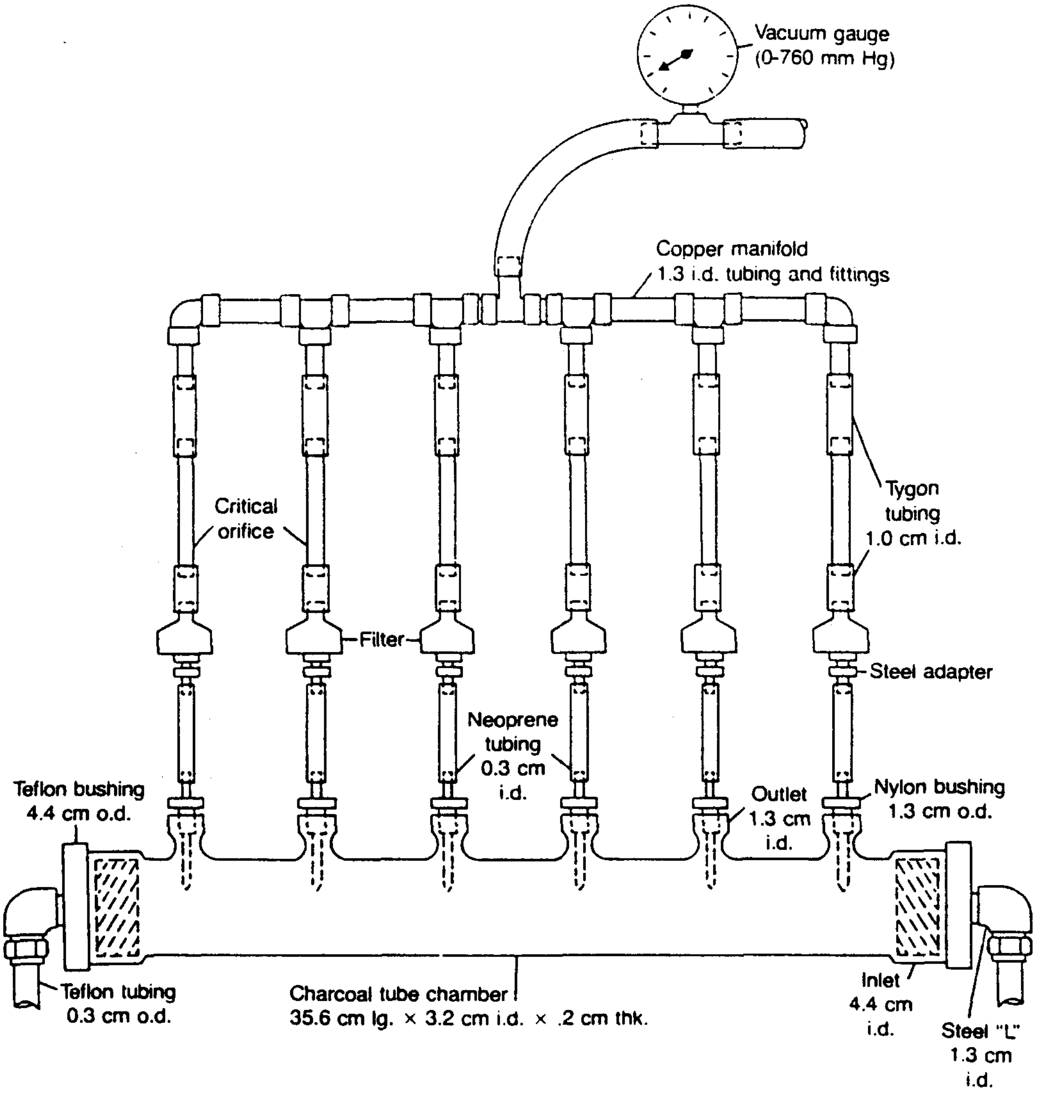

Figure 4 — Schematic of charcoal tube sampling method.

TABLE I
Charcoal Tube Analytical Test Parameters[A]

Compound	Column Type[B]	Gas Chromatograph Conditions: Temperature Settings (°C) Oven	Inj. Port	Detector
Ethanol[C]	B	70	80	90
Isopropyl alcohol	D	70	150	150
t-Butyl alcohol	D	65	120	200
n-Pentane	A	100	160	170
Cyclohexane	D	60	150	150
n-Hexane	D	65	100	100
n-Octane	D	60	100	100
Benzene	D	70	150	150
Toluene[D]	D	85	250	250
(VM+P) Naphtha	D	65	120	120
Ethyl benzene	A	190	250	250
Cumene	D	125	150	150
Methyl cellosolve[E]	B	130	200	200
Dioxane	A	100	110	120
Isopropyl acetate	A	170	180	190
Isobutyl acetate	A	170	180	190
Methylene chloride	A	50	200	200
Methyl chloroform	A	100	240	250
Methyl ethyl ketone	A	90	250	250
Mesityl oxide[E]	C	120	130	140
Methyl isobutyl ketone	A	150	200	200

[A] Desorbing solvent = CS_2 (unless specified otherwise). Volume of solvent = 1.5 mL.

[B] A = 0.1% SP 1000 on Carbopack C (glass) 1/4", 4-6 ft. 80/100 mesh.
B = 10% FFAP on Supelcoport (glass) 1/4", 4-6 ft. 80/100 mesh.
C = Same as B only stainless steel columns 1/8", 4-6 ft. 80/100 mesh.
D = 10% Carbowax 20M on Chromosorb W, AW-DMCS, 80/100 mesh, 6 ft. long × 6 mm O.D. × 4 mm I.D.

[C] Acetonitrile.

[D] 1% 2-butanol in CS_2.

[E] 10% methanol in methylene chloride.

efficiency and compared with the expected weight. The percentage error was the ratio of contaminant found on the charcoal tube to the expected weight of contaminant as determined from the known chamber concentration, the flow rate through the tube (50 cm^3/min), and the total sampling time. The experimental data are tabulated in Table II. The average breakthrough was calculated from the ratio of the weight found on the back section to the total weight collected on the exposed tube. A breakthrough value of 25% or higher invalidated the test.

Statistics

The statistical treatment of data is a combination of that recommended by NIOSH[7] and a conservative treatment used previously by one of the authors.[10,19,20] The pooled bias ratio B for each compound tested on charcoal tubes was obtained using Equation 1:

$$\hat{B} = \sum_{i=1}^{k} n_i B_i / \sum_{i=1}^{k} n_i \tag{1}$$

where: B_i is the average relative error for six charcoal tubes (n_i) exposed at each test level (k). These data are included in Table II.

The coefficient of variation CV_i is a measure of the pre- sion or reproducibility of the method. It includes both lytical and sampling sources of variation. The calculated total pooled coefficient of variation $\widehat{CV}_T$ is obtained by using experimental data in Equation 2:

$$\widehat{CV}_T = \left[\sum_{i=1}^{k} f_i (CV_i)^2 / \sum_{i=1}^{k} f_i\right]^{1/2} \tag{2}$$

where: $CV_i = S_i/\bar{X}_i$ denotes the coefficient of variation for each set of charcoal tubes at exposure levels i = 1 through k, sampling via critical orifices in place of constant flow sampling pumps, S_i is the standard deviation, $\bar{X}_i$ is the average charcoal tube-determined concentration, and f represents the degrees of freedom. These terms are all defined elsewhere.[7]

In order to establish a more practical coefficient of variation, the minimum sampling pump error was included by using Equation 3:

$$(\overline{\overline{CV}}_T)^2 = (\widehat{CV}_T)^2 + (CV_p)^2 \tag{3}$$

where: CV_p was assigned a minimum of 5% error similar to that used by NIOSH.[6]

The target total coefficient of variation $(CV_T)_o$ is the threshold value that $\overline{\overline{CV}}_T$ must be less than to guarantee that the total error in the sampling and analytical method is wit ±25% of the true concentration 95% of the time. (C depends on the true bias ratio B and is needed in order to carry out a statistical test at the 0.05 level.

Bush and Taylor[6,7] present both a figure and a table for establishing $(CV_T)_o$ values based on given known bias ratios, B.[19] The value of $\overline{\overline{CV}}_T$ must be demonstrated to be less than the critical coefficient of variation $(CV_T)_c$ to conclude $\overline{\overline{CV}}_T \le (CV_T)_c$ at the 0.05 statistical test level. These authors provide values for $(CV_T)_o$ for m = 18 and k = 3 levels. In many cases validation tests involve more than three exposure levels (Table II). Consequently, $(CV_T)_c$ can be calculated from a complicated expression given by Hald,[20] where:

$$(CV_T)_c = \text{Function of } [(CV_T)_o, f, n] \tag{4}$$

and the target coefficient of variation $(CV_T)_o$ is obtained by iteratively solving the expansion:

$$0.95 = \Phi\left(\frac{0.25 - B}{(CV_T)_o}\right) - \Phi\left(\frac{-0.25 - B}{(CV_T)_o}\right) \tag{5}$$

where: B is the pooled bias and $\Phi(x)$ is the standard normal distribution function.

The validation test at the 0.05 level may be carried out by comparing the calculated total pooled coefficient of va tion $\overline{\overline{CV}}_T$ to the critical coefficient of variation $(CV_T)_c$ value. If $\overline{\overline{CV}}_T \le (CV_T)_c$, the NIOSH accuracy criterion has been demonstrated to hold with 95% confidence.

TABLE II

Performance of Standard Charcoal Tubes Sampling Various Organic Contaminants in Air at 25°C, 80% Relative Humidity for Six Hours at 50 cm^3/min Using Critical Orifices to Control Flow[A]

Class/Compound	Maximum Capacity NIOSH Validated[B] (mg)	Test Levels (ppm) This Work	Analytical Results			% B.T.
			mg Calc'd	mg Found	% Error Bias, B_i	
Alcohols						
1) Ethanol	5.2	45	1.62	1.82	+11.0	17
		106	3.85	4.42	+14.8	21
				$\hat{B}$ =	+12.9	
2) Isopropyl alcohol	11.3	52	2.31	2.75	+18.9	0
		174	7.70	5.43	−29.5	0
				$\hat{B}$ =	− 1.8	
3) t-Butyl	9.9	18	0.97	0.94	− 3.1	0
		41	2.06	2.00	− 2.9	0
		64	3.29	2.98	− 9.4	0
		72	3.70	3.31	−10.5	0
				$\hat{B}$ =	− 6.5	
Aliphatics						
4) n-Pentane	18.0	28	1.57	1.85	+17.8	24.1
		64	3.58	3.48	− 2.8	23.6
		134	7.49	7.21	− 3.7	12.6
				$\hat{B}$ =	+ 3.8	
5) Cyclohexane	12.5	46	2.66	2.69	− 1.1	12.0
		87	5.40	6.23	+15.4	13.6
		271	16.80	17.70	+ 5.4	2.0
				B =	+ 6.6	
6) n-Hexane	21.7	16	1.05	1.04	− 1.0	0
		46	2.98	2.77	− 7.5	0
		184	11.90	11.80	− 0.6	0
				B =	− 2.8	
7) n-Heptane	21.0	72	5.41	6.31	+ 9.9	0
		103	8.16	9.04	+10.8	0
		266	18.21	20.1	+10.3	0
				$\hat{B}$ =	+10.3	
8) n-Octane	30	41	3.48	3.26	− 6.3	0
		87	7.38	6.70	− 9.2	0
		113	9.58	9.68	+ 1.0	0
		353	29.92	27.80	− 7.1	3.1
				B =	− 5.4	
Aromatics						
9) Benzene	7.2	3.1	0.162	0.156	− 3.7	0
		7.5	0.352	0.362	+ 2.8	0
		15.2	0.795	0.872	+ 9.7	0
		19.6	0.990	1.190	+20.2	0
		23.1	1.450	1.090	−24.8	0
		24.0	1.080	1.150	+ 6.5	0
		24.0	1.300	1.090	−16.2	0
				B =	+ 0.8	
10) Toluene	27.3	44	3.06	2.85	− 6.9	0
		53	3.61	3.92	+ 8.6	0
		56	3.79	3.75	− 1.1	0
		57	3.84	3.95	+ 2.9	0
				B =	+ 1.2	

TABLE II (Cont'd.)

Class/Compound	Maximum Capacity NIOSH Validated[A] (mg)	Test Levels (ppm) This Work	Analytical Results mg Calc'd	mg Found	% Error Bias, B_i	% B.T.
11) VM+P Naphtha	29.7	22	2.19	2.30	+ 5.0	0
		51	5.46	5.76	+ 5.5	0
		97	8.04	7.79	− 3.1	0
		252	18.80	20.30	+ 8.0	0
				$\hat{B}$ =	+ 3.9	
12) Ethyl benzene	32.4	31	2.54	2.77	+ 9.1	0
		65	5.33	5.50	+ 3.2	0
		124	10.15	11.50	+13.3	0
				$\hat{B}$ =	+ 8.5	
13) Cumene	22	16.8	1.48	1.46	− 1.4	0
		34.5	3.05	3.05	0.0	0
		116.0	10.23	10.60	+ 3.6	0
				$\hat{B}$ =	+ 0.8	
Ethers						
14) Methyl cellosolve	20.3	6.5	0.380	0.281	-26.1	0
		12.5	0.731	0.581	-20.5	0
		24.5	1.430	1.270	-11.2	0
				B =	-19.3	
15) Dioxane	26	36	2.40	2.12	-11.7	0
		81	5.39	4.52	-16.1	0
		179	11.90	9.41	-20.9	0
				B =	-16.2	
Esters						
16) Isopropyl acetate	26	97	6.84	8.25	+20.6	0
		229	16.14	19.28	+19.5	0
		508	35.90	24.70	-31.2	0
				B =	+ 3.0	
17) Isobutyl acetate	27.6	53	4.51	5.10	+13.1	0
		105	8.94	10.65	+19.1	0
		218	18.56	21.66	+16.7	0
				$\hat{B}$ =	+16.3	
Halogenated						
18) Methylene chloride	23.3	51.3	3.20	3.05	− 4.7	40
		110.0	6.83	6.74	− 1.3	33
				B =	− 3.0	
19) Methyl chloroform (1,1,1-trichloroethane)	36.2	31.0	3.08	3.27	+ 6.2	1
		63.9	6.36	6.84	+ 7.5	1.1
		132.0	13.10	15.60	+19.1	0.3
				$\hat{B}$ =	+10.9	
Ketones						
20) Methyl ethyl ketone	17.5	42.6	2.27	1.52	-33.0	0
		77.0	4.14	3.11	-24.9	0
		156.0	8.30	6.92	-16.6	6.2
				$\hat{B}$ =	-24.8	
21) Mesityl oxide	9.6	9.0	0.69	0.56	-18.2	0
		19.0	1.45	0.96	-37.8	0
		37.0	2.82	1.89	-33.0	0
				$\hat{B}$ =	-27.9	
22) Methyl isobutyl ketone	35	26	1.96	0.89	-54.6	0
		57	4.29	2.24	-47.8	0
		119	8.95	5.48	-38.8	0
				$\hat{B}$ =	-47.1	

[A] For 100 mg front section of charcoal tube, see Table IV.

TABLE III

Summary of Sampling Data Using Standard Charcoal Tubes at 25°C, 80% Relative Humidity and 50 cm^3/min — 6 Tubes Per Test (Most Tests)[A]

Class/Compound	Range (ppm) Tested	Avg. Error[B] (%) Found vs. Calc'd	$\overline{\overline{CV}}_T$[C]	Overall[D] Accuracy ±%	$(CV_T)_c$[E]
Alcohols					
Ethanol	45-106	+12.9	0.066	26.1	0.046
Isopropyl alcohol	52-174	- 1.8	0.143	30.4	0.060
t-Butyl alcohol	18.3-72	- 6.5	0.086	23.7	0.082
150 Butyl alcohol	20-140	+13.3	0.081	29.5	0.048
Aliphatics					
n-Pentane	28-134	+ 3.8	0.112	26.2	0.087
Cyclohexane	46-271	+ 6.6	0.108	28.2	0.076
n-Hexane	16-184	- 2.8	0.063	15.4	0.069
n-Octane	41-353	- 5.4	0.063	18.0	0.082
n-Heptane	76-241	+10.3	0.113	32.9	0.062
Aromatics					
Benzene	3.1-24	+ 0.8	0.060	12.8	0.101
Toluene	44.0-57	+ 1.2	0.086	18.4	0.093
(VM+P) Naphtha	21.7-252	+ 3.9	0.079	19.7	0.110
Ethyl benzene	31.0-124	+ 8.5	0.074	23.3	0.070
Cumene	16.8-115.8	+ 0.7	0.072	15.1	0.089
Ethers					
Methyl cellosolve	6.5-24.5	-19.3	0.065	32.3	0.024
Dioxane	36.0-179	-16.2	0.065	29.2	0.037
Esters					
Isopropyl acetate	97-508	+ 3.0	0.072	17.4	0.086
Isobutyl acetate	53-218	+16.3	0.064	29.1	0.037
Halogenated					
Methylene chloride	51.3-111	- 3.0	0.077	18.4	0.084
Methyl chloroform	31.0-132	+10.9	0.101	31.1	0.059
Ketones					
Methyl ethyl ketone	42.6-156	-24.8	0.075	39.8	0.001
Mesityl oxide	9.0-37	-29.7	0.117	53.1	0.000
Methyl isobutyl ketone	26.0-119	-47.1	0.099	66.9	0.000

[A] Six hour test exposures.

[B] Relative Bias Ratio B.

[C] $(\overline{\overline{CV}}_T)^2 = (\widehat{CV}_T)^2 + (CV_p)^2$ where $\widehat{CV}_T$ is the precision of the sampling and analytical method when critical orifices were used and CV_p is the average sampling pump error of ±5% $(CV_p)^2 = 0.0025$.

[D] Overall Accuracy = $[1.96\,(\overline{\overline{CV}}_T) + \text{Absolute Mean Bias } |\hat{B}|] \times 100$ where Mean Bias $|B|$ = average error.

[E] $(CV_T)_c$ is defined in Reference 20.

In the past the authors have treated laboratory validation data by calculating an overall system accuracy (O.S.A.) using Equation 6:(10)

$$\text{O.S.A.} = [2(\text{MCV}) + \text{Absolute Pooled Bias}] \times 100 \qquad (6)$$

where: M.C.V. is the mean coefficient of variation and the absolute pooled bias is $|\hat{B}|$.

The mean coefficient of variation (M.C.V.) and pooled coefficient of variation $\overline{CV}_T$ are identical. Equation 5, using the Bush and Taylor notation, can be expressed as Equation 7:

$$\text{O.S.A.} = [1.96(\overline{\overline{CV}}_T) + |\hat{B}|] \times 100 \qquad (7)$$

The coefficient 1.96 had been rounded off to 2 in the earlier validation reports that used Equation 6. If the O.S.A. is less than ±25%, the NIOSH accuracy criterion is satisfied. Both methods are used in the evaluation of the data presented in Table III.

Results and Discussion

The data obtained on 21 common organic airborne contaminants are summarized in Table III. These were obtained in conjunction with a test program conducted at the Du Pont Haskell Laboratory for Industrial Medicine and Toxicology. The main goal of this program was to establish experimental sampling rates for Du Pont Pro-Tek® Type G-BB organic vapor passive badges.(16) Standard charcoal tubes were included in this program as an additional independent check on the badge exposure chamber concentration. W the charcoal tube data were tabulated, it was found that l the 22 compounds tested did not meet the NIOSH accuracy criterion wherein $\overline{CV}_T \leq (CV_T)_c$, an extension of the NIOSH statistics described earlier. When the more conservative O.S.A. approach was used, nine of the group exceeded the ±25% accuracy requirement. These results were unexpected.

A sample of the calculations performed to obtain the data tabulated in Tables II and III is shown in Appendix A.

All of the aromatic compounds tested met NIOSH accuracy criterion except for ethyl benzene. In the other groups half of all compounds tested failed the accuracy criterion.

Methylene chloride was the only compound that had sufficient breakthrough to the back section of the charcoal tube and can be considered an invalid test. Breakthrough occurred even though the total amount found on the tube was only 13% of the saturation limit for 100 mg of charcoal(7) reported by NIOSH. Table IV summarized the data on the same compounds found in the NIOSH validation tests.(7) These data and the data in Table III have a minimum of 5% pump error ($(CV_p)^2 = 0.0025$) included in the $\overline{CV}_T$ values.

TABLE IV
Summary of NIOSH Charcoal Tube Validation Tests in Dry Air (at 0.5, 1.0, and 2.0× OSHA Standards)(19)

Compound	Sampling Conditions Used			Published Max. Capacity 100 mg Charcoal mg	CV_T[A]
	P&CAM S-	Flow (cm³/min)	Time (min)		
Ethanol	56	200	5	5.2	0.065
Isopropyl alcohol	65	200	12.5	11.3	0.064
t-Butyl alcohol	63	200	50	9.9	0.075
n-Pentane	379	67	30	18	0.055
Cyclohexane	28	200	13	12.5	0.066
n-Hexane	90	220	18	21.7	0.062
n-Octane	378	220	18	30.0	0.060
Benzene	311	200	10	7.2	0.059
Toluene	343	200	10	27.3	0.052
(VM+P) Naphtha	86	220	45	29.6	0.051
Ethyl benzene	29	200	50	32.4	0.041
Cumene	23	200	52.6	22.0	0.059
Methyl cellosolve	79	1000	53.5	20.3	0.068
Dioxane	360	220	44	26.0	0.054
Isopropyl acetate	50	220	37	26.0	0.067
Isobutyl acetate	44	220	45	27.6	0.065
Methylene chloride	329	50	15	23.3	0.073
Methyl chloroform	328	220	15	36.2	0.054
Methyl ethyl ketone	3	200	50	17.5	0.072
Mesityl oxide	12	200	50	9.6	0.071
Methyl isobutyl ketone	18	200	52.6	19.9	0.064

[A] Includes Minimum Pump Error; $CV_T^2 = CV_2^2 + (CV_p)^2$, $(CV_p)^2 = 0.0025$, CV_2 = analytical and sampling precision.

The overall averages of CV_T were slightly higher than reported in the NIOSH validation tests, although no judgment can be made about the accuracy of the charcoal tube method for any compound tested from the validation data as presented. The decision rule stated in the document is that $\overline{CV}_T$ must be less than 10.5%, which is the $(CV_T)_c$ for an unbiased method. Since the experimental protocol used did not contain an independent method, *e.g.*, certified mixed gas cylinders to calibrate on-line instrumentation, the data presented prove only that the charcoal tube method is precise but not necessarily accurate.

Conclusions

Laboratory tests to data indicate that the NIOSH charcoal tube sampling method has serious deficiencies when used to determine the true exposure concentration of many common industrial organic compounds in moist air. In view of the results presented, users are cautioned to consider charcoal tube sampling only as another independent monitoring procedure and not as a "reference standard," especially when comparisons are made with other sampling methods in field work.

Laboratory validation of charcoal tubes prior to field sampling is strongly recommended.

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APPENDIX

Sample Calculations — Toluene

Toluene (MW = 92)

Test Level 53 ppm for 6.0 hours

Expected Charcoal Tube pickup (Table II) calculated as follows:

1) 53.3 ppm = 200.4 mg/m^3 = 200.4 μg/L
2) (0.050 L/min)(360 min)(200.4 mg/m^3)(10^{-3} mg/g)
   = mg Expected
   = 3.61 mg Expected
3) % Error (Bias)(B_i) = 100(Found − Expected) Found
   = +8.6%
4) Mean Bias (Error) B $\Sigma n_i B_i$ Σn_i (Equation 1)
   n_i = 6
   B = 5[(−6.9) + (6)(+8.6) + (6)(−1.1) + (6)(+2.9)] 23
   = +1.2%

5) Table III

From experimental data:

$CV_1 = 5.3\%$; $n = 5$; $f = 4$
$CV_2 = 9.8\%$; $n = 6$; $f = 5$
$CV_3 = 3.3\%$; $n = 6$; $f = 5$
$CV_4 = 7.4\%$; $n = 6$; $f = 5$

Using Equation 2:

$\widehat{CV}_T = [\Sigma (CV_i)^2 fi / \Sigma f_i]^{1/2} = 7.0 = (CV_2)$ by NIOSH Definition of precision of analytical and sampling method without sampling pump error.

6) Using Equation 3:

$(\overline{\overline{CV}}_T)^2 = (\widehat{CV}_T)^2 + (CV_p)^2$ where $(CV_p)^2 = 0.0025$ the minimum pump error

7) $[(0.070)^2 + (0.0025)]^{1/2} = 0.086$ or $8.6\% = \overline{\overline{CV}}_T$ or (M.C.V.)

8) Using Equation 5 or the plot of $(CV_T)_o$ vs. Bias (%):

$(CV_T)_o = 0.127$

Gives $(CV_T)_c = 0.093$

9) Since $(CV_T)_c > (\overline{\overline{CV}}_T)$ the method meets NIOSH accuracy criterion.

10) Overall system accuracy by Equation 6:

O.S.A. = (8.6)(2) + (1.2) = ±18.4%

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