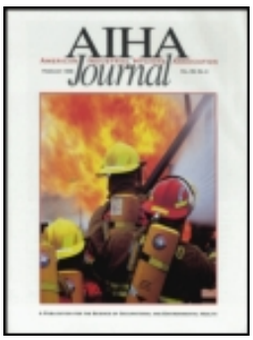

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Penetration of Methyl Isocyanate Through Organic Vapor and Acid Gas Respirator Cartridges*

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Methyl isocyanate (MIC) is a volatile, toxic chemical [Threshold Limit Value (TLV®) = 0.02 ppm] used to manufacture carbamate pesticides. The principal manufacturer of MIC is Union Carbide, and the site of production is Institute, West Virginia. In light of the December 1984 Bhopal, India disaster and possible safety problems at the Institute facility, NIOSH conducted this research as a basis upon which to recommend protective equipment that might be used in an emergency situation where extremely high MIC concentrations might be encountered. Both protective clothing and respirators were evaluated. In particular, NIOSH studied air-purifying respirators in order to assess their effectiveness against MIC vapor penetration. NIOSH does not recommend any air purifying respirator for MIC because of its high toxicity and lack of warning properties and because no effective end of service life indicator currently is available for MIC. This report addresses only MIC penetration through air-purifying cartridges at challenge concentrations designed to simulate emergency escape conditions. Another report addresses the protective clothing issue. The results presented are for two different manufacturers' organic vapor (OV) and acid gas cartridges. Penetration tests were conducted at three or four MIC challenge concentrations and at three different humidity conditions. In general, breakthrough times (1% of challenge concentration) were very short (<20 min). Also, high relative humidity was found to decrease the breakthrough time of MIC.

Introduction

Methyl isocyanate is an extremely hazardous compound because of its toxicity (TLV = 0.02 ppm), volatility and flammability. The NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards[1] contain a monograph on MIC that summarizes information on Permissible Exposure Limits (PEL), chemical and physical properties and potential health hazards. Recommendations for medical surveillance, respiratory protection and industrial hygiene practices are given. These recommendations are in accordance with good industrial hygiene and medical surveillance practices. Also, the NIOSH/OSHA Standards Completion Program contains a "Draft Technical Standard and Supporting Documentation for Methyl Isocyanate." The chemical and physical properties[2-4] and toxic effects[5] of MIC also have been reported.

Experimental Procedures

Materials

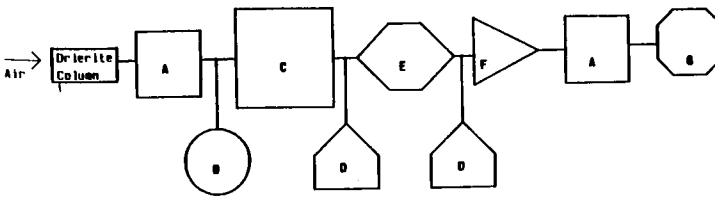
Methyl isocyanate was obtained from the Aldrich Chemical Company, Inc.[6] and was from Lot #3317A6. The hexane employed was obtained from Fisher Scientific (HPLC Grade with a UV Cutoff 195 mm). Also, the air was house air that was passed through a dryer, sorbent and high efficiency filter to remove any residual contaminants.

Detectors

The H-Nu, PI-101, Miran 1A, and Century OVA 108 direct reading instruments all were evaluated initially for MIC detectability. The Miran 1A General Purpose Infrared Gas Analyzer was used for the analytical monitoring of MIC because it was the most sensitive analytical technique immediately available. The Miran 1A is a single-beam, variable filter spectrometer, capable of scanning the infrared spectral range between 2.5 and 14.5 μm. The instrument is equipped with a gas cell having variable pathlength between 0.75 and 20.25 meters. Metal Bellows Corporation pumps Model MB-41 were used as sampling pumps. They have a flow rate of approximately 8 Lpm.

Experimental Design

The laboratory setup employed is shown in Figure 1. House air was passed through an in-line dryer to remove residual moisture. The inlet airflow was controlled by means of a



A - Flow Control Mechanism
B - Vapor Generator
C - Buffer Reservoir Tank
D - Vapor Detector
E - Cartridge Cell
F - Cold Trap or Sorbent Trap
G - Vacuum Source

Figure 1 — Experimental design.

*Mention of a company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH).

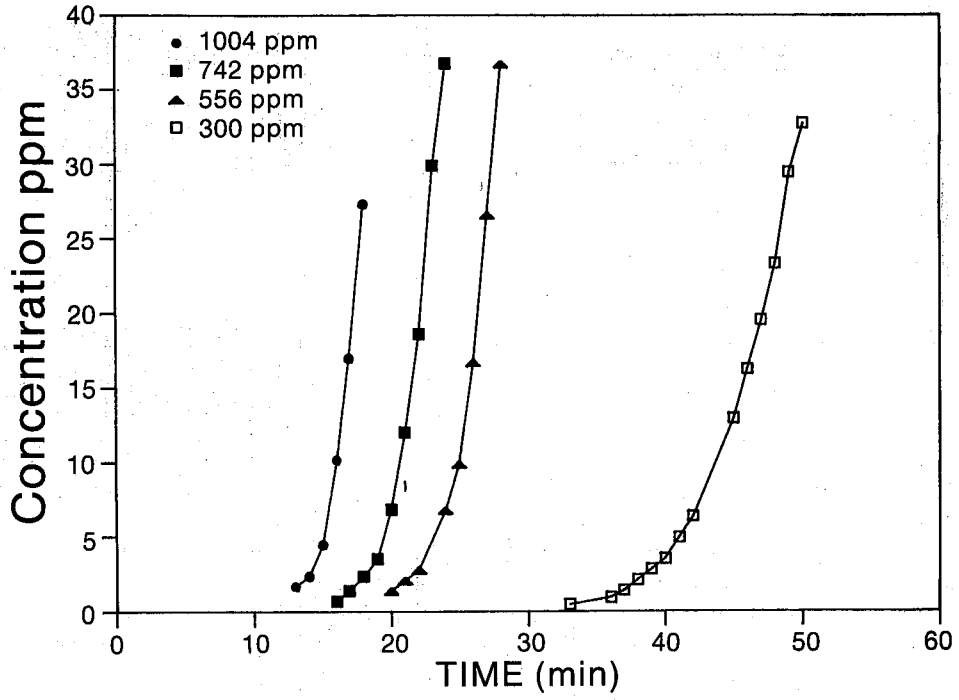


Figure 2 — Average MIC breakthrough of OV cartridges at dry conditions for Manufacturer A.

central valve (A). This flow rate can be varied from 60 to 120 Lpm but always is maintained at a flow rate that exceeds the flow rate pulled by the downstream vacuum source (G). A syringe pump was used to inject MIC into the airstream at a predetermined rate. By adjustment of syringe pump feed rate and the inlet air flow rate, a known upstream concentration can be generated. The upstream MIC concentration, however, was found to vary somewhat over the duration of any particular run. To reduce these fluctuations in the upstream concentration, a buffer tank was added to the system. The upstream MIC vapor concentration (Co) was monitored continually by means of an infrared detector (IR). When humidified conditions were necessary, a Miller-Nelson Research Inc. Model HCS-201 Flow-Temperature-Humidity Control System was placed in line.

The airstream containing the challenge MIC vapor was pulled through the cartridge cell housing that contained either a single cartridge or a pair of cartridges, depending on

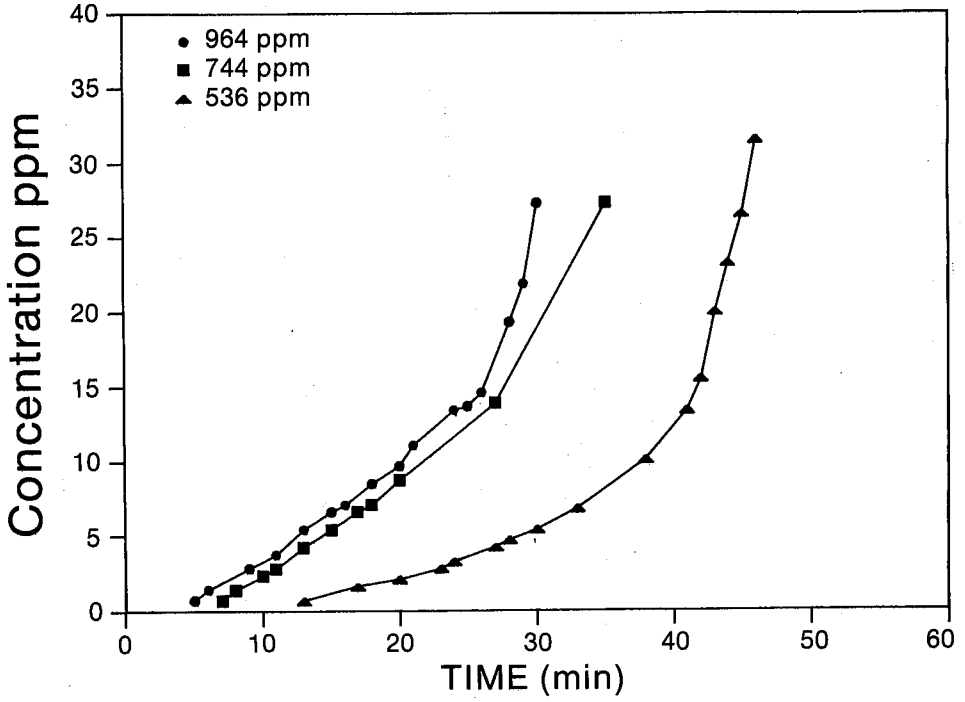


Figure 3 — Average MIC breakthrough of OV cartridges at dry conditions for Manufacturer B.

TABLE I
MIC Breakthrough and Capacity Data at Dry Conditions

Manufacturer	Average Challenge Concentration (ppm)	Average 1% Breakthrough Time (min)	Capacity[A] g/g
A	1004	16.1	0.035
	742	20.2	0.033
	556	23.3	0.030
	300	39.4	0.011
B	964	20.1	0.039
	744	18.4	0.033
	536	29.9	0.031

[A]g adsorbed/g of sorbent.

the manufacturer's respirator cartridge design. Immediately downstream from the cartridges was another IR detector that monitored the breakthrough concentration as a function of exposure time. The downstream flow then was passed through a sorbent scrubber to remove residual vapors before reaching the vacuum source.

Both the upstream and downstream IR detectors were calibrated each day before experiments were conducted. The IR instrumental conditions were adjusted for the concentration range of interest. The upstream concentration varied from 280 to 1100 ppm, whereas the downstream concentration range of interest was between 0 and 50 ppm. Both IRs were calibrated by injection of known quantities of MIC into a closed-loop calibration setup. The IR absorbance was monitored as a function of the MIC concentration. The upstream calibration was done with the use of neat MIC. The downstream calibration required the use of a 10% MIC/90% hexane solution and the IR absorption due to hexane was subtracted from the total.

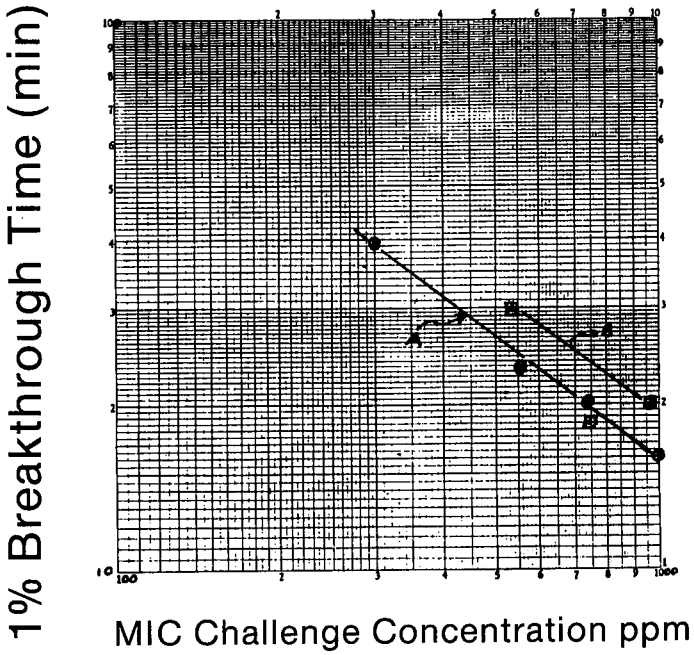


Figure 4 — MIC breakthrough as a function of challenge concentration at dry conditions.

The lower limit of detection was determined by two different methods. A known amount of liquid MIC was injected into a large carboy (50 L) and was allowed to vaporize; then an aliquot was injected into the closed loop. In the other method, a head space sample of MIC vapor at 20°C (vapor in contact with liquid MIC) was injected into the closed loop. The lower limit of detection was 0.20 ppm by the former method and 0.32 by the latter. The minimum detectable concentration claimed by the manufacturer is 0.6 ppm.

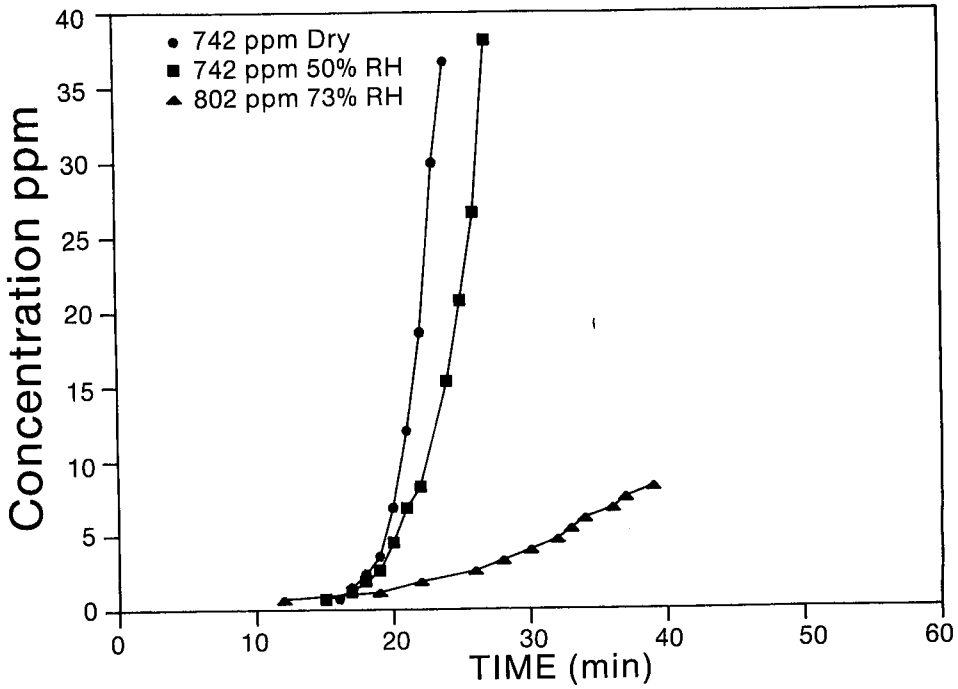


Figure 5 — Average MIC breakthrough of OV cartridges at various RH conditions for Manufacturer A.

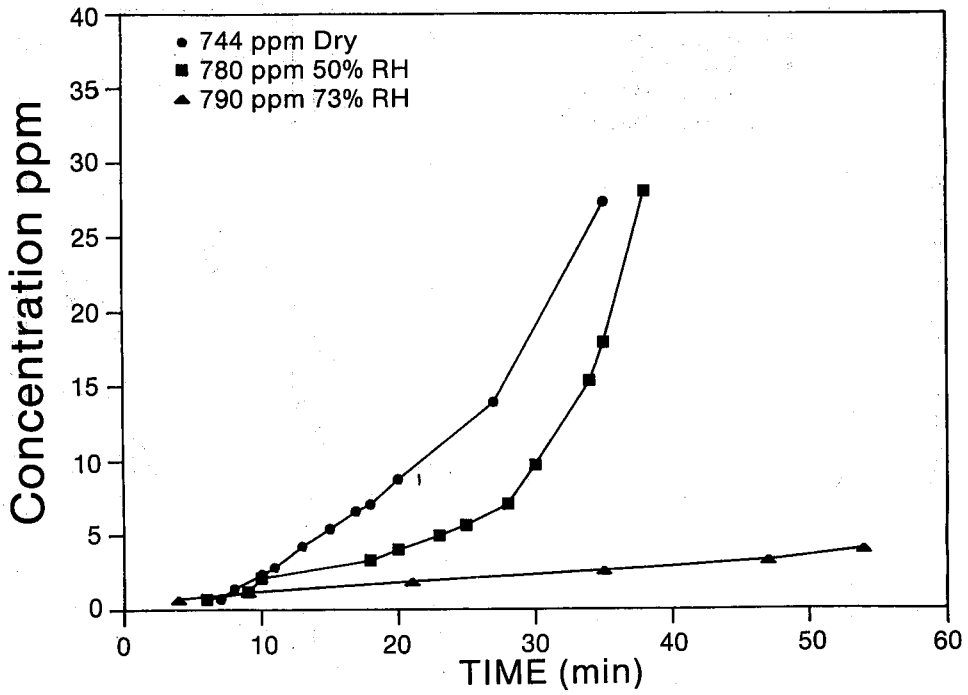


Figure 6 — Average MIC breakthrough of OV cartridges at various RH conditions for Manufacturer B.

During these experiments the following IR conditions were used:

0 - 0.100	absorbance scale
11.6	wavelength
20.25 m	path length
1.0	response
1.0	slit width

This lower limit of detection is approximately 20 times the TLV from MIC (0.02 ppm).

The cartridges tested were all "as received" from the manufacturer with no preconditioning. Two manufacturers' products were evaluated — one having a single cartridge arrangement and the other a dual cartridge. The cartridges were weighed and placed in the cell holder. The cell holder was connected to the downstream vacuum source and the flow rate through the system adjusted to 64 Lpm by means of a standard dry test meter. When all the adjustments had been made, the inlet gas stream containing the MIC was placed on line and the upstream and downstream absorbance values were monitored as a function of time.

After the breakthrough test was completed, the cell holder was removed from the system and disassembled. Final cartridge weights were determined. Next, the cartridges were dismantled and the sorbent removed. The empty cartridge then was weighed, thus permitting the calculation of the sorbent weight.

Results

Organic Vapor Cartridges

Breakthrough data for OV cartridges of Manufacturer A at dry conditions (as received cartridges with dried air stream) for challenge concentrations of 1004 ppm, 742 ppm, 556 ppm and 300 ppm were obtained. The average breakthrough times *vs.* breakthrough concentration for these challenge

TABLE II
Methyl Amine Breakthrough of OV Cartridges at 64 Lpm by Certification Test Method

Manufacturer	% RH	Challenge Conc.ppm	Initial Cartridge Weight (g)	Precond. Cond.	Wt. After Precond. (g)	Cartridge Case Weight (g)	Sorbent Weight (g)	Δ Wt. Precond. (g)	Δ Wt. Change During Test (g)	Time to 2 ppm Breath Min	Time to 5 ppm Breath Min	Time to 10 ppm Breath Min
B	76.5	1148	140.0	-	-	44.5	95.5	-	+1.5	-	5.7	6.2
B	76.5	1148	140.0	-	-	44.5	95.5	-	+1.5	-	5.0	5.5
B	50.0	1148	139.1	-	-	44.5	94.6	-	+0.9	-	4.7	4.9
B	50.0	1148	140.9	-	-	44.9	96.0	-	+0.2	-	4.6	4.8
B	50.0	1161	140.0	85%RH/25Lpm/6hr	158.1	44.1	95.9	+18.1	+1.8	3.1	-	27.1
B	50.0	1161	141.0	85%RH/25Lpm/6hr	159.0	44.9	96.1	+18.0	+1.0	4.8	-	25.2
A	50.0	1020	92.0	85%RH/25Lpm/6hr	107.1	29.9	62.1	+15.1	0.0	-	1.8	18.2
A	50.0	1020	93.5	85%RH/25Lpm/6hr	108.5	29.5	64.0	+15.0	+0.4	-	1.6	17.8
A	71.5	1148	93.2	-	-	30.0	63.2	-	+1.0	-	3.7	4.0
A	76.5	1148	91.0	-	-	29.9	61.1	-	+1.0	-	3.5	3.7
A	50.0	1148	93.0	-	-	29.9	63.1	-	+0.9	-	2.7	3.0
A	50.0	1148	94.0	-	-	30.0	64.0	-	+0.9	-	3.2	3.5

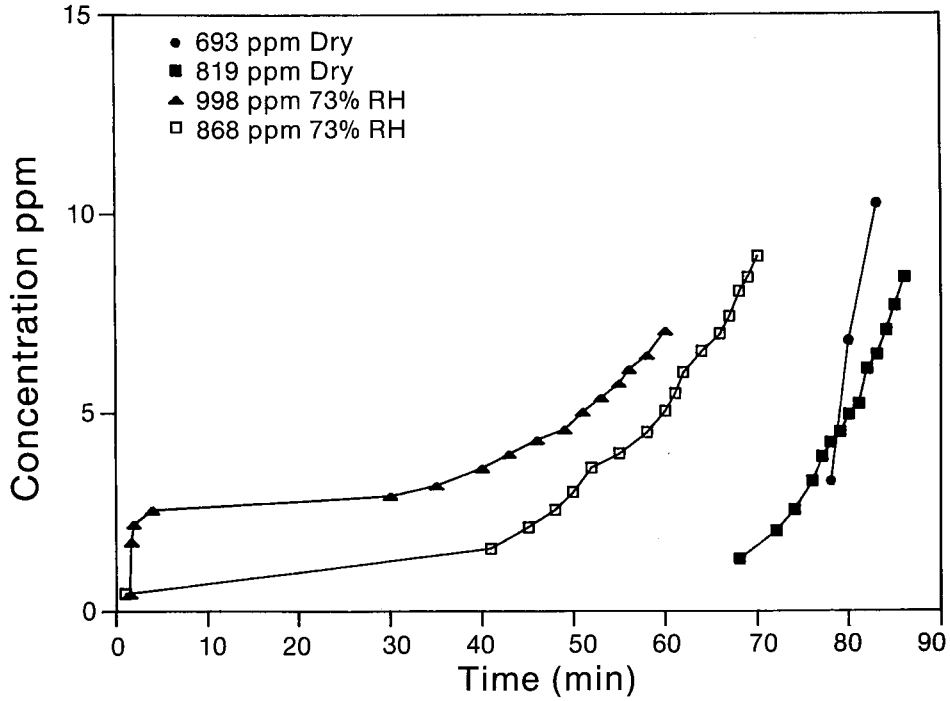


Figure 7 — MIC breakthrough of acid gas cartridges for Manufacturer A.

concentrations is illustrated in Figure 2. Similar data for OV cartridges from Manufacturer B are illustrated in Figure 3. These data clearly show that at high MIC challenge concentrations, which might be encountered in an emergency situation, MIC is poorly adsorbed on OV cartridges. This point is reinforced by the observation that, at the lowest challenge concentration studied (≃ 300 ppm), a breakthrough time of only about 30 min was observed, and this breakthrough concentration was approximately 20 times the TLV for MIC.

Table I presents a summary of the data obtained for the dry runs of Manufacturers A and B. Included in this table is the calculated capacity of the sorbent (g adsorbent)/(g of sorbent) when the breakthrough time at 1% of the inlet concentration was used. These values reflect the low adsorption capacity of charcoal for MIC. Also, as expected, when the challenge concentration decreases, the adsorption capacity also decreases. The breakthrough time variation as a function of challenge concentration was investigated. The average 1% breakthrough time as a function of challenge

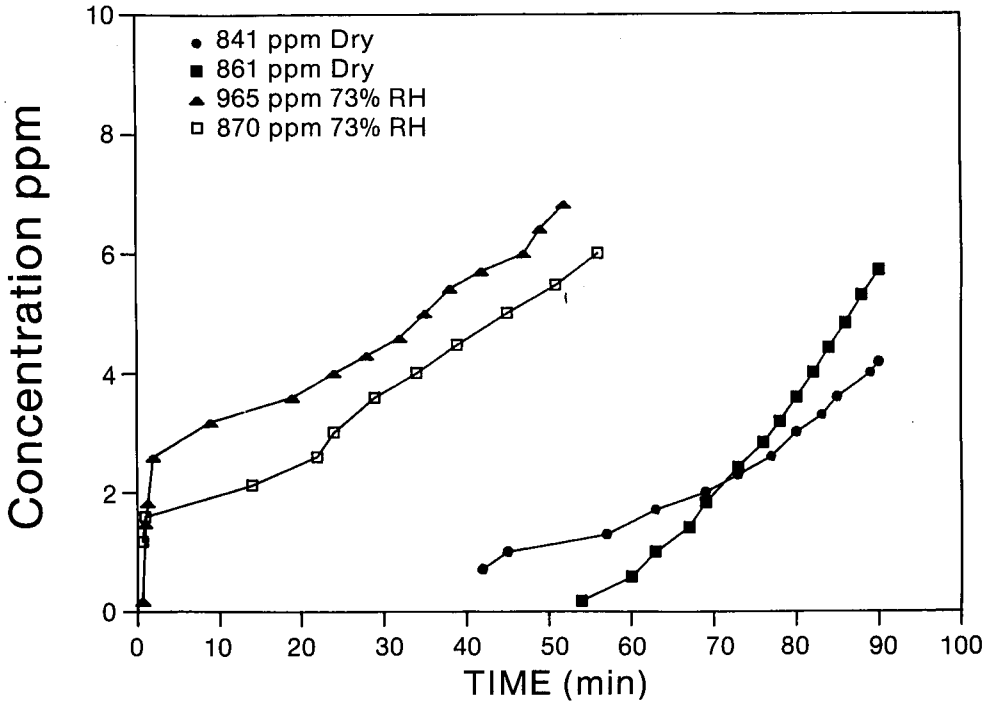


Figure 8 — MIC breakthrough of organic vapor/acid gas cartridges for Manufacturer B.

TABLE III
MIC Breakthrough Results Employing Jonas Model Stacked OV Cartridges at Dry Conditions for Manufacturer B

Breakthrough Concentration (ppm)	Breakthrough Time for Cartridge #1 (min)	Breakthrough Time for Cartridge #2 (min)	Breakthrough Time for Cartridge #3 (min)	Breakthrough Time for Cartridge #4 (min)
0.8	8.2	26.4	44.6	64.2
1.6	8.3	27.5	-	-
2.3	9.9	28.6	47.5	67.1
2.9	-	29.1	-	-
3.6	10.5	-	48.3	68.0
4.3	-	29.5	-	-
5.0	-		48.8	68.5
5.6	11.1	29.9	-	-
7.0	-	30.3	49.4	69.4
9.0	-	-	49.8	-
9.7	-	30.8	-	-
10.4	12.0	-	50.1	70.1
11.7	-	31.1	-	-
13.2	-	-	-	70.6
13.8	12.4	-	50.6	-
14.4	-	31.4	-	-
15.2	-	-	-	70.9
17.2	12.8	31.7	-	71.2
18.0	-	-	51.1	-
18.6	-	31.9	-	-
20.7	13.1	32.0	51.3	71.5

concentration for the cartridges of Manufacturers A and B at dry conditions also is shown in Table I. These data were plotted on log-log axes (log 1% breakthrough time *vs.* log challenge concentration), as shown in Figure 4. From this plot an estimate of breakthrough time can be obtained for a given challenge concentration over a limited range. Extrapolation outside this limited range can be extremely dangerous.

Next, OV cartridges of Manufacturers A and B were run at elevated relative humidities. Both 50% and 73% RH were used in these studies, with the challenge concentration being between 750 and 800 ppm. The average breakthrough curves for Manufacturer A cartridges at 50% and 73% RH are illustrated in Figure 5. The 50% RH data are not significantly different from the dry condition data. At 73% RH, however, the onset of breakthrough is faster, but the rate of increase of the breakthrough concentration with time is suppressed significantly. Likewise, the average breakthrough curves for Manufacturer B cartridges at 50% and 73% RH are presented in Figure 6. Exactly the same trend was seen with Manufacturer B cartridges as with Manufacturer A cartridges.

Given these results, a set of cartridges was run at 73% RH to see if an increase is absorbance occurred at 3.4λ that probably could be associated with mono methyl amine, a decomposition product of methyl isocyanate. This experiment verified an increase in absorbance at 3.4λ and suggests that the suppression of the MIC breakthrough concentration curve at 73% RH was probably due to the formation of methyl amine at or near the charcoal surface. Thus, additional experiments were performed in order to determine the breakthrough characteristics of methyl amine with OV cartridges. These experiments were done with the use of the methyl amine certification test with OV cartridges. Results for "as received" and "preconditioned" cartridges are found in Table II. As expected, the OV cartridges are ineffective in adsorbing mono methyl amine. Cartridges that had been

TABLE IV
Cartridge Weight Data for MIC Employing Jonas Model Stacked OV Cartridges at Dry Conditions for Manufacturer B

Cartridge #	Run Concentration (ppm)	Initial Cartridge Weight (g)	Cartridge Case Weight (g)	Final Cartridge Weight (g)	Initial Charcoal Weight (g)	Δ Wt. (g)	Capacity[A] (g/g)
1	945	69.0570	22.3574	72.3998	46.6996	3.3428	0.0716
2	948	68.0443	22.2853	70.9387	45.7590	2.8944	0.0633
3	964	70.1623	22.3016	72.7216	47.8607	2.5593	0.0535
4	945	70.5125	22.0375	71.6093	48.4750	1.0968	0.0226

[A]Capacity = g adsorbed/g of sorbent.

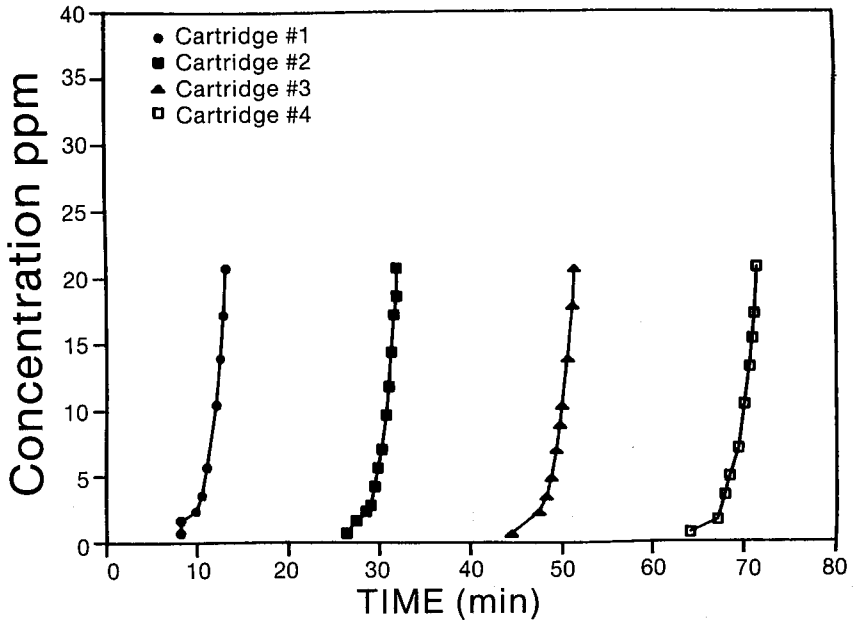


Figure 9 — MIC breakthrough results employing Jonas Model stacked OV cartridges at dry conditions for Manufacturer B.

pretreated at high relative humidity conditions, however, showed increased methyl amine adsorption because of the presence of adsorbed water on the charcoal sorbent. This is the same effect that probably is occurring during the MIC runs at 73% RH. In fact, when acid gas (AG) and OV/AG cartridges were studied against a MIC challenge vapor, the same phenomenon was observed for the 3.4λ absorption. Also, when one set of ammonia/methyl amine cartridges from Manufacturer A was tested against MIC at approximately 750 ppm and at dry conditions, a breakthrough time of <2 min was observed.

Acid Gas and Organic Vapor/Acid Gas Cartridges

It was thought that because of the high reactivity of MIC, acid gas cartridges which might act as a catalyst might be effective. Duplicate runs for Manufacturer A's acid gas cartridges at dry and 73% RH were completed, and the corresponding breakthrough curves are illustrated in Figure 7. The results at dry conditions gave breakthrough times greater than 60 min, but when these same acid gas cartridges were tested at a high humidity (73%), instantaneous MIC breakthrough was observed. This instantaneous breakthrough concentration persisted at a steady level (<4 ppm) for approximately 30 min before any futher increase in the level of MIC breakthrough resulted. Similar results were obtained for Manufacturer B's OV/AG cartridges, as displayed in Figure 8. It should be noted that Manufacturer A's AG cartridges actually lost weight when run at dry conditions. Also, as expected, rather large weight gains were observed at 73% RH, mostly because of water uptake.

Jonas Model Results on Organic Vapor Cartridges

Since NIOSH has been conducting research on the evaluation of the Jonas Model for predicting organic vapors breakthrough characteristics, one final experiment was conducted with Manufacturer B's cartridges at dry conditions. Four cartridges were stacked in series and challenged with MIC to see if the Jonas[7-14] breakthrough model applied. This model states that the breakthrough characteristics are directly proportional to sorbent weight. The data obtained for the respective four cartridges in series are presented in Table III with the weight and calculated capacity data in Table IV. The four breakthrough curves are presented in Figure 9.

The 1% breakthrough times and the corresponding sorbent weights are:

Time to 1% Breakthrough (min)	Cumulative Sorbent Weight (g)
11.9	46.6996
30.8	92.4586
50.0	140.3193
69.9	188.7943

The above 1% breakthrough times are all corrected to a concentration value of 950 ppm. This was done by assuming linear behavior of the challenge concentration with breakthrough time (1% BT × CC)/950. A plot of these 1% breakthrough times *vs.* the sorbent weight gave a linear relationship (Figure 10) in accordance with the modified Wheeler Equation.[11] Results from a least squares analysis are as follows:

slope = .4076
Υ intercept = -7.0998
R^2 = 0.9999

The adsorption capacity (W_e) was calculated from the slope when the breakthrough time at 1% of the inlet concentration was used as follows:

$$\text{slope} = W_e / C_o Q \quad (1)$$
$$0.4076 = W_e / 2.239 \times 10^{-6} (64\,000)$$
$$W_e = 0.0584 \text{ g/g}$$

where

$$C_o = \frac{950 \text{ ppm } (57.05)}{10^9 (24.205)} = 2.239 \times 10^{-6}$$

When 47.198 g as the average weight of sorbent per cartridge and a fill volume of 119 cc are used, the resulting bed-packing density is 0.3966 g/cm^3. The first order rate constant (k_v) at a concentration ratio C_o/C_x (C_o = challenge concentration and C_x = breakthrough concentration) of 1% then can be determined as follows:

$$\text{intercept} = \frac{-W_e \rho \ln C_o/C_x}{k_v C_o} \quad (2)$$

$$-7.0998 = \frac{-0.0584\ (0.3966)(4.6052)}{k_v\ (2.239 \times 10^6)}$$

$$K_v = 6710 \text{ min}^{-1}$$

The critical bed weight was found to be 17.42 g. This means that a bed of 17.42 g of charcoal in this configuration would give instantaneous MIC breakthrough.

The adsorption space available in the carbon sorbent to adsorb the vapor is calculated from the adsorption capacity (W_e) as follows:

$$W_v d_e = W_e \quad (3)$$

where d_e is the density for MIC (0.967 g/cm^3).

This calculation employs the concept of volume pore filling of Bering *et al.*[15] The adsorption space (W_v) was found to be 0.060 cm^3/g. Cartridges from the same manufacturer but from a different lot gave W_v values of $\simeq$ 0.15 cm^3/g for acetone at 1060 ppm and $\simeq$0.22 cm^3/g for chloroform at 1000 ppm. The W_v value for MIC is significantly lower and reflects the fact that MIC is weakly adsorbed on charcoal sorbent.

Conclusions

This study showed that none of the commercially available air-purifying cartridges tested provided protection against MIC breakthrough at high MIC challenge concentrations that might be expected during an emergency situation. Organic vapor cartridges tested at dry conditions against a 300 ppm MIC challenge concentration gave a breakthrough time of approximately 30 min, but the breakthrough concentration was 20 times the TLV for MIC. OV cartridge results at 50% RH were not significantly different from the dry condition data. At 73% RH, however, the onset of breakthrough for the OV cartridges was earlier, but the rate of increase in the breakthrough concentration was slower. Organic vapor/acid gas and acid gas cartridges gave breakthrough times greater than 60 min at dry conditions against the high MIC challenge concentrations. These same cartridges showed instantaneous MIC breakthrough when tested at 73% RH.

Sorbent capacity data for the OV cartridges confirmed that MIC was weakly adsorbed on charcoal. All the results that were obtained supported and emphasized the importance of NIOSH's recommendation that any air purifying respirator should not be used for MIC because of the MIC's high toxicity and lack of warning properties and because no effective end of service life indicator is currently available for MIC. Thus, only supplied air respirators should be used, even for escape only purposes, when MIC is the suspected contaminant.

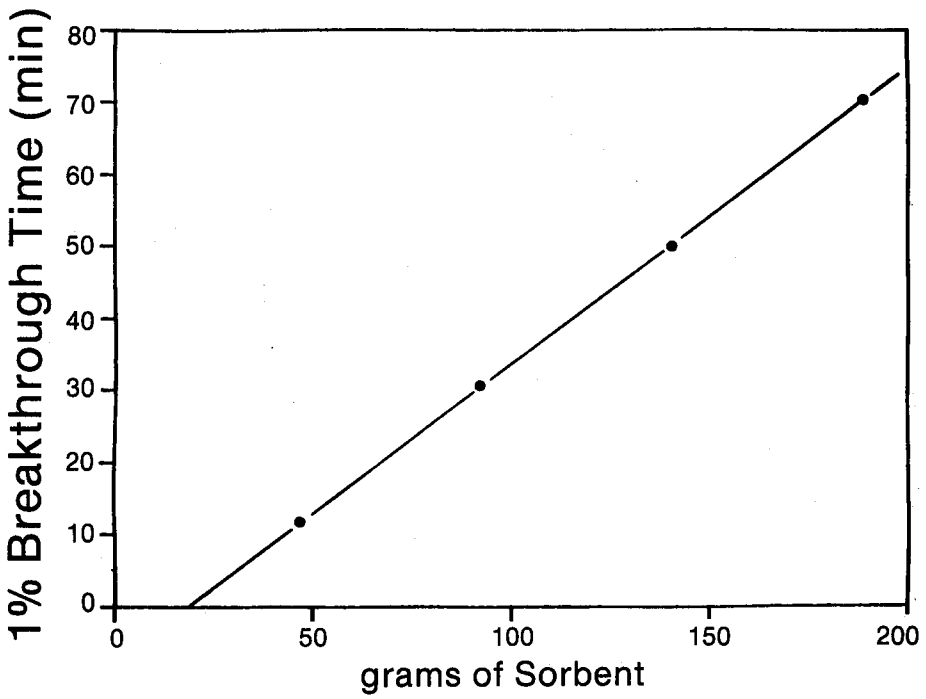


Figure 10 — One percent MIC breakthrough time as a function of sorbent weight at dry conditions for Manufacturer B.

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