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Criteria and Test Methods for Certifying Air-Purifying Respirator Cartridges and Canisters Against Radioiodine

October 1, 1978—September 30, 1982

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CRITERIA AND TEST METHODS FOR CERTIFYING AIR-PURIFYING RESPIRATOR CARTRIDGES AND CANISTERS AGAINST RADIOIODINE

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ABSTRACT

A project has been completed which provides experimental data and recommendations for establishing a standard test procedure and acceptance criteria for air-purifying respirator cartridges and canisters used for airborne radioiodine. Previous experimental work with methyl iodide vapor was extended to generate elemental iodine and measure its removal by charcoals. A special apparatus was constructed and used to simultaneously measure penetrations of radioiodine and normal iodine vapor species through beds of various charcoals. Normal methyl iodide (I-127) was selected as the most representative vapor species for testing and its limitations were identified. Effects of testing and use conditions (bed depth, contact time, concentration, relative humidity, temperature, flowrate, and flow cycling) were studied to identify testing requirements. Temperature and simulated breathing flow cycling were shown to have much more significance than was previously realized. Recommendations for testing and approval include considering the effects of all these parameters. An apparatus designed and built for testing has been delivered to the National Institute for Occupational Safety and Health. In one related study the desorption of triethylenediamine (TEDA), a charcoal impregnant for organic iodide removal, was found to be insignificant at normal canister use conditions.

I. INTRODUCTION

The main goal of this project has been to provide the Nuclear Regulatory Commission (NRC), the National Institute for Occupational Safety and Health (NIOSH) Testing and Certification Branch (TCB), respirator manufacturers, and respirator users with data, recommendations, and proven test methods for certifying air-purifying respirators against radioiodine. Since facepiece fit is being determined at Los Alamos and elsewhere in other studies, the main concern in this project was with the air-purifying canister or cartridge used with facepieces.

Steps which have been taken to accomplish this goal are

(1) Survey and analysis of the literature relating to air-purifying respirators, vapor adsorption, and radioiodine air cleaning. Contacts with professionals experienced in these fields.

(2) Design and construction of an experimental apparatus for sorbent testing, including generation and detection systems for nonradioactive ^{127}I vapor species.

(3) Experimental study of the adsorption of methyl iodide on a variety of potential respirator sorbents and examination of the effects of environmental and cartridge design parameters on this adsorption.

(4) Experimental study of the adsorption of elemental iodine vapors under limited conditions.

(5) Experimental study of the adsorption of hypoiodous acid (HOI) vapors.

(6) Design and construction of facilities for the use of radioiodine for sorbent testing and development of radioiodine generators and detectors.

(7) Experimental study of the adsorption of iodine vapor species tagged with ^{131}I for comparisons of results with those obtained using stable ^{127}I species.

(8) Studies of the effects of relative humidity, temperature, flowrate, and concentration on cartridge performance and service life.

(9) Measurements of desorption rates of charcoal impregnants used to enhance methyl iodide removal.

(10) Evaluation of effects of cyclic flow on efficiencies and service lives of potential radioiodine canisters.

(11) Development of final acceptance tests, apparatus, and criteria to be recommended to NRC for approval of respirator cartridges against radioiodine.

(12) Publication of results of this project and transfer of the test procedures and techniques developed to the NIOSH TCB and assistance to them in the development of an approval schedule.

Items 8, 9, and 10 have been added to the original plan to address concerns which have arisen as the project developed. In addition, a complete, ready-to-use test apparatus has been built for the NIOSH TCB to use for certification testing.

A preceding progress report[1] covered the first three of the above steps and included the background for this project. This report includes and organizes work reported since September 1978 in quarterly letter reports, presentations at professional meetings, and publications. With the exceptions of some journal publications to follow, this is the final report for this project.

II. ELEMENTAL IODINE GENERATION AND ADSORPTION ON ACTIVATED CHARCOAL

A. Objectives

Testing of a selected adsorbent, an unimpregnated activated charcoal, for adsorption of elemental iodine at ppm challenge concentrations was done to examine the usefulness of I_2 generation and detection methods and to demonstrate the kinds of results that might be expected in a respirator cartridge test.

B. Generation

One I_2 generation technique used a flow of air (10 L/min) to pick up I_2 and H_2O evaporating from an aqueous solution ($\leq 10^{-3}$ moles/L). Relative humidity resulting from H_2O evaporation was about 50%. The challenge and test bed breakthrough concentrations were measured using calibrated oxidant meters (Mast Model 724-5). The challenge concentration (C_o) of I_2 generated

in air was directly proportional to I_2 concentration in solution $[C_0$ (mg/m$_3$) = 26400 $[I_2]$ (moles/L)]. Both concentrations decreased linearly with time as I_2 evaporated faster than H_2O.

Another generation technique involved the sublimation of I_2 crystals at controlled temperatures into a flowing air stream. Challenge concentrations of 8-30 mg/m^3 (1-4 ppm), determined by weight losses and air flow rates (10 L/min), were relatively steady for up to a week.

C. Retention

The activated charcoal used for these studies was 6/16 mesh from Union Carbide.

Fractional bed breakthrough C_B/C_0 from I_2 generation from solutions increased from zero to a constant value in a time interval (10-120 min) dependent on bed condition and challenge concentration. This limit value of C_B/C_0 was constant over a wide range (X 300) of C_0 and decreased exponentially with bed depth, D, i.e., $C_B = C_0 e^{-bD}$. All of these observations suggest that this initial bed penetration is controlled by kinetic adsorption processes rather than by adsorbent capacity. It should, therefore, be equal to adsorption efficiency at much lower challenge concentrations.

Retention studies of I_2 generated from crystals used beds of 6/16-mesh charcoal, 2.4-cm diameter and usually 1.25 cm deep, which corresponds at 10 L/min to a linear flow velocity of 22 m/min. Relative humidities of 50% and 90% were used. In these longer term experiments at constant C_0, after the initial constant bed breakthrough was subtracted out, a subsequent increase in penetration developed more slowly, requiring up to 7 d to reach an additional 10% bed penetration. This was due to loss of capacity as active sites were being used up.

This subsequent breakthrough curve was best described by the equations of the Statistical Moments Theory, as was previously found for methyl iodide.[1] An I_2 challenge concentration effect (Fig. 1) was observed: $t_B = kC_0^{-0.5}$ (t_B = breakthrough time for a selected fractional penetration C_B/C_0), similar to what was observed for CH_3I. Again, this implies that such cartridge lifetimes, determined at ppm levels using normal iodine, would be conservative for much lower levels expected in

CHALLENGE CONCENTRATION (ppm)
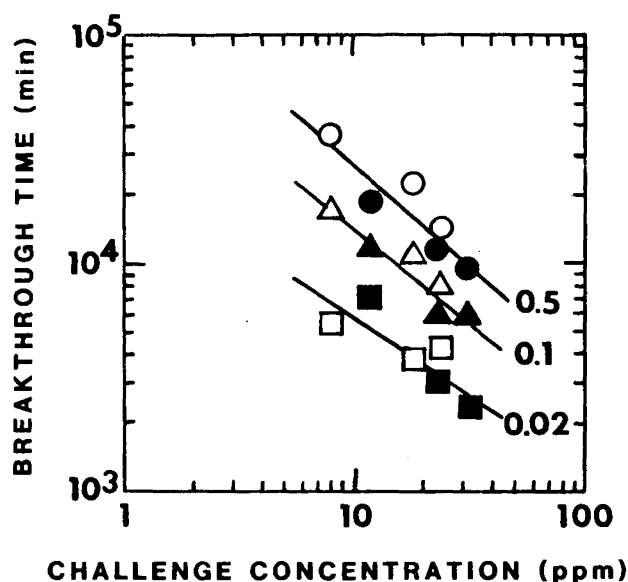
Fig. 1. Iodine breakthrough times for a 6/16-mesh Union Carbide activated charcoal bed, 1.25 cm deep, 2.4-cm diam, 10-L/min air flow. Open symbols are for 50% relative humdity and solid symbols are for 90% relative humidity experiments. Fractional bed penetrations: □ for 0.02, △ for 0.1, ○ for 0.5.

radioiodine environments. However, due to the long experimental times involved, the determination of cartridge lifetimes may not be a practical way of measuring and comparing cartridge performances. The observed initial breakthrough may be a more useful indicator of cartridge performance.

Five types of potential radioiodine adsorbents were compared for I_2 adsorption efficiency at the following conditions:

2.4-cm-diam × 1.25-cm deep beds.
50% relative humidity.
0.0127-g I_2 in 100-ml H_2O generator solution.
10-L/min (22.1-m/min) air flow rate.
The measured penetration fractions were
0.27% Westvaco WV-H, coal charcoal, not impregnated.
0.14% Sutcliffe Speakman 207A, 1.5% KI impregnated.
0.15% Coast Engineering Silver Zeolite, AgZ.
0.072% Sutcliffe Speakman 208C, 5% TEDA impregnated.
0.032% Witco 337, petroleum charcoal, not impregnated.

III. RADIOIODINE STUDIES—EXPERIMENTAL

A. Flow System

The apparatus used to measure the penetrations of volatile iodine and radioiodine compounds through test beds, canisters, and cartridges is diagrammed in Fig. 2 and shown in Fig. 3. It was built inside a fume hood to exhaust any toxic vapors which might have been released. Radioiodine solutions and contaminated sorbents were contained for further safety within a glovebox with charcoal and HEPA exhaust filters. Vapor generation and test bed exposures were done within the glovebox. Compressed air was filtered, regulated for proper flow rate, and humidified before entering the glovebox. An electronic mass flow meter (Datametrics 800-L) which monitored airflow was periodically checked using a dry test meter (Singer DTM-325) at the test bed location. Humidification was accomplished by passing air through the headspace over a heated water reservoir. A humidity monitor/controller (Phys-Chemical Research Corp.) which regulated water temperature was calibrated with a dew point hygrometer (EG&G 911) at the test bed location. Water level was maintained automatically by a conductive liquid-level control (Lumenite Electronic Co.).

A "Standard Operating Procedure for Use of ^{131}I in the Testing of Respirator Components"[2] was prepared and approved by internal review. It describes the experimental apparatus, procedures, and precautions to be used with this radionuclide.

B. Generation Methods

Vapors were generated in two ways, shown in Fig. 2. Liquid methyl iodide and methyl radioiodide sealed in a Teflon permeation tube were released at a steady rate by

Fig. 2. Experimental apparatus for testing air-purifying respirator cartridges and canisters using radioiodine and normal iodine vapor species.

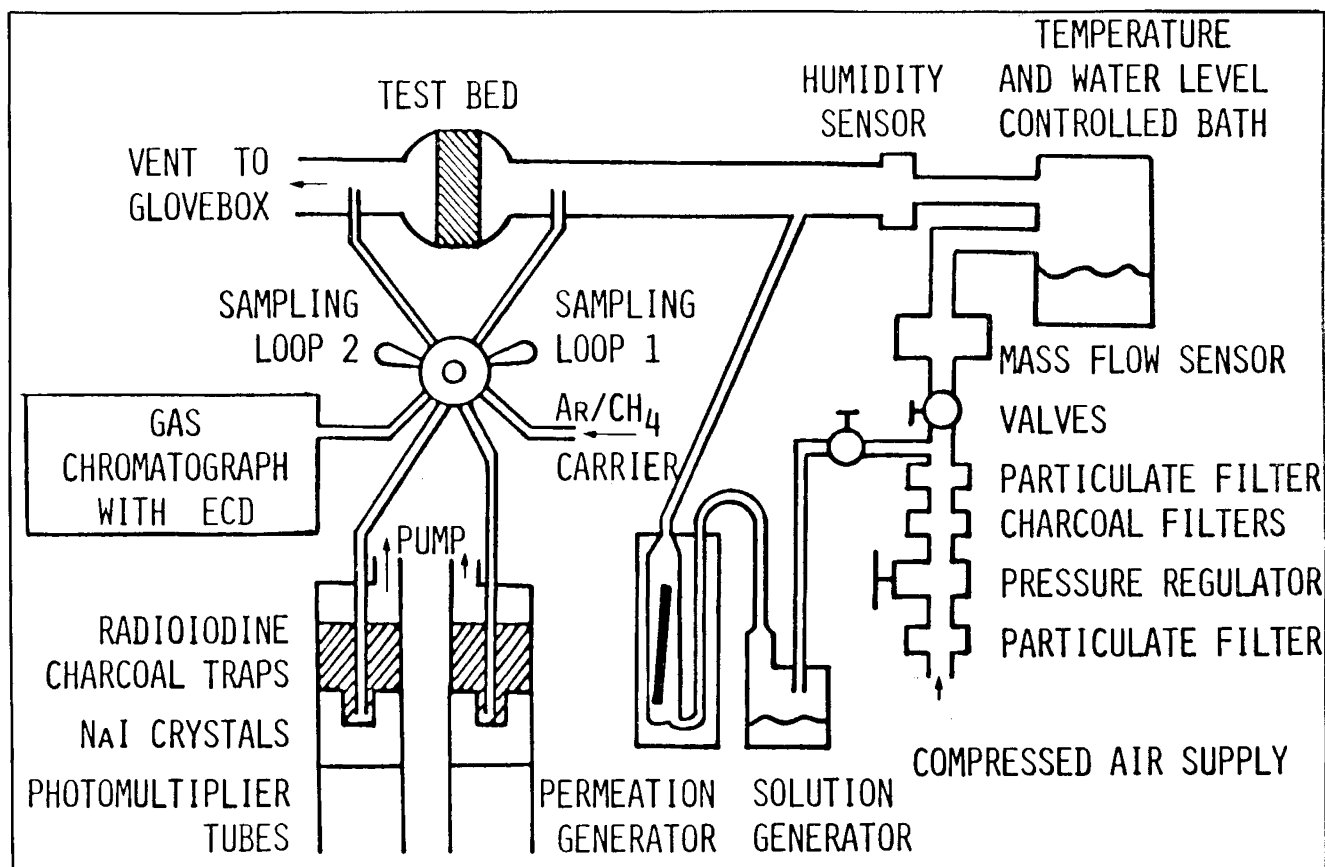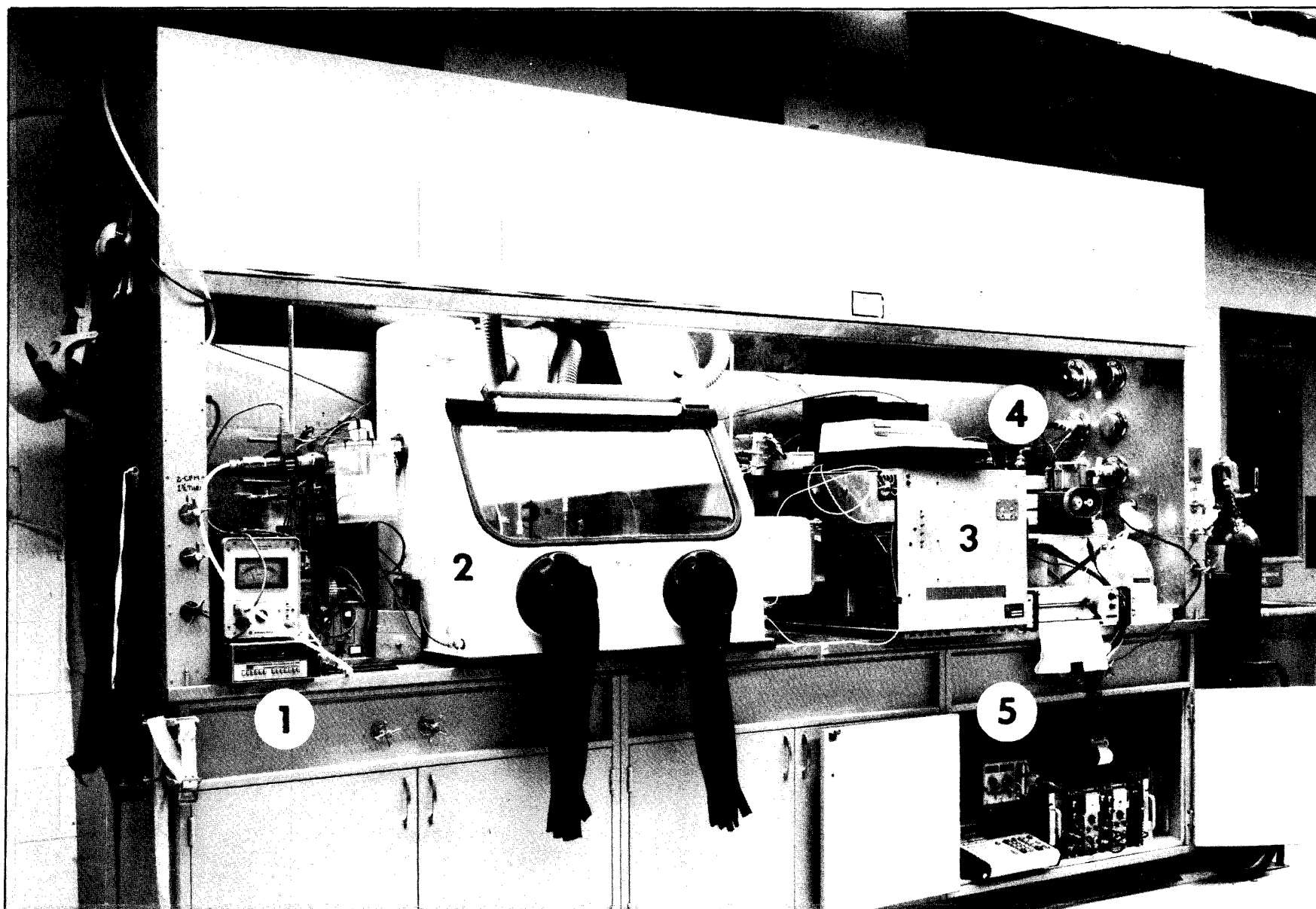Fig. 3. Experimental apparatus for testing air-purifying respirator cartridges and canisters using radioiodine and normal iodine vapor species. (1) Airflow and humidity control section. (2) Glove box for radioiodine containment. (3) Gas chromatograph and automated sampling valve for methyl iodide measurements. (4) Charcoal traps and scintillation crystals for radioiodine mesurements. (5) Counting electronics and data logger.

permeating into a 500-cm³/min airflow. Temperature control (25-70°C ± 0.1°C) of this permeation tube was by the Calibration System (Analytical Instrument Development, Inc., Model 303). Alternately, methyl radioiodide ($CH_3^{131}I$), elemental radioiodine ($^{131}I_2$), and hyporadioiodous acid ($HO^{131}I$) were generated from aqueous solutions. A syringe was used to inject 10 mL of solution into 100 mL of distilled water or other reagent solution in the glass container in the lower center of Fig. 2. The volatile iodine compounds in this stirred mixture entered the head space and were swept by 500 cm³/min of air through Teflon and glass tubing into the main airflow. Water vapor was also generated. Output of volatiles from solution dropped exponentially from the time of injection. Generator output and main airstream passed through sufficient length of 2.4-mm-i.d. glass tubing and two elbows to mix thoroughly before entering the test bed. Sections of the glass flow system and the test bed were connected with O-ring seals and clamps. Challenge air and test bed effluent air were sampled continuously through Teflon tubes connected to the glass system and into the gas chromatograph and charcoal beds.

The technique of generating volatile iodine species from aqueous solutions for the testing of sorbent beds or respirator cartridges has proved to be quite useful. Concentrations in water (and in air) decrease with time approximately exponentially, depending on species volatility and, in the case of CH_3I, the rate of stirring of the solution. One advantage of this generation method is that a range of challenge concentrations is produced in a single experiment. This can give information about the adsorption isotherm of the test bed. Another advantage for inorganic species, particularly, is that generation is from a source similar to field sources, such as reactor coolant waters or spent fuel cooling pools. It is also possible that experimental generator solutions can be matched (pH, additives, etc.) to actual aqueous field sources.

C. Detection Methods

The detector for methyl iodide was a gas chromatograph (Varian 1520) with a linearized electron capture detector (Tracor Instruments). Air from upstream and downstream of the test bed was drawn (0.8 L/min) through matched Teflon sampling loops attached to a 10-port valve (Valco Instrument Co.) of Hastalloy-C (for inertness). This valve was pneumatically actuated by a

digital valve sequence programmer (Valco Instrument Co.) to alternately inject the upstream and downstream air at 5-minute intervals. The chromatographic column was 1.8 m × 4-mm-id., glass packed, with 15% OV-7 on 100/120-mesh Chromosorb G. Operating conditions were 100°C and 20-cm³/min 19:1 Ar:CH₄ carrier gas. An electronic peak integrator (Spectra Physics Minigrator) quantitated the methyl iodide peaks and recorded elapsed times. Calibrations of this analytical system were made using weighed permeation tubes to generate known methyl iodide concentrations in air.

The radiometric detectors continuously collected and measured ^{131}I from the 0.8-L/min air samples passing through the gas chromatograph sampling valve. Fig. 2 shows the charcoal trap and 7.6-cm-diam × 7.6-cm-thick NaI (Tl) well-type (52-mm-deep × 29-mm-diam) scintillation crystal with integral photomultiplier tube (Harshaw Chemical Co.). High-efficiency charcoals were used: 5% TEDA-impregnated (Barnebey Cheney CN 2762) for $CH_3^{131}I$ and activated charcoal (Union Carbide ACC) for $^{131}I_2$ and $HO^{131}I$. The majority of radioiodine was collected at the bottom of the well, resulting in good detection efficiencies (~0.5) for the 0.364-MeV gamma ray. Each detector for upstream and downstream air had its own preamplifier, amplifier, single-channel analyzer, and counter (all from Ortec). They shared the power bin (Ortec), high-voltage power supply (Canberra), timer (Ortec), and printer (Ortec). Linear-log rate meters (Mech-Tronics) were used for count rate monitoring. Detector counts were taken from 5-minute intervals and printed together. Each detector trap and crystal was shielded by 5 cm of lead to reduce background counts. Fresh charcoal was placed in the detector traps for background counts before each new bed was tested. The detectors were compared almost daily for relative sensitivities by sampling the same radioiodine-containing air.

D. Reagents

The source for radioiodine 131 was ICN Chemical and Radioisotope Division, Irvine, CA. Methyl radioiodide was ordered as 5 mCi ^{131}I in 3 mL of total methyliodide. Stated purity was a least 99%. Two milliliters were used to fill a permeation tube and 1 mL was dissolved in 1 L of double-distilled water. This aqueous solution (2.3 g/L or 0.016 mol/L) was used 10 mL at a time for generating as described above. Radioiodine in the form of NaI in 0.05-N NaOH was

purchased in a 5-mCi amount. Stated purity was at least 99% with an $^{127}I/^{131}I$ ratio less than 10. This material of about 1-mL volume was added to 1-L H_2O containing 0.127 g of dissolved I_2 (0.127 g/L or 5×10^{-4} mol/L). Isotope exchange occurred to form $^{131}I_2$. This solution was used to generate both $^{131}I_2$ and HOI^{131}. For $HO^{131}I$, 10 mL of this latter solution were injected into 100 mL of 4×10^{-3} mol/L $NaIO_3$ at pH = 2 to cause the reactions:[3]

$$2I_2 + IO_3^- + 6H^+ + 2H_2O = 5 \ H_2OI^+$$

$$H_2OI^+ + H_2O = HOI + H_3O^+$$
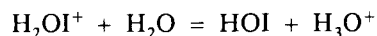
No attempt was made to determine the extent of HOI production, since no analytical method is known which distinguishes this unstable species from I_2.

E. Test Beds

Air-purifying respirator canisters and cartridges were obtained from three U.S. commercial sources: Mine Safety Appliances Company (MSA), Pittsburgh, PA; Norton Company, Safety Products Division, Cranston, RI; and Scott, Health/Safety Products, South Haven, MI. They each claimed, by labelling or personal manufacturer information, to be of some use for protection against iodine for radioiodine vapors. Each type contained a particulate filter followed by a sorbent bed containing a coarse-grained charcoal. Some of the charcoal sorbents were reportedly impregnated with reactive chemicals for radioiodine removal, such as triethylenediamine (TEDA) and KI_3 ($KI + I_2$). The distinction which is made in this paper between canisters and cartridges is that the latter are used in pairs and are physically smaller. For some experiments beds of 2.4-cm diam were prepared from charcoals taken from canisters. The term "test bed" will be used in this report to refer to a canister, a cartridge, or an experimental bed. Table I lists characteristics of the canisters and cartridges and their charcoal contents.

IV. RADIOIODINE STUDIES—RESULTS AND CONCLUSIONS

A. Comparison of Vapor Species

Penetration test results at high humidity (97 ± 3%) for the three radioiodine vapor species are tabulated in Table II for five canisters (64 L/min) and in Table III for four cartridges (32 L/min). Pulses of challenge vapor were generated from solution at 2-hour intervals. Two-hour average penetrations and standard deviations (given in

TABLE I. Characteristics of Canisters and Cartridges Tested

| Source | Type | Designation | Charcoal Bed Geometry[a] | | | Charcoal Impregnants[b] |
			Cross Section (cm²)	Depth (cm)	Volume (cm³)	(Weight Percent)
MSA	Canister	GMR-I	110[c]	3.2	350	5% KI_3
	Canister	GMR-I(TEDA)[d]	110[c]	3.2	350	5% KI_3, 2% TEDA[e]
	Canister	GMR-S	110[c]	3.2	350	Metal and Ammonium Salts[f]
Scott	Canister	600252-75	87	3.8	330	5% TEDA
	Canister	282 OAP-R	87	3.8	330	Metal and Ammonium Salts[f]
	Cartridge	604550-75	48	1.3	62	5% TEDA
	Cartridge	604403-75	48	1.3	62	5% TEDA
Norton	Cartridge	Type I[g]	44	2.4	106	5% TEDA
	Cartridge	Type II[h]	44	2.4	106	5% TEDA

[a]Measured from opened canisters.
[b]Best information from manufacturers.
[c]Oval cross section.
[d]The GMR-I (TEDA) designation is used for GMR-I canisters manufactured after July 1979 through at least April 1980.
[e]TEDA = triethylenediamine.
[f]Whetlerized charcoal.
[g]Granule size, 8-16 mesh.
[h]Granule size, 12-20 mesh.

TABLE II. Radioiodine Test Results for Canisters[a]

Canister Type	Test Vapor	Average Percent Instantaneous Penetrations (and Standard Deviations)[b]				
		0-2 h	2-4 h	4-6 h	6-8 h	8-10 h
Scott 600252-75	$CH_3{}^{131}I$	-0-	---	0.24	---	---
			---	(0.02)		
		1.07	-0-	0.61	---	---
		(0.06)		(0.05)		
	$^{131}I_2$	-0-	-0-	-0-	---	---
	$HO^{131}I$	---	-0-	0.10	0.08	-0-
				(0.03)	(0.03)	
GMR-I (TEDA)	$CH_3{}^{131}I$	0.24	4.43	6.09	---	---
		(0.08)	(0.16)	(0.17)		
		0.99	2.46	7.54	---	---
		(0.41)	(0.73)	(1.06)		
	$^{131}I_2$	0.71	0.10	0.10	---	---
		(0.04)	(0.02)	(0.02)		
	$HO^{131}I$	---	0.08	-0-	-0-	-0-
			(0.04)			
GMR-I	$CH_3{}^{131}I$	3.34	8.40	21.29	---	---
		(0.52)	(0.53)	(0.65)		
	$^{131}I_2$	0.17	0.07	-0-	---	---
		(0.02)	(0.01)			
	$HO^{131}I$	---	-0-	0.07	0.17	0.11
				(0.03)	(0.07)	(0.03)
Scott 282 OAP-R	$CH_3{}^{131}I$	19	98	100	---	---
		(2)	(4)	(7)		
	$^{131}I_2$	-0-	0.07	0.18	---	---
			(0.01)	(0.02)		
	$HO^{131}I$	---	-0-	-0-	0.27	0.75
					(0.04)	(0.04)
GMR-S	$^{131}I_2$	-0-	-0-	-0-	---	---
	$HO^{131}I$	-0-	-0-	-0-	---	---

[a] 64 L/min, 97 ± 3% RH.
[b] Zero value (-0-) means not significantly greater than zero at the 95% confidence level. Dash (---) means not measured.

parentheses) were determined by linear regression analysis of 5-minute counts in the downstream detector versus the upstream detector. Relative sensitivity of the two radioiodine detectors determined by daily calibrations was taken into account. Any penetrations calculated to be within 95% confidence levels of zero were considered as zero and listed as -0-. In only two cases was more than one canister or cartridge of a type tested for a given radioiodine vapor. Therefore, these results cannot reflect variations within a given type. At least three of each canister or cartridge were tested.

Methyl iodide was the vapor form of radioiodine that most readily penetrated the respirator canisters and cartridges which were tested. Penetrations of $^{131}I_2$ and $HO^{131}I$ at high humidity were low ($\leq 0.75\%$) and, with one exception, did not increase significantly with exposure and loading. Since methyl iodide is the most volatile organic iodide compound, other organic iodides should be retained on these canisters or cartridges with the same or higher efficiencies. Therefore, methyl iodide

TABLE III. Radioiodine Test Results for Cartridges[a]

Cartridge Type	Test Vapor	Average Percent Instantaneous Penetrations[b]		
		0-2 h	2-4 h	4-6 h
Norton Type I	$CH_3^{131}I$	0.03	1.94	3.34
		(0.01)[c]	(0.06)	(0.60)
	$^{131}I_2$	-0-	-0-	-0-
Norton Type II	$^{131}I_2$	-0-	-0-	-0-
Scott 604403-75	$CH_3^{131}I$	1.18	9.27	11.50
		(0.33)	(0.29)	(0.34)
	$^{131}I_2$	0.04	-0-	-0-
		(0.01)		
Scott 604550-75	$CH_3^{131}I$	1.98	10.71	12.87
		(0.17)	(0.99)	(0.90)

[a]32 L/min, 97 ± 3% RH.
[b]Zero value (-0-) means not significantly greater than zero at the 95% confidence level.
[c](Standard deviations).

should be used as the test species to determine the upper-limit penetration of vapors containing iodine.

Milo Kabat and coworkers at Ontario Hydro have challenged four cartridges and canisters with CH_3I, HOI, and I_2 forms of radioiodine.[3] The results shown in Table IV confirm that HOI and I_2 removal and retention efficiencies are greater than or essentially equal to those for CH_3I.

B. Methyl Iodide Versus Methyl Radioiodide

Cumulative percent penetrations through three types of impregnated charcoals are compared for methyl iodide (Fig. 4) and for methyl radioiodide (Fig. 5). The test beds, 3.75 cm deep by 2.4-cm diameter, consisted of charcoals taken from MS GMR-I, GMR-I (TEDA), and Scott 600252-75 canisters. Each bed was preconditioned for 2 hours at the test conditions of 3-L/min airflow and 86 ± 3% relative humidity before being challenged with 1.5-ppm (7-mg/m³) methyliodide tagged with ^{131}I. Cumulative fractional methyl radioiodide penetrations were calculated directly from 5-minute interval counts of radioiodine trapped in the detectors. Cumulative fractional penetrations of methyl iodide were calculated by integrating instantaneous upstream and downstream concentrations determined by gas chromatography. The 5% TEDA-impregnated charcoal from the Scott canister

was the most efficient, allowing nearly constant 1.5 ± 0.5% penetration of both methyl iodide and radioiodine throughout the experiment. The GMR-I (5% KI_3, 2% TEDA) was less efficient at about 10 ± 2% methyl iodide penetration and 5 ± 1% methyl radioiodine penetration after an initial equilibration period. The GMR-I (5% KI_3) charcoal was most efficient at the beginning of the experiments but rapidly and steadily deteriorated to give a 60% cumulative fractional methyl iodide penetration and a 17% cumulative fractional methyl radioiodide penetration by 100 minutes.

Results from seventeen experiments with iodized charcoals are compared in Fig. 6, which shows $CH_3^{131}I$ cumulative percent penetration versus CH_3I cumulative percent penetration. The data points all fall below the equality (dashed) line, i.e., CH_3I penetration greater than $CH_3^{131}I$ penetration. Also, in the region of practical interest (less than 10% penetration) the difference is an apparently only and constant factor, about two in these cases.

A more extensive comparison of fractional penetrations for Scott (5% TEDA) beds is summarized in Fig. 7. These results are from 14 experiments at two humidities for two generation methods and for three bed depths (1.25-3.75 cm). Each graphed point represents the average of 20 to 30 measurements for a given experiment. The penetration values all fall close to the theoretical (dashed) equality line. Therefore, for this type of sorbent (TEDA only) measurements of molecular CH_3I penetrations are direct measurements of the ^{131}I penetration when the radioiodine challenge is in the form of $CH_3^{131}I$.

A fourth type of charcoal, from an MSA GMR-S canister, was tested to compare methyl iodide and radioiodide penetrations. This Whetlerized charcoal is impregnated with metal and ammonium salts but contains no impregnants that react with methyl radioiodide. Therefore, removal of ^{131}I in CH_3 ^{131}I can occur only by physical adsorption of the molecule. Cumulative fractional penetrations of methyl iodide and methyl radioiodide are compared in Fig. 8 for duplicate experiments. The data points closely fit the equivalence line until the amount desorbing from the test bed equals that entering it. Then there was a slight deviation in the direction of greater radioiodine penetration than methyl iodide penetration. This deviation is explained as the result of forming volatile iodides other than methyl iodide. The radioiodine detector is not compound specific, but the gas chromatograph is and would not measure the other iodides. Instantaneous fractional penetrations (effluent concentration/challenge concentration) of methyl iodide

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TABLE IV. Comparisons of Radioiodine Species Removal Efficiencies by Kabat*

Adsorber Type	Radioiodine Species	Airflow L/min	Range of Percent [131]I	
			Adsorption (3h)	Desorption (2h)
GMA-H Cartridge	CH_3I	20	98.13-99.29	3-11
	HOI		99.24-99.90	0.2-1.5
	I_2		99.92-99.96	<0.1-0.11
GMI-H Cartridge	CH_3I	20	99.95-99.96	0-< 0.1
	HOI		99.87-99.92	< 0.1
	I_2		99.92-99.96	0.19-0.33
Canadian C1 Canister	CH_3I	40	52-47	41-46
	HOI		99.2-99.6	0.3-0.5
	I_2		98.5	1.1
MSA-Type N Canister	CH_3I	40	99.91-99.93	0.14-0.59
	HOI		99.21-99.93	0.1
	I_2		99.87-99.96	<0.1-0.15

*From Reference 3. 95 percent RH, 25°C.
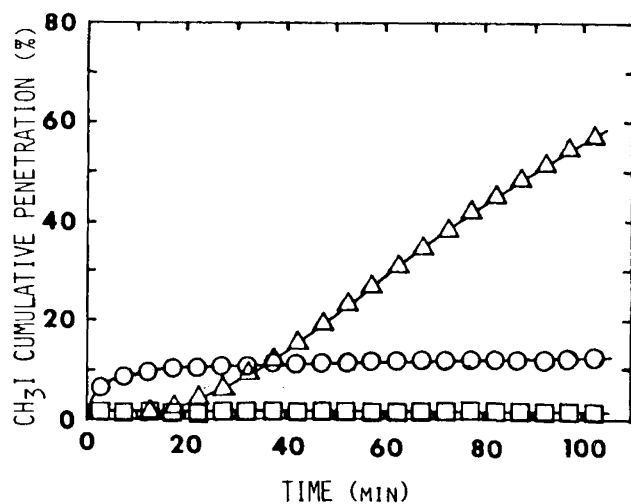
Fig. 4. Methyl iodide cumulative percent penetrations as functions of time for charcoals from three respirator canisters: □, Scott 600252-75 (5% TEDA); ○ , MSA GMR-I (5% KI_3 + 2% TEDA); △, MSA GMR-I (5% KI_3).

Fig. 5. Methyl radioiodide cumulative percent penetrations as functions of time for charcoals from three respirator canisters: □ , Scott 600252-75 (5% TEDA); ○ , MSA GMR-I (5% KI_3 + 2% TEDA); △, MSA GMR-I (5% KI_3).
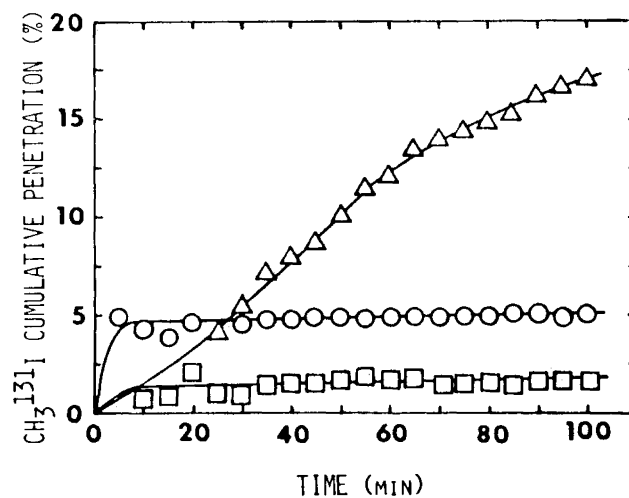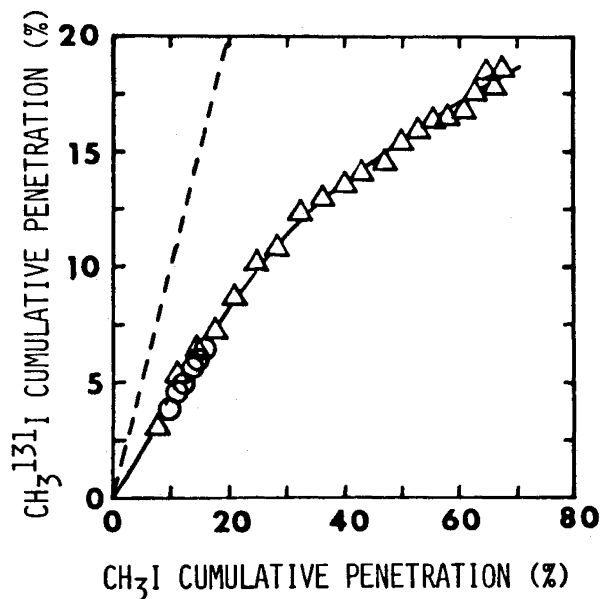
Fig. 6. Comparisons of cumulative percent penetrations of methyl radioiodide and methyl iodide for two 5% KI_3 charcoals: △, GMR-I; ○, GMR-I (TEDA).
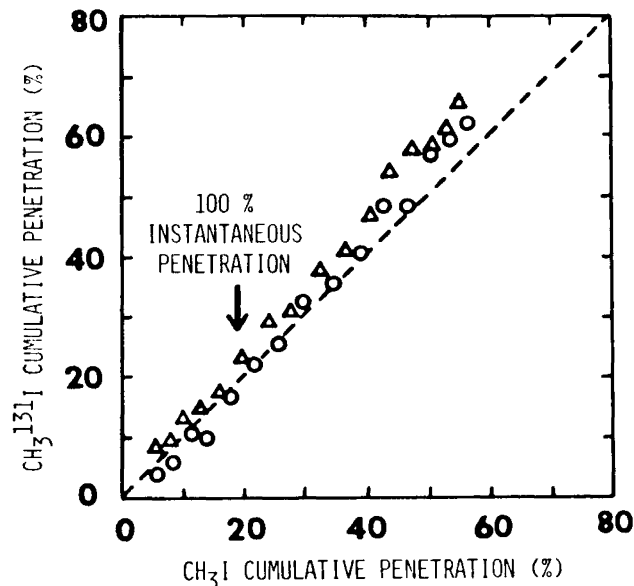

Fig. 8. Comparisons of cumulative percent penetrations of methyl radioiodide and methyl iodide for Whetlerized charcoal (GMR-S) for two separate experiments (△ and ○).
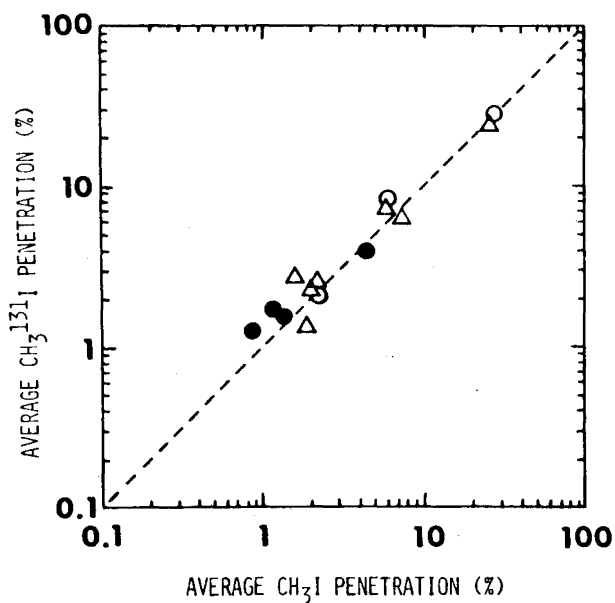

Fig. 7. Comparison of average percent penetrations of methyl radioiodide and methyl iodide for a 5% TEDA-impregnated charcoal (Scott 600252-75). Permeation tube generation: ○ , 97% RH and ●, 85% RH; aqueous solution generation: △, 97% RH.

increased with time and even exceeded 100% as the vapor adsorbed at the beginning was displaced in the air. Breakthrough times of methyl iodide averaged 33 ± 3 minutes at 0.1%, 49 ± 6 minutes at 1%, and 68 ± 8 minutes at 10% instantaneous penetration.

Normal methyl iodide can be used to determine the upper limit of penetration to be expected for methyl radioiodide. Isotope equivalent efficiencies have been demonstrated for sorbents not impregnated with normal iodine or iodide. Normal methyl iodide tests cannot measure the removal of ^{131}I by isotope exchange on iodized charcoals and, therefore, give a high (conservative) estimate of methyl radioiodide penetrations. However, there are currently no commercial radioiodine canisters or cartridges which have charcoals impregnated with iodide only. The GMR-I canister with 5% KI_3 packing is no longer available.

C. Effects of Bed Depth and Contact Time

Another series of experiments with the TEDA and KI_3 impregnated respirator canister charcoals was done to establish the rate orders of methyl iodide and radioiodide

removal. The ranges of test conditions were

Bed depth: 1.25-3.75 cm
Bed diameter: 2.4 cm
Airflow rate: 1.8-4.2 L/min or 6.7-15.3 cm/s
Bed residence time: 0.16-0.75 s
Relative humidity: 86 ± 3%
Concentrations: 6-1200 nCi/m³ ^{131}I and 0.19-72 mg/m³ CH_3I
Conditioning Period: 2 hours

Seventeen tests with methyl radiodide generated from a permeation tube were done using iodized charcoal from an MSA GMR-I canister. In each test the methylradioiodide instantaneous penetration remained nearly constant, while methyl iodide instantaneous penetration increased steadily with time until it exceeded 100%. When the logarithms of methylradioiodide penetration percents were plotted against bed contact times, a straight line with an intercept of 1.0 resulted (Fig. 9). This indicates that the methylradioiodine removal reaction (isotope exchange) is simple first order in meth-
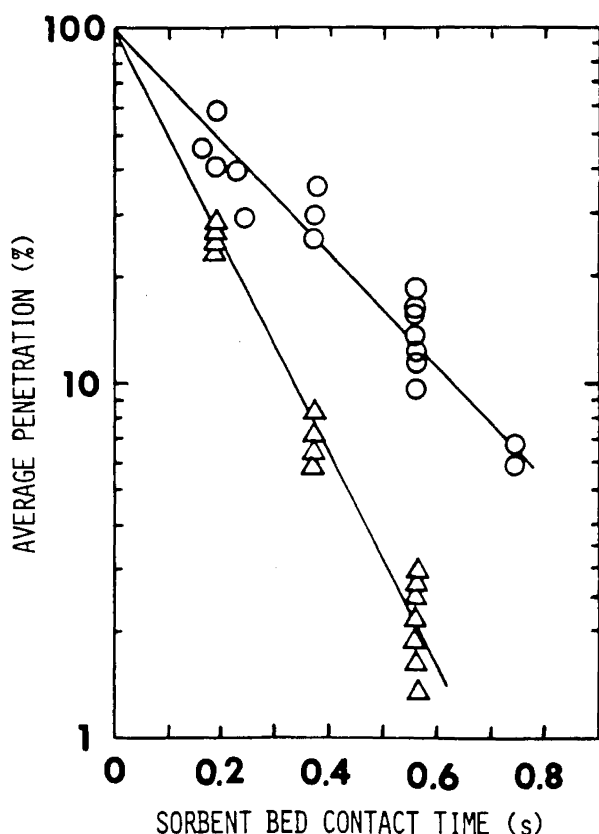

Fig. 9. Average instantaneous percent penetrations as logarithmic functions of bed contact times: ○ methyl radioiodide for a 5% KI₃ charcoal (GMR-I); △, methyl iodide and methyl radioiodide for a 5% TEDA charcoal (Scott).

ylradioiodide concentration. The range of airflow rates was not large enough to notice the velocity effects found later.

Ten such experiments using 5% TEDA charcoal from Scott 600252-75 canisters were also done at similar conditions. Semilog plots for penetration percents (both methyl iodide and radioiodide) versus bed contact times (Fig. 9) showed that the chemisorption reaction is also described by a simple first-order rate. Both methyl iodide and radioiodide are removed from air at the same rate. Four experiments were also done at different bed depths (1.25-5.0 cm) using charcoal from MSA GMR-I (TEDA) canisters. Penetrations of methyl iodide and radioiodine during each run were both constant but not equal. The difference for this mixed impregnant (2% TEDA and 5% KI₃) sorbent is due to isotope exchange which removes the ^{131}I from the methylradioiodide but leaves a molecule of methyl iodide. Average first-order rate coefficients calculated from the slopes of plots such as Fig. 9 are listed in Table V.

The reaction of TEDA impregnant with methyl iodide vapor is by first-order kinetics. The isotope exchange of iodide impregnant to remove the radioiodine from methylradioiodide is also by first-order kinetics. Effluent vapor concentrations decreased exponentially with bed depth. These results indicate that removal efficiency was independent of vapor concentrations within the bed. This is an important conclusion, since the radioiodine concentrations to be encountered in nuclear environments are many orders of magnitude lower than the ppm concentrations required for a nonradiometric test. The first-order kinetics also implied that contact time of vapor within the sorbent bed is critical. Contact time is determined by canister geometry and airflow rate (i.e., workload). A high flow rate should be chosen for a canister test to approach the upper limit of average vapor penetration. The arbitrary test standard is 64 L/min for canisters and 32 L/min for individual cartridges used in pairs.[4]

Canister charcoals containing 5% TEDA impregnant were more effective for methyl iodide removal than those containing 5% KI₃ impregnants and are more efficient for methyl radioiodide removal than those without, except for short periods with fresh canisters.

D. Effects of Challenge Concentrations

Five tests were made with 5% KI₃-impregnated charcoal under these conditions:

TABLE V. First-Order Rate Coefficients for Methyl Iodide and Radio-iodide Removal[a]

Charcoal Impregnant	Charcoal Source	Rate Coefficient (s^{-1})		
		Total $CH_3^{131}I$	Total CH_3I	Isotope Exchange[b]
5% TEDA	Scott 600252-75	6.9 ± 0.5	7.1 ± 0.3	None
5% KI$_3$	GMR-I	3.6 ± 0.3		3.6 ± 0.3
5% KI$_3$ + 2% TEDA	GMR-I (TEDA)	4.9 ± 0.1	3.0 ± 0.1	1.9 ± 0.2

[a]2-h preconditioning at 86% RH.
[b]Difference of preceding two columns.

3.75-cm depth × 2.5-cm-diam bed.

1.8-L/min airflow: 6.6 cm/s; 0.57s bed contact time, 86% RH; 2-hour equilibration before testing 0.19-3.8 mg/m^3 CH$_3$I.

0.0061-0.125 µCi/m^3 ^{131}I.

Challenge concentrations varied over a factor of 20. Breakthrough times (t$_B$) of CH$_3$I for 1%, 10%, and 50% instantaneous penetrations were nearly the same for all challenge concentrations (Table VI.) Individual breakthrough times were used to calculate the breakthrough capacities plotted versus challenge concentrations in Fig. 10. The linearity of these plots indicated that CH$_3$I adsorption and desorption occurred according to a simple linear isotherm (Henry's law). Other charcoals which have been tested with CH$_3$I have not indicated linear isotherms.[1]

The Wheeler adsorption equation[5] predicts the logarithm of penetration as a linear function of time for low penetrations (<15%), and such plots have been reported for CH$_3$I. The penetration curves for the experiments reported here with the iodized charcoal consistently fit the Statistical Moments Theory (SMT) equations[6] and an empirical exponential $C/C_0 = at^b$ equation better than the Wheeler equation. For example, four data sets at penetrations less than 15% yielded the correlations in Table VII.

The consistent failure of the Wheeler equation to give the best fit of penetration results from many experiments brings to question its use in extrapolating to define initial penetration at initial exposure. However, it will always give a conservative (higher) initial value relative to the true one due to the curvature of the breakthrough curve.

TABLE VI. Effects of Challenge Concentrations

CH$_3$I				CH$_3$ ^{131}I	
Conc. (mg/m^3)	Breakthrough Times (min)			Conc. (nCi/m^3)	Percent Penetration[a]
	t1%	t10%	t50%		
0.19	6.8	18.0	39.6	6.1	12.3
0.41	2.4	14.7	41.5	13.6	16.0
1.29	3.8	15.4	41.8	42.6	9.7
2.19	7.4	20.5	45.8	72.3	15.4
3.78	3.4	15.1	38.7	124.7	11.5
Average	4.8	16.7	41.5	Average	13.0
Std. Dev.	2.2	2.5	2.7	Std. Dev.	2.7

[a]Average instantaneous penetration after the initial period in which physical adsorption was significant.
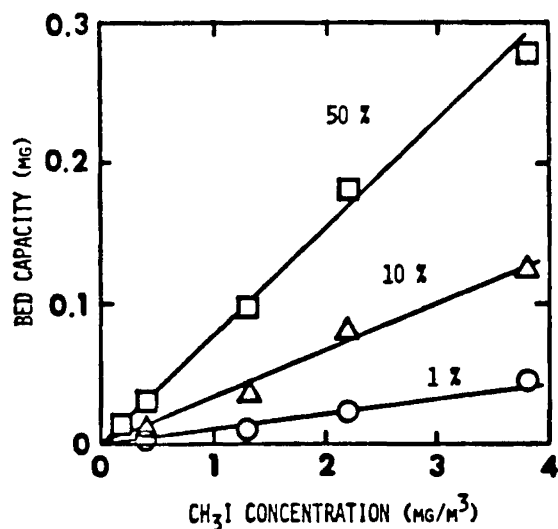
Fig. 10. Dynamic adsorption isotherms at three instantaneous penetration fractions for methyl iodide and MSA GMR-I (2% KI_3) charcoal.

For the above experiments, the Wheeler equation gave an initial penetration value of 0.33% (std. dev = 0.18%) to be compared with the SMT initial value of 0.094%. One of the best fits of the breakthrough curves was for a $C/C_0 = at^b$ empirical equation which has three difficulties: (1) it has no theoretical basis; (2) it does not allow extrapolation of penetration to initial exposure time; and (3) extrapolated values vary rapidly at short times, for this example, 0.020 at 0.5 minutes, 0.073% at 1 minute, and 0.265% at 2 minutes.

E. Cartridge Comparisons

Four cartridges, all containing 5% TEDA-impregnated charcoals, were tested with methylradioiodide at 0, 2, and 4-hour exposure times to 32 L/min, 97 ± 3% RH air. Methyl iodide penetrations again increased with exposure times. Maximum penetrations (humidity equilibrations) were reached in about 3-4 hours. Average penetrations measured during 4-6 hours by gas chromatography and by radiometric counting are listed in Table VIII. The values from the two methods are in good agreement. Cartridges with larger sorbent volumes (Table I) of similar sized and impregnated charcoals gave lower penetrations. That this can be attributed to increaded bed contact time is shown in Fig. 11. This semilog plot also includes data from Table II for the Scott 600252-75 canister. The average first-order rate coeficient is $17.6s^{-1}$ (standard deviation = 1.3 s^{-1}). This correlation should be useful for improving efficiencies by redesigning canisters and cartridges.

The larger canisters (used alone) were more effective for methyl iodide removal than cartridges (used in pairs) even though the flow rate through each cartridge was half as much. Also, the cartridges deteriorated in efficiency more rapidly due to high humidity. Magnitudes of efficiencies can be correlated with volumes of charcoal and bed contact times.

Insufficient data are available to rate cartridges and canisters for radioiodine removal. Variations within brands and types have not been established. Also, their contents are subject to change by the manufacturers. These unknowns emphasize the need for an ongoing certification program. Such a program to be carried out in the NIOSH Testing and Certification Branch is an ultimate product of this project.

TABLE VII. Fits of Penetration Data to Equations

Equation	Linear Correlation Coefficient, r
Wheeler: $\ln(C/C_0) = \ln a + b\, t_B$	0.9256
Exponential: $\ln(C/C_0) = \ln a + b \ln t_B$	0.9999
SMT: $\dfrac{t_B - m_1 + m_3/6m_2}{X_B} = -\sqrt{m_2} + \dfrac{m_3}{6m_2} X_B$	0.9999

TABLE VIII. Cartridge Penetration Fractions of Methyl Iodide and Methyl
Radioiodide after Equilibration at High Humidity[a]

Cartridge Type	Average Percent Instantaneous Penetrations (and Standard Deviations)		Bed Contact Time(s)	Charcoal Granule Mesh
	CH_3I	CH_3 ^{131}I		
Norton Type I	3.75	3.34	0.20	8-16
	(0.76)	(0.06)		
Norton Type II	1.50		0.20	12-20
	(0.15)			
Scott 604403-75	13.24	11.50	0.12	8-16
	(0.59)	(0.34)		
Scott 604550-75	16.52	12.87	0.12	8-16
	(0.61)	(0.90)		

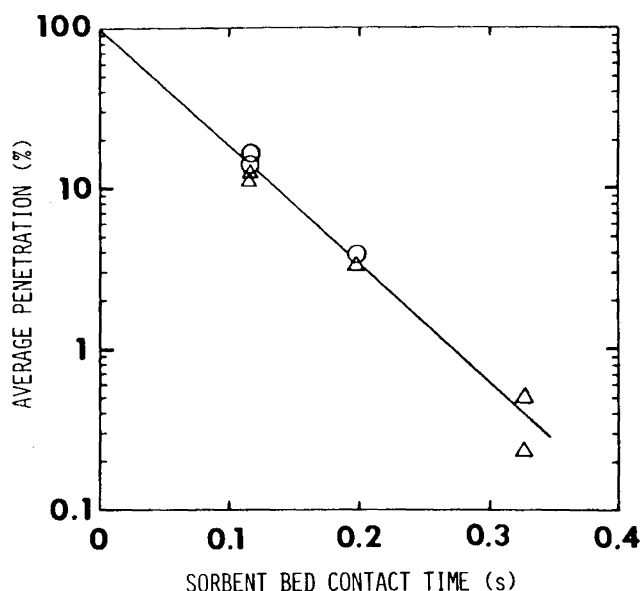[a]32 L/min, 97 ± 3% RH, 4h.

Fig. 11. Dependence of average instantaneous percent penetrations on bed contact times for canisters and cartridges containing 5% TEDA-impregnated charcoals: O , methyl iodide; △, methyl radio-iodide.

V. EFFECTS OF USE CONDITIONS

A. Relative Humidity

1. **Comparisons of Water Vapor and Methyl Iodide Loading.** When canisters or cartridges were tested more than once with methyl radioiodide at 2-hour intervals

while continuously exposed to very high humidity (95 ± 3% RH) air, increasing penetrations were usually observed. This is illustrated by the results in Tables II and III. Such an effect could be due to (1) loading the test bed with methyl iodide in previous tests and/or (2) loading it with water vapor by exposure to large volumes of high humidity air. Studies were done to sort out these effects using Scott 600252-75 canisters (5% TEDA charcoal) at 64-L/min airflow rate. Methyl iodide was generated from aqueous solutions (0.23 g/100 mL) at selected times while a canister was exposed to high (97 ± 3% or medium (50 ± 3%) relative humidity air. Penetration results versus exposure times are shown in Fig. 12. Box
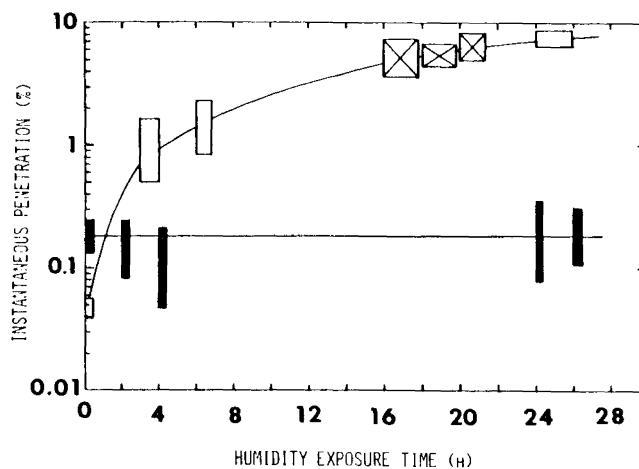

Fig. 12. Average instantaneous percent penetrations of methyl iodide through Scott 600252-75 (5% TEDA) canisters as functions of exposure times: □, 97% RH; ■ , 50% RH.

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sizes represent ranges of data obtained. In the first experiment (open rectangles) a fresh canister was tested after 0, 3, 6, and 24-hour exposures to 97% RH air. Penetrations increased by over two orders of magnitude. In the second experiment another canister was exposed at this humidity for 16 hours before being tested at 16, 18, and 20 hours. These data (shown as rectangles with x's) fell on the same curve as those from the first experiment. In the third experiment (solid rectangles) another canister was tested at the 50% RH and 0, 2, 4, 24 and 26-hour exposures. Even for the longest time and highest bed loading the penetration at 50% RH was not significantly changed from the beginning.

A Norton Type II cartridge (12-20 mesh, 5% TEDA) was challenged with 1.7-ppm (7.6-mg/m^3) methyl iodide at 32-L/min air and 90% RH (Fig. 13). During the first 3 hours, the penetration fraction increased nearly 2 orders of magnitude to 1% where it remained constant for at least 19 hours. Since the bed was being loaded constantly with methyl iodide and there was no change in penetration fraction after 3 hours, the initial change must be attributed to something other than sorbent exhaustion by methyl iodide loading. Apparently, 3 hours was required for the charcoal to become equilibrated with water vapor in equilibrium with the 90% RH air. The larger canisters require more time (Fig. 12). The adsorbed water vapor either blocks access of methyl iodide vapor to the TEDA impregnant or removes TEDA effectiveness by hydrolysis:

$$N(CH_2CH_2)_3N + H_2O = N(CH_3CH_2)_3NH^+ + OH^-$$
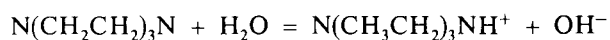
When the challenge of a vapor to a test bed is at a high enough concentration and continuous, the bed will become loaded and will decrease in efficiency of vapor removal. The resulting increase in penetration with time is called a breakthrough curve. Breakthrough times for selected penetration fractions are often dependent on the vapor challenge concentration. At high relative humidities charcoal beds become loaded with water vapor, also increasing penetration of test vapor with time. The above experiments have shown that for efficient sorbents at low challenge concentrations or loadings, the relative humidity effect may be the most significant. Therefore, the time of exposure of a canister or cartridge to high humidity air is an important parameter in a test procedure or a usage protocol.

2. **Equilibrium Penetrations.** A charcoal bed at equilibrium with the water vapor in the air entering it does
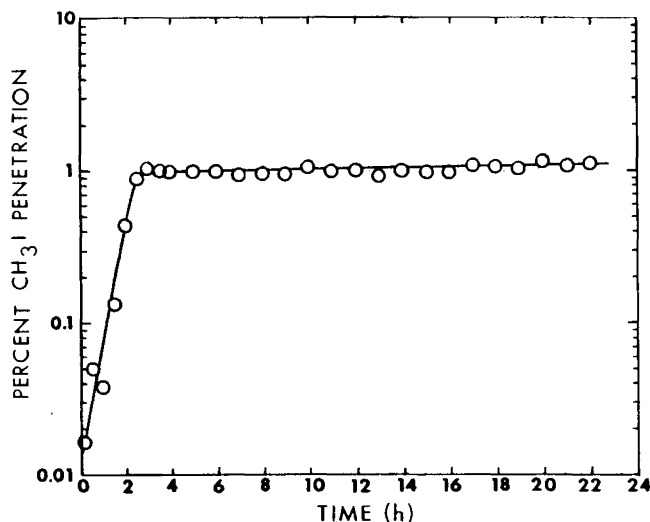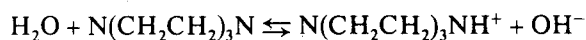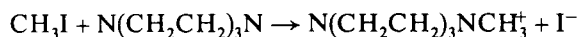

Fig. 13. Effect of exposure time on methyl iodide instantaneous penetration for a fresh Norton Type II cartridge tested at 90% RH, 32-L/min airflow, and 1.7-ppm (7.6-mg/m^3) methyl iodide.

not exhibit heating due to additional water vapor adsorption (see Section V. A.4.). Also, the penetration is often maximized at such equilibrium. A Scott cartridge (642-TEDA-H) containing 5% TEDA-impregnated charcoal was exposed at 32-L/min airflow, 0.57 mg/m^3 (0.13 ppm) CH$_3$I, 27 ± 0.4°C, and 50, 71, and 91% RH. After equilibrium was reached at each humidity penetration, measurements were made at 7- or 10-more-minute intervals and averaged.

These values of the equilibrium CH$_3$I penetration fraction P$_E$ were related to water vapor concentration in air [H$_2$O] by

$$P_E = \exp(-47/[H_2O]) .$$

This is consistent with the simple competitive mechanism:

$$CH_3I + N(CH_2CH_2)_3N \rightarrow N(CH_2CH_2)_3NCH_3^+ + I^-$$

$$H_2O + N(CH_2CH_2)_3N \leftrightarrows N(CH_2CH_2)_3NH^+ + OH^-$$

where water vapor reacts with TEDA, making it unavailable for CH$_3$I removal.

Larger MSA canisters, also containing 5% TEDA charcoal, were also measured for methyl iodide penetration at several humidities. Flow rate was 64 L/min and relative humidities ranged from 50 to 85%. Penetrations at water vapor equilibrium, P$_E$, were less sensitive to [H$_2$O] changes than in the case of the Scott cartridges

with one-fifth as much charcoal. Times required for fresh MSA canisters to reach water vapor equilibrium varied from 9.5 hours at 75% RH to 16 hours at 50% RH.

At relative humidities above 75% the CH_3I penetration at water vapor equilibrium was not the highest penetration value. This is illustrated in Fig. 14 with penetration fraction versus time curves for MSA canisters containing 5% TEDA charcoal. At 85% RH a maximum penetration of 7.6% was reached at 450 minutes as compared with an equilibrium penetration of 4.1% (std dev = 0.2%). This maximum is attributed to the displacement by water of CH_3I previously physically adsorbed. Such a maximum is commonly seen at all humidities with various charcoal beds.

Conclusions reached from studying humidity effects for equilibrated canisters are the following: (1) We now understand how water vapor reduces the efficiencies of TEDA-impregnated charcoal beds. It is by tying up the impregnant and making it unavailable for reaction with methyl iodide. (2) Long times, up to 16 hours, required to reach humidity equilibrium limit the practicality of using penetration at humidity equilibration as a measurement of canister performance. (3) Since the penetration at high humidity equilibrium is not the highest value which occurs, its usefulness for canister or cartridge performance specification is questionable.

3. **Service Lives.** Measurement of service life, the time required to reach a selected penetration fraction, is an alternative to measurement of penetration at humidity equilibrium. Service lives of air-purifying canisters and
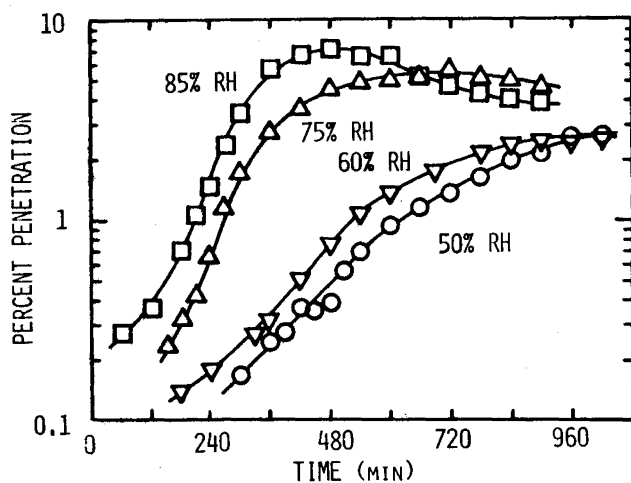
cartridges decrease with increasing relative humidity of the air passing through them. This is illustrated by the results in Fig. 14. If 1% is chosen as the maximum penetration to be allowed, the service lives t_p for fresh MSA 5% TEDA canisters decrease from 635 minutes at 50% RH to 200 minutes at 85% RH. Another selected penetration value would give another set of service lives. For example, tests of three fresh GMR-I (TEDA) canisters at 64 L/min yielded the results in Table IX.

An empirical relationship was found which described the effects of relative humidity on service lives (t_p) of fresh canisters. Log t_p versus log $[H_2O]$ (or log percent RH) plots were found to be linear with slopes between 2 and 3. Fig. 15 shows such plots for MSA 5% TEDA canisters at 64 L/min airflow, Scott 5% TEDA canisters (600252-75) at 64-L/min airflow, and Scott 5% TEDA cartridges (642-TEDA-H) at 32-L/min airflow. The two brands of canisters, which have nearly the same volumes of charcoal, had equivalent service lives (Fig. 15). Even at half the airflow rate the cartridges with much smaller charcoal volume had much shorter service lives which were more seriously affected by humidity. Similar data with MSA GMA canisters containing unimpregnated activated charcoal were also linear on a log t_p versus log $[H_2O]$ plot.

The usefulness of this relationship for a certification program is for extrapolating from one humidity to another. It may allow the selection of two humidity conditions for evaluating canisters and cartridges. Also, the selected test humidities could be high (70-100%) where service lives are shorter and where, therefore, test times would be shorter. This is desirable for maximum efficiency of a certification test program.

Fig. 14. Humidity effect on methyl iodide breakthrough curves at 64 L/min for MSA 5% TEDA charcoal.

TABLE IX. Service Life (±5 min) at Three Relative Humidities

Penetration Fraction	Percent Relative Humidity		
	60	80	100
0.0002	145	85	30
0.0005	185	105	35
0.001	225	135	45
0.002	275	155	55
0.005	375	195	65
0.01	455	215	75
0.02	555	245	95
0.05	705	305	135
0.1	855	475	235

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RELATIVE HUMIDITY AT 25°C
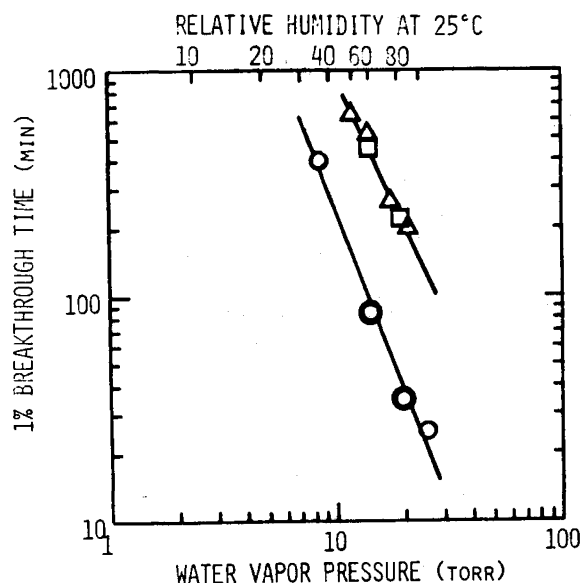
Fig. 15. Correlations of relative humidity and service life (1% breakthrough) for canisters (□, Scott and △, MSA) and a cartridge (○ , Scott) containing 5% TEDA charcoals.

4. Humidity Heating. The adsorption of water vapor from air passing through charcoal-packed canisters and cartridges heated the air to significant extents for long periods. Temperature rises for Scott canisters (642-TEDA-H) at 32-L/min airflow and three humidities are shown in Fig. 16. The maximum increase of 10°C (18°F) was observed for the highest (85%) relative humidity at about 5 minutes from initial exposure.
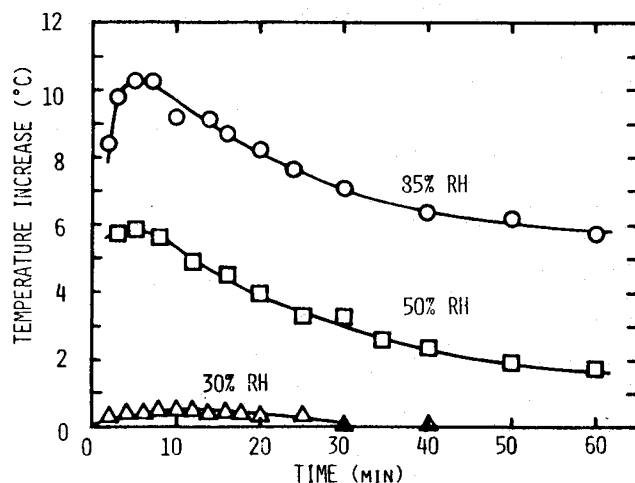
Measurable heating (+0.2°C) continued for periods up to 340 minutes for this series. Other cartridges and canisters (64 L/min) showed similar heating effects.

Dew points were measured for air leaving test cartridges as well as for air entering them. This allowed determination of the rates of water vapor adsorption at times throughout an experiment. Temperature increases were proportional to water vapor concentration decreases. This relationship was used to calculate heats of adsorption ranging from 4 to 9 kcal/mole.

Humidity heating effects are important to note since (1) they can make air-purifying respirators less comfortable to wear and (2) they complicate the descriptions of how canisters work. The comfort effect is more relevant to the user than to the certification test.

B. Temperature

1. Equilibrium Penetrations. Ambient air temperatures for applications of air-purifying respirators can vary. In addition, as mentioned above, air drawn through a canister can be heated by water vapor adsorption on the adsorbent. Temperature effects can be complex since higher temperatures enhance chemical reactions (chemisorption) with impregnants but reduce physical adsorption of vapors.

In a series of experiments with Scott cartridges (642-TEDA-H) at 32-L/min airflow, temperature of entering air was varied from 26.4 to 38.0°C. Test cartridges were equilibrated at dew points from 15.1 to 25.7°C before methyl iodide penetrations were measured at the equilibration humidities (50-75% RH). Fig. 17 shows a plot
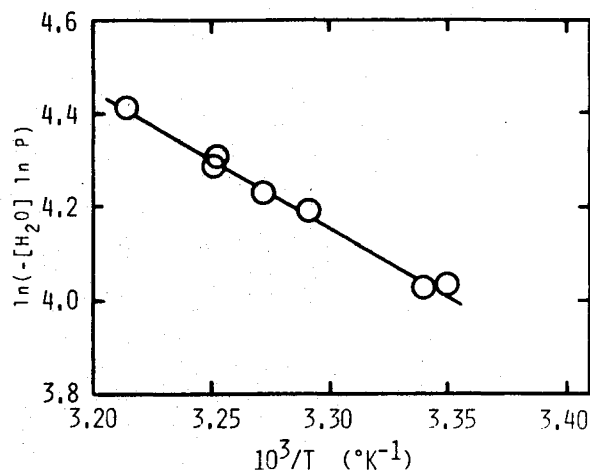

Fig. 16. Humidity heating effects for a Scott 5% TEDA cartridge at 32-L/min airflow.

Fig. 17. Clapeyron plot to correlate equilibrium methyl iodide penetration with dewpoint and air temperatures.

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of $\ln (-[H_2O] \ln P_E)$ versus $1/T$, which turns out to be linear with a slope of $3020°k^{-1}$.

The usefulness of this data is in sorting out the interrelated effects of relative humidity, ambient temperature, and dew point temperature. The following semiempirical equations were derived from data for this cartridge:

$$\ln P_E = -0.0096 \, t_c \exp\left[\frac{5300}{T_{DEW\ POINT}} - \frac{3020}{T_{AMBIENT}}\right]$$

$$\ln P_E = \frac{-0.96 \, t_c}{(\%RH)} \exp\left[\frac{2280}{T_{AMBIENT}}\right]$$

The exponent $5300/T_{DEW\ POINT}$ comes from the dependence of saturation vapor pressure of water on temperature. At constant dew point, i.e., at constant water vapor concentration, equilibrium penetration of methyl iodide decreases with increasing ambient temperature. However, when relative humidity is held constant, equilibrium penetration actually increases at higher ambient temperature. This is due to the higher water vapor concentration for fixed humidity at higher temperatures.

2. **Penetration and Service Lives.** We have done experiments to determine how much effect the temperature of inspired air has on the efficiencies and service lives of fresh (unequilibrated) canisters and cartridges for methyl iodide. First, we observed that such an effect does exist, even over a limited expected range of use temperatures (15-35°C or 59-95°F). This is illustrated in Fig. 18 by data obtained with a Mine Safety Appliances

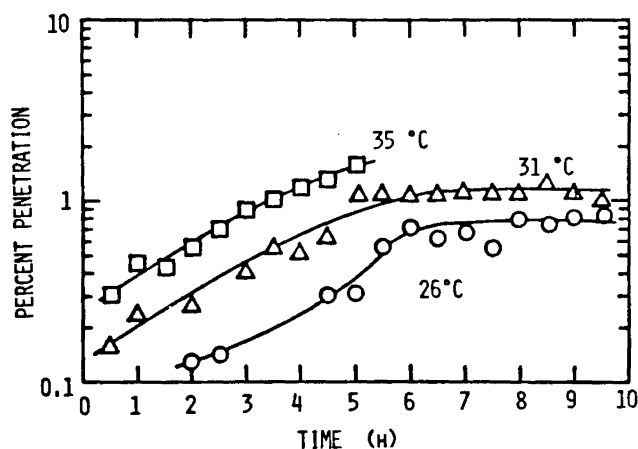Company (MSA) canister containing charcoal with two impregnants, 2% TEDA and 5% KI_3. The breakthrough curves show increased penetrations for increased temperatures at all experimental times. When logarithms of percent penetration were plotted against temperatures, we obtained apparently straight lines. Fig. 19 shows such plots for the MSA canister (2% TEDA, 5% KI_3) and a Scott 642 cartridge (5% TEDA). Similar results were obtained with an MSA-GMA canister containing unimpregnated activated charcoal. In all three cases, the temperature effects corresponded to approximately doubling the penetration for each 5°C (9°F) increase in temperature.

The parameters of air temperature (T), relative humidity (RH), and dew point temperature (DP) are interrelated and cannot independently affect service lives (breakthrough times at selected penetrations). Therefore, we have studied temperature effects first with RH constant and then with DP constant. As before, methyl iodide is the test vapor, since it is the most penetrating vapor form of iodine we have found.

At constant RH, increasing temperatures shift breakthrough curves to higher penetrations and, consequently, result in shorter service lives (Fig. 20). Canisters and cartridges containing three types of charcoal were studied at constant RH. The result (Table X) shows significant service life decreases with increasing temperatures, up to 15% decrease per °C (8% per °F).

Fig. 18. Air temperature effect on methyl iodide breakthrough curves at 64 L/min and 50% RH for an MSA 2% TEDA, 5% KI_3 canister.
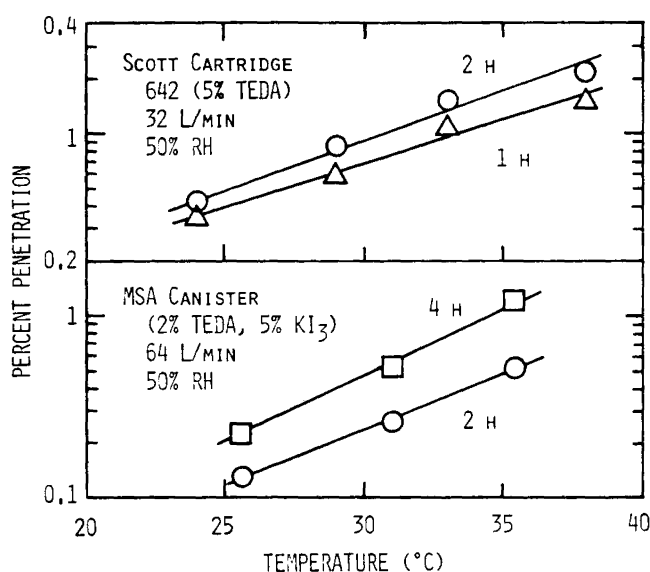

Fig. 19. Effects of air temperature on methyl iodide penetration at selected times after initiating flows of 50% RH air.
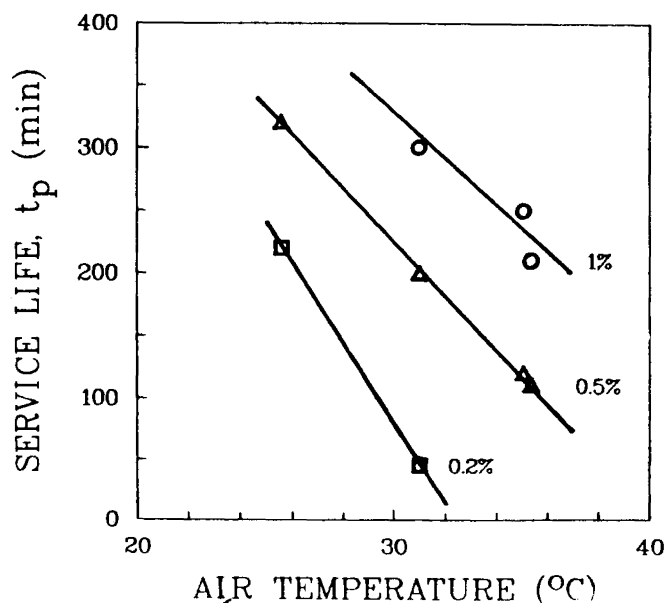
Fig. 20. Effect of air temperature on service lives at constant 50%
RH for an MSA canister (2% TEDA, 5% KI₃) at 64 L/min.

TABLE X. Temperature Effects on Service Lives at Constant Humidity

Charcoal Type	Percent RH	T Range (°C)	Percent CH_3I Penetration	Service Life Decrease (Percent Per°C)
2% TEDA, 5% KI₃	52	30-35	1	4
	50	31-35	1	4
		26-35	0.5	7
		26-31	0.2	15
Activated	50	25-34	1	7
	70	25-30	50	5
		25-30	10	5
		25-30	1	5
5% TEDA	50	29-38	1	9

In one case (2% TEDA, 5% KI₃), the temperature effect varied with penetration fraction selected to define service life.

At constant DP (i.e., constant water vapor concentration in air), service lives increased significantly with increasing temperatures (Fig. 21). This is due to the combined effects of less water adsorption (air/charcoal equilibrium shift) and enhanced reaction of methyl iodide with triethylenediamine (TEDA) impregnant. The main reason for doing constant DP studies was our hope that temperature effects would be less significant. This did not turn out to be the case. Average increases in service lives at 1% penetration were 12% per °C at 19°C DP and 3% per °C at 24°C DP.

The conclusion of these studies is that temperature can affect service lives much more than the 1-10% reduction per 10°C increase reported in the literature.[7] Therefore, temperatures at which cartridges and canisters are tested must be more closely controlled than ±2.5°C specified in CFR 30, Part II.[4] Also, the units must be tested at maximum T and RH of expected use or tested at lower values with extrapolations of service lives to the worst
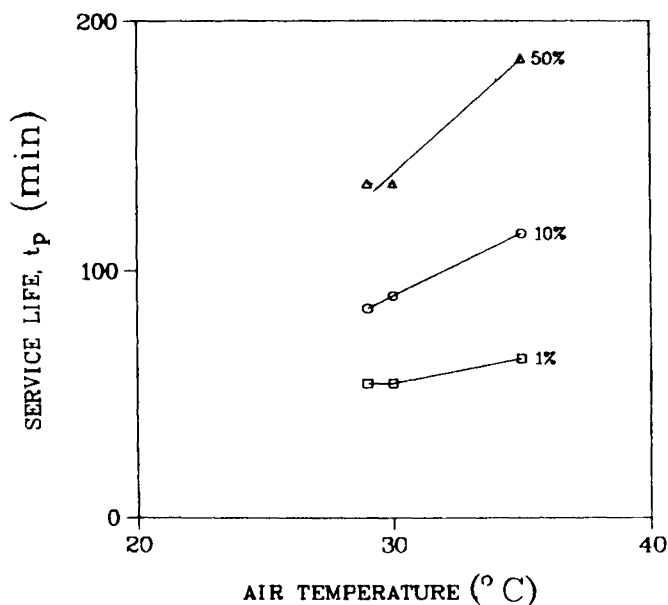
Fig. 21. Effect of air temperature on service lives at constant 24°C
dewpoint for an MSA canister (2% TEDA, 5% KI₃) at 64 L/min.

case conditions. Users must be made aware of the potential for reduced service life when these units are used at even more elevated temperatures.

C. Flowrate

A canister with 2% TEDA, 5% KI₃ impregnated charcoal was tested at 30°C and two RH, DP, and airflow rates. The results shown in Table XI clearly indicate that service life is inversely proportional to airflow rate. This confirmation of a well-established relationship was necessary, since in this case service life is determined by water vapor loading rather than the contaminant (methyl iodide) vapor loading.

D. Reproducibilities of Service Life Measurements

The question was raised as to what reproducibilities can be expected for service life determinations, considering variabilities due to manufacturing and testing. Results of limited studies are shown in Table XII. Precision was worst for high protection factors and short times where bed deterioration due to humidity was most rapid. These results and other experiences indicate that at 1% penetration for one batch of cartridges or canisters a reproducibility of 10% relative standard deviation of service life is reasonable. Reproducibility between batches can only be determined with more extensive testing.

TABLE XI. Effects of Airflow Rate and Humidity on Service Life*

Flowrate (L/min)	Dew Point (°C)	Relative Humidity Percent	Service Life (±5 min) at Penetrations	
			1 Percent	10 Percent
32	19	52	175	300
64	19	51	80	---
32	24	71	115	195
64	24	67	55	105

*30°C; 2% TEDA, 5% KI₃ canisters.

TABLE XII. Reproducibilities of Service Life Measurements

Charcoal Type	Temperature (°C)	% Relative Humidity	Flowrate (L/min)	Number of Measurements	Percent Penetration	Service Life (Min) Average	Service Life (Min) Std. Dev.	% Relative Std. Dev.
5% TEDA	30	70	32	6	3	46	6.3	14
					5	66	4.6	7
					10	98	4.2	4
					20	150	12.2	8
2% TEDA, 5% KI₃	30	70	64	5	1	128	10.4	8
5% TEDA	25	90	32	3	0.02	25	24	96
					0.05	48	18	38
					0.1	85	0	0
					0.2	105	10	10
					0.5	132	7	5

VI. EFFECTS OF CYCLIC FLOW (BREATHING PATTERNS)

A. Background

The effects of variable flow rates and flow (breathing) patterns on the average efficiency needed to be determined also. Evidence is available (Section IV. C.) that the efficiency of a sorbent bed for removing vapors from air decreases with increasing airflow rate. There are data which demonstrate, among other things, that peak inspiration flow rates can be very high (200 L/min) at moderate work loads.[8,9] Therefore, at the peak of inspiration in the breathing cycle, the efficiency may be very poor and certainly will be very different from that at the standard 64-L/min test airflow.

The work of Gary Nelson[10] is widely misinterpreted as showing no such effect. Actually, he demonstrated only that, in a limited number of cases, the cartridge capacity (lifetime) was unaffected by airflow rate or cycling. In the cases of highly toxic vapors (radioiodine, other radionuclides, carcinogens, etc.) the sorbent bed efficiency, rather than its capacity, is the limiting factor in determining usefulness. This is because only low levels in air are expected to be encountered, resulting in low bed loading.

Experimental measurements and theoretical computations were done to identify and quantitate the effects of cyclic flow patterns. Average efficiencies for a given breathing cycle (work load) were measured and related to instantaneous efficiencies throughout the cycle.

B. Computer Modeling Study

A computer program was written which could calculate canister penetrations of methyl iodide based on assumed airflow rate and reaction kinetics of removal. Breathing patterns of airflow were taken from the work of Silverman et al.,[9] who measured and characterized inhalation and exhalation curves at ten work rates for resistances approximating those of gas masks and other breathing apparatus. Their Table 4 provided four parameters used to simulate the varying flows:

R = respiration rate (per minute)
A = maximum inspiratory flowrate (L/min)
I = fraction of total cycle that is inspiration
F_m = minute volume, mean inspiratory flowrate over an entire breathing cycle (L/min)

Only the inspiration flow was considered since exhalation is usually through an exhalation valve, rather than through the canister. During expiration, flow through the canister was set at zero.

The equation which best fits the experimental breathing curves was a linear combination of sinusoidal and ellipsoidal functions:

$$F = A_1 \sin\left(\frac{\pi t}{t_I}\right) + A_2\left[1 - \left(\frac{2t}{t_I} - 1\right)^2\right]^{1/2},$$

$$0 \leq t \leq t_I,$$

where

F, F_m = instantaneous and average volumetric flowrates (L/min)

t_I = I/R, the average time for inspiration (min)

A_1, A_2 = constants selected for each work rate to match the experimental values of maximum flowrate, A, such that

$$A = A_1 + A_2 \text{ and } F_m = \left(\frac{2}{\pi}A_1 + \frac{\pi}{4}A_2\right) I$$

Table XIII lists the input parameters and calculated values of A_1, and A_2 for ten workrates. The (trapezoidal) integrated flowrates for the best fit curves are given in the last column.

A second assumption was that the canister was equilibrated at a set of temperature and relative humidity conditions, where the removal of methyl iodide was described by first-order kinetics (Section IV. C.):

$$P = \exp[-kt_c]$$

where

P = penetration fraction of methyl iodide

k = first-order rate coefficient for removal (per sec)

t_c = bed contact time (sec) = 60V/F

V = charcoal bed volume (L)

These equations were combined to calculate instantaneous and integral flowrates and penetration fractions for steady and cyclic flows for selected values of k and V in the ranges of experimental values. The constant flowrate required to give a penetration equal to that of the cyclic flow was also calculated.

The simplest case, where k is a velocity-independent constant, was computed first with the results shown in Table XIV for k = 17.6 s^{-1} and V = 330 cm^3, both experimental values (Section IV. E.). Average cyclic flow penetrations were much higher than those for equal steady flowrates. Higher steady flowrates (2.0 to 3.6 times) were required to give penetrations equal to the cyclic flow penetrations. The effects of varying the product k V on the cyclic penetration (P_c), steady penetration (P_s), and ratio were given by

$$\ln P_c = -c\,(k\,V),$$

$$\ln P_s = -s\,(k\,V),$$

$$P_c/P_s = \exp[(s-c)\,(k\,V)],$$

TABLE XIII. Input and Calculated Parameters for Fitting Experimental Breathing Curves

Average Flowrate (L/min)	Maximum Flowrate (L/min)	Respiration Rate (per min)	Inspiration Fraction	Best Fit Constants		Integrated Flowrate (L/min)
				A_1 (L/min)	A_2 (L/min)	
9.1	37	14.8	0.382	35.20	1.79	9.0
13.2	44	17.5	0.431	26.42	17.58	13.1
19.8	60	18.7	0.464	29.92	30.08	19.6
27.0	78	20.7	0.479	32.89	45.11	26.7
28.2	79	22.0	0.487	27.83	51.17	27.9
36.2	101	22.5	0.490	36.62	64.38	35.8
48.9	128	27.4	0.512	33.76	94.24	48.4
64.4	160	32.5	0.519	10.61	149.39	63.7
81.3	192	34.2	0.539	-0.26	192.26	80.4
90.3	240	42.0	0.514	86.13	153.87	89.3

TABLE XIV. Cyclic and Steady Flow Results Calculated for a Constant Rate Coefficient*

Integrated Flowrate (L/min)	Average Penetration Fraction			Equivalent Steady Flowrate (L/min)	Flowrate Ratio
	Cyclic Flow	Steady Flow	Ratio		
9.0	2×10^{-5}	2×10^{-17}	1×10^{12}	32.2	3.58
13.1	1×10^{-4}	3×10^{-12}	3×10^{7}	38.2	2.92
19.6	0.0011	2×10^{-8}	5×10^{4}	50.9	2.60
26.7	0.0047	2×10^{-6}	2×10^{3}	64.9	2.43
27.9	0.0051	4×10^{-6}	1280	66.0	2.36
35.8	0.0145	6×10^{-5}	244	82.3	2.30
48.4	0.0340	0.0007	46	102.0	2.13
63.7	0.0675	0.0042	16	129.3	2.03
80.4	0.1046	0.0131	8	154.4	1.92
89.3	0.1423	0.0202	7	178.7	2.00

*$k = 17.6 \text{ s}^{-1}$, $V = 330 \text{ cm}^3$.

where for each workrate c and s are average values of 60/F for cyclic and steady flows, respectively. The penetration ratio is a function of k V and, therefore, a function of the penetration fraction (P_c or P_s). At the penetration fraction of most interest for determining cartridge service life, $P_c = 0.01$, and at a total breathing rate of 64 L/min (32 L/min through each of two cartridges of volume 165 cm³), k V = 4.962, P_s = 0.000087, and $P_c/P_s = 115$.

Since experiments were showing much smaller cyclic flow effects (see below), the simplest model was modified to include velocity dependence of the rate coefficient. Dietz, Blachly, and Jonas observed a nonlinear increase of the first-order rate coefficient with increases in linear flow velocity for methyl iodide removal by impregnated charcoals.[11] Others have also observed this phenomenon.[12-15] Including the velocity, v_R (cm/sec), dependence,

$$\ln P = -k \, v_R^n V/F$$

where k is a "true" constant. Wheeler has shown theoretically that the value of n should be 0.5 for the case of a mass transfer-limited rate.[5] Dietz et al.[11] obtained n values of 0.45 to 0.58 for their hexamethylenetetramine/iodine/sodium hydroxide-impregnated charcoals. The data of May and Polson[13] has been used to calculate the n values for a 5 per cent TEDA-impregnated charcoal shown in Table XV. These results show a relative humidity dependence for n, which ranged from 0.23 to 0.42.

TABLE XV. Rate Coefficient Velocity Dependence Calculated from the Data of May and Polson[a]

Percent Relative Humidity	Velocity Range (cm/s)	Coefficient[b] Range (s^{-1})	Log-Log Least Squares Fit		
			Number of Points	n	Correlation (r^2)
50	17.5-101.3	40.7-85.8	4	0.42	1.000
60	17.7-101.7	34.5-67.1	4	0.38	0.999
80	17.3-103.2	25.4-42.3	8	0.29	0.970
94	17.5-101.5	21.2-31.8	4	0.23	0.994

[a] Reference 13.
[b] kv^n.

The computer program was modified to include linear velocity dependence in the above penetration equation. Results shown in Table XVI were computed from n = 0 to 0.75, average F = 64 L/min (32 L/min through each of two cartridges), and k V selected so that P_c = 0.01. Computed equivalent (P_s = P_c = 0.01) steady flowrates are listed in the last column.

The value of n = 0.7 was used with the computer program and the parameters of Table XIII to calculate the results in Table XVII for ten workrates.

Cyclic/steady penetration ratios for P_c = 0.01 varied from 2.49 to 5.13. Steady/cyclic flowrate ratios for P_c = P_s = 0.01 ranged from 1.90 to 2.76, with all but the lowest two workrates in the range 2.0 ± 0.2. The flowrate ratios for the extreme case of n = 0 were also in this range for cyclic breathing rates of 48 L/min and above (Table XIV). The cyclic/steady flowrate ratio is less variable than the penetration ratio and is a possible way to take into account cyclic flow effects.

TABLE XVI. Computed Values for Selected Velocity Parameters*

Steady n	Average Penetration Fraction			Equivalent Steady Flowrate (L/min)
	Cyclic Flow	Steady Flow	Ratio	
0.00	0.01	8.7×10^{-5}	115	64.6
0.50	0.01	0.0019	5.3	58.9
0.67	0.01	0.0036	2.8	58.1
0.70	0.01	0.0040	2.5	58.6
0.75	0.01	0.0046	2.2	59.3

*Assumed 32 L/min through each of two cartridges and breathing curve corresponding to 64-L/min total flowrate.

TABLE XVII. Results Computed for a Velocity-Dependent Rate Coefficient* and One Percent Cyclic Flow Penetration

Integrated Flowrate (L/min)	Average Penetration Fraction		Equivalent Steady Flowrate (L/min)	Flowrate Ratio
	Steady Flow	Ratio		
9.0	0.00195	5.13	24.8	2.76
13.1	0.00254	3.94	31.2	2.38
19.6	0.00296	3.38	42.8	2.18
26.7	0.00318	3.14	56.0	2.10
27.9	0.00328	3.05	57.5	2.06
35.8	0.00335	2.99	72.9	2.04
48.4	0.00364	2.75	93.6	1.93
63.7	0.00375	2.67	121.2	1.90
80.4	0.00402	2.49	146.8	1.83
89.3	0.00378	2.65	169.2	1.89

*$k_r = k V_R^{0.7}$, V = 330 cm^3.

C. Experimental Study

A Scott Breathing Simulator (Scott Aviation Corporation, Lancaster, NY, Part No. 800116) was used to produce cyclic flow patterns. It is a dual-piston pump operated by a motorized cam to simulate a breathing pattern. The cam used in these experiments was designated 622 KGM. Total volumetric flowrate of air was adjusted with the pump speed control and measured downstream of the test bed with a dry test meter (Singer Model DTM-325) over at least 20 cycles. A series of check valves and a filtered air supply were used so that during half of the cycle backflow through the cartridge was prevented. This was to simulate one-way (inspiration) flow through a cartridge on a typical air-purifying respirator. A 20-L polyethylene bottle was used to mix methyl iodide from the permeation tube with the main airflow to smooth out possible variations in challenge concentrations due to cycling airflow. Total flow volume over a time corresponding to a full number of cycles (20-25) was measured with a dry test meter downstream of the test bed to determine average flowrate. Other than these modifications, the experimental apparatus was the same as that described in Sections III and VIII.

Test beds of 7.5-cm diam and 0.5 to 1.5-cm depth were packed with varying amounts of 5 percent TEDA-impregnated charcoal (Barnebey Cheney CU 2762) to obtain a range of penetration fractions at selected relative humidities (25-95 per cent) and ambient temperature (23 ± 1°C). Airflow was maintained at 32 L/min for both steady and cyclic (20.5 cycles/min) situations. After the test bed was equilibrated at the selected relative humidity, penetration fractions of methyl iodide were determined at 10-min intervals, alternating steady and cyclic flow for about 2-hour periods. The resulting measurements were averaged and a standard deviation was calculated. Alternating flow patterns for the same test bed eliminated the significant between-bed variations experienced in earlier experiments.

Results summarized in Table XVIII show definite penetration differences for the cyclic and steady flow cases. Cyclic flow penetration was greater by factors from 1.2 to 4.2. However, there was no consistent correlation of ratio with penetration fraction, contrary to the computer calculations. This suggests that the real situation is complicated by unknown factors (e.g., relative humidity, granule size, packing density, bed depth, etc.) having unknown effects.

Additional experiments were done with other charcoals to explore the generality of the cyclic flow effect. Comparisons of penetrations at cyclic and steady flow conditions (32 L/min) were done with several cartridges, canisters, and beds packed with 52-55g of charcoal (7.5-cm diam). The measured cyclic/steady penetration ratios and experimental conditions are given in Table XIX. Figure 22 shows breakthrough curves obtained for two 5% TEDA charcoals, one which showed a definite cyclic flow effect (1.6 times higher penetrations) and one which did not. Likewise for the other charcoals, some showed an effect and others did not. There was no obvious way to predict when the cyclic flow would give a higher methyl iodide penetration or how much higher it would be.

The significance of the cyclic flow effect is seen in Fig. 22 for the Scott charcoal. There appear to be two separate breakthrough curves differing by the factor of 1.6. The end-of-service life, defined as penetration reaching 1%, is 300 min for steady airflow but only 180 for cyclic airflow at 32 L/min. At 1.5% the differences are much greater (>>500 min vs. 260 min).

A maximum penetration at about 120 min was observed for the Willson/Inco 5% TEDA charcoal breakthrough curve (Fig. 22). This has been seen before for this and other charcoals and is attributed to bed heating by water vapor adsorption (see Section V.A.4.). Both the cyclic flow and steady flow penetration followed the same breakthrough curve.

D. Conclusions

Both the computational and experimental approaches to determining cyclic/steady penetration ratios led to the same conclusion: significant differences between breakthrough fractions at selected bed conditions (time of use, humidity, temperature, average flowrate, etc.) can exist for a variety of charcoals. The limited experimental and computed data acquired so far do not reveal the factors determining the existence or magnitude of this effect for any given charcoal. It is of great interest for a variety of respirator applications, not merely radioiodide removal, to identify these critical parameters. The existence of a cyclic flow effect impacts on manufacturing, testing, certification, approval, and use of chemical air cleaning respirator cartridges and canisters.

TABLE XVIII. Experimental Results of Cyclic Flow Study at 32 L/min
for One 5% TEDA Charcoal (BC CU-2762)

Relative Humidity %	Cyclic (C) or Steady (S) Flow	Average Penetration	Standard Deviation	Ratio (C/S)
25	C	0.025	0.003	4.2
	S	0.006	0.001	
	C	0.145	0.019	1.3
	S	0.112	0.010	
50	C	0.045	0.005	1.9
	S	0.023	0.002	
	C	0.076	0.013	1.7
	S	0.045	0.005	
	C	0.086	0.007	1.6
	S	0.055	0.012	
75	C	0.304	0.027	1.3
	S	0.238	0.022	
86	C	0.081	0.005	2.5
	S	0.032	0.003	
	C	0.067	0.008	3.5
	S	0.020	0.001	
95	C	0.512	0.012	1.2
	S	0.443	0.028	
	C	0.177	0.008	1.7
	S	0.101	0.007	

An immediate concern for this project is how to take into account cyclic flow effects on methyl iodide penetration. Three options have been considered:

1) Define end-of-service life of a canister or cartridge at a lower penetration fraction (e.g., 0.5% instead of 1%).
2) Double the testing airflow rate.
3) Use a breathing simulator pump for testing.

The first option would require identifying a constant or average cyclic/steady flow penetration factor. Tables XVIII and XIX show a significant range for this ratio. Furthermore, this option would penalize those manufacturers using charcoals which have no such effect and may hinder the development of more effective sorbents. For example, the Willson/Inco cartridge in Fig. 22 would have failed (>1%) entirely instead of having a service life of about 45 min.

The second option, doubling the steady airflow, is based on the computed results in Tables XVI and XVII, which show that this approximately compensates for cyclic flow at a variety of conditions. Unfortunately, the experimental results reveal a more complicated situation. This option also has the same objections as the first. Humidity effects would be more than doubled by doubling the airflow rate. And modifications would be required for the existing testing apparatus. The third option also would require modifying the existing apparatus by 1) inserting a breathing simulator pump and one-way valves between the filtered air supply and the humidity chamber, 2) inserting a 20-L buffer volume between the methyl iodide generator and the test bed, and 3) changing the method of average flow rate monitoring (volumetric average instead of an instantaneous flowmeter readout). The question remains as to

TABLE XIX. Cyclic/Steady Flow Penetration Ratios for a Variety of Charcoals.

Charcoal Source and Type[a]	Original Unit	Packed Bed[b]	Preconditioned (% RH)	Run Relative Humidity (%)	Number of Comparisons	Average Cyclic/Steady Penetration Ratio
Norton OV Cartridge, (7500-1)	X		No	75	2	1.0 ± 0.1
		X	No	85	2	1.0 ± 0.1
MSA OV Cartridge, GMA (44.35)	X		35	50	3	1.3 ± 0.1
MSA OV Canister, GMA-C	X		50	85	3	1.0 ± 0.1
MSA Canister, GMR-I, 5% KI$_3$		X	No	85	4	1.0 ± 0.1
MSA Canister,[c] 5% KI$_3$, 2% TEDA		X	No	85	4	1.7 ± 0.2
MSA Canister,[c] 5% TEDA		X	95	95	4	1.0 ± 0.1
Scott Canister, 5% TEDA (600252-75)		X	No	85	7	1.6 ± 0.1
		X	85	95	2	1.7 ± 0.2
Barnebey Cheney 5% TEDA (CU-2762)		X	No	85	1	1.9 ± 0.2
		X	85	85	4	1.8 ± 0.2
Willson/Inco Cartridge,[c] 5% TEDA (Lot B)	X		No	85	2	1.3 ± 0.1
	X		95	95	1	1.3 ± 0.1
Willson/Inco Cartridge,[c] 5% TEDA (Lot V)	X		No	85	4	1.0 ± 0.1
		X	No	85	1	0.9 ± 0.2
		X	No	85	2	1.2 ± 0.2

[a]Impregnants and amounts based on manufacturers' information.

[b]55 g in 7.5-cm-diam bed.

[c]Prototypes supplied by manufacturers.
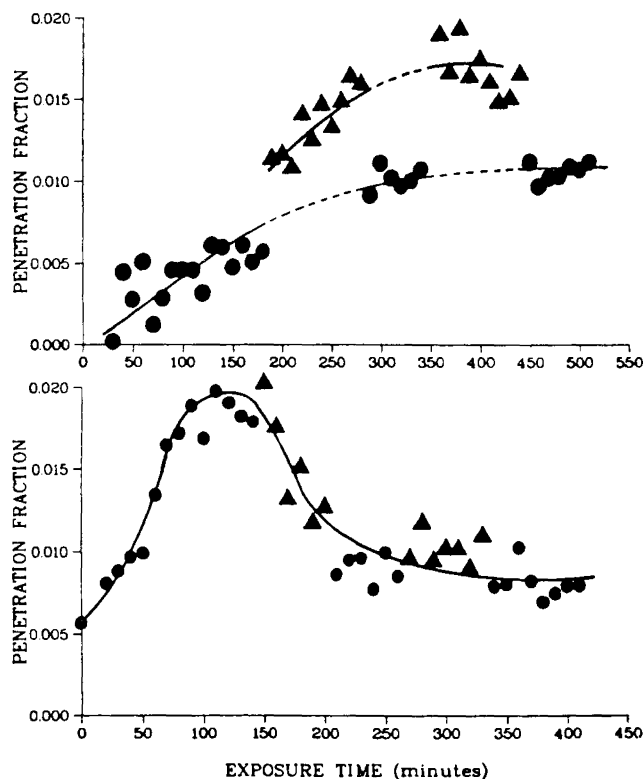
Fig. 22. Breakthrough curves alternating steady flow (●) and cyclic flow (▲) for two 5% TEDA charcoals. Upper curve: Scott (55g, 7.5-cm diam). Lower curve: Willson/Inco (52g, 7.0-cm diam). 85% RH, 32 L/min.

which breathing curve parameters to use and how critical are they to the final penetration results.

The third option appears to be the most desirable, at least until more data are developed. The selection of parameters would be no more arbitrary than the selection of an average breathing rate, usually 64 L/min, for testing. The data of Silverman et al.[9] are available to make these selections less arbitrary.

VII. DESORPTION OF TEDA FROM IMPREGNATED RESPIRATOR CHARCOALS

A. Background

Data reported earlier (Section IV.) have shown that TEDA $[N(C_2H_4)_3N]$ is an effective charcoal impregnant for the trapping of organic forms of radioiodine from air. Four canister manufacturers have plans to continue or begin packing their radioiodine canisters with 5% by weight TEDA-impregnated charcoals.

This compound has a normal boiling point of 174°C but is known to sublime readily at room temperatures. The volatility of the pure crystals has brought up the question of the volatility of TEDA impregnated in activated charcoals. The reason for this concern is the possible release of significant amounts of this amine of unestablished toxicity from sorbents, especially in air-purifying canister applications.

There are no toxicological data available for TEDA; however, TEDA belongs to the class of organic aliphatic amines, many of which have been shown to be toxic. Threshold Limit Values (1982)[16] for similar amines are

	mg/m³	ppm
Ethylamine	18	10
Diethylamine	30	10
Triethylamine	40	10
Etylenediamine	25	10
Diethylenetriamine	4	1

By structural and functional similarities, TEDA can be considered moderately toxic with a concern level of 1 ppm or greater. Vapor pressures measured over the range 50-110°C have been extrapolated to give 0.58 torr at 25°C. However, there was no information available on the volatility of desorption rate of TEDA impregnated on activated charcoal.

To supply data to answer these concerns we have measured TEDA desorption from commerical impregnated charcoals.

B. Apparatus and Procedures

The apparatus used for measuring TEDA desorption is diagrammed in Fig. 23. The detector for TEDA in air was a photoionization detector through which air samples are drawn. Detector response was amplified and attenuated with the electrometer component and recorded on a strip chart. The detector was calibrated by sublimation of TEDA crystals at 30.0°C into flowing air. Weight loss rate and diluent air flow rates were measured and used to calculate calibration concentrations.

A gas chromatograph oven was used to control temperatures (70-120°C) of test beds, the air entering them, and the sampling lines. Charcoal samples of 1-4 cm³ volume were packed into stainless steel tubes and held in place by glass wool. This resulted in bed depths of 1.4-5.6 cm.
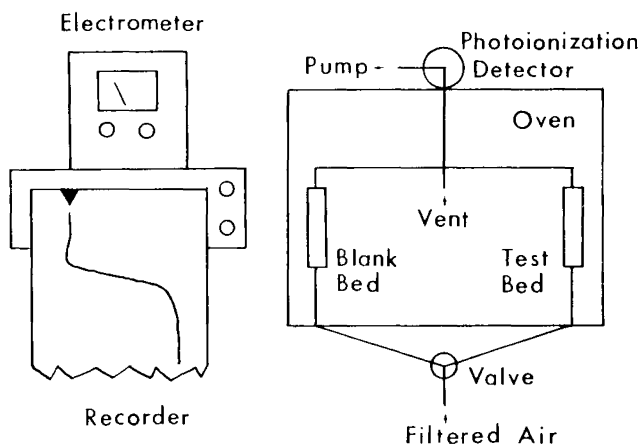
29

Fig. 23. The apparatus used for studies of TEDA desorption from charcoals.

Compressed air from cylinders was passed through a filter of activated charcoal before use. It was quite dry initially. For higher humidity studies a fraction or all of the airflow was passed through the headspace of a water reservoir. Resulting relative humidities were determined using a dew point hygrometer.

Two charcoal beds were placed in the oven in such a way that the airflow could be switched by a valve to either. One bed contained unimpregnated activated charcoal and the other the test charcoal. Air flowed through the former to the detector during oven equilibration. Upon reaching a steady detector baseline signal the airflow was switched to the test bed. An upscale signal shift occurred.

Such signal shift measurements were repeated at the same conditions, often using a fresh bed. At least three temperatures were used for each charcoal. Signal shifts recorded on the strip were measured with a ruler, multiplied by attenuation factors, and compared with calibration curves to get TEDA concentrations (mg/m^3).

Three kinds of TEDA-impregnated charcoals from 5 commercial sources have been studied for TEDA desorption. Four of these contained a 5% by weight loading of TEDA. Another had a mix impregnated—2% TEDA and 5% KI$_3$. And one charcoal was impregnated 5% with a new compound called "C-Alkyl TEDA" or "Heavy TEDA," which has an alkyl group, such as ethyl, added to one or more of the ethylene bridges. The main objective is to make a higher molecular weight compound with lower volatility. The added alkyl group should not affect the reactive nitrogens. Another charcoal, impregnated with 5% KI$_3$ only,

was also tested under the same conditions to provide a reference and to identify any iodine release upon heating.

C. Results and Conclusions

Since breathing through a respirator cartridge is not at a fixed, constant flow rate, we first studied the effect of airflow velocity. The results shown in Fig. 24 for one of the 5% TEDA charcoals show the absence of effect of flow rate over the range 1.6—6.8 cm/s. This implies that the air was TEDA saturated and the volatilization rate was rapid.

Since bed depths also vary for different designs of cartridges and canisters, we also varied this parameter. Again, no effect was observed (Fig. 25). This result, combined with no velocity effect, implies that the air passed through the impregnated charcoal was saturated with TEDA vapor, in other words, at equilibrium.

Humidity was also varied over a range from 5% to 99% RH at 25°C. Dew points of -18 ± 4°C, 15.1 ± 1.4°C, and 24.8 ± 0.7°C were measured at test conditions of 70°C, 90°C, and 110°C. At 25°C these dew points correspond to relative humidities of 4%, 54%, and 99%. Increasing water vapor concentrations decreased the response of the photoionization detector. When this response change was taken into account, no detectable changes in TEDA desorption rates were
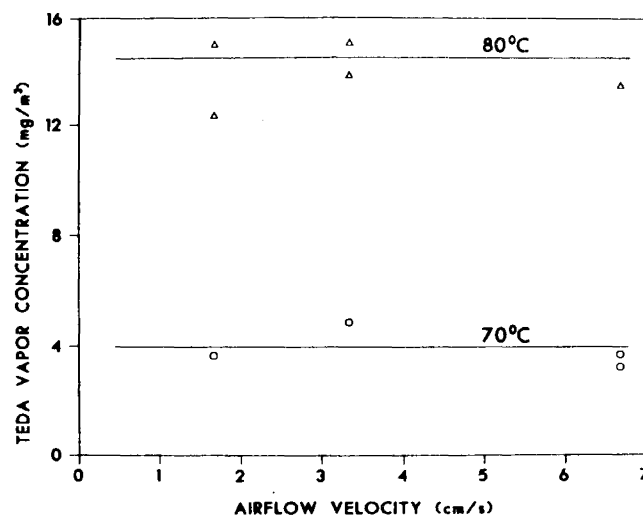

Fig. 24. Effect of airflow velocity on TEDA vapor desorption concentration at two temperatures.
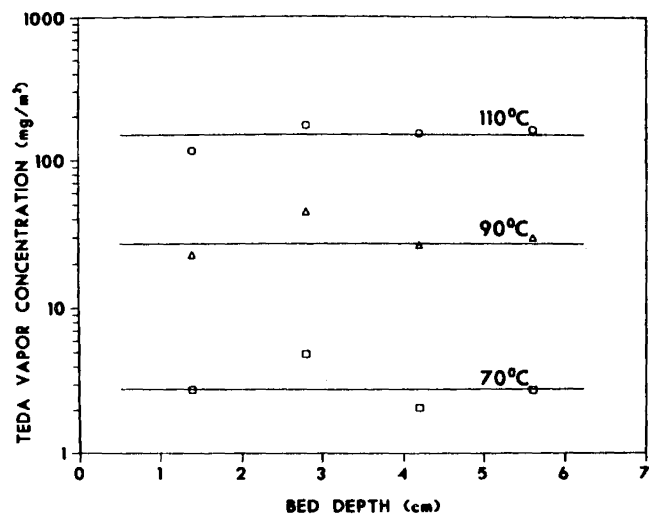
Fig. 25. Effect of bed depth on TEDA vapor desorption concentration at three temperatures.

observed over these ranges of experimental parameters. Only dry air was used in other experiments.

For the ordinary 5% TEDA charcoals, desorption concentrations varied widely (Fig. 26). For example, at 90°C the range was 4 to 48 mg/m³. The mixed impregnant charcoal gave a value of 6 mg/m³, at the lower end of this range. No iodine or other desorbing vapors were detected from the 5% KI_3 (only)-impregnated charcoal up to 120°C.

The differences in desorption rates for the four 5% TEDA charcoals are significant. They may be due to impregnation methods or due to the charcoal base

characteristics (activity, surface area, pore structure, pore size, etc.).

Fig. 27 shows a comparison of desorption concentrations of TEDA and Heavy TEDA. Both charcoals were from the same manufacturer, who said the same base charcoal was used. Note that the Heavy TEDA desorption was about 10 times lower than that for TEDA. This is what was expected. Efficiencies for trapping methyl iodide have been found to be similar for both impregnants.

As we have seen from Figs. 26 and 27, Clapeyron equation plots (log C versus 1/T) are linear. This was expected from analogy with evaporation and sublimation processes. The slopes of these plots are directly proportional to heats of desorption. The range of measured heats of desorption is shown in Table XIX. The average is 25 kcal/mol, much higher than the 14-kcal/mol heat of TEDA sublimation from pure crystals. The difference is due to TEDA-charcoal interactions. The 25-kcal/mol average corresponds to a doubling of desorption concentration with every 5°C rise in temperature.

Another use of the Clapeyron equation plots is extrapolation to lower temperatures where TEDA desorption is too small to measure directly. Such extrapolations to 25°C yielded the TEDA vapor concentrations shown in Table XX.

The most important conclusion from these studies is shown in this table: the maximum desorbed TEDA vapor concentration at 25°C was calculated to be 0.12
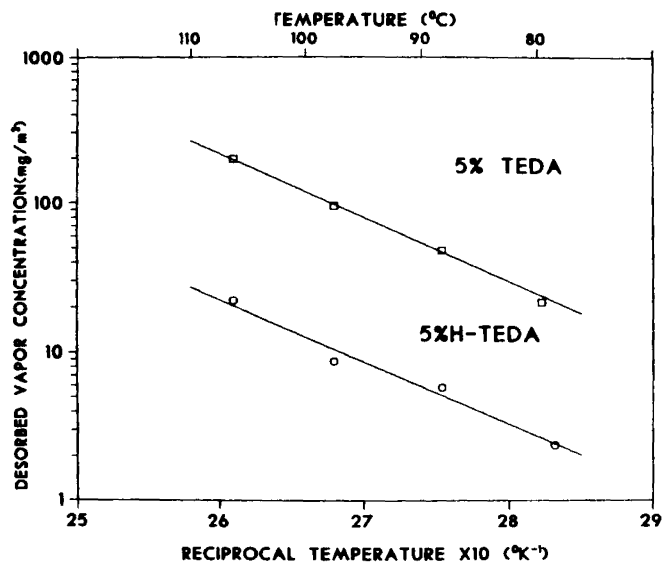

Fig. 26. Clapeyron plots for TEDA vapor desorbed from 5% TEDA charcoals into flowing air.

Fig. 27. Clapeyron plots for vapor desorbed from a "normal" TEDA charcoal and a "heavy" TEDA charcoal.

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mg/m^3. No toxicological data are available for TEDA, but this is well below the Threshold Limit Values for similar amines, which range from 4 mg/m^3 for diethylenetriamine to 40 mg/m^3 for triethylamine.[16] Therefore, there should be no toxic hazard from using TEDA-impregnated charcoals up to the 5% by weight level.

VIII. TEST APPARATUS DEVELOPMENT

During the course of this project several experimental apparatuses have been built and used for challenging and testing sorbent beds, canisters, and cartridges. The two earliest apparatuses have been described elsewhere[1] and in Section III and Fig. 2 of this report.

After experiments with radioiodine were completed the analytical instrumentation for sampling and measuring methyl iodide in air was redesigned and rebuilt. Goals were compactness, simplicity, automation, and low cost. Sampling valves and loops were mounted in a heat valve oven (Carle Instrument Inc., Model 4300) to overcome the problem of water condensation during high humidity tests. A more efficient gas chromatograph column packing (Porapak Q-S) for separating methyl iodide from air was found. This made possible smaller columns that also could be mounted in the valve oven and eliminated the need for a separate large gas chromatograph. Two sampling valves were ganged by gears for simultaneous sampling upstream and downstream of a test canister. This eliminated the need for interpolating between peak areas of alternate samples when making comparisons. Simultaneous sampling requires different times of arrival

of methyl iodide peaks to the electron capture detector (Valco Instrument Co., Model 140B). Each sample passes through its own column (1.0 or 0.6 m long) with its individually controlled carrier gas flow rate to accomplish this. A third valve momentarily vents the effluent from both columns to keep air from passing through the detector. A downstream sampling loop 10 times larger than the upstream one gives methyl iodide peaks closer together in size during the earlier stages of bed penetration. These improvements, the substitution of a dew point hygrometer (EG&G, Model 911) for a resistance type hygrometer, and high output generation of methyl iodide from permeation tubes were major steps to the final test apparatus design.

The final test apparatus, pictured in Fig. 28, contains in one unit on wheels (1) air flow, humidity, and temperature control, (2) methyl iodide generator, (3) sampling pumps and automatic samplers, (4) dual column gas chromatograph with sampling valves and electron capture detector, and (5) data integrator with chart recorder. It requires for operation (1) compressed air, (2) distilled water, (3) argon/methane carrier gas, and (4) electric power. Two Respirator Cartridge/Canister Test Systems have been built, one for our use and one for NIOSH. The capabilities are

Temperature: Ambient—40°C
Dew Point: ≤25°C
Airflow Rate: ≤100 L/min (Constant)
Penetration Fraction: ≥0.001
Challenge Concentration: ≥0.1 ppm CH$_3$I

Advantages of having two units include the capabilities to confirm testing results, to help NIOSH with

TABLE XX. Triethylenediamine Desorption

Charcoal Impregnants	Heat of Desorption (kcal/mol)	Vapor Concentration at 25°C (mg/m^3)
5% TEDA	19.6	0.12
	23.2	0.032
	31.6	0.0003
	26.6	0.0036
2% TEDA +5% KI$_3$	28.5	0.0011
5% H-TEDA	19.0	0.016

troubleshooting, and to provide backup in case of major breakdowns.

A detailed and descriptive operations manual for this test system has been written[17] and will not be repeated here. The table of contents is given in the Appendix of this report to illustrate the information provided to the NRC and NIOSH. It includes diagrams, photographs, specifications, instructions, precautions, and component manuals.

The first draft was subjected to an evaluation suggested by Donald Campbell of NIOSH. Five technicians and staff members not familiar with the apparatus were given the instructions and apparatus and asked to perform a cartridge test. These evaluations revealed some unclear and out-of-sequence instructions and provided useful suggestions for improvements. The final draft was once again evaluated in this way to make sure the changes had been effective.

In the light of the discovery of significant cyclic flow effects, this apparatus and manual will need to be modified to include a breathing simulator pump and associated parts (Section VI.D.).

IX. DEVELOPMENT OF APPROVAL CRITERIA FOR RADIOIODINE CANISTERS

A. History

Preliminary proposals for approval (acceptance) criteria were presented and discussed at NRC and NIOSH in February 1981. Testing conditions proposed were 0.3-ppm CH^3I challenge at 64 L/min, 25°C, and two humidities, 50% and 85% RH, for freshly opened (not equilibrated) canisters. Acceptable service lives proposed were 8 hours at 50% RH and 3 hours at 85% RH, which extrapolates to 2 hours' minimum at 100% RH.

Further discussions and additional experiments led to a revised set of proposals in April 1981. Testing at a higher temperature (30°C) was added. Close control of RH (±2%) and T (±1°C) was required. A reproducibility requirement of ±10% on service life measurements was proposed, as was identifying service life in terms of total breathed volume, instead of in terms of time of use. A knowledgeable industrial hygienist or supervisor would then be able to calculate a service life based on T, RH, and work level. These ideas were discussed over the next several months with various interested parties.

In November 1981, meetings were held in Rockville, MD, with NRC and NIOSH personnel to refine some of these proposals. We identified probable maximum use conditions (90°F or 32°C; 100% RH). The proposal of user discretion in setting service life based on data to be provided on work rates and breathing volumes was rejected, since it was felt that user knowledge was often inadequate and the radioiodine has no warning properties in case of overuse. We identified some additional use restrictions (interferences, storage, maximum concentration, facepiece performances, etc.) that must be part of the approval. Another revised set of testing conditions (30°C and 25°C at 50% RH and 85% RH) was proposed. Steps necessary for follow-up of this meeting were agreed upon.

The ANSI Ad Hoc Respirator Testing and Approval Subcommittee meeting in Los Alamos in December 1981 was another good opportunity to discuss relevant subjects with representatives from many industry and government organizations.

Approval requirements were modified to allow several classes of approvals by humidity range (high and moderate) and minimum service life for 1% penetration:

Designation	Minimum Service Life
High Humidity, Half Hour	30 minutes at 30°C and 100% RH
High Humidity, One Hour	60 minutes at 30°C and 100% RH
Moderate Humidity, One Hour	60 minutes at 30°C and 75% RH
Moderate Humidity, Two Hours	120 minutes at 30°C and 75% RH

The reasons for more than one class of approvals are (1) to allow some current canisters to be approved and (2) to provide incentive for manufacturers to develop improved canisters for higher classes (i.e., High Humidity, Eight Hours) of approval.

The approval schedule should also include periodic testing to verify shelf life claims of manufacturers.

Additional use restrictions that must be put into the regulations for use and on approval labels include

1. Not to be used in the presence of organic solvent vapors.

2. To be stored in sealed, humidity barrier packaging in cool, dry environments.

3. Service life is to be calculated from the time of unsealing including periods of non-exposure.
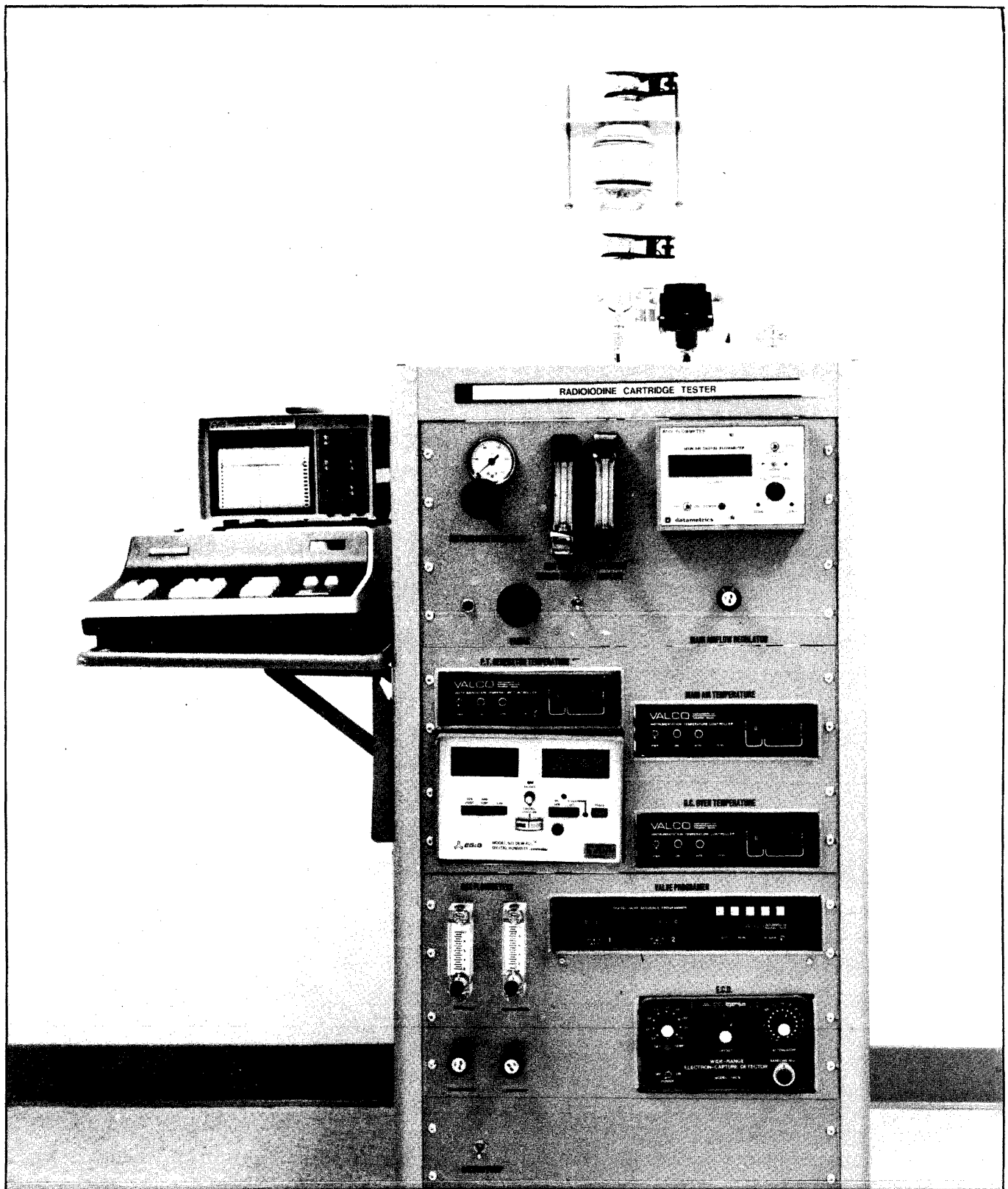
Fig. 28. Apparatus developed for testing radioiodine cartridges and canisters using methyl iodide.

4. To be used with a facepiece capable of providing protection factors greater than 100, as determined by testing with a HEPA filter and aerosol.

5. Not to be used in challenge concentrations of total organic iodide, including nonradiometric iodide, greater than 1 ppm.

Also in December 1981, NIOSH initiated by internal memo procedures for establishing an approval schedule on the following conditions: (1) NRC will first establish administrative controls, (2) Los Alamos will provide NIOSH with the testing equipment, (3) approval will be for methyl iodide, the testing agent, only. NRC then can allow use for other iodine vapor species based on Los Alamos and other data.

B. Current Recommendations

The current recommendations for radioiodine cartridge and canister testing conditions and acceptance criteria are summarized in Table XXI. Also listed are the current criteria from the U.S. Code of Federal Regulations[4] for organic vapor canisters for comparison. The latter are called current recommendations, rather than final ones, since discussions will continue in the regulatory process.

Testing should be done at two relative humidities and at 64-L/min cyclic airflow for canisters and 32-L/min cyclic airflow for cartridges used in pairs. Challenge concentration should be 1-ppm methyl iodide, although this is not a critical parameter. Units are to be tested as received and freshly opened. Tests at 25°C were eliminated since 30°C represents a more severe con-

dition and provides a safety factor for use at less severe conditions. The maximum testing humidity was reduced from 85% to 75%, since at 30°C the latter corresponds to a dew point of 25°C, the maximum practically attainable without placing the testing apparatus in a warm (>25°C) room or environmental chamber. Linear extrapolation of results to 100% at 30°C using log service life versus log RH plots is recommended. Triplicate instead of duplicate service life determinations will better define reproducibility and the need for additional testing.

X. ASSISTANCE TO NIOSH IN ESTABLISHING A TESTING AND CERTIFICATION PROGRAM

All data, conclusions, and proposals generated from this project have been shared with the NIOSH TCB from the beginning. This has been accomplished by visits to one another's laboratories, in-person and telephone conversations, trip reports, progress reports, public presentations, and publications.

A final test apparatus described in Section VIII was built and shipped to the NIOSH TCB for their use in certification testing. An extensive operation manual was prepared and also given to NIOSH. Follow-up visits to the Morgantown, WV, laboratories are planned to help NIOSH in setting up and using this equipment. Los Alamos will also be available for telephone consultations, as needed. The duplicate apparatus at Los Alamos will be useful for identifying and correcting problems NIOSH may encounter, as well as for performing interlaboratory comparisons of test results.

TABLE XXI. Testing Conditions and Acceptance Criteria for Organic
Vapor Chin-Style Gas Mask Canisters

Test Parameter	CFR Title 30, Part 11.102	Radioiodine Proposal
Vapor	CCl_4	CH_3I
Concentration	5000 ppm	1 ppm
Relative Humidity	50 ± 5%	50; 75% (±2%)
Temperature	25 ± 2.5°C	30 ± 1°C
Total Airflow		
As Received	64 L/min	64 L/min Cyclic Flow
Equilibrated	32 L/Min	
Equilibration	3-As Received	All As Received
(6 H at 64 L/min)	2-At 25% RH	3-At 50% RH
	2-At 85% RH	3-At 75% RH
Maximum Penetration	0.1% (5ppm)	1% (0.01 ppm)
Minimum Service Life	12 min	30 min at 100% RH*
		60 min at 75% RH

*Extrapolated from 50% and 75% RH.

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