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Carbon Tetrachloride Replacement Compounds for Organic Vapor Air-Purifying Respirator Cartridge and Activated Carbon Testing— A Review

This article reviews efforts by researchers and organizations around the world to identify chemicals as substitutes for carbon tetrachloride in measuring activated carbon activity (adsorption capacity) or organic vapor air-purifying respirator cartridge (or other packed carbon bed) breakthrough times. Such measurements usually are done to determine if a minimum performance standard is met. Different criteria have been established, supporting data developed and used, and conclusions reached. This article presents relevant published, unpublished, obscure, and recalculated data which the reader can use to make a choice of replacement chemical and testing conditions. No recommendations for a specific replacement chemical are endorsed or promoted in this review.

Keywords: activated carbon, carbon tetrachloride, cartridges, respirators, substitution

Organic vapor cartridges and canisters are used with air-purifying respirators to remove toxic gases and vapors from inspired air. These cartridges and canisters contain activated carbon granules in a packed bed, which adsorb organic vapors from air flowing past them. Carbon tetrachloride (CCl_4) has long been recognized as the standard test vapor used by the carbon industry to measure activity (equilibrium adsorption capacity) of activated carbon (ASTM D3467–94).(1) Also, CCl_4 has been used as a testing chemical to measure organic vapor cartridge breakthrough time (service life, time to reach a selected concentration of vapor in air coming out of a cartridge at selected test conditions) for comparison with minimum standards (e.g., 30 CFR 11(2) and 42 CFR 84(3)). This compound is particularly suited for carbon testing, because it is water-immiscible and shows extreme deleterious effects of reduced adsorption capacity at high carbon moisture levels from exposures to high relative humidities. Further, it is easy to generate at high concentrations (over 10,000 ppm), is nonflammable, is easy to measure experimentally (spectroscopic and chromatographic methods), and is nonexplosive.

However, CCl_4 has the disadvantages as a test chemical of being a toxic, environmentally unfriendly (atmospheric ozone depleting) compound. CCl_4 has been cited as a potential occupational carcinogen(4–6) and has been identified as a potential contributor to stratospheric ozone depletion. As a result of amendments to the Montreal Protocol (1990),(7) the mandated global phase-out of industrial CCl_4 use by the year 2000 was established. The Environmental Protection Agency has proposed to make its stratospheric ozone protection regulations (40 CFR, Part 82) conform to the requirements of Title VI of the Clean Air Act Amendments of 1990 (Public Law 101–549).(8) Although cartridge and carbon testing with CCl_4 has been insignificant compared with past industrial use, banning its industrial manufacture and use has directly affected its availability and desirability for such testing.

Criteria for an ideal replacement testing chemical for CCl_4 include the following: It should (1) be relatively nontoxic, (2) be readily available, (3) give identical results for critical measured properties (e.g., adsorption capacity or breakthrough time) in all conditions, (4) be affected by adsorbed water to the same extent as CCl_4, (5) be nonflammable, and (6) not be ozone depleting.

This article reviews efforts by researchers and organizations around the world to identify chemicals as substitutes for CCl_4 in measuring activated carbon activity (adsorption capacity) or organic vapor air-purifying respirator cartridge (or other packed carbon bed) breakthrough times. Such measurements usually are done to determine if a minimum standard is met. It is not within the scope of this article to recommend or endorse a specific test chemical, test conditions, or acceptance criteria.

ASTM—SPECIFIED REPLACEMENTS FOR DETERMINING CARBON ACTIVITY

The American Society for Testing and Materials (ASTM) established a test for determining activated carbon activity (% uptake by weight of carbon) designated D3467–94; Standard Test Method for Carbon Tetrachloride Activity of Activated Carbon.(1) Activity of an activated carbon reflects the micropore volume and is a relative measure of the degree of completion of the activation process. It can serve as a means of quality control for activated carbon intended for removal of gases and vapors from air. This method determines the equilibrium gravimetric absorption capacity of a known weight of dry carbon at a CCl_4 concentration of 250 ± 10 mg/L in dry air, a temperature of 25 ± 1°C, and a total airflow rate of 1670 ± 15 mL/min (superficial flow velocity of 10 m/min through the sample tube).

However, in the latest versions of this standard ASTM recommends no longer using this test, but rather an n-butane adsorption test, which is part of D5228–92 (reapproved 1996).(9) An activated carbon bed of known volume and mass is saturated with pure, dry n-butane. The mass adsorbed at saturation is used to calculate the n-butane activity. Adsorption capacity, and therefore activity, depends on the gas or vapor adsorbed. A correlation between n-butane activity values and CCl_4 activity values has been established with 175 comparison data points, which sets the CCl_4 activity equal to 2.57 times that of n-butane.(9) A new standard, D5742–95, Standard Test Method for Determination of the Butane Activity of Activated Carbon,(10) was issued in August 1995 with the same procedures and conditions for determining activated carbon activity. The correlation with CCl_4 activity is shown graphically and given as a factor of 2.55. Therefore, CCl_4 activity is proportional to n-butane activity. n-Butane is relatively nontoxic and not ozone depleting, but is flammable. Dry conditions can be maintained for laboratory testing, such that differences in water effects are irrelevant.

ASTM D5020–89, Standard Test Method for Chlorofluorocarbon Activity of Activated Carbon, was issued in February 1990.(11) It is based on the work of Sosa and Underhill,(12) in which they compared activities obtained with four less toxic chlorofluorocarbons (CFCs, Freon™, refrigerants) with those of CCl_4. CFC-114 (1,2-dichlorotetrafluoroethane), a gas at ordinary temperatures, was selected for this ASTM standard. Conditions are the same as those in D5228–92, except for a 10-min exposure time. The correlation from 18 activated carbons was CCl_4 activity = 0.10 + 0.985 times the CFC-114 activity. (12) Unlike n-butane, CFC-114 is a concern for stratospheric ozone depletion, but is much less flammable.

U.S. BUREAU OF MINES—STUDY OF ALTERNATIVES FOR SERVICE LIFE TESTING

Swab and Ferber at the U.S. Department of the Interior, Bureau of Mines, selected Freon (CFC) 113 (1,1,2-trichloro-1,2,2-trifluoroethane) from among three Freon types screened as test materials for measuring breakthrough times of respirator cartridges in place of CCl_4.(13) The brand and specifications of the approved chemical cartridge used were not given. The average Freon 113/CCl_4 breakthrough time ratio was 0.67 for two airflows (32 and 64 L/min), 1000 ppm, and 50% relative humidity (RH). Breakthrough concentration used was not mentioned. The standard deviation was 0.04 for five sets of comparisons. Single comparisons for Freon 11 (fluorotrichloromethane) and Freon 21 (dichloromonofluoromethane) gave breakthrough time ratios relative to CCl_4 of 0.38 and 0.15, respectively. This was a preliminary study and did not result in any Bureau of Mines recommendation. Freon 113 is a concern for stratospheric ozone depletion, but is relatively nontoxic and nonflammable. It is water immiscible, like CCl_4, but effects of adsorbed water on it have not been established.

NIOSH—BREAKTHROUGH TIME COMPARISONS

The National Institute for Occupational Safety and Health (NIOSH) has been mandated to use CCl_4 for testing and certifying organic vapor/gas cartridges and canisters by 42 CFR 84.(3) Cartridges/canisters are tested as-received from the applicant or after preconditioning at 25% or 85% RH. Varying flow rates, challenge concentrations of CCl_4, and breakthrough time criteria are employed. Because of the CCl_4 toxicity and environmental and availability problems, NIOSH instituted a program to find a suitable replacement chemical for CCl_4 in evaluating organic vapor and gas cartridges and canisters. Four chemicals (ethyl acetate, pentane, hexane, and heptane) were selected for testing based on their physical characteristics, toxicity, and reported activated carbon adsorption characteristics.(14–17)

Nonpowered Air-Purifying Respirator Cartridges

The first NIOSH study dealt with nonpowered organic vapor air-purifying respirator (APR) cartridges.(18) Respirator organic vapor/gas cartridge screening experiments were done to identify potential replacement chemicals, challenge concentrations, and test conditions that would produce cartridge breakthrough times equivalent to those for the certification CCl_4 tests at 1000 ppm.(3) They were performed at 50% RH, 80% RH, 25°C ± 2°C, and at a constant flow rate consistent with the certification criteria on as-received (not preconditioned) cartridges from the manufacturer. Various challenge concentrations of CCl_4 (control), ethyl acetate, pentane, hexane, and heptane were used.

Conclusions from this first study(18) for the four potential replacement compounds were as follows:

- The ethyl acetate breakthrough time data at 1000 ppm were similar to the baseline 1000-ppm CCl_4 control data. However, the main objection to the use of ethyl acetate was its water solubility. In the presence of water it may not be representative of immiscible chemicals, such as CCl_4 or hydrocarbons.
- Pentane breakthrough time data at 500 ppm were closest to the CCl_4 1000-ppm control. Follow-up calculations determined that a 550-ppm pentane challenge should give breakthrough times even more in agreement.

TABLE I. Breakthrough Time Comparisons for Organic Vapor APR Cartridges (NIOSH)

	Manufacturer B Organic Vapor Cartridges, 111 g Carbon			Manufacturer C Organic Vapor Cartridges 84 g Carbon			Manufacturer C Organic Vapor/Acid Gas Cartridges, 92 g Carbon		
	5 ppm Breakthrough Times (min)								
Conditions	1000 ppm CCl_4	1000 ppm n-Hexane	550 ppm Pentane	1000 ppm CCl_4	1000 ppm n-Hexane	550 ppm Pentane	1000 ppm CCl_4	1000 ppm n-Hexane	550 ppm Pentane
Preconditioned 25% RH Test: 32 L/min 50% RH^A	220	179	222	211	192	232	202	179	218
Preconditioned 85% RH Test: 32 L/min 50% RH^A	106	120	129	118	127	175	80	84	88
As-received Test: 64 L/min 25% RH	106	87	121	105	86	115	101	87	111
As-received Test: 64 L/min 50% RH^A	101	90	111	98	85	111	90	81	99
As-received Test: 64 L/min 80% RH	69	71	69	77	73	76	68	71	63

^{A}Specified in 42 CFR 84 (Ref. 3).

- The n-hexane breakthrough time data at 1000 ppm were close to the 1000-ppm CCl_4 baseline data.
- A heptane concentration of at least 1250 ppm would be needed to produce breakthrough times near the 1000-ppm CCl_4 baseline data.

The replacement chemicals and challenge concentrations that showed equivalency with the 1000 ppm CCl_4 controls, based on breakthrough time as the sole critical evaluation criteria, were pentane at 550 ppm and n-hexane at 1000 ppm. Ethyl acetate was eliminated based on its water solubility, even though its breakthrough time at 1000 ppm was equivalent to that of 1000-ppm CCl_4.

Both pentane and n-hexane were evaluated in additional side-by-side testing against 1000-ppm CCl_4 using the certification experimental set-up and testing procedures at the following five test conditions:

(1) preconditioned at 25% RH, tested at 50% RH and 32 L/min,
(2) preconditioned at 85% RH, tested at 50% RH and 32 L/min,
(3) as-received, tested at 25% RH and 64 L/min,
(4) as-received, tested at 50% RH and 64 L/min, and
(5) as-received, tested at 80% RH and 64 L/min.

Conditions 1, 2, and 4 represent the 42 CFR 84 testing scheme. The results(18) from the side-by-side study presented in Table I led to these conclusions relevant to substitutes.

- The breakthrough times for the 1000-ppm CCl_4 controls and the 550 ppm pentane and 1000 ppm hexane were confirmed to be similar (±22% with one exception) for all three cartridges, one of them an organic vapor/acid gas cartridge.
- Using breakthrough time as the critical criterion, more than one test chemical could be used to replace CCl_4 for testing organic vapor cartridges.

Follow-up testing of nonpowered organic vapor APR cartridges at three test conditions was done to measure correlation and reproducibility with better statistics.(19) The three test conditions were 1000 ppm CCl_4 at 50% RH (64 L/min), 550 ppm pentane at 80% RH (64 L/min), and 1000 ppm n-hexane at 80% RH (64 L/min). The CCl_4 conditions represented the most critical organic

TABLE II. Breakthrough Times (NIOSH) Estimated To Be Equivalent to the CCl_4 Standard at Selected Conditions and Reproducibilities Measured for As-Received Cartridges from One Manufacturer

Test Solvent	Concentration (ppm)	Relative Humidity (%)	Flow Rate (L/min)	Number of Cartridges	Measured Average 5 ppm Breakthrough Time (min)	Standard Deviation (min)	Ratios of Measured Averages	Estimated Breakthrough Time (min)	95% Confidence Interval on Estimate (min)
Carbon Tetrachloride^A	1000	50	64	6	100.9	4.3	1.00 (reference)	50 (reference)	
Pentane	550	80	64	10	73.2	3.4	0.73	40	35–45
Pentane	550	50	64	10	113.5	3.4	1.12		
n-Hexane	1000	80	64	10	70.3	3.2	0.70	37	33–42
n-Hexane	1000	50	64	10	86.7	1.8	0.86		

^{A}Specified in 42 CFR 84 (Ref. 3).

TABLE III. Summary of Chin-Style Canister Breakthrough Data (NIOSH)

Challenge Chemical	Relative Humidity (%)	5 ppm Breakthrough Time (min) at Challenge Concentration							
		1000 ppm	2000 ppm	2500 ppm	4000 ppm	5000 ppm	7000 ppm	7500 ppm	10000 ppm
Carbon tetrachloride	50	140	70			37			21
	50					40			18
	50					36			
	80					33			
	80					39			
	80					35			
Ethyl acetate	50	127	56			25		20	
	50	125							
	80	78	44			17		11	
	80	98							
	80	99							
Pentane	50	79	57		38	33		23	
	50				38				
	80	74	50		36	30		21	
	80				41				
n-Hexane	50	106	55			29	21		
	80	97	54			33	21		
Heptane	50			59		26		19	
	80			57		26		16	

vapor certification criteria observed for cartridges. All tests were performed on as-received cartridges. Averages and ratios of breakthrough times are shown in Table II. The minimum acceptable breakthrough time according to 42 CFR 84 is 50 min for 1000 ppm CCl_4, 64 L/min, 50% RH, and 25°C. Table II also shows estimates of the breakthrough times for pentane and n-hexane equivalent to 50 min for CCl_4 at the selected conditions. Reproducibility results also are shown in Table II.

Nonpowered APR Chin-Style Canisters

In another study,(20) nonpowered APR organic vapor chin-style canisters were tested by NIOSH against the same four potential CCl_4 replacement solvents: ethyl acetate, pentane, n-hexane, and heptane. In the case of chin-style canisters, screening tests were done to identify replacement chemical/challenge concentration combinations, which give breakthrough times similar to the 5000-ppm CCl_4 certification test criteria for chin-style canisters. The summary of the breakthrough data collected on chin-style canisters is presented in Table III for various challenge concentrations for the different solvents tested at both 50% and 80% RH.

The best candidate for chin-style canister direct comparison with the 5000-ppm CCl_4 standard test condition was found to be a 4000-ppm pentane challenge. This conclusion was based solely on breakthrough time comparisons with the 5000-ppm CCl_4 results. Ethyl acetate was again eliminated from further studies due to its water solubility. Table IV presents the results of a follow-up study. Breakthrough time data for the CCl_4 controls at the two certification conditions (as-received and preconditioned at 85% RH) were compared with the as-received test data at 80% RH for a 4000 ppm pentane challenge. The chin-style canister data, especially for Manufacturer B, suggests that the most severe 42 CFR 84 test (shortest average breakthrough time) was with 85% RH preconditioned canisters against CCl_4 at 5000 ppm, 50% RH, 32 L/min, and 25°C. The test method for chin-style canisters employing the pentane 4000 ppm challenge concentration on as-received canisters gave reproducible results.(19) At the 50% RH condition a mean breakthrough time of 38 min with a standard deviation of 1.4 (range 36–40) was obtained for 10 tests; at the 80% RH test condition a mean of 35 min with a standard deviation of 2.3 (range 33–41) was obtained for 10 tests.

TABLE IV. Organic Vapor Cartridge Breakthrough Time Comparisons for Chin-Style Canisters (NIOSH)

		5000 ppm CCl_4, AR, 64 L/MIN, 50% RH, 25°C[A]		5000 ppm CCl_4, 85% Preconditioned, 32 L/min, 50% RH 25°C[A]		4000 ppm Pentane, AR, 64 L/min, 80% RH 25°C	
Manufacturer	Run	Carbon Weight (g)	5 ppm Breakthrough Time (min)	Carbon Weight (g)	5 ppm Breakthrough Time (min)	Carbon Weight (g)	5 ppm Breakthrough Time (min)
A	1	249.5	52	232.6	49	243.3	51
	2	237.2	57	236.0	38	245.3	51
B	1	200.0	42	198.1	18	203.7	37
	2	200.3	35	204.7	29	204.9	37
C	1	134.3	46	134.5	42	154.0	45
	2	135.7	45	149.5	41	154.5	44

[A] Specified in 42 CFR 84 (Ref. 3).

TABLE V. Summary of FM/BM Canister Breakthrough Data (NIOSH) at 64 L/min for As-Received Canisters

Challenge Chemical	Relative Humidity (%)	5 ppm Breakthrough Time (min) at Challenge Concentration: 1000 ppm	2000 ppm	5000 ppm	7000 ppm	7500 ppm	9000 ppm	10,000 ppm	12,000 ppm	15,000 ppm	20,000 ppm^{A}
Carbon tetrachloride^{A}	50			215				118		41^{B}	28^{B}
	50							116^{B}			
	80			225				122		38^{B}	28^{B}
	80							89^{B}			
Ethyl acetate	50	672^{B}	378	184^{B}		118^{B}		88			
	80	464^{B}	291	175^{B}		104^{B}		76			
Pentane	50			153		120		96	83		
	80			139		108		97	80		
n-Hexane	50		290	165	121	96					
	50					86					
	80		271	157	112	105					

^{A}Specified in 42 CFR 84 (Ref. 3).
^{B}Canister Lot B. Unmarked are canister Lot A from the same manufacturer.

Nonpowered Front-Mounted/Back-Mounted Canisters

Even larger carbon capacity, nonpowered, front-mounted/back-mounted (FM/BM) canisters also were tested against these potential replacement chemicals.(21) However, it should be noted that the challenge concentrations for these potential replacement chemicals have upper-use concentration restrictions due to lower-flammability limits (LFLs). The LFLs for these are significantly lower than the CCl_4 challenge concentration of 20,000 ppm specified in 42 CFR 84:(3) ethyl acetate, 22,000 ppm; pentane, 15,000 ppm; n-hexane, 11,000 ppm; and heptane, 10,500 ppm. Warning: These three hydrocarbons are extremely flammable; therefore, sparks and open flames must be avoided when they are used.

Two production lots of one manufacturer's organic vapor FM/BM canisters (average 739 g carbon, otherwise specifications not given) were used throughout these tests. A summary of the breakthrough time data for CCl_4 (5000–20,000 ppm), ethyl acetate (1000–10,000 ppm), pentane (5000–12,000 ppm), and n-hexane

TABLE VI. Organic Vapor FM/BM Canister Breakthrough Time Correlation Data (NIOSH)

Test Substance/Condition	Challenge Concentration (ppm)	% Relative Humidity	Run #	Carbon Weight (g)	5 ppm Breakthrough Time (min)
Carbon tetrachloride, as-received, 64 L/min, 25°C	10,000	50	1	743.0	126
			2	748.6	98
			3	728.0	101
			4	723.8	121
		80	1	748.3	99
Carbon tetrachloride, preconditioned 85% RH, 32 L/min, 25°C	10,000	50	1	731.7	173
Carbon tetrachloride, as-received, 64 L/min, 25°C^{A}	20,000	50	1	733.0	38
			2	744.1	39
			3	741.8	52
			4	732.8	52
Carbon tetrachloride, preconditioned 85% RH, 32 L/min, 25°C^{A}	20,000	50	1	729.8	17
			2	731.2	23
Pentane, as-received, 64 L/min, 25°C	10,000	50	1	725.7	80
			2	716.7	74
			3	748.2	97
		80	1	742.1	76
			2	748.7	72
			3	753.2	73
			4	746.3	94
			5	746.5	82
Pentane, preconditioned 85% RH, 32 L/min, 25°C	10,000	50	1	746.2	122
			2	743.4	128

^{A}Specified in 42 CFR 84 (Ref. 3).

TABLE VII. Breakthrough Time Data (NIOSH) for Powered Air-Purifying Respirator Cartridges

		5 ppm Breakthrough Time (min)			
		Carbon Tetrachloride, 1000 ppm, 50% RH, 25°C[A]		Pentane 550 ppm, 80% RH, 25°C	Hexane 1000 ppm, 80% RH, 25°C
Manufacturer	Flow Rate (L/min)	85% RH Preconditioned Cartridges	As-Received Cartridges	As-Received Cartridges	As-Received Cartridges
V	115	33 31 41 33 29	142 149	124 121	88 100
W	115	70 95	178 187	141 128	131 127
X	115	79 60	148 139	133 133	97 97
Y	170	92 64	184 181	146 143	126 114 99
Z	170	40 38	175 159 170	114 121 111	112 111

[A]Specified in 42 CFR 84 (Ref. 3).

(2000–9000 ppm) at 50% and 80% RH is presented in Table V. Flow rate was 64 L/min.

Breakthrough time data for the as-received FM/BM canisters at 50% and 80% RH for CCl_4 controls and pentane are presented in Table VI. These tests were done with a different lot of canisters from the same manufacturer as those in Table V. Data for CCl_4 at challenge concentrations of 20,000 ppm (per 42 CFR 84)(3) or 10,000 ppm are presented. Pentane data were generated only at 10,000 ppm because pentane's LFL is 15,000 ppm. Evaluation of these FM/BM canister data revealed that the most severe 42 CFR 84 test (shortest average breakthrough time) was with 85% RH preconditioned canisters tested against CCl_4 at 20,000 ppm, 50% RH, 32 L/min, and 25°C. The minimum 5 ppm breakthrough time requirement for this test is 12 min; the average and range measured (Table VI) were 20 ±3 min.

From these data it was clear that the LFL restriction would not allow high enough pentane concentrations to match breakthrough times with the most severe 42 CFR 84 test. At a challenge concentration of 10,000 ppm pentane for as-received canisters at 80% RH, 64 L/min, 5 ppm breakthrough, and 25°C, a breakthrough time of 50 min was estimated to be equivalent to the minimum acceptable 12 min for the CCl_4. This was determined by comparing the CCl_4 preconditioned, 85% RH, 32 L/min, 25°C data with the pentane as-received, 80% RH, 64 L/min, 25°C data. Due to the limited number of data points (Table VI), a nonparametric method of elimination was used. All CCl_4 controls were paired with pentane tests and direct estimates were obtained relative to the 12-min breakthrough time for CCl_4. The resulting 50-min breakthrough time is the median of all pairwide estimates. However, all test data were obtained for only one supplier's FM/BM canisters and, thus, the data may not represent all such canisters.

TABLE VIII. Calculated Breakthrough Times and Ratios from Freundlich-Like ($t = AC^{-B}$) Parameters for Concentration Dependence from Littleton and Feeney(23)

	Data Fit Parameters		10 ppm Breakthrough Time (min)	Ratio to CCl_4	10 ppm Breakthrough Time (min)	Ratio to CCl_4
	A	B	1000 ppm		5000 ppm	
Carbon tetrachloride	113,787	0.92	198	1.00	45	1.00
Ethyl acetate	106,702	0.91	199	1.00	46	1.02
Chloroform	66,230	0.84	200	1.01	52	1.15
Dichloromethane	5276	0.59	90	0.45	35	0.77
Trichloroethylene	82,617	0.85	233	1.18	59	1.32
Diethyl ether	29,717	0.79	127	0.64	36	0.79
Acetone	13,179	0.67	129	0.65	44	0.97
Pentane	53,584	0.86	141	0.71	35	0.79
Hexane	116,860	0.95	165	0.83	36	0.80
Heptane	104,307	0.94	158	0.80	35	0.77
Octane	87,519	0.92	152	0.77	35	0.77

TABLE IX. Calculated Breakthrough Times and Ratios from Freundlich-Like ($t = AC^{-B}$) Parameters for Concentration Dependence from Smith[(25)]

	Data Fit Parameters		1000 ppm		5000 ppm	
	A	B	10 ppm Breakthrough Time (min)	Ratio to CCl_4	10 ppm Breakthrough Time (min)	Ratio to CCl_4
Carbon tetrachloride	166,100	0.941	250	1.00	55	1.00
Pentane	68,300	0.861	178	0.71	45	0.81
Methyl acetate	40,800	0.779	188	0.75	64	0.98
Hexane	246,300	1.003	240	0.96	48	0.87
Cyclopentane	35,500	0.753	198	0.78	58	1.08
Heptane	234,600	0.995	243	0.97	49	0.89
Octane	130,400	0.918	230	0.92	52	0.96
Cyclohexane	211,700	0.974	253	1.01	53	0.96
Acetone	3450	0.451	154	0.62	75	1.38
Bromochloromethane	48,800	0.782	220	0.88	82	1.14
o-Xylene	181,000	0.943	268	1.07	69	1.07
Ethyl acetate	97,800	0.859	259	1.04	65	1.16
Butanone	377,000	1.029	309	1.24	59	1.07
Toluene	299,500	0.988	325	1.30	66	1.21

Note: Seventy percent RH, 30 L/min, and 20°C.

Powered Air-Purifying Respirator Cartridges

Powered APR (PAPR) organic vapor cartridges from five manufacturers were similarly evaluated at the following four conditions:[(19)]

(1) CCl_4 control with 85% preconditioned cartridges tested at 1000 ppm, 50% RH, and 25°C; minimum acceptable breakthrough time = 25 min.

(2) CCl_4 control with as-received cartridges tested at 1000 ppm, 50% RH, and 25°C; minimum acceptable breakthrough time = 50 min.

(3) Pentane on as-received cartridges tested at 550 ppm, 80% RH, and 25°C.

(4) Hexane on as-received cartridges tested at 1000 ppm, 80% RH and 25°C.

Test flow rates were 115 L/min for tight-fitting facepieces or 170 L/min for loose-fitting hoods or helmets. The test results (Table VII) show that the most severe (shortest breakthrough times) PAPR organic vapor cartridge test condition under the requirements of 42 CFR 84.207 and 84.1156 is the 85% RH preconditioned cartridges with CCl_4 testing performed at 1000 ppm, and 50% RH, 25°C. The minimum breakthrough time requirement is 25 min at a 5-ppm breakthrough concentration.

Pentane results on as-received PAPR cartridges tested at 550 ppm, 80% RH, 25°C, and a flow rate of 115 L/min for tight-fitting facepieces or 170 L/min for loose-fitting hoods or helmets are presented in Table VII. Similarly, hexane data on as-received cartridges tested at 1000 ppm, 80% RH, 25°C, and the appropriate flow rate are also presented in Table VII. From the model (Weibull regression) the point estimates for pentane and hexane

TABLE X. Ratios of 5 ppm Breakthrough Times to Those of Carbon Tetrachloride with Freundlich-Like ($t = AC^{-B}$) Parameters from the Data of Nelson[(26)]

Concentration (ppm)	Flow Rate (L/min)	Preconditioning (% RH)[A]	Relative Humidity (% RH)	Carbon Tetrachloride (min)	Ethyl Acetate Ratio	Methyl Ethyl Acetate Ratio	Heptane Ratio
500	32	AR	50	220.9	0.91	0.88	0.90
1000	32	AR	50	112.0	1.03	1.11	0.90
2000	32	AR	50	55.9	1.19	1.27	0.87
3000	32	AR	50	44.2	0.88	1.11	0.82
5000	32	AR	50	25.2	1.16	1.04	0.85
7500	32	AR	50	16.7	1.11	1.06	0.77
10,000	32	AR	50	13.0	0.88	1.10	0.78
15,000	32	AR	50	6.9	1.13	1.38	
1000	32	AR	80	85.8	1.09	1.16	1.06
1000	32	AR	85	75.2	1.09	1.24	1.15
1000	15	AR	70	212.9	1.09	1.19	0.96
1000	16	25	50	222.5	1.01	1.22	0.88
1000	16	85	50	114.1	1.63	1.56	1.57
Freundlich-like fit parameters (AR and 50% RH data)			B	0.981	0.954	0.915	0.995
			A	101171	83816	65795	98005
Average breakthrough time ratio to CCl_4 (excluding 85% RH preconditioning)					1.05	1.15	0.90

[A] AR = as-received, no preconditioning.

TABLE XI. Breakthrough Times and Ratios from the Data of Moyer et al.[16]

			Carbon Tetrachloride					
Cartridge Lot	Concentration (ppm)	Relative Humidity (% RH)	5 ppm Breakthrough Time (min)	Average Carbon Weight (g)	Pentane	Hexane	Heptane	Ethyl Acetate
					Breakthrough Time Ratios to Carbon Tetrachloride			
B	750	50	75.2	48.22	0.71	1.07		
A	750	50	93.4	35.94				0.77
A	1000	50	59.3	33.08				0.83
B	1000	50	52.2	48.12	0.86	1.23	1.29	
B	1500	50	32.7	47.68		1.34	1.41	
A	1500	50	44.6	33.67				0.83
A	2000	50	31.4	35.55				1.10
		Average Ratios			0.78	1.21	1.35	0.88
B	750	80	64.8	47.70	0.69	1.00		
A	750	80	63.9	36.31				1.09
A	1000	80	48.7	33.34				1.02
B	1000	80	44.4	47.78	0.77	1.09	1.40	
B	1500	80	29.1	48.06		1.46	1.30	
A	1500	80	37.4	34.52				0.92
A	2000	80	30.0	34.69				1.08
		Average Ratios			0.73	1.18	1.35	1.03

were determined using the CCl_4 breakthrough data for the 85% RH preconditioned cartridges tested at 1000 ppm, 50% RH, 25°C, appropriate flow rate, and minimum breakthrough time of 25 min as the control criteria. The corresponding pentane point estimate was 50 min (95% CI = 37–67). The hexane point estimate was 52 min (95% CI = 37–72).

As of the writing of this article and to the authors' knowledge NIOSH has made no recommendations or standards changes for replacement of CCl_4 as a test vapor. Perhaps the results summarized in this article will provide a basis for such action.

ANSI—REVIEWS OF DATA TO SELECT A REPLACEMENT VAPOR

The American National Standards Institute (ANSI) is a consensus standard organization. The current ANSI Z88.8 committee[22] has sought a CCl_4 replacement vapor for testing air-purifying organic vapor respirator cartridges. Again, the desirable characteristics of equivalent breakthrough times and lesser toxic and environmental concerns were discussed. Published comparative data were augmented by unpublished data supplied by some committee members from their organizations. Some of this follows.

Littleton and Feeney[23] have published correlations of breakthrough times as functions of concentration for a variety of vapors, including CCl_4. Testing conditions were in accordance with EN141 (70% RH, 30 L/min, 10 ppm breakthrough, 20°C) with Class A2 filters. They used a Freundlich-type equation[24] for breakthrough times (min) of the form:

$$t = A\,C^{-B} \tag{1}$$

with two empirical data-fit parameters, A and B. Those parameters are used here to back-calculate breakthrough times for 11 compounds at 1000 and 5000 ppm (Table VIII). Ratios of breakthrough times to those of CCl_4 are also given in this table. One use of presenting results in this way is for comparisons of the vapor concentration effect Parameter B. For identical values of B for two compounds, breakthrough time ratios for the two compounds would be independent of concentration. Ethyl acetate, hexane, heptane, and octane have B values within ±0.03 of CCl_4. Ethyl acetate, hexane, and heptane also have similar values of A. However, the ratios to CCl_4 closest to unity at both 1000 and 5000 ppm are those for ethyl acetate.

Breakthrough time measurements by Smith[25] for 14 compounds and Class A2 cartridges containing 270 cm^3 (225 g) unimpregnated coconut activated carbon also were summarized by Freundlich-type fits. Test conditions were 70% RH, 30 L/min, 10 ppm breakthrough, 20°C. Table IX shows these fit parameters and calculated breakthrough times and ratios to CCl_4 at 1000 and 5000 ppm. Cyclohexane and o-xylene have B values within ±0.03 of CCl_4; cyclohexane has the breakthrough time ratio closest to unity at 1000 ppm and second closest at 5000 ppm. Note: the last column of Table V of Reference 25 was improperly sorted. The correctly sorted values appear in the second column of Table IX.

Nelson[26] reported breakthrough times for half-mask cartridges for four compounds at a wide range (500–15,000 ppm) of vapor concentrations and several humidities and airflow rates. Nelson adjusted the times to a common carbon weight of 54.8 g, which was the average carbon weight in the cartridges. Table X lists the adjusted times for CCl_4 and ratios of breakthrough times of three other compounds to those of CCl_4. Data at 1000 ppm are averages of three measurements. Temperatures were 25°C except for 20°C for the 70% RH test. The data for as-received cartridges at 32 L/min and 50% RH have been fit to the Freundlich-type equation to get the A and B fit parameters shown in Table X. Heptane has the closest match of A and B parameters to CCl_4, but ethyl acetate has the average ratio closest to unity. At the one high-humidity (85% RH) preconditioning condition, breakthrough time ratios were much higher (1.56–1.63) than for no preconditioning. This shows that CCl_4 is more affected than the other three compounds by preadsorbed water. Nelson also reported that he (and three of four other laboratories he contacted) had difficulties in generating pentane vapors using a syringe pump. Even at sea level, pentane (normal boiling point = 36°C) vaporizes in the syringe; at higher altitudes this problem is more severe.

As previously discussed in the NIOSH section, Moyer et al.[18] compared breakthrough times for vapors of four compounds with those of CCl_4. Two significantly different lots of commercial organic vapor cartridges were used. Table XI shows their reported

TABLE XII. Comparisons of Carbon Tetrachloride and Ethyl Acetate Average Breakthrough Times

	Breakthrough Time Average (min)		Concentration (ppm)		Relative Humidity (%)				
Reference	CCl$_4$	Ethyl Acetate	Challenge	Breakthrough	Preconditioning[A]	Test	Average Carbon Weight (g)	Airflow (L/min)	EA/CCl$_4$ Time Ratio
25	97.5	102.0	2000	5	AR	40	116	57	1.05
25	41.5	46.5	5000	5	AR	40	116	57	1.12
25	22.5	23.5	10000	5	AR	40	116	57	1.04
25	90.5	101.5	2000	5	AR	50	116	57	1.12
25	41.5	45.5	5000	5	AR	50	116	57	1.10
25	21.0	24.5	10000	5	AR	50	116	57	1.17
25	91.5	98.5	2000	5	AR	60	116	57	1.08
25	42.0	48.5	5000	5	AR	60	116	57	1.15
25	21.5	26.0	10000	5	AR	60	116	57	1.21
25	94.5	95.0	2000	5	AR	80	116	57	1.01
25	41.0	44.5	5000	5	AR	80	116	57	1.09
25	20.0	23.5	10000	5	AR	80	116	57	1.18
25	249.7	259	1000	10	AR	70	97	30	1.04
25	54.9	65.0	5000	10	AR	70	97	30	1.18
30	8.5	29.0	5000	5	80	80	116	57	3.41[B]
30	130.2	150.0	1000	5	AR	50	116	60	1.15
30	54.0	51.7	5000	5	AR	50	116	40	0.96
30	38.0	32.5	10000	5	AR	50	301	60	0.86
30	24.0	24.5	15000	5	AR	50	301	60	1.02
30	31.4	101.0	1000	5	85	50	116	60	3.22[B]
26	220.9	200.8	500	5	AR	50	55	32	0.91
26	112.0	115.1	1000	5	AR	50	55	32	1.03
26	55.9	66.8	2000	5	AR	50	55	32	1.19
26	44.2	38.8	3000	5	AR	50	55	32	0.88
26	25.2	29.3	5000	5	AR	50	55	32	1.16
26	16.7	18.6	7500	5	AR	50	55	32	1.11
26	13.0	11.4	10000	5	AR	50	55	32	0.88
26	6.9	7.8	15000	5	AR	50	55	32	1.13
26	85.8	93.3	1000	5	AR	80	55	32	1.09
26	114.1	185.9	1000	5	85	50	55	16	1.63[B]
26	222.5	224.9	1000	5	25	50	55	16	1.01
26	75.2	82.3	1000	5	AR	85	55	32	1.09
26	212.9	233.0	1000	5	AR	70	55	15	1.09
26	120.0	121.0	1000	5	AR	25	55	32	1.01
26	111.0	117.0	1000	5	AR	50	55	32	1.05
26	22.5	55.0	1000	5	85	85	55	32	2.44[B]
27	92.0	88.7	1000	5	AR	50	45	32	0.96
27	74.9	76.3	1000	5	AR	80	45	32	1.02
28	30.3	35.5	15000	5	AR	80	227	64	1.17
28	50.6	51.8	10000	5	AR	50	227	64	1.02
28	31.1	34.7	15000	5	AR	50	227	64	1.12
16	91.4	74.2	750	5	AR	50	35	32	0.81
16	61.2	69.5	750	5	AR	80	35	32	1.14
16	62.8	59.2	1000	5	AR	50	35	32	0.94
16	48.8	55.2	1000	5	AR	80	35	32	1.13
16	45.7	45.3	1500	5	AR	50	35	32	1.00
16	38.7	39.1	1500	5	AR	80	35	32	1.01
16	32.5	35.0	2000	5	AR	50	35	32	1.08
16	31.0	35.4	2000	5	AR	80	35	32	1.14
16	121.7	78.0	1000	5	AR	80	193	64	0.64
16	69.7	55.7	2000	5	AR	50	193	64	0.80
16	61.6	44.0	2000	5	AR	80	193	64	0.71
21	118.2	88.3	10000	5	AR	50	739	64	0.75
21	122.1	76.3	10000	5	AR	80	739	64	0.62
29	99.0	97.5	1000	5	AR	50	44	32	0.98
29	82.8	83.5	1000	5	AR	70	44	32	1.01
29	73.8	78.0	1000	5	AR	80	44	32	1.06
					Average =				1.02
					Standard Deviation =				0.14

[A] AR = as received.

[B] Average and Standard Deviation were calculated without these outliers.

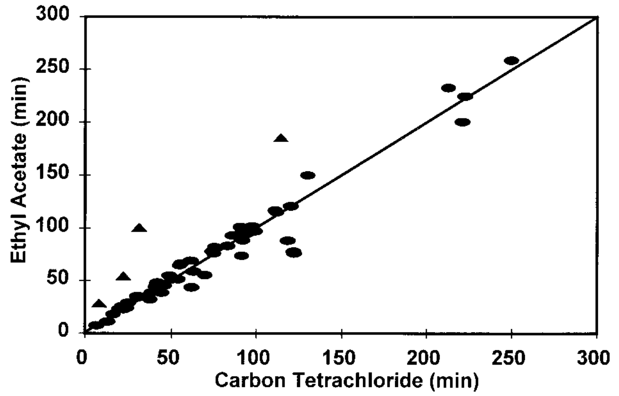

FIGURE 1. Comparison of breakthrough times of ethyl acetate with those of CCl_4. Triangles represent prehumidified carbon conditions. Data from Table XII.

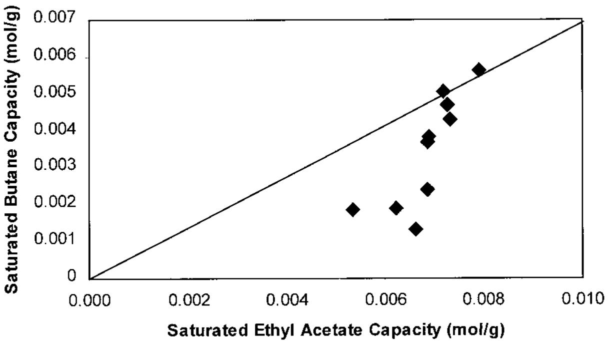

FIGURE 2. Comparisons of butane saturation molar capacities with those of ethyl acetate for 10 respirator activated carbons, 4 of them designated for acid gas removal as well as for organic vapors. The line represents a ratio of 0.7.

data summarized as CCl_4 breakthrough times and ratios of times for the other compounds to those of CCl_4. These are not actual measurements, but values calculated from 5 ppm breakthrough times normalized to the average carbon weights used in the corresponding CCl_4 measurements and fits. Ethyl acetate produced average breakthrough time ratios closest to unity at the two testing relative humidities, 50% and 80% RH.

The ANSI Z88.8 committee has selected ethyl acetate as its primary replacement compound for CCl_4.(22) Comparison data between CCl_4 and ethyl acetate, in addition to the abovementioned sources, were supplied to the ANSI Z88.8 Subcommittee by Monahan,(27), Grunberg,(28) Wilmes,(29) Smith.(30) Table XII lists measured breakthrough times for varieties of cartridges and canisters, vapor concentrations, airflows, and humidities. Breakthrough times of ethyl acetate are compared witvh those of CCl_4 in Figure 1. In this graph the triangles, and in Table XII the superscripts B, on the time ratios indicate those measurements for which the cartridges were preconditioned at high humidities (80–85%RH) before testing. These four data are statistically significant (>3 standard deviations) outliers from the as-received and low humidity preconditioning ratios. The remainder of the data fall close to the equivalence line in Figure 1. The average ethyl acetate/CCl_4 ratio without these four outliers is 1.02, with a standard deviation of 0.14 (n=53).

The conclusion from these comparisons was that ethyl acetate breakthrough times are equivalent to those of CCl_4, except in those cases where the cartridge is significantly preloaded with water. The effects of the preloaded water are solution and possibly hydrolysis of ethyl acetate. Stavitskaya(31) demonstrated ethyl acetate hydrolysis on oxidized carbon containing metal cations and measured rates of hydrolysis. The extent of hydrolysis of ethyl acetate in a respirator cartridge depends on the water loading, the period of contact of ethyl acetate vapor with the carbon bed and water, and catalytic properties of the carbon. Because the products

TABLE XIII. Conclusions from European Comparison Trials of 1993

Compound	Advantages[A]	Disadvantages[A]
Carbon tetrachloride	easily detected nonflammable	high toxicity, carcinogenic environmentally unfriendly
n-Pentane	easily detected low toxicity	boiling point < 65°C log concentration vs. log time plot has lower slope than for other organics
n-Hexane	similar breakthrough time to CCl_4 easily detected	LEL only 1.1% v/v (volume ratio)
n-Heptane	easily detected low toxicity	slightly longer breakthrough time than CCl_4 (need to increase test time or concentration)
Cyclohexane	easily detected slightly shorter breakthrough time than CCl_4 (possible to reduce test concentrations)	LEL only 1.2% v/v
2-Butanone	similar breakthrough time to CCl_4 higher LEL than others	high water solubility
Ethyl acetate	low toxicity high LEL breakthrough time similar to CCl_4	high water solubility reproducibility suspect
Propyl acetate	high LEL breakthrough time similar to CCl_4	high water solubility poor reproducibility

[A] LEL = Lower Explosive Limit.

TABLE XIV. Carbon Tetrachloride Replacement Interlaboratory Trial Summary Data

Chemical	Cartridge Manufacturer	Mean Breakthrough Time (min)	Standard Deviation (min)
Carbon tetrachloride	Protector	114.58	20.82
	Racal	186.67	17.06
	Siebe	163.25	19.36
Cyclohexane	Protector	101.50	21.46
	Racal	172.78	18.57
	Siebe	130.09	16.82
Butanone	Protector	134.80	15.55
	Racal	177.89	23.39
	Siebe	146.42	14.90

Note: 1000 ppm, 30 L/min per cartridge, 70 ± 2% RH, 20 ± 2 °C, and 10 ppm breakthrough concentration.

of hydrolysis—ethyl alcohol and acetic acid—are quite water-soluble, ethyl acetate breakthroughs would be delayed, as observed.

The ANSI Z88.8 committee has specified testing organic vapor respirator cartridges as-received from a freshly opened package, just as they are most often used.(22) Therefore, large water preloading and ethyl acetate hydrolysis during testing would not be a problem with ethyl acetate vapor. However, it is recognized that combination cartridges may have some water preloaded intentionally to activate reactive removal of acid gases, alkaline gases, and so forth.

Because of the potential interference of adsorbed water with ethyl acetate testing, the ANSI Z88.8 committee draft allows a second test vapor, butane. A maximum saturation ratio of 0.7 moles butane per mole ethyl acetate has been measured for six organic vapor and four organic vapor/acid gas carbons (Figure 2).(32) Therefore, in the draft standard, test concentrations of butane were reduced by this factor relative to ethyl acetate (e.g., 700 ppm butane equivalent to 1000 ppm ethyl acetate), keeping the acceptable breakthrough times the same.

THE EUROPEAN APPROACH

During development of alternative test methods for organic vapor testing, European approvals were conducted under three standards: European Norm (EN) 141 for negative pressure respirators,(33) pre-European Norm (prEN) 146 for PAPRs with loose-fitting hoods or helmets,(34) and prEN 147 for PAPRs with tight-fitting masks.(35) The *pr* indicates a method under development. The latter two of these have been finalized and renumbered EN 12941 and EN12942,(36,37) respectively, from 1999 onward. In each of these standards there were three classifications according to the size of respirator. Under standard EN 141, approvals are given for the filter alone, so that it can be used on any approved respirator. For the powered air system standards the filter is considered part of a system; it is approved only with the associated blower and headpieces. Testing is conducted after a period of vertical shock rough handling. In the case of PAPRs, environmental conditioning is additionally required.

EEC Directive 594/91 from the European Commission required that all uses of CCl_4, including laboratory uses, were to cease after January 1, 1995. The consequent changes to the European Norms proceeded via a process of committee meetings, with representation from the different member countries. Certain member countries have their own committees dealing with matters of respiratory protection. Necessary testing to provide data also was organized and acted on through these committees. CEN technical committee TC79 SC4 undertook the job of determining a replacement for CCl_4.

Initial screening of some candidate replacement compounds was undertaken in 1993, and results were compiled into a report(38) and presented at a meeting of CEN TC79 SC4. This report summarized testing by three different institutes, along with literature data, to compare with CCl_4 the properties of the compounds n-hexane, 2-butanone (methyl ethyl ketone), n-pentane, cyclohexane, n-heptane, ethyl acetate, and propyl acetate. The conclusions regarding each of these are given in Table XIII. Candidates were considered on the basis of toxicity, flammability, detectability, test reproducibility, water solubility, and similarity in performance to CCl_4. From these tests, it was decided to select two compounds for further study: cyclohexane and butanone.

A series of tests was organized in 1994 by Associated Octel Co. to compare these candidate compounds. Thirteen laboratories across Europe, plus one in Canada, conducted trials on filters from a range of suppliers to determine which compound gave the best interlaboratory correlation.(39) A matrix of studies was compiled that spread the testing of filters from three suppliers among 14 test laboratories with three test chemicals: CCl_4, cyclohexane, and butanone. Additional studies on filters from one supplier of three size classifications, and the effects of prehumidification, were evaluated. Data from these trials are given in Table XIV. Statistical

TABLE XV. Comparisons of Former and Revised European Organic Vapor Standards

				Carbon Tetrachloride (Former Standard)		Cyclohexane (Revised Standard)	
Standard	Class	Pre-Treatment	Flow Rate per Cartridge (L/min)	Challenge Concentration (ppm)	Required Time (min)	Challenge Concentration (ppm)	Required Time (min)
EN 141	A1	20 min vertical shock	30	1000	80	1000	70
	A2		30	5000	40	5000	35
	A3		30	10000	60	8000	55
EN12941	A1	Environmental[A] plus 20 min vertical shock	[B]	500	80	500	70
EN12942	A2		[B]	1000	80	1000	70
	A3		[B]	5000	40	5000	35

Note: All tests at 70% relative humidity and 10 ppm breakthrough concentration
[A] Environmental conditioning is for 72 hours hot/humid exposure and 72 hours cold exposure at conditions defined by the manufacturer.
[B] Flow rates are set according to the blower output.

TABLE XVI. Summary of Japanese Test Requirements for Organic Vapors Formerly Requiring Carbon Tetrachloride, but Now Specifying Cyclohexane Test Vapor

Standard	Test Designation	Concentration (ppm)	Flow (L/min)	Breakthrough Time (min)
	Negative Pressure Respirators			
Japan	Direct Connection Small Size	300	30	50
JIS T 8152	Direct Connection	3000	30	30
(1981)	Separate	5000	30	100
	Separate O.V./CO	5000	30	30
	Powered Air-Purifying Respirators			
Japan	Grade L	300	[A]	50
JIS T 8157	Grade M	3000	[A]	30
(1991) (3)	Grade H	5000	[A]	100

Note: All tests at 50% relative humidity with no pretreatment and 5 ppm breakthrough concentration.
[A] Flow rates are set according to the blower output.

analysis of the data showed that the consistencies in data for replicates at the same test facility were high, with relative standard deviations lying between 0.7 and 12.9%. Deviations in results among laboratories lay between 9.1 and 21.1%. Data were accumulated to determine effective ratios of data to use to compare testing results.

Studies(39) also were conducted on filters of three size classifications from one supplier to determine typical breakthrough times for revising the required times in test standards. The relatively low lower explosive limit of cyclohexane of 1.2% (12,000 ppm) meant that the test concentration for the largest filter classification was reduced from the 10,000 ppm used with CCl_4 to 8,000 ppm for these trials.

A measurement also was made of the effect of prehumidification on the test results. Whereas prehumidification has been a standard feature of tests in the NIOSH requirements, it is not a feature of European standard tests. However, the effect of moisture on carbon is significant, as there exist in Europe varieties of filters designed to remove contaminants of several types. Filters capable of removing the combination of organic vapors, inorganic gases, acid gases, and ammonia are not uncommon. These filters require a level of moisture on the carbon to aid removal of the chemically reacted gases. This moisture acts to hinder the removal of many organic vapors. It is therefore necessary to select a standard test compound that is negatively affected by water adsorbed on the carbon. Reduced adsorption capacity leading to a low test breakthrough time will be the consequence of too much moisture on the carbon at the time of approval (or manufacture, if performed as a quality assurance test). Breakthrough time should indicate suitability of the carbon for removal of the widest range of organic compounds.

In 1995, Common European Norm Technical Committee 79 (CEN TC 79) moved to replace CCl_4 with cyclohexane. New revisions of the affected standards were issued incorporating the change.(40) The limitation of lower explosive limit led to a reduction in the test concentration for the EN 141 A3 classification from 10,000 to 8000 ppm. Because observed breakthrough times with cyclohexane were lower than those for CCl_4, other factors being equal, the required breakthrough times in the standards were reduced. New and old test criteria are given in Table XV.

A further series of interlaboratory trials was conducted in 1996.(41) A total of 15 laboratories in Europe and Canada were involved, comprising 7 independent test agencies, 6 filter manufacturers, and 2 carbon producers. All conducted the same test using the revised A2 canister requirement with cyclohexane. The results were compared for repeatability and reproducibility. Each laboratory performed triplicate tests on standard canisters, and also gave a detailed account of the test method. Conclusions were as follows:

(1) The repeatability: the difference between two single test results

TABLE XVII. Summary of Successful Substitutions of Vapors for Carbon Tetrachloride in Activated Carbon Testing

Source	Measurement	Substitution	Adjustment Factor[A]
ASTM	carbon activity	butane gas for 250 mg/L CCl_4	2.55
Sosa & Underhill	carbon activity	CFC-114 gas for 250 mg/L CCl_4	0.1 + 0.985 x
Swab & Ferber	breakthrough time	1000 ppm CFC-113 for 1000 ppm CCl_4	1.5
Moyer et al.			
APR cartridges	breakthrough time	550 ppm pentane for 1000 ppm CCl_4 or	1.0–1.25
		1000 ppm hexane for 1000 ppm CCl_4	1.0–1.3
Chin-style canisters	breakthrough time	4000 ppm pentane for 5000 ppm CCl_4	0.82
FM/BM canisters	breakthrough time	10000 ppm pentane for 20000 ppm CCl_4	
		as-received at 50% RH	0.54
		preconditioned at 85% RH	0.16
PAPR cartridges	breakthrough time	550 ppm pentane for 1000 ppm CCl_4[B] or	0.50
		1000 ppm hexane for 1000 ppm CCl_4[B]	0.48
ANSI Z88.8	breakthrough time	various conditions ethyl acetate for CCl_4	1.02
Europe	breakthrough time	500–10000 ppm cyclohexane for CCl_4	1.14
Japan	breakthrough time	300–5000 ppm cyclohexane for CCl_4	1.0

[A] Breakthrough time multiplier to make the substitution measurement equivalent to that for CCl_4 use. See text and tables for more details.
[B] Other test conditions differed.

found on identical test material by one analyst within a short time interval will exceed the repeatability on average not more than once in 20 cases in the normal and correct use of the method. The value of repeatability found was 3.8 min.

(2) The reproducibility: the difference between two single and independent results found by two operators working in different laboratories on identical test materials will exceed the reproducibility on average not more than once in 20 cases in the normal and correct use of the method. The value of reproducibility found was 10.6 min.

No pattern was discerned relating differences in test methods to the variability of results.

THE JAPANESE APPROACH

Use of industrial respirator filters in Japan is subject to meeting the requirements of Japanese Industrial Standards and Ministry of Labour Performance Regulations.(42) The standard JIS T 8152 applies for gas masks (negative-pressure APRs),(43) and JIS T 8157 for PAPRs.(44) A Ministry of Labour regulation covers use of gas masks in industry but does not permit the use of chemical cartridge PAPRs.

In a study on CCl_4 replacement reported in 1993, the Koken Co. evaluated benzene, toluene, n-heptane, and trichloroethylene.(45) They concluded that n-heptane and benzene gave almost identical performance to CCl_4. Candidate compounds studied at the Ministry of Labour laboratories(46) were trichloroethylene, n-pentane, n-hexane, n-heptane, cyclohexane, and toluene. Of these, cyclohexane was found to have the closest correlation to CCl_4 for all the sizes of canisters in the standard. Cyclohexane was recommended to the Ministry of Labour as the alternative test compound for organic vapor filters. A revision to the regulations was enacted April 1, 1996, using cyclohexane in place of CCl_4 at the same testing conditions and acceptance requirements (Table XVI).

CONCLUSIONS

Efforts around the world to identify substitute activated carbon test vapor(s) and conditions have reached differing results. Table XVII summarizes the conclusions reached in various studies and standards settings. It appears that several chemical vapors can be used for replacing CCl_4 in establishing equivalent or relative minimum adsorption capacities or breakthrough times (acceptable test lives). None meets all the criteria of an ideal replacement chemical; that is, that it should (1) be relatively nontoxic, (2) not deplete the ozone, (3) give identical results for critical measured properties (e.g., adsorption capacity or breakthrough time) at all conditions, (4) be affected by adsorbed water to the same extent as CCl_4, and (5) be nonflammable. The user or organization choosing a replacement chemical must decide which characteristics have priority for the application and testing conditions under consideration.

Testing conditions, particularly high-humidity preconditioning, must be considered when selecting a substitute test vapor. Adsorbed chemicals may be blocked and/or displaced to differing extents by adsorbed water. Breakthrough times relative to CCl_4 may be decreased or increased at higher humidities. Some chemicals, like ethyl acetate, may dissolve and/or hydrolyze and thereby show more retention (longer breakthrough times) than predicted from comparison data at drier conditions.

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