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Evaluation of Carbon Tetrachloride Replacement Agents for Use in Testing Nonpowered Organic Vapor Cartridges

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Carbon tetrachloride has been used for years as a standard material for evaluating charcoal's ability to adsorb organic materials. It has also been the standard organic compound for testing organic vapor breakthrough characteristics of respirator cartridges and canisters. However, due to the potential carcinogenic characteristic of carbon tetrachloride and the lack of commercial availability, a suitable substitute organic vapor cartridge test agent is needed. Four potential replacement agents were tested (ethyl acetate, pentane, *n*-hexane, and heptane). Initially, testing was performed using the stacked-cartridge test system. This screening method identified replacement agent challenge concentrations which gave breakthrough characteristics equivalent to 1000 parts per million (ppm) carbon tetrachloride. Breakthrough time was the critical criterion. Two test conditions (550 ppm pentane and 1000 ppm n-hexane) were selected for side-by-side testing with 1000 ppm carbon tetrachloride. The results show that for the most stringent test condition ("as received" cartridges tested at 64 L/min and 80% relative humidity) the breakthrough times for two different manufacturers' organic vapor cartridges were identical for these three test conditions (1000 ppm carbon tetrachloride, 550 ppm pentane, and 1000 ppm *n*-hexane). Pentane's lower toxicity makes it the replacement agent of choice. MOYER, E.S.; PETERSON, J.A.; CALVERT, C.: EVALUATION OF CARBON TETRACHLORIDE REPLACEMENT AGENTS FOR USE IN TESTING NONPOWERED ORGANIC VAPOR CARTRIDGES. APPL. OCCUP. ENVIRON. HYG. 10(9):761–768; 1995.

The National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) have prepared and published occupational health guidelines for various chemical substances.[1] As part of the carbon tetrachloride guidelines, a special note indicates that the International Agency for Research on Cancer evaluated the data on carbon tetrachloride and concluded that it causes cancer. The American Conference of Governmental Industrial Hygienists 1991–1992 booklet of Threshold Limit Values[2] lists carbon tetrachloride with an A2 designation, which indicates chemical substances "associated with industrial processes, which are suspect of inducing cancer, based on either limited epidemiological evidence or demonstration of carcinogenesis in one or more animal species by appropriate methods."[2]

As a result of the toxicity of carbon tetrachloride, NIOSH instituted a program to find a suitable replacement substance for carbon tetrachloride in evaluating organic vapor (OV) and gas cartridges and canisters. Further, the Environmental Protection Agency recently proposed to conform its stratospheric ozone protection regulations (40 CFR, Part 82) to the requirements of Title VI of the Clean Air Act Amendments of 1990 (Public Law 101-549). This will result in the phasing-out of carbon tetrachloride production. Thus, it became essential to conduct the testing necessary to find an acceptable replacement test substance for carbon tetrachloride. This report presents data collected on OV cartridges designed for use on nonpowered, negative-pressure respirators.

Background

The current respirator certification regulations for chemical cartridges mandate testing in accordance with 30 CFR, Part 11,[3] Sections 11.162-8 and 11.183-7. Cartridges are tested "as received" from the applicant or after preconditioning at 25 or 85 percent relative humidity (RH). Varying flow rates and times are employed in the testing. A summary of the certification tests for OV and gas cartridges is given in Table 1. The rationale for equilibrating the cartridges at 25 or 85 percent RH, followed by testing at 50 percent RH and at a reduced flow rate, has been questioned.[4] It is thought that testing of as received cartridges over a broad range of RHs at the higher flow rate, 64 L/min, appears more indicative of use-type conditions.[4] Further, such testing might, in fact, constitute an improved and more realistic performance standard for testing OV and gas respirator cartridges. Truly, the fact that testing would be done under conditions more representative of use-type conditions is the most significant reason for justifying such a testing scheme.

The experimental work consisted of initial screening (phase one), followed by side-by-side testing against carbon tetrachloride (phase two). Four possible replacement agents (ethyl acetate, pentane, n-hexane, and heptane) were selected for screening based on their physical characteristics and toxicity, as well as reported charcoal adsorption characteristics.[5–8] Screening experiments tested cartridges as received from the manufacturer at 50 percent RH, 80 percent RH, and 25° ± 2°C with no preconditioning being performed. These tests were performed on a stacked-cartridge configuration which resembled a packed column or sorbent bed.[9] These tests were conducted at various challenge concentrations of carbon tetrachloride (control), ethyl acetate, pentane, n-hexane, and

TABLE 1. Summary of Organic Vapor Cartridge Certification Tests

Type of Respirator	Test Condition	Test Flow Rate (L/min)	Number of Tests	Minimum Life[A] (min)
Chemical cartridge organic vapor	As received	64	3	50
Chemical cartridge organic vapor	Equilibrated 25% RH	32	2	50
Chemical cartridge organic vapor	Equilibrated 85% RH	32	2	50
Powered air-purifying tight-fitting	As received	115[B]	3	50
Powered air-purifying tight-fitting	Equilibrated 25% RH	115[B]	2	25
Powered air-purifying tight-fitting	Equilibrated 85% RH	115[B]	2	25
Powered air-purifying loose-fitting hood or helmet	As received	170[B]	3	50
Powered air-purifying loose-fitting hood or helmet	Equilibrated 25% RH	170[B]	2	25
Powered air-purifying loose-fitting hood or helmet	Equilibrated 85% RH	170[B]	2	25

Test conditions are: 1000 ppm carbon tetrachloride and 50 percent RH; the minimum life is determined at 5 ppm breakthrough concentration.
[A]Cartridges designed for use against more than one type of agent; the minimum life shall be one-half of that shown above for each type of gas or vapor.
[B]Flow rate shall be the effective flow rate of the device, but not less than this flow rate.

heptane at 50 percent RH, 80 percent RH, and 25°C. (Warning: Ethyl acetate, pentane, n-hexane, and heptane are extremely flammable. Sparks and open flames must be avoided. Buildup of vapors in closed containers must also be avoided.) The purpose of the screening study was to identify potential replacement agents, challenge concentrations, and test conditions that would produce cartridge breakthrough times equivalent to the 1000 ppm carbon tetrachloride test.

The replacement agent(s)/challenge concentration conditions which showed equivalence with 1000 ppm carbon tetrachloride, based on breakthrough time as the critical evaluation criterion, were considered for further side-by-side testing against 1000 ppm carbon tetrachloride. This final side-by-side testing was to confirm that the test agent(s)/challenge concentration conditions gave cartridge breakthrough times equivalent to carbon tetrachloride at the most severe test condition. The side-by-side testing also determined which test condition was the most critical: equilibrated cartridges, as per 30 CFR, Part 11; or as received cartridges run at a higher test RH (80%). Finally, the side-by-side tests were to be run in accordance with the certification test procedure rather than the stacked-cartridge method used for the initial screening of the replacement test agents.

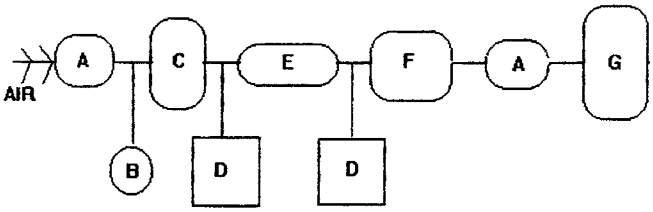
The breakthrough time data from the initial screening were used to select the agents for the side-by-side testing. The sole selection criterion was equivalency of breakthrough time with the 1000 ppm carbon tetrachloride 30 CFR, Part 11 certification test. However, other factors such as toxicity of the agent at the challenge concentration, water insolubility comparable to carbon tetrachloride, laboratory safety issues, and the existence of a suitable analytical detection system had to be considered.

The modified Wheeler equation was used for evaluating all the initial screening data.[9] The equation is as follows:

$$t_b = \frac{W_e}{C_o Q}\left[W - \frac{\rho_\beta Q}{k_v} \ln (C_o/C_x)\right] \qquad (1)$$

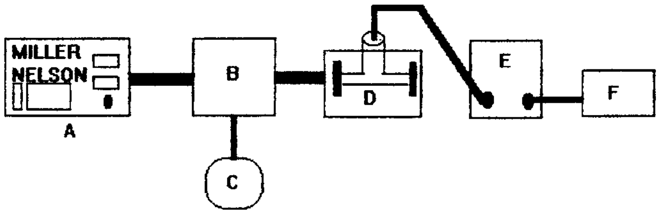
where:

t_b = breakthrough time (min)
C_x = exit concentration (g/cm^3)
C_o = inlet concentration (g/cm^3)
Q = volumetric flow rate (cm^3/min)
W = weight of adsorbent (g)
ρ_β = bulk density of the packed bed (g/cm^3)
W_e = kinetic adsorption capacity or equilibrium adsorption capacity at an arbitrary ration of C_x/C_o (g/g)
k_v = first-order rate constant of adsorption (per min)



A – FLOW CONTROL MECHANISM
B – VAPOR GENERATOR
C – BUFFER RESERVOIR TANK
D – MIRAN 1A GAS ANALYZER
E – CARTRIDGE CELL
F – SORBENT SCRUBBER
G – VACUUM SOURCE

FIGURE 1. Stacked-cartridge test system.



A. MILLER-NELSON RELATIVE HUMIDITY FLOW CONTROLLER
B. RESERVOIR
C. SYRINGE PUMP
D. CARTRIDGE CELL HOLDER
E. MIRAN 1A GAS ANALYZER
F. VACUUM PUMP

FIGURE 2. Carbon tetrachloride certification test system.

TABLE 2. Organic Vapor Cartridge Breakthrough Time (t_b) against 1000 ppm Carbon Tetrachloride for Stacked Cartridges of Manufacturer A at Equivalent of 64 L/min for Pair Configuration

% RH	Cumulative Charcoal Weight (Grams) Single Cartridge[A,B]	Calculated[C] Charcoal Weight (g) if in Pair Configuration	t_b Corrected to 1000 ppm (Minutes)		
			5 ppm	10 ppm	15 ppm
50	33.840	67.680	61.2	63.6	64.9
	66.137	132.274	156.0	158.1	159.2
	99.045	198.090	239.3	241.4	242.7
	131.121	262.242	333.4	335.7	336.0
50	33.334	66.668	64.4	67.4	68.5
	67.363	134.726	155.1	158.7	160.7
	100.622	201.244	249.6	253.9	258.4
	133.498	266.996	360.0	364.1	366.7
80	33.247	66.494	46.3	49.6	51.2
	67.738	135.476	110.3	113.5	115.0
	101.342	202.684	178.8	182.7	184.5
	136.443	272.886	246.7	250.7	253.0
80	33.236	66.472	51.3	52.9	54.5
	64.757	129.514	118.0	119.7	121.4
	97.027	194.054	190.0	192.1	193.8
	130.313	260.626	262.8	264.6	266.9

[A]Stacked single cartridges run at 32 L/min.
[B]Lot 1.
[C]Calculated = twice the single cartridge weight

The values for C_o, C_x, and Q are established by the experimental test conditions, as is the temperature that remains constant. The value of ρ_β—which is dependent on the fill weight, granular size, shape of the adsorbent, and fill volume—can be determined experimentally and is part of the manufacturer's production criteria.

Plots of breakthrough times (t_b) as a function of bed weight (W) gave a straight line where the slope and intercept allowed calculation of the kinetic adsorption capacity and the adsorption rate constant. The slope is equal to W_e/C_oQ, the y-axis intercept is equal to

$$\frac{-W_e\rho_\beta}{k_\nu C_o}\ln\frac{C_o}{C_x} \tag{2}$$

and the critical bed weight (W_c) is equal to ρ_β Q ln $(C_o/C_x)/k_\nu$. By knowing the slope, a value for W_e (kinetic adsorption capacity) can be determined. By inserting W_e into the y-axis intercept relationship, one can calculate the kinetic adsorption rate constant k_ν. Also, k_ν could be calculated from the x-axis intercept value.

The two test agent/challenge concentration systems which best satisfied the above criteria were selected for direct side-by-side carbon tetrachloride testing to compare the present 30 CFR, Part 11 test methods[3] with data generated on as received cartridges. The five test conditions were: (1) preconditioned 25 percent RH and tested at 50 percent RH and 32 L/min, (2) preconditioned at 85 percent RH and tested at 50 percent RH and 32 L/min, (3) as received tested at 25 percent RH and 64 L/min, (4) as received tested at 50 percent RH and 64 L/min, and (5) as received tested at 80 percent RH and 64 L/min. Conditions 1, 2, and 4 represent the present 30 CFR, Part 11 testing scheme, while conditions 3, 4, and 5 represent the testing scheme NIOSH is considering for future implementation.

Experimental Method

Phase one entailed the stacked-cartridge method for screening possible replacement agents and determining replacement challenge concentration. This technique, which monitors breakthrough time as a function of sorbent weight, was used because it is more discriminating than running single cartridges. Manufacturer A cartridges (pair configuration) were used, and the phase one stacked-cartridge experiments were performed at a test flow of 32 L/min.

Two different lots of cartridges were used for the initial screening, but only comparisons within a single lot were considered so as to eliminate lot-to-lot variation. The stacked-cartridge testing system is as shown in Figure 1. Dried air is passed through an in-line dryer/sorbent system to remove residual moisture and contaminants. The inlet air is controlled to regulate the temperature, humidity, and flow rate. This flow

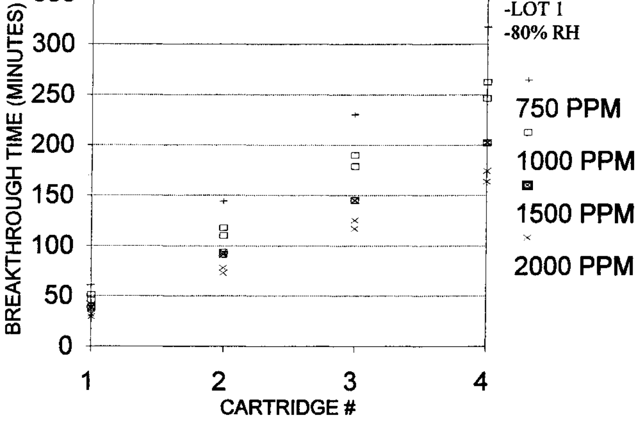


FIGURE 3. Carbon tetrachloride breakthrough data.

TABLE 3. Wheeler Constants for Manufacturer A Cartridges Against Carbon Tetrachloride at 5 ppm Breakthrough

					Slope				Intercept			Cartridge Wheeler Constants	
Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope	T	Pr>/T/	Y-Axis Intercept	T	Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	K_v Rate Constant ($-min^{-1}$)	W_c Critical Bed Weight (g)
1	750	50	8	0.998	3.945	59.32	0.0001	−48.36	−7.74	0.0002	0.596	4768	12.3
2	750	50	3	0.999	2.526	37.30	0.0171	−46.61	−6.61	0.0956	0.381	4457	18.5
1	750	80	8	0.999	2.455	177.02	0.0001	−25.22	−19.08	0.0001	0.339	5286	11.2
2	750	80	3	0.999	1.917	40.92	0.0156	−26.65	−5.52	0.1140	0.289	5852	13.9
1	1000	50	8	0.996	2.859	39.89	0.0001	−35.23	−5.41	0.0017	0.576	4842	14.6
2	1000	50	10	0.975	1.944	17.67	0.0001	−41.35	−3.04	0.0161	0.391	4080	25.3
1	1000	80	8	0.985	2.051	19.61	0.0001	−19.70	−2.07	0.0838	0.413	6281	9.6
2	1000	80	12	0.987	1.515	27.96	0.0001	−27.98	−3.94	0.0028	0.305	4666	18.5
1	1500	50	10	0.995	1.975	40.55	0.0001	−21.93	−5.22	0.0008	0.596	5932	11.1
2	1500	50	8	0.990	1.158	24.87	0.0001	−22.52	−3.72	0.0099	0.350	4761	19.5
1	1500	80	8	0.995	1.581	36.00	0.0001	−17.15	−4.12	0.0062	0.477	6181	10.9
2	1500	80	7	0.999	0.941	168.30	0.0001	−16.16	−23.97	0.0001	0.284	5434	17.2
1	2000	50	8	0.998	1.420	51.72	0.0001	−19.06	−7.14	0.0004	0.572	5402	13.4
1	2000	80	8	0.995	1.330	35.35	0.0001	−16.17	−4.52	0.0040	0.535	5819	12.2

rate can be varied up to 190 L/min, but must always exceed the flow rate pulled by the downstream vacuum source (G). This ensures that there is always positive overflow from the buffer reservoir to prevent atmospheric air from entering the system. The challenge concentrations for these experiments were generated and controlled using a syringe pump or Laboratory Data Control Minipump® (Riviera, Florida) to feed solvent to the airstream at a predetermined rate. By adjusting the pump feed rate and the inlet air flow rate, a known upstream concentration (C_o) could be established.

To reduce fluctuation in the upstream concentration, a buffer tank was added to the system. The upstream vapor concentration (C_o) and the downstream concentration (C_x) were continually monitored by means of a Miran 1A (Foxboro, Massachusetts) general-purpose infrared gas (IR) analyzer equipped with a variable path length gas cell. The analytical wavelength and minimum detectable limits, as specified by the manufacturer, with a 20-m cell for the test agents, were as follows: carbon tetrachloride, 12.6 μm and 1.1 ppm; ethyl acetate, 8.3 μm and 0.1 ppm; pentane, 3.4 μm and 0.2 ppm; n-hexane, 3.4 μm and 0.2 ppm; and heptane, 3.4 μm and 0.1 ppm.

The conditioned air stream (50 or 80 percent RH at 25°C) containing the challenge agent was then pulled through the cartridge cell housing which can contain from one to four cartridges in series. Another Miran 1A IR detector was located immediately downstream of the cartridges to monitor the breakthrough concentration as a function of exposure time. The exiting vapors were then passed through a sorbent scrubber before reaching the vacuum source.

The cell arrangement consisted of anodized aluminum pieces which had been machined to accept a specific commercially available OV respirator cartridge. The spacer units allowed for the stacking of one to four cartridges in series to resemble a packed column of varying bed length and sorbent weight, as well as containing sampling ports for the consecutive sampling of the gas downstream of each cartridge. Four breakthrough time versus breakthrough concentration measurements were obtained during a single experiment.

The data collection system operated similarly to the system previously described in the scientific literature.[9,10] The system was updated with a Hewlett-Packard (HP) series 200 computer in combination with an HP 3497A data acquisition system. In addition, all data were stored on a 3½-inch disk for future data analysis.

The phase two side-by-side testing was done per the present certification testing procedure with only minor modification. This test system is as shown in Figure 2. The testing conditions were the five noted earlier for conducting the side-by-side carbon tetrachloride testing comparison. Two different manufacturers' cartridges (B and C) were tested during the phase two side-by-side testing. Manufacturer B cartridges (single-

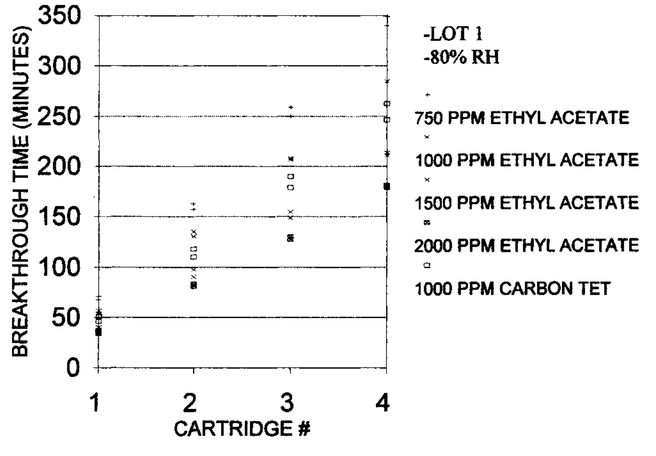


FIGURE 4. Carbon tetrachloride versus ethyl acetate breakthrough data.

TABLE 4. Wheeler Constants for Manufacturer A Cartridges Against Ethyl Acetate at 5 ppm Breakthrough

				Slope				Intercept				Cartridge Wheeler Constants	
Lot	**Challenge Concentration (ppm)**	**% RH**	**No. of Points**	R^2	**Slope**	**T**	**Pr>/T/**	**Y-Axis Intercept**	**T**	**Pr>/T/**	W_e **Kinetic Adsorption Capacity (g/g)**	K_v **Rate Constant** $(-min^{-1})$	W_c **Critical Bed Weight (g)**
1	750	50	8	0.997	2.925	47.45	0.0001	−32.97	−5.43	0.0016	0.253	5438	11.3
1	750	80	8	0.994	2.528	31.08	0.0001	−22.14	−2.74	0.0338	0.219	7073	8.8
1	1000	50	8	0.999	2.356	77.74	0.0001	−28.69	−9.55	0.0001	0.272	5371	12.2
1	1000	80	8	0.998	2.083	57.24	0.0001	−20.02	−5.50	0.0015	0.240	6819	9.7
1	1500	50	8	0.998	1.774	55.71	0.0001	−22.53	−7.01	0.0004	0.307	5630	12.7
1	1500	80	8	0.999	1.584	63.79	0.0001	−20.39	−8.21	0.0002	0.274	5505	12.9
1	2000	50	4	0.999	1.342	46.61	0.0005	−13.25	−4.39	0.0482	0.310	8147	9.9
2	2000	50	4	0.995	1.211	19.90	0.0025	−23.50	−3.00	0.0953	0.279	4883	19.4
1 and 2	2000	50	8	0.958	1.211	11.72	0.0001	−12.19	−1.01	0.3534	0.279	8704	10.1
1	2000	80	8	0.999	1.319	82.16	0.0001	−13.37	−8.35	0.0002	0.304	7328	10.1

cartridge configuration) were of the OV type. Manufacturer C cartridges were of the OV type and organic vapor/acid gas (OV/AG) type cartridges (pair configuration). The major differences between the certification test system and the stacked-cartridge experiments were: (1) the air was pushed through the cartridges rather than being pulled through with a vacuum source, (2) a single or cartridge pair was mounted on a holder as employed on the respirator rather than stacking single cartridges in series, (3) the challenge concentration was determined gravimetrically (time-weighted average) rather than instantaneously over the entire test, (4) the breakthrough time was only determined at 5 ppm, and (5) a Teflon® needle resting on heated glass beads was employed when generating pentane.

The test agents evaluated were as follows: (1) carbon tetrachloride, Fisher Scientific, Pittsburgh, Pennsylvania, certified American Chemical Society (ACS) spectranalyzed, or Aldrich Chemical Company, Milwaukee, Wisconsin, ACS reagent 99 percent; (2) ethyl acetate, Fisher Scientific, certified ACS spectranalyzed; (3) n-pentane, Fisher Scientific, high pressure liquid chromatography (HPLC) grade; (4) n-heptane, Fisher Scientific, HPLC grade; and (5) n-hexane, either Fisher Scientific, certified ACS 99 mol% pure, or J.T. Baker Chemical Company, Phillipsburg, New Jersey, HPLC 97 percent. House air which was passed through a dryer/sorbent system to remove contaminants was used.

Results and Discussion

Breakthrough data for manufacturer A's cartridges against carbon tetrachloride for lot 1 and lot 2 serve as baseline data. Comparisons with other test agents were made within the same lot of cartridges, since it has been reported[11] that significant lot-to-lot variability can occur. Lot 1 data at 50 and 80 percent RH for stacked-cartridge experiments against a carbon tetrachloride challenge concentration of 1000 ppm are given in Table 2. Similar data for lot 1 stacked cartridges against carbon tetrachloride challenges of 750, 1500, and 2000 ppm were obtained, and Figure 3 is a plot of the 80 percent RH data. Similar data were collected for lot 2 cartridges at challenge concentrations of 750, 1000, and 1500 ppm of carbon tetrachloride at 50 and 80 percent RH. The Wheeler constants[9] which were calculated for both lots of cartridges at the various carbon tetrachloride challenge concentrations are presented in Table 3. These data represent the baseline data against which other compounds are compared.

Lot 1 cartridges were used in the testing of ethyl acetate. The breakthrough data for the stacked-cartridge phase one screening experiments at 50 and 80 percent RH against ethyl acetate concentrations of 750, 1000, 1500, and 2000 ppm were obtained. A typical graph of breakthrough time versus sorbent weight for the various ethyl acetate challenge concentrations is shown in Figure 4 (80% RH). Figure 4 also contains the 1000 ppm carbon tetrachloride baseline data for comparison. The Wheeler constant calculations at the various ethyl acetate challenge concentrations are presented in Table 4. These data show that the 1000 ppm ethyl acetate data are similar to the baseline 1000 ppm carbon tetrachloride data. But the main objection to the potential use of ethyl acetate is its water solubility, which

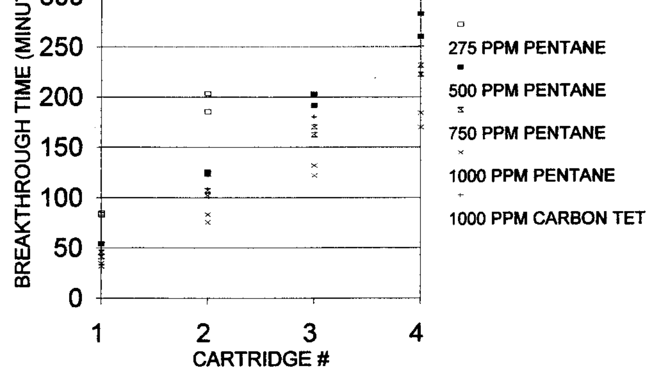


FIGURE 5. Carbon tetrachloride versus pentane breakthrough data.

TABLE 5. Wheeler Constants for Manufacturer A Cartridges Against Pentane at 5 ppm Breakthrough

Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope: Slope	Slope: T	Slope: Pr>/T/	Y-Axis Intercept	Intercept: T	Intercept: Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	Cartridge Wheeler Constants: K_v Rate Constant ($-min^{-1}$)	Cartridge Wheeler Constants: W_c Critical Bed Weight (g)
2	275	50	6	0.958	3.746	9.55	0.0007	−40.36	−1.03	0.3594	0.097	5836	10.8
2	275	80	6	0.991	2.408	21.33	0.0001	−28.99	−2.55	0.0631	0.063	5271	12.0
2	500	50	8	0.996	2.445	39.01	0.0001	−34.52	−4.32	0.0050	0.116	5171	14.1
2	500	80	8	0.992	1.549	27.04	0.0001	−19.08	−2.60	0.0406	0.073	5850	12.3
2	750	50	8	0.989	1.746	22.98	0.0001	−31.05	−3.24	0.0178	0.124	4398	17.8
2	750	80	8	0.997	1.323	45.31	0.0001	−18.18	−4.89	0.0027	0.094	5316	13.7
2	1000	50	8	0.999	1.396	81.21	0.0001	−22.34	−10.22	0.0001	0.132	5234	16.0
2	1000	80	8	0.995	1.030	35.04	0.0001	−15.16	−4.06	0.0067	0.097	5697	14.7

introduces another variable, solubility of ethyl acetate in water occupying the micropores of the carbon structure.

The next agent investigated was pentane. Breakthrough stacked-cartridge data were obtained at 275, 500, 750, and 1000 ppm challenge concentrations for cartridge lot 2. The 80 percent RH data are plotted in Figure 5, and the Wheeler constants are given in Table 5. The 1000 ppm carbon tetrachloride data are included in Figure 5 for comparison, and show that the pentane breakthrough time data at 500 ppm are the closest to the carbon tetrachloride baseline curve.

Data for n-hexane were obtained for the stacked-cartridge configuration at challenge concentrations of 500, 750, 1000, and 1500 ppm. The breakthrough time versus sorbent weight data were employed in calculating the Wheeler constants, and are presented in Table 6. These data indicate that the n-hexane 1000 ppm data compare with the 1000 ppm carbon tetrachloride data and therefore n-hexane is a possible replacement agent.

The final agent tested was heptane. Heptane data were collected at 800, 1000, 1250, and 1500 ppm with the stacked cartridges. Table 7 presents the Wheeler constants calculated from the breakthrough time versus sorbent weight data. The data indicate that a challenge concentration of at least 1250 ppm is needed to give breakthrough times of the same order, as seen with 1000 ppm carbon tetrachloride. Based on these data and safety considerations, heptane was not deemed a suitable replacement agent.

The screening data identified potential replacement agents and challenge concentrations for additional testing. The evaluation was based solely on the equivalency of breakthrough time as compared with the 1000 ppm carbon tetrachloride control. The two best replacement candidates (pentane and n-hexane) were selected for direct comparison with carbon tetrachloride at the five conditions stated earlier in this report. These conditions represent the 30 CFR, Part 11 testing scheme with additional testing of as received cartridges at 25 and 80 percent RH (64 L/min). The first testing condition was pentane at 550 ppm, and the second was n-hexane at 1000 ppm. The results for manufacturer B OV cartridges and manufacturer C OV and OV/AG cartridges against 1000 ppm carbon tetrachloride (control), 550 ppm pentane, and 1000 ppm n-hexane are given in Table 8.

Table 8 reveals some interesting observations. First, the most stringent 30 CFR, Part 11 test condition (i.e., that which gave the shortest breakthrough time) for the OV cartridges was as received cartridges tested at 50 percent RH and 64 L/min. Second, the OV/AG cartridges' most stringent 30 CFR, Part

TABLE 6. Wheeler Constants for Manufacturer A Cartridges Against n-Hexane at 5 ppm Breakthrough

Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope: Slope	Slope: T	Slope: Pr>/T/	Y-Axis Intercept	Intercept: T	Intercept: Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	Cartridge Wheeler Constants: K_v Rate Constant ($-min^{-1}$)	Cartridge Wheeler Constants: W_c Critical Bed Weight (g)
2	500	50	3	0.999	3.234	122.56	0.0052	−45.09	−16.74	0.0380	0.182	5311	14.0
2	500	80	3	0.999	2.328	43.94	0.0145	−30.18	−5.48	0.1149	0.131	5811	13.0
2	750	50	8	0.993	2.435	28.49	0.0001	−37.32	−3.42	0.0142	0.206	5188	15.3
2	750	80	7	0.999	1.827	59.91	0.0001	−22.19	−6.29	0.0015	0.155	6505	12.1
2	1000	50	8	0.999	1.786	66.46	0.0001	−22.00	−6.50	0.0006	0.202	6729	12.3
2	1000	80	8	0.999	1.528	78.95	0.0001	−24.73	−10.21	0.0001	0.172	5098	16.2
2	1500	50	8	0.999	1.427	79.51	0.0001	−24.25	−10.60	0.0001	0.242	5320	17.0
2	1500	80	8	0.999	1.260	129.09	0.0001	−18.47	−14.82	0.0001	0.213	6149	14.7

TABLE 7. Wheeler Constants for Manufacturer A Cartridges Against Heptane at 5 ppm Breakthrough

Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope: Slope	Slope: T	Slope: Pr>/T/	Y-Axis Intercept	Intercept: T	Intercept: Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	Cartridge Wheeler Constants: K_v Rate Constant ($-min^{-1}$)	Cartridge Wheeler Constants: W_c Critical Bed Weight (g)
2	800	50	6	0.982	2.587	14.82	0.0001	−30.89	−1.78	0.1505	0.271	6693	11.9
2	800	80	6	0.981	2.394	14.30	0.0001	−35.29	−2.07	0.1067	0.251	5513	14.7
2	1000	50	8	0.981	2.100	17.70	0.0001	−33.63	−2.22	0.0685	0.275	5260	16.0
2	1000	80	8	0.997	1.974	46.79	0.0001	−32.08	−5.90	0.0011	0.259	5219	16.3
2	1250	50	8	0.989	1.815	22.75	0.0001	−29.09	−2.85	0.0293	0.298	5490	16.0
2	1250	80	8	0.998	1.700	56.51	0.0001	−32.46	−8.38	0.0002	0.279	4628	19.1
2	1500	50	8	0.996	1.629	37.87	0.0001	−31.63	−5.77	0.0012	0.320	4652	19.4
2	1500	80	6	0.974	1.129	12.25	0.0003	−16.55	−1.79	0.1483	0.222	6150	14.7

11 test condition was 85 percent RH preconditioned tested at 32 L/min and 50 percent RH. Third, all cartridges, even the OV/AG, had breakthrough times in excess of 50 minutes at all five test conditions. Fourth, the breakthrough times for the OV and OV/AG cartridges were of the same magnitude. Fifth, of all the tests performed, the most severe test condition was as received cartridges tested at 80 percent RH and 64 L/min.

The breakthrough times for manufacturer B and manufacturer C OV cartridges as received and tested at 64 L/min and 80 percent RH against 1000 ppm carbon tetrachloride were 68.6 and 76.6 minutes, respectively. The breakthrough times for manufacturer B and manufacturer C OV cartridges against 550 ppm pentane at the same test conditions (64 L/min and 80% RH) were 68.8 and 76.1 minutes, respectively. The breakthrough times for these OV cartridges against 1000 ppm n-hexane were 70.6 and 73.2 minutes. This indicates that 550 ppm pentane and 1000 ppm n-hexane should be suitable replacement agents for 1000 ppm carbon tetrachloride based on breakthrough times. However, correlation studies needed to be conducted to confirm these findings. Further, since it was shown that the most severe test condition was as received cartridges tested at 64 L/min and 80 percent RH, a strong case can be made to switch to a testing regimen that employs only as received cartridges and tests them at realistic use-type conditions (25, 50, and 80% RH).

Conclusions

The data show that, based on breakthrough time as the critical criterion, numerous test agents could be used instead of carbon tetrachloride for testing organic vapor cartridges. In fact, side-by-side testing of 1000 ppm carbon tetrachloride, 550 ppm pentane, and 1000 ppm n-hexane gave equivalent breakthrough times at the most severe test condition, which was as received cartridges tested at 80 percent RH and 64 L/min. But since pentane is considerably less toxic than n-hexane (600 and 50 ppm OSHA permissible exposure limits, respectively), pentane is the test agent of choice. Further, since the present 30 CFR, Part 11 equilibration tests are less discriminating than testing as received cartridges at use-type conditions, the test regimen should test as received cartridges at 25, 50, and 80 percent RH with a flow rate of 64 L/min.

TABLE 8. Cartridge Breakthrough Time Comparison Summary

Conditions	Breakthrough Time t_b (Minutes) Against 1000 ppm Carbon Tetrachloride: Mfg B OV	Mfg C OV/AG	Mfg C OV	Breakthrough Time t_b (Minutes) Against 1000 ppm *n*-Hexane: Mfg B OV	Mfg C OV/AG	Mfg C OV	Breakthrough Time t_b (Minutes) Against 550 ppm Pentane: Mfg B OV	Mfg C OV/AG	Mfg C OV
Preconditioned 25% RH test: 32 L/min 50% RH	219.6	201.9	210.5	178.9	178.7	191.6	222.0	217.9	232.3
Preconditioned 85% RH test: 32 L/min 50% RH	106.3	80.3	118.3	119.8	83.8	126.6	128.6	87.7	175.2
As received test: 64 L/min 25% RH	106.3	101.3	104.7	87.1	86.7	86.2	120.7	111.1	115.1
As received test: 64 L/min 50% RH	100.9	89.6	97.7	89.8	81.1	84.7	110.6	99.2	110.5
As received test: 64 L/min 80% RH	68.6	68.2	76.6	70.6	70.6	73.2	68.8	63.1	76.1

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