

Replacement of Carbon Tetrachloride as an Organic Vapour Respirator Filter Test Agent

Simon J. Smith

Racal Filter Technologies Ltd., Brockville, Ontario, Canada

Abstract

Carbon tetrachloride is currently the standard agent for testing organic vapour respirator filters by approval bodies world-wide. It is due to be phased out in the near future by international agreement as it has been identified as a possible factor in ozone depletion. A satisfactory replacement test chemical is required, and so a study to aid selection of a suitable alternative was made to assist this process. Selection criteria included price, toxicity, detectability, ease of use, similarity of performance across a range of concentrations, and influence of adsorbed moisture on the adsorbent carbon on the test results.

Experimental evaluation was made of the effects of concentration, test humidity and pre-adsorbed moisture on a range of suitable candidates in standard tests on organic vapour filters, approximating North American and European filter approval procedures. The effects of concentration on penetration time for the candidate compounds were determined over a decade of concentration, and in most cases these were generally similar to carbon tetrachloride. Humidity of the test air had little effect on results, but pre-humidification of filters had substantial effect for lower molecular weight, water immiscible compounds.

Cyclohexane and n-pentane were selected as the overall best candidates. Results of independent studies for changes to the European and North American standards agree with these conclusions.

Introduction

Filters for use in respiratory protection are subject to approval testing for performance. This is normally undertaken by a regulatory agency which tests the filters according to a standard protocol. The four principal test standards for respirator filters effective world-wide are:

- Those of the National Institute for Occupational Safety and Health (NIOSH) in the Code of Federal Regulations 30CFR11

- Those agreed by the member countries of the European Community, as European Norm (EN) standards
- Those of Japan in JIS T series standards
- Those of Australia and New Zealand in standard AS/NZS 1716.

Carbon tetrachloride is currently used as the organic vapour filter test agent in all of these. It has

been identified as contributing to ozone depletion, and its usage will be severely curtailed from 1996 (Environment Canada, 1992). The approach of this ban, combined with the concomitant increase in price has spurred efforts in various countries to seek an alternative to carbon tetrachloride for respirator filter testing. Decisions are being made as to the choice of replacement compound.

Current Organic Vapour Test Methods

All approval agencies require a test for proving organic vapour filters which is based on the same basic principle. A test mixture of carbon tetrachloride of known concentration is generated by evaporation of the liquid into humid air, and this is applied to the filter. The concentration of carbon tetrachloride downstream of the filter is monitored by a dedicated detector. Tests are performed at ambient temperature using defined conditions of vapour concentration, air flow rate and humidity, "break-through concentration" (concentration of effluent at which level the filter is considered to be no longer effective) and required breakthrough time - the time before which the breakthrough concentration must not be observed. Precise methods for the testing vary, but the basic equipment layout is depicted in Figure 1. Test conditions for each approval authority are indicated in Table 1.

The conditions and limits are defined in the various standards. Each standard has three or more levels of test. These accommodate the approval of small face-fitting cartridges, larger face-fitting canisters and body-mounted filters of high capacity. Conditions of flow, temperature, humidity and break point are generally constant, the differentiation between classifications being made by different test concentrations. Tests are designed to be accomplished in a time frame convenient for laboratory

Racal Filter Technologies has been involved in the research testing of replacement compounds to meet the needs both of the National Institute for Occupational Safety and Health (NIOSH) and of standards under the European Norms.

testing and none exceed 100 minutes. NIOSH has extra standards for high concentration/short duration emergency escape use, and Australia/New Zealand have a standard for low concentration use. Constant flow rates are chosen to approximate normal breathing flow rates in most cases. In cases where pairs of filters are used on a face-piece, the flow through each for individual test is halved.

Conditions for tests on powered air purifying respirator chemical filters are given in Part B of Table 1. They are covered by in the Australian standard AS/NZS 1716, where testing for powered air purifying respirator (PAPR) filters is conducted at a flow rate of 30 LPM and the required break time adjusted to match the usage of the PAPR filters. In North America, PAPRs are covered by a supplement to the NIOSH standards. In Japan, the latest issue of standard JIS T 8157 provides test conditions for PAPR filters, though this is not yet in effect. In Europe, the latest revisions of standards EN 146 and EN 147 cover PAPRs.

All agencies except Japan require some pre-treatment of filters. For NIOSH, certain samples are pre-humidified to a limited extent prior to testing, for EN and Australian standards, filters are subjected to a simulated transportation shock.

Approaches for Selection of a Replacement Compound

The relative importance of selection criteria for a replacement compound vary with the viewpoint of those concerned. It is preferable to have a compound with as low toxicity, and minimal environmental effects as possible. Scientific formalists will seek a compound that most closely resembles the behaviour of carbon tetrachloride in all aspects. Operators of test laboratories are seeking the safest, cheapest and most convenient replacement that will provide discriminating data. Approval agencies would be

interested in reproducibility across a range of carbon types and product classifications. Respirator users would be interested in a compound that provides an effective indication of workplace performance. One compound may not satisfy all of these needs. Data have been accumulated in this work to address all of these points of view, and to assist the determination of a replacement. Test procedures were undertaken based on the advice of researchers at NIOSH and in Europe.

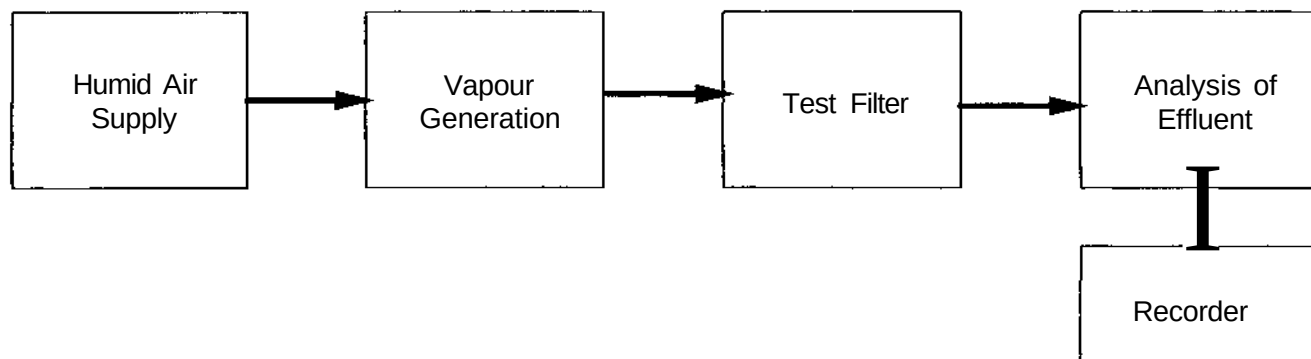


Figure 1a. Components of organic vapour test equipment.

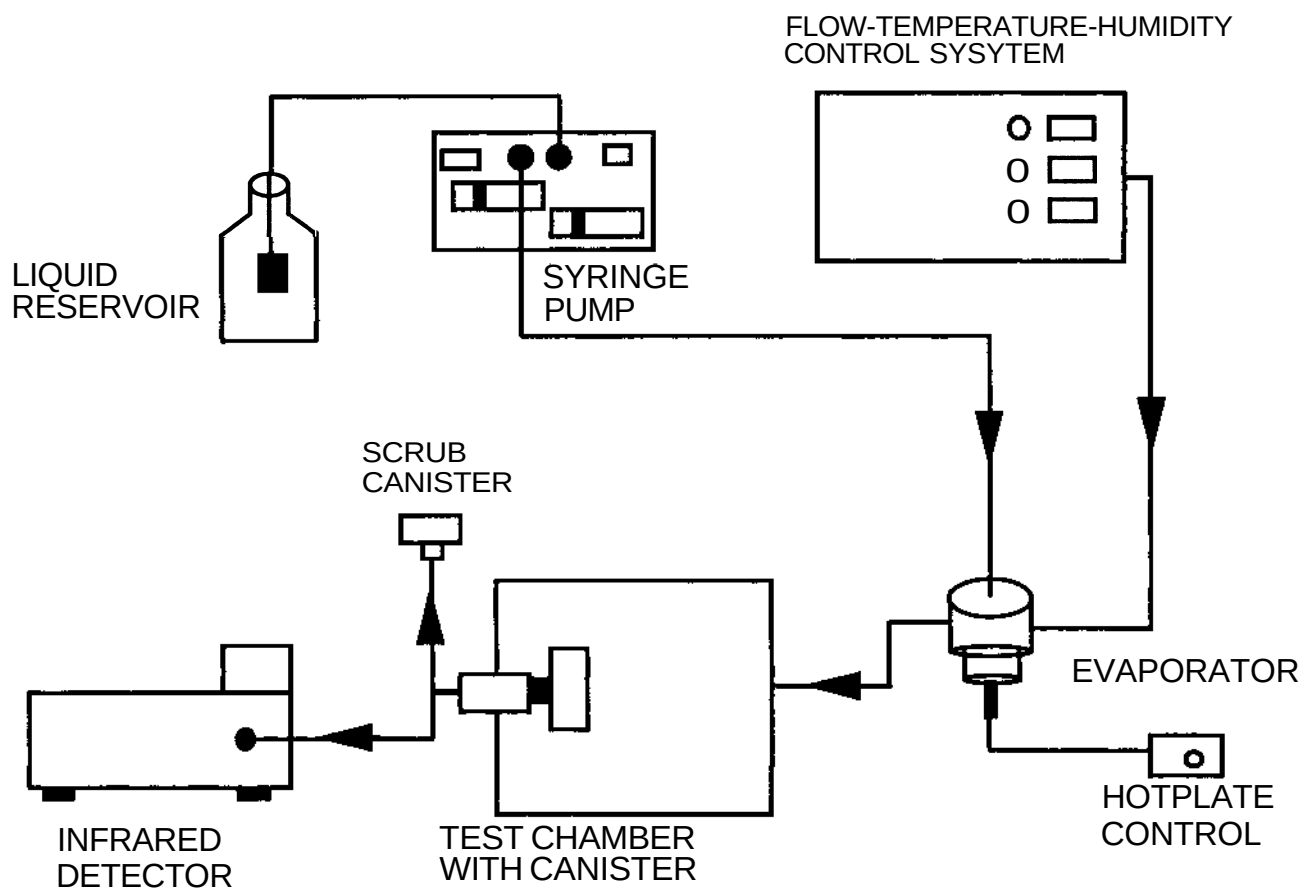


Figure 1b. Layout of organic vapour test equipment.

Figure 1. Organic vapour test apparatus.

Table 1. Summary of tests for organic vapours requiring carbon tetrachloride.

Country/Standard	Test Designation	Pre-Treatment	Concentration ppm	Flow LPM	Humidity % R.H.	Break Point ppm	Break Time min.	Uptake at Break, g
A. Negative Pressure Respirators								
Japan	Direct Connection	None						
JIS T 8152	Small Size		300	30	50	5	50	2.8
(1981)	Direct Connection		3,000	30	50	5	30	17.0
	Separate		5,000	30	50	5	100	94.6
	Separate O.V./CO		5,000	30	50	5	30	28.4
European	Class A1	20 minutes	1,000	30	70	10	80	15.1
Community	Class A2	Vertical Shock	5,000	30	70	10	40	37.8
EN 141 (1990)	Class A3		10,000	30	70	10	60	113.5
Australian/N.Z.	AUS	20 minutes	1,000	30	70	5	20	3.8
Standard	Class A1	Vertical Shock	1,000	30	70	10	80	15.1
AS/NZS 1716	Class A2		5,000	30	70	10	40	37.8
(1994)	Class A3		10,000	30	70	10	60	113.5
	Class G		50	30	70	10	15	0.1
North American		(1)		(2)				
NIOSH	Cartridge As							
30 CFR 11	Received		1,000	64	50	5	50	20.2
(1972)	Cartridge Humidified	Pre-Humidification	1,000	32	50	5	50	10.1
	Canister As Received		5,000	64	50	5	12	24.2
	Canister Humidified	Pre-Humidification	5,000	32	50	5	12	12.1
	Chest-Mounted As							
	Received		20,000	64	50	5	12	96.8
	Chest-Mounted							
	Humidified	Pre-Humidification	20,000	32	50	5	12	48.4
	Escape As Received		20,000	64	50	5	12	96.8
	Escape Humidified	Pre-Humidification	20,000	32	50	5	12	48.4

Table 1. Continued.

Country/Standard	Test Designation	Pre-Treatment	Concentration ppm	Flow LPM	Humidity % R.H.	Break Point ppm	Break Time min.	Uptake at Break, g
B. Powered Air Purifying Respirators								
Japan	Grade L	None	300	(4)	50	5	50	
JIS T 8157 (1991)	Grade M		3,000		50	5	30	
(3)	Grade H		5,000		50	5	100	
Eur. Community	Class A1	20 minutes	500	(4)	70	10	80	
prEN 146/147 (5)	Class A2	Vertical Shock	1,000		70	10	80	
(1993)	Class A3		5,000		70	10	40	
Australian/N.Z.	Class A1	20 minutes	1,000	30	70	10	(6)	
Standard	Class A2	Vertical Shock	5,000	30	70	10		
AS/NZS 1716	Class A3		10,000	30	70	10		
North American		(7)		(8)			(9)	
NIOSH	Cartridge As							
30 CFR 11	Received		1,000	115/170	50	5	50	
(Supplement)	Cartridge Humidified	Pre-Humidification	1,000	115/170	50	5	25	
	Canister As Received		5,000	115/170	50	5	12	
	Canister Humidified	Pre-Humidification	5,000	115/170	50	5	6	

- Notes:
1. Pre-humidification with air at 25% or 85% Relative Humidity for 6 hours at 25 LPM for cartridge, 64 LPM other types.
 2. Flow rate is halved if filter also provides protection against another contaminant class, e.g., acid gases.
 3. Standard is issued but not implemented.
 4. Flow rate for test determined by total flow output of PAPR, varies with each type.
 5. Standard is issued in preliminary form, not yet implemented.
 6. Breakthrough time for test calculated from formula based on PAPR flow output, number of filters and class.
 7. Pre-humidification with air at 25% or 85% Relative Humidity for 6 hours at 115 or 170 LPM.
 8. Flow rate 115 LPM for tight fitting systems (masks), 170 LPM for loose fitting systems (hoods, helmets).
 9. Breakthrough time is halved if filter also provides protection against another contaminant class, e.g., acid gases.

Properties of Carbon Tetrachloride and Replacement Compounds

Carbon tetrachloride offers certain desirable properties for its use as a filter test agent, and it is useful to consider these when examining alternative test agents. It is non-flammable, available with good purity, currently inexpensive, water immiscible and readily detectable by an infrared spectrophotometer. It has been considered "typical" of organic solvents, against which organic vapour filters will see service. Paradoxically, its low permitted exposure limit and high odour threshold means that a filter system cannot be recommended for general protection against it in the workplace. Its undesirable properties are its effect on the environment as a contributor to ozone depletion, and the toxic effects—it is a carcinogen, mutagen, teratogen and neurotoxic.

A compound to replace carbon tetrachloride would ideally offer properties matching the useful ones while avoiding the undesirable ones. These are summarized and quantified where possible in Table 2.

Table 2 includes data for:

1. Toxicity—this is a consideration when disposing of tested filters, but not so much a concern during the test, as the challenge chemicals are contained within the equipment.

2. The lower explosive limit—the higher test concentrations may approach explosive levels for some compounds.
3. Ease of use—notably to find a replacement that can be used in existing test equipment with minimum modification.
4. Price—this is significant as a determining factor as the tests for the highest class of protection for NIOSH and EN standards can use up to 100 g of test chemical. This eliminates many branched alkanes from consideration, as the price of pure isomers can be high.

Suitable candidates can be drawn from the following classes: linear alkanes, branched alkanes, cycloalkanes, aromatic hydrocarbons, esters and ketones. A chlorinated alternative to carbon tetrachloride was tested also. These compounds and their properties are listed in Table 3. Prices are given for 1990 to enable comparison with the carbon tetrachloride price before escalation due to the impending ban (Aldrich, 1990). In 1995, carbon tetrachloride is priced at \$4.09 per 100 g (Aldrich 1994). Water miscibility, based on polarity is also included, as this is considered to contribute to the effect of humidity on the test agent.

Test Rationale

Method for Comparing Performance

Similarity to carbon tetrachloride can be estimated by determined by measuring the effect of concentration on breakthrough time of the filter for potential replacement candidates. It has been reported that the relationship of filter lifetime (T) with concentration (C), all other factors being constant, follows the formula:

$$T = A \cdot C^{-B} \text{ or } \log T = \log A - B \log C$$

Nelson et al. (1976a), Littleton et. al. (1992). For direct proportionality, B is equal to one, but in practice, it is usually slightly less. If the concentration and time are plotted on logarithmic axes, the slope of the best fit line is -B, and the intercept A. Plotting the generated data in this manner enables comparison of the effects of concentration to be made over a wide range.

Comparison of a Range of Organic Compounds

Test conditions were based on the anticipated requirements of the updated NIOSH standard for organic vapour testing (Moyer, 1993), and on European standards.

1. Tests to NIOSH Requirements. Tests were made on an approved organic vapour filter with a range of replacement candidates at flow rates used for PAPR testing. Four concentrations were used to establish the break time/concentration plots according to the equation.
2. Tests to European Requirements. Tests were undertaken at flow rates used in European/Australian/Japanese standards on a canister meeting European Class A2.

Table 2. Target properties of replacement compounds.

	Criterion	Carbon Tetrachloride	Desired	Comment
"Similarity"	Boiling Point Concentration Time Over Carbon Type	77°C	70-90°C Must be demonstrated Must be demonstrated	Typical low range of common solvents
Non-Flammability		Non-flammable	L.I.L. $< 1\%$, $> 20\%$ preferred	10,000 g/g used for EN A3 tests 20,000 preferred for NIOSH Escape Tests
Purity		$> 99\%$	$> 99\%$	
Price		\$0.61 per 100 g (1977)	$< \$100$ per 100 g ref.	
Equipment Compatibility	Boiling Pt. Non-corrosive Non-polymerizing Stable	Adequate Adequate Adequate Adequate	$> 50^\circ\text{C}$ Required Required Required	Avoid dispensing directly
Detectability		Infrared/Halogen	Infrared F.I.D.	
Repeatability		Miscible in water	Debated	
Toxicity	Exposure Limits Toxic Effects	TLV Carcinogen, mutagen, teratogen	High TLV Not carcinogen, mutagen, teratogen	
Environmental	Ozone friendly Low-cost disposal Low desorption	Not suitable Poor Adequate	Required Required Required	

Table 3. Potential replacement compounds and properties.

Compound	Rel. Molecular Mass	Boiling Point (C°)	LC ₅₀ L (%) ¹	TL _V (ppm) ²	Price (US\$/100 g) ³	Toxicology (RTECS) ⁴	Miscibility ⁵	Toxicity
Acetone	58.1	56.2	2.5	750	0.59	M-I	S	Yes
Amyl Acetate	130.2	142	1.1	100	\$5.40		S	No
Bromochloromethane	128.4	68.1	None	200	\$2.35	S	I	Yes
Butanone	72.1	79.6	1.4	200	\$1.11	M-I	S	Yes
Carbon Tetrachloride	153.8	76.5	None	2	\$0.61	C-M-I	I	Yes ^S
Cyclohexane	84.2	80.7	1.2	100	\$1.36	M	I	Yes
Cyclopentane	58.1	49.2	1.1	600	\$1.92		I	Yes ^S
Ethyl Acetate	88.1	77.1	2.2	400	\$0.81	M	S	Yes
Ethylbenzene	106.2	136.2	1.0	100	\$2.22	M-I	I	Yes ^S
Heptane (n-)	100.2	98.4	1.05	400	\$1.26		I	Yes
Hexane (n-)	86.2	68.7	1.1	50	\$5.46	M-I	I	Yes
Isooctane	114.2	99.2	1.0	75	\$1.10	M	I	Yes
Methyl Acetate	74.1	57.9	3.1	200	\$2.15	M	S	Yes
Octane (n-)	114.2	125.7	1.0	300	\$6.83		I	Yes
Pentane	72.1	36.1	1.4	600	\$1.59		I	Yes
Propyl Acetate	102.1	101.6	1.8	200	\$0.34		S	Yes
Toluene	92.1	118.6	1.2	100	\$0.84	M-I	I	Yes
Xylene (o-)	106.2	144.4	1.1	100	\$1.45		I	Yes

¹ LEI = Lower Explosive Limit
² TL_V = Threshold Limit Value (ACGIH)
³ Obtained from 1990-1991 Aldrich Catalogue
⁴ C = Carcinogen, N = Notagen, T = Teratogen
⁵ S = Soluble, I = Insoluble

Effect of Carbon Type

The different source materials from which respirator carbons are made, commonly coconut shell, coal or peat, may impart differences in performance characteristics in the activated carbon used in respirator filters. This has not been investigated in this work as all tests were made on coconut shell based products.

Certain filters are intended for removal of more than one type of contaminant. The commonest of these are filters used for acid gases and organic vapours. In Europe, the combination of organic vapour, acid gas and ammonia is not uncommon. The removal of non-organic gases is achieved usually by the addition of chemicals to the surface of the carbon by impregnation from aqueous solution, followed by drying to various extents. Filters with impregnated carbons are therefore likely to contain some adsorbed moisture after this. In fact, for removal of acid gases or ammonia, a certain level of adsorbed water is beneficial, but this water will itself adversely affect the removal of many organic vapours. It is important that an organic vapour test agent reflect this, to indicate the potential for early vapour penetration in the workplace if too much adsorbed water is present.

Effect of Test Humidity

All current test protocols require testing with humid air: 50% (NIOSH and Japan) and 70%

(Europe and Australia) are relative humidities of choice. Water will adsorb on activated carbons in competition with organic compounds and may inhibit their removal to some extent. The effects of relative humidity have been reviewed and studied (Moyer 1983, Nelson 1976b). To establish how important the test humidity was, four replacement candidates were evaluated at five humidities, and the breakthrough time versus concentration plots compared.

Generally, test conditions do not simulate typical workplace conditions except perhaps for emergency escape. In the workplace, there is continuous exposure of filters to humid air, and often to a relatively low level of contaminant while in use. The filter is likely to become equilibrated with water at the ambient temperature and humidity. To be representative, a test agent for filters should be able to indicate the effect of adsorbed moisture. Therefore tests on pre-adsorbed moisture were undertaken as described below.

Effect of Pre-Adsorbed Moisture

Deliberate pre-humidification of filters is currently called for in certain of the NIOSH filter tests, and its effects were studied for some compounds here. Pre-humidification of the canisters with 80% R.H. air to constant weight was followed by testing with 80% R.H. air, and results compared with those for non pre-humidified canisters.

Experimental

Test Procedure

The layout of the test equipment used for organic vapour testing at Racal Filter Technologies Ltd. is shown in Figure 1. Humidified air was supplied by a flow-temperature-humidity controller (Miller-Nelson Research Inc.). The flow rate, temperature and humidity were verified by a calibrated flow meter and wet/dry bulb hygrometer before every test. The humid air passed over a hot plate, on to which was fed the organic liquid from a continuous feeding syringe pump (Pharmacia P-500). The liquid evaporated into the airstream which then passed through a mixing baffle and into the test chamber which contained the filter. Air temperature was controlled by room conditions, and was not otherwise regulated. All tests were in the range 23 to 25°C. Downstream of the filter, a portion (3 litres per

minute) of the air was fed to an infrared spectrophotometer (Miran 1B2) which was calibrated to analyse the compound of interest. The detector output was logged on a chart recorder. The remaining effluent was fed through a second filter, so that no vapour was released from the equipment. Flow, temperature, humidity were checked using calibrated equipment before every test, and detector response was calibrated using a sample loop before each set of tests. The concentration of the test vapour was determined by calculation from the air flow rate, time and the weight change of the container from which it was drawn.

Pre-Humidification

This was undertaken by connecting filters to the output of a flow-temperature-humidity controller

(Miller-Nelson Research Inc.) and passing humid air into them until constant weight was achieved. The air humidity was verified by a calibrated hygrometer before filter exposure. Several filters could be humidified at once using a manifold.

Test Materials

This work was undertaken principally in support of the powered air purifying respirator filters manufactured by Racal. For this study, filters manufactured to NIOSH organic vapour PAPR

"Cartridge" standard which contained 270 cc of unimpregnated coconut shell activated carbon were used. For part of this, smaller filters meeting the performance requirements of class A2 in the European EN 141 or Australian AS 1716 standards were used, which contained 225 cc of the same type of activated carbon. The carbon was a standard commercially available grade.

All test Chemicals were obtained from Aldrich Chemical Co. as HPLC grade, except for Bromochloromethane, supplied by Ethyl Corporation.

Results

Comparison of Concentration-Breakthrough Time Response for a Range of Organic Compounds

1. *Tests to NIOSH Requirements.* Twelve candidate compounds were tested using a filter with 270 cc of carbon with airflow at a constant 57 LPM and 23 to 25°C, generally with organic vapour concentrations of 1,000, 2,000, 5,000 and 10,000 ppm. The break concentration used was 5 ppm. Experiments were performed at two humidities: 50 and 80% R.H. Two or three measurements were made as indicated in Table 4 and averages plotted in Figure 2. Correlation coefficients for the lines all exceeded 0.99. The flow rate corresponds to powered air purifying respirator flow rates for North American products, and is equivalent to 2 cubic feet per minute, this being the flow through one filter of three used on a PAPR system.
2. *Data for the Effect of Test Humidity.* Additional tests were made at 22, 40, and 60% R.H. for four of the compounds, to demonstrate the effect of a wide range humidity on the performance. Data for carbon tetrachloride are illustrated in Figure 3.

3. *Tests for European Requirements.* Data were obtained for filters corresponding to a European A2 product. A larger range of compounds was tested, at 1,000 and 5,000 ppm only in air at 70% R.H. and 30 LPM, with break point 10 ppm.

Slopes and intercepts were calculated for each of the logarithmic breakthrough time versus concentration plot lines. These are assembled in Table 5 for comparison. Tests with cyclopentane were limited due to poor sensitivity of the infrared detector to this compound.

Effect of Pre-Adsorbed Moisture

Data are summarized in Figure 4 which shows the mean breakthrough times for pairs of tests on filters "as received" (containing the base level of moisture) and after equilibration to constant weight in air at 80% R.H. at 23°C. The relative drop in performance is indicated over each set of data. Water uptakes for these filters were 55 to 59 g, and with the carbon weight approximately 116 g, this represents about 47 to 51% weight uptake.

Discussion

Comparison of Concentration-Breakthrough Time Response for a Range of Organic Compounds

The data plotted in Figure 2 for these compounds illustrate that there is general similarity in performance of standard filters over a wider range of

concentrations. Derived slope and intercept data from Figure 2 are in Table 5. Slopes for compounds with boiling points over about 80°C are all seen to be similar, and approach unity. Below this temperature, boiling point and slope correlate approximately, so that slopes down to about -0.5 are noted for the lower boiling compounds. The given intercept

Table 4. Data for concentration-time plots.

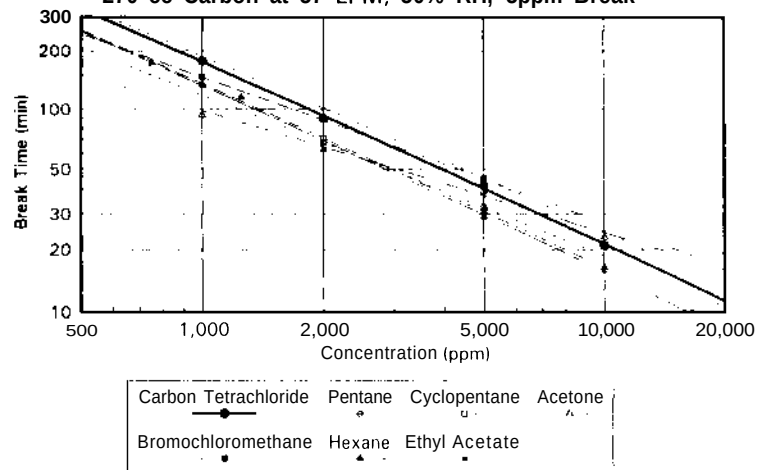
Tests of 270 cc Organic Vapour Cartridges
Break Times in minutes

Flow Rate: 57 LPM
Break Point: 10 ppm

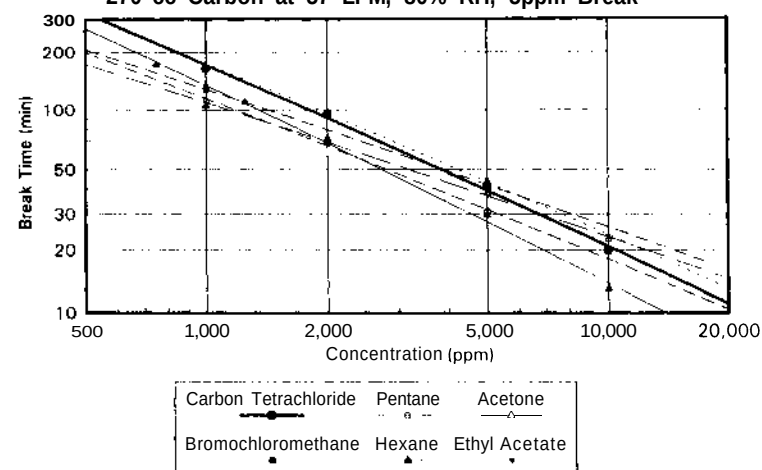
		Percent Relative Humidity									
Compound	Conc./ ppm	22		40		50		60		80	
Butanone	1,000									187	18
	2,000	117	120	116	117	99	100	109	112		
	5,000	53	53	54	54	47	48	49	50	47	4
	10,000	28	28			29	29	27	28	27	2
Carbon Tetrachloride	1,000					172	183			163	16
	2,000	93	99	97	98	88	93	89	94	92	9
	5,000	42	43	41	42	41	42	42	42	41	4
	10,000	21	22	22	23	21	21	21	22	20	2
Cyclohexane	1,000					159	168			158	16
	2,000	90	92	87	89	85	90	85	86	85	9
	5,000	39	40	36	36	38	38	35	36	37	3
	10,000	20	20	19	20	20	20	19	19	18	1
Ethyl Acetate	2,000			100	104	100	103	98	99	94	9
	5,000			46	47	45	46	48	49	44	4
	10,000			23	24	24	25	26	26	23	2
Acetone	1,000					90	97			103	10
	2,000					68	69			68	7
	5,000					38	40			38	3
	10,000					22	24			22	2
Bromochloromethane	1,000					146	148			103	10
	2,000									68	7
	5,000					45	45			38	3
	10,000									22	2
Cyclopentane	2,000					66	70				
	5,000					32	33				
Heptane	1,000					158	159			146	15
	2,000					79	81			76	7
	5,000					34	34			34	3
	10,000					16	18			18	1
Hexane	750					174	174	170		153	17
	1,000					134	126	147		125	13
	1,250					114	116	117		105	11
	2,000					56	64	68		67	6
	5,000					28	29	30		29	3
	10,000					15	17	17		11	1
Octane	2,000					73	76			76	7
	5,000					29	31			32	3
	10,000					15	15			16	1
Pentane	1,000					132	137			109	11
	2,000					71	73			67	7
	5,000					31	32			30	3
	10,000					16	16				
Toluene	1,000					214	222			195	20
	2,000					101	109			105	10
	5,000					45	45			44	4
	10,000					25	25			23	2

a. Comparison of Organic Vapours Boiling $<80^{\circ}\text{C}$

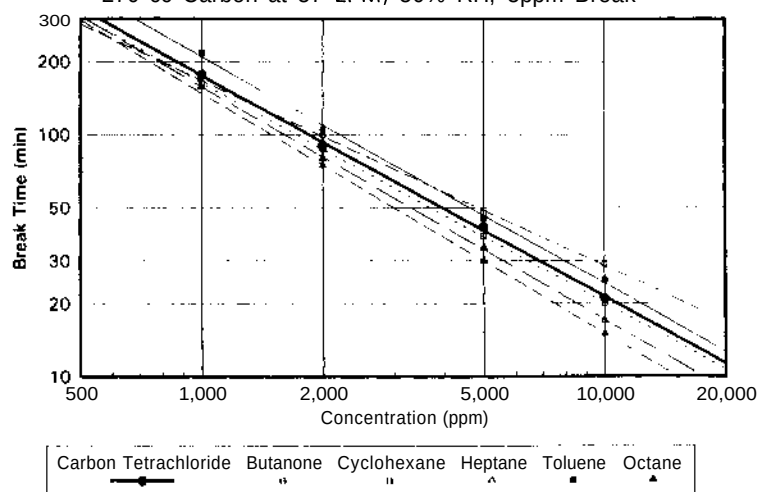
270 cc Carbon at 57 LPM, 50% RH, 5ppm Break

**b. Comparison of Organic Vapours Boiling $<80^{\circ}\text{C}$**

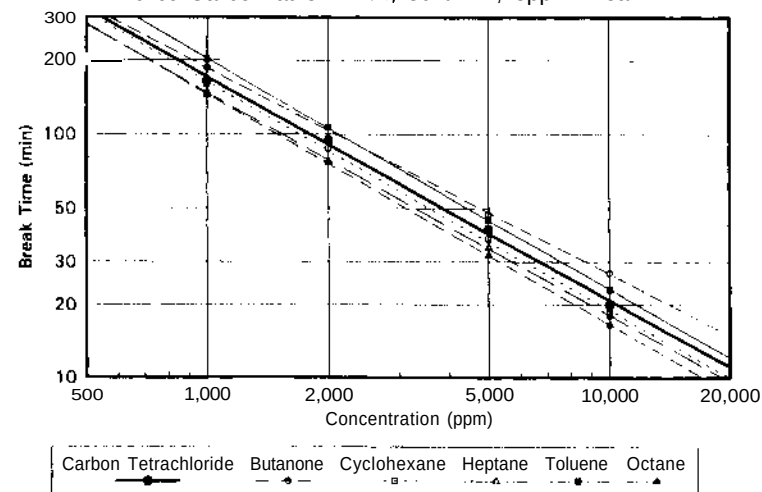
270 cc Carbon at 57 LPM, 80% RH, 5ppm Break

**c. Comparison of Organic Vapours Boiling $>80^{\circ}\text{C}$**

270 cc Carbon at 57 LPM, 50% RH, 5ppm Break

**d. Comparison of Organic Vapours Boiling $>80^{\circ}\text{C}$**

270 cc Carbon at 57 LPM, 80% RH, 5ppm Break

**Figure 2. Comparison of organic vapours.**

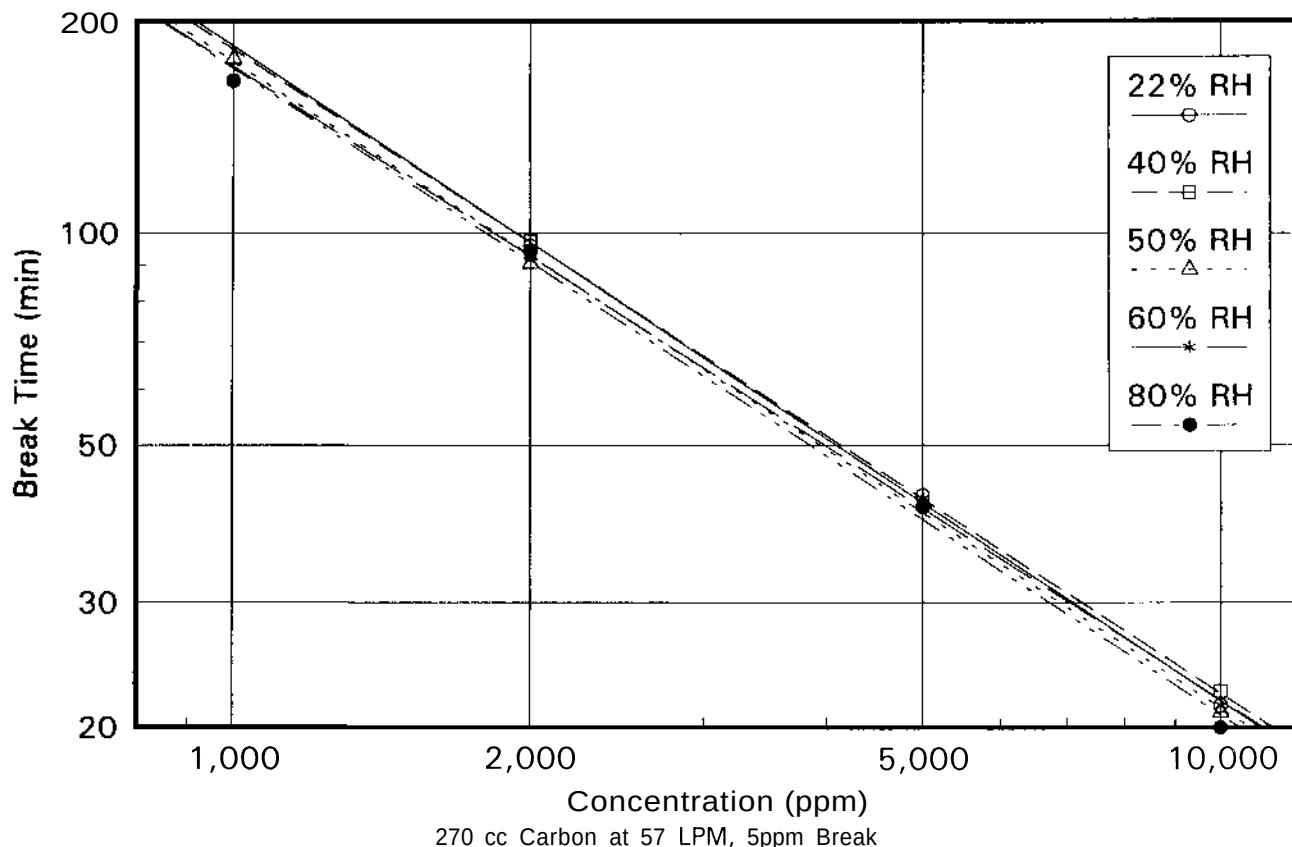


Figure 3. Effect of humidity on carbon tetrachloride.

values, representing the time for 5 ppm breakthrough at Log C = 0 or 1 ppm challenge, have no practical meaning, and are only useful for interpolation of values in these plots.

The tests on filters under "European" conditions in the right hand column of Table 5 gave different slope and intercept values. This would be expected as the combination of a smaller filter and lower flow rate results in a higher gas residence time. In the latter case this is 0.45 seconds compared with 0.28 seconds for the NIOSH-type study. However, in general the data correlate with those from the main series of tests.

These data help in the selection of a replacement compound which gives as close reproduction of the current carbon tetrachloride test as possible. The

four closest compounds from these trials are cyclohexane, n-pentane, octane and ethyl acetate.

Effect of Test Humidity

The data show that there is very little effect of the humidity of the test atmosphere on the performance of the test agents. The closeness of data for carbon tetrachloride is illustrated in Figure 3. These tests are of relatively short duration, so it would be expected that the level of water removed by the filters during this time is low relative to that required to saturate the carbon surface. There was a tendency to shorter break times with increasing humidity. Effects of competition for adsorptive sites under the test conditions are considered to be very slight, and so the test humidity has little effect, even at high humidities.

Table 5. Slopes and intercepts from replacement compounds.

Compound	270 cc Canister 57 LPM, 5 ppm break										225 cc Canister 30 LPM	
	22% R.H.		40% R.H.		50% R.H.		60% R.H.		80% R.H.		70% R.H.	
	Slope	Intercept	Slope	Intercept	Slope	Intercept	Slope	Intercept	Slope	Intercept	Slope	Intercept
Butanone	-0.895	107,500	-0.893	68,600	-0.768	33,800	-0.865	78,900	-0.842	62,800	-1.029	245,300
Carbon Tetrachloride	-0.927	111,700	-0.912	99,600	-0.917	98,800	-0.897	84,800	-0.916	95,900	-0.941	35,500
Cyclohexane	-0.940	116,000	-0.939	109,200	-0.912	89,300	-0.935	104,300	-0.935	104,800	-0.974	130,400
Ethyl Acetate			-0.909	103,800	-0.883	83,400	-0.825	52,700	-0.866	69,200	-0.859	243,600
Acetone					-0.610	6,670			-0.672	11,300	-0.451	211,700
Bromochloromethane					-0.736	23,700			-0.692	15,300	-0.782	3,480
Cyclopentane					-0.805	31,000					-0.753	166,100
Heptane					-0.965	123,800			-0.913	81,300	-0.995	68,300
Hexane					-0.929	81,300			-0.988	123,900	-1.009	48,800
Octane					-0.996	144,300			-0.935	92,700	-0.918	40,800
Pentane					-0.922	79,000			-0.802	29,100	-0.861	377,000
Toluene					-0.938	137,100			-0.943	137,400	-0.988	299,500
Methyl Acetate											-0.779	97,800
o-Xylene											-0.943	181,000

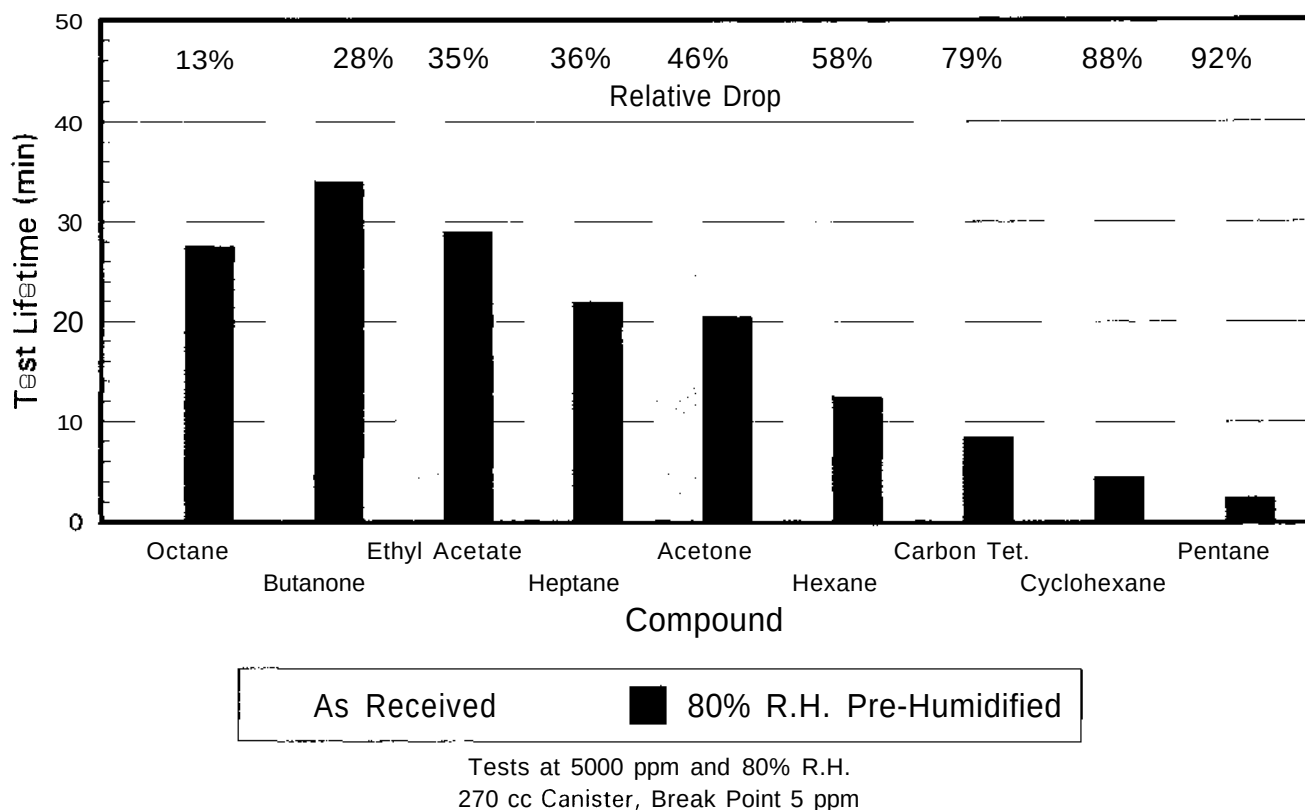


Figure 4. Effect of pre-humidification on organic compound tests.

Effect of Pre-humidification

Pre-humidification had a much greater effect than test humidity. It has been suggested that uptake of highly water soluble organic compounds might be enhanced by humidity pre-conditioning (Moyer 1983). In these tests, it was noted that the filter lifetime for the pre-equilibrated samples was always lower than those not treated. The relative drop was greatest for lower boiling compounds, and generally for those less miscible with water. In cases where the effect of the pre-equilibration was significant, the effect of test humidity was still quite slight.

Choice of Replacement Compound

Tables 3 and 5 show compound information and summary data.

Toxicity

Toxicity ruled out certain compounds from inclusion in Table 3. From consideration of TLV and toxic effects, the most favoured compounds are acetone, cyclopentane and n-pentane.

Price

This was used also to limit the inclusion of compounds in Table 3 to those with a cost under U.S.\$10 per 100 g, so all were reasonable. Compounds with the best prices are acetone, propyl acetate, ethyl acetate and toluene.

Practical Factors

Some of the compounds with boiling points below 40°C, notably n-pentane, can cause difficulties when a regular syringe pump liquid feed system was used. The liquid vaporized in the syringe barrel and feed lines if care was not taken to keep them cool. This problem can be avoided with adaptation of the equipment by operation with cooling or by a change to an evaporation vessel arrangement. This would add to the cost of immediate changeover.

Detection by infrared spectrophotometer was difficult for cyclopentane as the detection limit was so high.

Toluene was observed to attack rubber seals used in certain kinds of syringe pump systems.

Reproducibility Across a Range of Filter Types

Data on different filter sizes at different flow regimes correlated, though were not identical. More work needs to be done to measure performance against different base materials and impregnations.

Correlation with "Real Workplace"

As discussed, test compounds that are strongly affected by humidity will provide a good representation of performance in the workplace. The data in Figure 4 illustrate comparative performance. Compounds that are strongly affected by the presence of

moisture such as cyclohexane and n-pentane are therefore representative in this regard.

Test Flow Rates

In line with the main purpose of the study, the bulk of tests were undertaken at PAPR flow rates (57 LPM). The data are considered to be valid at negative pressure flow rates for NIOSH purposes (64 LPM). Tests undertaken at the negative pressure test conditions used in Europe (30 LPM) show that the relative performance of replacement compounds was generally the same.

Conclusions

Summary of Points of Interest

In limiting the choice of materials tested to a few commonly available organic compounds, there was similarity in performance over a range of concentrations when tested against a standard protocol on organic vapour filters. No compound could be eliminated due to significantly different or inconsistent performance under these conditions.

It was noted that for the range covered, test humidity had very little effect on the performance, but the effect of pre-humidification was highly significant and would be a major factor in the choice of a "representative" compound.

Overall Conclusion

Cyclohexane meets all the criteria well. n-Pentane is also considered to be acceptable, providing that arrangements are made to accommodate the effects of its low boiling point.

Known Selections

At the time of writing, it is known that NIOSH has selected n-pentane for use in all types of test as a replacement for carbon tetrachloride (Moyer, 1993), though they do allow laboratories to use alternatives if correlation to n-pentane can be demonstrated. The European Community has selected cyclohexane (Malloy, 1994). Test conditions differ from those previously used for carbon tetrachloride. For cyclohexane, a lower concentration for the highest class of test (A3) has been chosen to be well below the lower explosive limit.

Other Factors

It is worthwhile to comment on certain of the considerations made in the selection process.

1. *Exact Replacement with Compound of Identical Performance.* The data indicate that cyclohexane, n-pentane, octane and ethyl acetate are all reasonably similar to carbon tetrachloride in terms of matching the relationship of breakthrough time to concentration.
2. *Representative Compounds—Effect of Humidity.* The compounds showing the beneficial property of a strong effect on test results of pre-humidified carbon were n-pentane, cyclohexane and hexane.
3. *Convenience—Practical Factors.* There were difficulties noted with n-pentane due to evaporation of the liquid in the feed system, with the infrared detection of cyclopentane and because of the solvent properties of toluene.
4. *Safety and Price.* Acetone is certainly the leader in this regard. It is cheaper than carbon tetrachloride, and has high lower explosive limit and threshold limit value. It is readily available, and does not necessitate any modification of test apparatus. However, the effect of pre-humidification and differences in breakthrough time concentration response rule it out from further consideration.

Of the compounds closely similar in performance, octane is the least favourable because of its high price.

Quick Reference

Table 6 shows the properties in Table 3 as a star rating, together with other measurements made in

this work. This may assist in the assessment of desirability of replacement compounds.

Acknowledgements

The author wishes to thank Carrie Andress, Luis Bernardo and Monika Simon of Racal Filter Technologies Ltd. for undertaking practical aspects of this work, and to express gratitude to Ernest Moyer of NIOSH (U.S.A.), Paul Malloy of Associated Octel (U.K.), Andrew Capon of Racal (U.K.), John Devine of WorkCover Authority (Australia) and Yoshimi Matsumura of Ministry of Labour (Japan) for information and assistance in the prosecution of this work.

Table 6. Summary of data.

Compound	Price	TLV	LEL	Water Effect	Immiscible in Water	Detectability		Equipment Required	Comments
Acetone	***	***	***	46%	X	✓	✓	Any	
Bromochloromethane	**	**	***		✓	✓		Any	
Butanone	***	**	**	28%	X	✓	✓	Any	
Cyclohexane	***	***	**	88%	-	-	-	Any	Close data fit
Cyclopentane	**	***	*		✓		✓	Any	
Ethyl Acetate	***	**	**	35%	X	✓	✓	Any	Close data fit
Heptane	***	**	*	36%	-	-	-	Any	
Hexane	*	*	**	58%	-	-	-	Any	
Methyl Acetate	**	**	***		X	-	-	Any	
Octane	*	**	**	10%	-	-	-	Any	
Pentane	**	***	**	92%	-	-	-	Not syringe	Close data fit
Toluene	***	*	*		✓	✓	✓	Any	
o-Xylene	***	*	*		✓	✓	✓	Any	

Price per 100 g	TLV (ACGIH)	LEL
*** <\$1.50	*** >500 ppm	*** >2.0%
** \$1.50-\$5.00	** 150-500 ppm	** 1.25-2.0%
* >\$5.00	* <150 ppm	* <1.25%

References

- Aldrich Chemical Company Inc., Catalogue 1990-1991. 1001 West Saint Paul Avenue, Milwaukee, Wisconsin 53233 U.S.A.
- Aldrich Chemical Company Inc., Catalogue 1994-1995. 1001 West Saint Paul Avenue, Milwaukee, Wisconsin 53233 U.S.A.
- Australian/New Zealand Standard AS/NZS 1716:1994 "Respiratory Protective Devices," Standards Australia/Standards New Zealand 1994.
- Code of Federal Regulations Title 30 Part 11 (30 CFR 11), 37th Federal Register Part 6244, 1972.
- "Criteria used by NIOSH for Certifying Powered Air Purifying Chemical Cartridge Respirators," C. Coffey, NIOSH, Morgantown, W.V., 1983.
- Dept. of Environment, Canada, "Fourth Meeting of the Parties to the Montreal Protocol, November 23-25, Copenhagen, Denmark," 9 Dec. 1992.
- European Standard EN 141:1990, "Specification for Gas Filters and Combined Filters Used in Respiratory Protective Equipment," European Committee for Standardization, Brussels.
- European Standard EN 146:1990, "Specification for Gas Filters and Combined Filters Used in Respiratory Protective Equipment," European Committee for Standardization, Brussels.
- European Standard EN 147:1990, "Specification for Gas Filters and Combined Filters Used in Respiratory Protective Equipment," European Committee for Standardization, Brussels.
- Japanese Industrial Standard JIS T 8152-1981, "Gas Masks," Japanese Standards Association.
- Japanese Industrial Standard JIS T 8157-1991, "Powered Air Purifying Respirators," Japanese Standards Association.
- Littleton, C. J. and Feeney, J. R. "The Effect of Challenge Concentration on the Gas Life of Respirator Filters," J. Int. Soc. Resp. Prot. 9 (4) pp. 6-13 (1992).
- Malloy, P., Associated Octel, Private Communication (1994).
- Moyer, E.S., "Review of Influential Factors Affecting the: Performance of Organic Vapor Air-Purifying Respirator Cartridges," Am. Ind. Hyg. Assoc. J., 44(1), 46-51 (1983).
- Moyer, E.S., NIOSH, Private Communication (1993).
- a. Nelson, G.O. and Harder, C.A. "Respirator Cartridge Efficiency Studies VI. Effect of Concentration," Am. Ind. Hyg. Assoc. J. 37 pp. 205-216 (1976).
- b. Nelson, G.O. Correia, A.N. and Harder, C.A., "Respirator Cartridge Efficiency Studies VII. Effect of Relative Humidity and Temperature," Am. Ind. Hyg. Assoc. J. 37 pp. 280-288 (1976).