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ESTIMATION OF THE RESIDUAL ADSORPTION CAPACITY — OF CHARCOAL FILTERS

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**DEPARTMENT OF NATIONAL DEFENCE
CANADA**

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**ESTIMATION OF THE RESIDUAL ADSORPTION CAPACITY
OF CHARCOAL FILTERS**

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J.A. Wheat and J.C. Hyde

Pilot Plant

NBC Defence Division

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ABSTRACT

A method has been developed for estimating the residual adsorption capacity of charcoal filters. Since the method is non-destructive and uses a low concentration of a non-toxic gas, it can be applied to installed collective protectors. It can also be used as a non-destructive, laboratory test method for protective mask canisters or other small charcoal filters.

In laboratory experiments, beds of charcoal were challenged with Freon-113 and the time required for the exit concentration to reach 0.005% of the inlet concentration was determined. It was demonstrated that break time was related to the amount of material adsorbed on the charcoal and also to the length of time in service.

Break time also depended upon flow rate, inlet concentration, temperature, relative humidity and bed depth. Equations were developed to relate the break time of beds of fresh charcoal with these five variables. To estimate the residual capacity of a filter, its measured break time would be compared with the break time calculated for a bed of fresh charcoal. A graphical method of carrying out the calculations is given.

RÉSUMÉ

Une méthode a été développée afin d'estimer la capacité rémanente d'absorption des filtres au charbon. Puisque la méthode est non-destructive et utilise une basse concentration de gaz non-toxique, elle peut-être appliquée aux protecteurs collectifs déjà installés. Elle peut-être aussi employée comme méthode non-destructive dans un laboratoire pour vérifier le dispositif filtrant du masque protecteur ou tout-autres filtres contenant du charbon.

Dans des essais de laboratoire, des lits de charbon furent soumis à des gaz de Freon-113 et le temps requis pour que la concentration de sortie atteigne le niveau de 0.005% de la concentration pénétrante a été déterminé. Il a été démontré que le temps de cassure avait une relation au montant de matériel absorbé par le charbon et au temps en remise.

Le temps de cassure dépendait aussi au taux d'écoulement, à la concentration pénétrante, à la température, à l'humidité relative et à la profondeur du lit. Des équations mathématiques ont été dérivés pour relier le temps de cassure d'une quantité fraîche de charbon à ces variables.

Pour estimer la capacité rémanente du dispositif filtrant, le temps de cassure déterminé par essai est comparé au temps calculé d'une quantité fraîche de charbon. Une méthode graphique pour simplifier les calculs est donnée.

INTRODUCTION

Filters containing beds of activated, gas-adsorbent charcoal are used in air flow systems to remove noxious vapors from the air. Applications include removal of odorous and other vapors from air in air-conditioning systems, containment of radioactive vapor in nuclear reactors (1), and collective protection against CW agents, particularly of spaces used by the military including vehicles and ships. For the last two applications, the adsorption capabilities of the charcoal are required only in the event of an accident or a CW attack. However, air may be passed through the filters continuously once they are placed in service. Contaminants in the air are thus adsorbed on the charcoal reducing its available adsorption capacity. It is important to know the residual capacity of installed charcoal filters so that they can be replaced with new ones to ensure adequate protection against accident or attack. This report describes a laboratory investigation to develop a non-destructive method of estimating the residual adsorption capacity of installed charcoal filters.

One basic method for estimating the adsorption capacity of a charcoal bed is to challenge it with a test gas until it is detected at a pre-determined concentration in the effluent from the filter. Since the test must be non-destructive, the test gas has to be non-toxic and must either desorb from the charcoal or not appreciably reduce its adsorption capacity. The penetration of a test gas through a charcoal filter depends upon many factors including properties of the charcoal, shape and size of the bed, flow velocity, inlet concentration, temperature, relative humidity and, of course, properties of the gas. A strongly adsorbed test gas will take a long time to penetrate the bed and will not readily desorb following the test. A less strongly adsorbed gas will give a shorter testing time and will deposit a smaller amount of material on the charcoal but will be more sensitive to the presence of moisture.

The same basic method of challenging a filter installation with a test gas can also be used to detect leaks through charcoal filters or through seals around the filters. The Atomic Energy Commission at its Savannah River Laboratory (1,2,3) employed halogenated hydrocarbons as tracers for this purpose so that the electron capture type detector which is very sensitive to halides could be used. At first (1) Freon-12 (F-12) was employed as a test gas. Later (2,3), F-112 was found to be the best of the compounds examined for this particular purpose. It could be detected at a concentration of 0.001 ppm and was found to be affected less by moisture and flow velocity than the others. Properties of several halogenated hydrocarbons mentioned in this report are given in Table I.

TABLE I

Physical Properties of Halogenated Hydrocarbons

Formula	CCl_2F_2	CHCl_2F	CCl_3F	$\text{CCl}_2\text{F}-\text{CClF}_2$	$\text{CCl}_2\text{F}-\text{CCl}_2\text{F}$
Freon designation	F-12	F-21	F-11	F-113	F-112
Formula weight	120.9	102.9	137.4	187.4	203.9
Melting point, °C	-158	-135	-111	-35	23.8
Boiling point, °C	-29.8	8.9	23.8	47.6	92.8
Liquid density 30°C, g/ml	1.292	1.354	1.464	1.553	1.634

This Freon-112 method for detecting leaks was used by DREO to determine the effects of shock and vibration on 1000 cfm charcoal filters. Subsequently, using laboratory test beds, the work to be described in this report was started in order to adapt the leak detection method to the estimation of residual life of installed charcoal filters.

Freon-12 had been suggested (4) for this purpose but from the AEC investigations described above the higher boiling Freons, such as F-112, would be expected to be more suitable. Following some preliminary investigations with F-112, F-113 was found to be a more suitable test gas for measurement of adsorption capacity because it gave more convenient penetration times and yet was still more strongly adsorbed than water.

Stamulis and Thompson of the Naval Research Laboratory described (5) a test method in which a filter was challenged with a short pulse of carbon dioxide instead of a continuous flow of tracer gas. The emerging pulse was flat and drawn out for a fresh bed but was sharp and short, like the inlet pulse, for an exhausted bed. Thus, the pulse height was related to the residual capacity of the charcoal filter. In experiments to be described later, the pulse technique with halogenated hydrocarbons did not appear to be as promising as the continuous injection method.

The experimental technique adopted, therefore, was to subject test beds to a continuous flow of known concentrations of Freon-113 in air at controlled flow rate, temperature and relative humidity, and to measure the outlet concentration as a function of time from the start of injection. The time for the outlet concentration to reach 0.005% of the inlet concentration was defined as the break time. Equations were then developed to relate break time with flow parameters and bed depth.

EXPERIMENTAL

CHARCOAL

The charcoal used in this investigation was Pittsburgh Activated Carbon Company Type BPL granular carbon. This is a vapor phase type charcoal made from bituminous coal. The following physical properties were taken from the manufacturer's data sheet.

Total surface area, N ₂ , BET method	1050-1150 m ² /g
Carbon tetrachloride adsorption, wt %	60-65
Pore volume	0.8 cm ³ /g
Bulk density	0.5 g/cm ³
Particle density (Hg displacement)	0.8 g/cm ³
Real density (He displacement)	2.1 g/cm ³

This material was screened using an 18 inch vibrating separator and the fraction passing 10 mesh but retained on 20 mesh was used in the experiments. The screen analyses given in Table II were determined with Tyler series test sieves and a Ro-Tap shaker. The surface volume average particle size of batch No. 1 was 1.02 mm and of batch No. 2 was 0.96 mm. This average particle size is defined (6) by the equation

$$d_{sv} = \frac{\sum fd^3}{\sum fd^2} = \frac{1}{\sum w/d} \quad (1)$$

where f is the number of particles of diameter d and w is the weight fraction of diameter d . It is related to the ratio, S_v , of particle surface area to particle volume by

$$S_v = \frac{\text{Surface area}}{\text{Particle volume}} = \frac{6}{d_{sv}} \quad (2)$$

TABLE IIScreen Analyses of Charcoal Used in Test Beds

Mesh Size Range (Tyler Series)	Weight percent	
	Batch 1	Batch 2
- 10	0.4	0.0
10 - 14	30.4	25.2
14 - 20	55.0	53.0
20 - 28	13.0	20.0
28 - 35	1.0	1.4
35 -		0.4

APPARATUSTest Bed

A refillable, screw-top canister, which was 4-1/8 inches inside diameter and deep enough to accommodate up to 1.5 inches of charcoal, was used for the test bed. The charcoal was retained as in the Canadian protective mask canister by a pad of a bulky non-woven fabric and a perforated diaphragm on both the top and bottom of the bed. The top diaphragm was kept in place by one of a set of sleeves of varying depth to serve as a spacer between the diaphragm and the screw top.

Air Supply

Air was supplied by a sliding vane compressor and the flow rate measured by a calibrated rotameter. Relative humidity was regulated, as shown in Fig. 1, by passing a portion of the air through either a silica gel drying chamber or a water bubbler and then recombining with untreated air. Wet and dry bulb thermometers were used to measure relative humidity of the air, either after being put through the test bed or else by-passed around it. Air temperature was adjusted by passing the air through a coil immersed in a water bath.

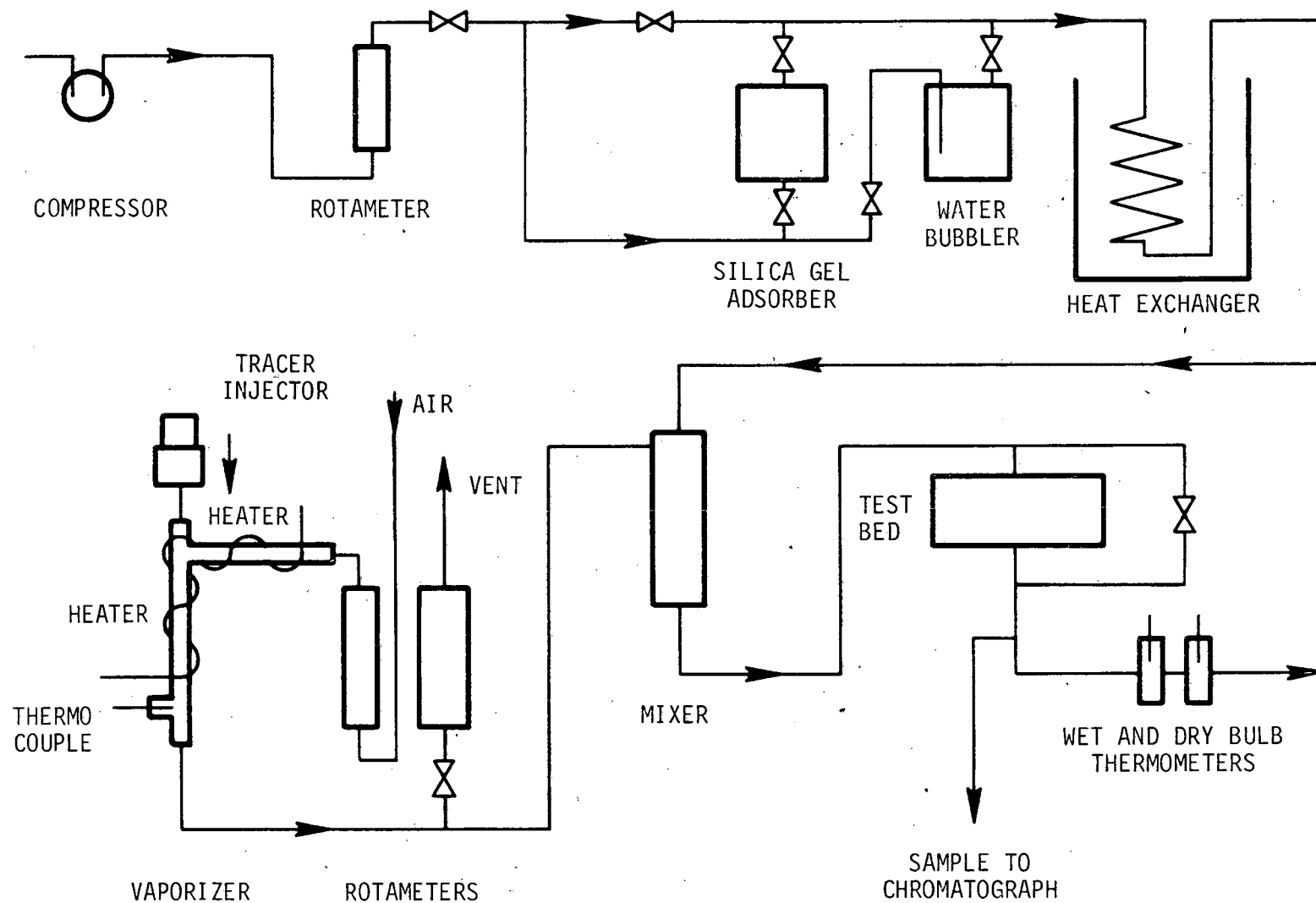


Fig. 1. Diagram of apparatus used to measure break time of charcoal beds.

Tracer Injector

Liquid tracer was metered into a vaporizer from a hypodermic syringe in a Portable Infusion-Withdrawal Pump (Harvard Apparatus Company). The vaporizer consisted of a 15 cm length of 9 mm OD glass tubing mounted vertically. A serum bottle rubber cap stopper was fitted over the top end of the vaporizer and the hypodermic needle of the injector syringe inserted through it. A small amount of glass wool was placed in the vaporizer to prevent any liquid from dropping through the vaporizer. A metered air flow of 1.5 liters/min entered the vaporizer through a side arm near the top. The side arm and the vaporizer were insulated and heated electrically to vaporize the injected liquid and to prevent freezing at the hypodermic needle when using Freon-112. Power to the heater was regulated with a variable transformer to give an air temperature at the bottom of the vaporizer just above the boiling point of the Freon being injected.

A portion of the Freon-containing air was vented through a rotameter and the balance mixed with the main air stream. The flow to the main air stream was the difference between the flow to the vaporizer and the vented flow. The volume of Freon vapor was negligible compared to the volume of air. Desired Freon concentration in the air to the test bed was obtained by varying the motor speed of the injection pump, the size of the syringe and the fraction of the vaporizer air diverted to the main air stream.

Detector

A gas chromatograph with an electron capture detector (Varian Aerograph Model 600D) was used to measure test gas concentration down stream from the test bed. The electron capture detector is very sensitive to halogens while being relatively insensitive to hydrocarbons. It is also sensitive to oxygen, so it was preceded by a chromatographic column to separate oxygen and Freon. Dry nitrogen carrier gas was passed continuously through the column and the detector. A sample stream of air was continuously drawn by vacuum through a one milliliter loop on a sample valve. By operating the valve this one milliliter sample was injected into the carrier gas.

The chromatographic column was a five foot length of 1/8 inch stainless steel tubing with a packing of 5% SC30 Silicone on 60/80 Chromasorb W housed in a thermostated oven. Column temperature and nitrogen pressure were adjusted to provide separation of the oxygen and Freon components of the sample. With Freon-113, an oven temperature of 40°C and a nitrogen pressure of 8 psi provided adequate separation of the peaks and cleared the column fast enough to allow samples to be injected at one minute intervals. The chromatograph was operated at an attenuation such that the standing current was nearly full scale of the recorder on a 1 mv range. At this setting, the entire oxygen peak was on scale and Freon-113 concentrations as low as 0.005 ppm could be measured.

METHODS

Testing Procedure

For each test, fresh charcoal was measured out volumetrically and placed in the screw top canister. Air was brought to the desired temperature and relative humidity with the test bed by-passed, and was then put through the charcoal until relative humidity became constant. Flow of air and Freon to the vaporizer were adjusted and discharged through the vent along with some back flow from the main air stream to ensure that no Freon went to the test bed. Chromatograph sampling was started and, if no peaks were present in the Freon position, the vent valve on the vaporizer was closed rapidly to divert the required portion of Freon-loaded air into the main air stream. Air was sampled at 1 min intervals until Freon peaks indicated a downstream concentration greater than 0.005% of the inlet concentration.

Charcoal Loading

To produce known amounts of loading, liquid toluene was injected into an air flow of 1.5 l/min heated to 70°C to give a concentration of 230 ppm when mixed with a main air streamflow rate of 6 cfm. Toluene injection was not started until the charcoal was in equilibrium with air at 25°C and 30% relative humidity.

Standardization of the Detector

In addition to the sampling valve, the chromatograph was equipped with an injector port and vaporizer so that liquid samples could be injected and vaporized into the carrier gas. These samples were injected into the vaporizer with a syringe through a rubber septum.

At the conclusion of each test, a standardization was carried out by injecting 1, 2, 3, 4, 5 and 6 microliter samples of a standard solution containing 3×10^{-4} g of Freon-113 per microliter of chromatograph quality n-hexane. Each microliter of this solution contained an amount of Freon-113 equivalent to 0.004 ppm of Freon in the one milliliter sample of air from the test loop. Freon peak heights were measured and plotted against equivalent ppm in air. Over this range of 0.004 to 0.024 ppm, response of the instrument was linear.

EXPERIMENTAL RESULTS

PRELIMINARY EXPERIMENTS

Freon-112, the test gas that was used for leak detection, was used for the initial trials in which experimental techniques were developed and the importance of some of the experimental conditions was established. With an inlet concentration of 10 ppm, which was suitable for leak detection, Freon-112 did not penetrate a one inch bed in a short enough time to be a useful test method. Concentrations up to 375 ppm were tried for a while but were then decreased to 86 ppm to reduce the heating effect of Freon adsorption.

When the pulse technique was tried with half-minute bursts of 1000 ppm of F-112, there was no penetration unless the bed was nearly saturated with toluene because the Freon was so strongly adsorbed. Also, the pulse was drawn out by Freon that was slowly desorbing. Freon-11, which has a boiling point of 24°C compared with 93° for F-112, penetrated an unloaded bed immediately. One minute bursts of Freon-113, like Freon-112, did not penetrate beds of fresh charcoal. With further investigation, a method of using a pulse of a suitable halogenated compound might have been devised but the continuous injection procedure appeared to be more promising and the pulse method was not tested further.

Freon-113 was then tried with continuous injection and found to be a more suitable test gas than F-112. At inlet concentrations low enough to avoid heating effects, it gave break times that were more useful and convenient. In addition, it would give faster desorption from charcoal following the testing of an actual filter installation. As a further advantage, it was much easier to handle because it is a liquid at normal room temperatures. The freezing point of F-112 is 23.8°C so heating was required to ensure that it remained in liquid form in the injection apparatus, particularly at the discharge from the hypodermic needle.

To determine the effect of loading the charcoal bed with another adsorbate on the penetration time of F-113, a series of tests was carried out with different amounts of toluene adsorbed on the test bed. For this series, toluene was adsorbed in the afternoon, the filter left overnight then equilibrated again for one hour with air at 25°C and 30% relative humidity before injecting Freon-113 to determine the penetration time. The inlet concentration was 130 ppm and the flow velocity was 64.6 ft/min which is about the same as the rated flow velocity for a typical charcoal filter. The bed depth was 0.73 in. Results of this test, which are given in Table III, showed that penetration time of F-113 was in fact related to the amount of material adsorbed on the charcoal before the test.

TABLE III

Effect of Toluene Loading on Freon Break Time

Toluene load on charcoal, g/g	Break time, min
0.0	29
0.025	21
0.042	17
0.067	11
0.083	4
0.100	3
0.117	2

BREAK TIME MEASUREMENTS

A series of measurements was planned to relate toluene loading to penetration time with velocity, inlet concentration, bed depth, temperature, and relative humidity as parameters. One difficulty was that replicate tests with partially loaded beds showed a large variation. This may have been at least partly caused by variation between tests of the distribution of toluene along the bed. Because of this and because such a relationship would be strictly valid for only the one particular adsorbate, it was decided to make measurements only for unloaded beds of charcoal. In a test of an actual filter installation, then, the experimentally determined break time could be compared to the estimated break time for a fresh bed tested at the same conditions.

The object of the investigation was therefore to derive the relationship of break time (t_B), with temperature (T), relative humidity (RH), inlet concentration (C), air flow velocity (V), and bed depth (L). This can be expressed as

$$t_B = f(T, RH, C, V, L) \quad (3)$$

Properties of the charcoal were not included since beds of the same charcoal were used for all the runs. Additional work would be required to determine the effects of charcoal particle size and the differences between charcoals with different adsorption characteristics. It seems reasonable, however, to suppose that gas adsorbent charcoals in industrial air filters would all be somewhat similar in adsorption properties and even more so in particle size. In practice, therefore, the effects of charcoal properties would likely be small compared with the other parameters in equation (3).

Table IV lists all break time measurements with corresponding test parameters except those for one series of tests at relative humidities between 30 and 55% which are presented later. The temperature correction method is explained in the following section.

TABLE IV
Listing of Experimental Results

Inlet Concn, ppm	Flow velocity, ft/sec	Bed depth, inches	Temperature, °C	Relative humidity, %	Break time, min	Break time corrected to 25°C				
97	48.5	0.51	25	30	18.8					
					21.2					
		0.73			68.2					
					73.0					
		1.10			139.0					
	64.6	0.51				10.0				
						10.8				
		0.73				28.2				
						38.7				
		1.10				102.2				
						101.0				
	123.0	93.2								
	180.0	101.1								
130	80.8	0.51	25		10.7					
					27.1					
		1.10			73.2					
		48.5			0.44				10.0	
									11.4	
	0.51		9.6							
			16.0							
	0.73		52.4							
			59.0							
	64.6	0.51				8.5				
						9.2				
5.9										
0.58		11.0								
		33.0								
0.73		33.3								
	24.2	18.3								
	31.8	24.1								
	57.2	32.1								
	59.3	33.3								

TABLE IV (cont'd)

Inlet Concn, ppm	Flow velocity, ft/sec	Bed depth, inches	Temperature, °C	Relative humidity, %	Break time, min	Break time corrected to 25°C	
130	64.6	0.73	25	0	24.2		
				5	25.3		
				10	34.4		
				15	29.5		
				20	24.0		
				25	32.4		
			1.10		30	75.0	
	80.8					4.1	
						3.9	
						6.6	
						13.2	
						22.0	
						17.0	
					62.1		
97	48.5	1.10	25	55	100.5		
						57.6	
	64.6	1.10				68.7	
						45.6	
						51.7	57.4
						46.8	52.0
						65.3	57.0
						58.7	44.5
						86.0	56.2
						107.3	60.3
130	64.6	0.51	25		2.2		
					2.6		
					4.5		
					9.5		
					9.8		
		13.6					
		6.8					
		16.3	12.3				
		8.3	6.3				
		8.1	6.1				
	0.88	25			22.0		
	80.8	0.73			8.5		

CORRELATION OF RESULTS

EFFECT OF TEMPERATURE

Break times at different temperatures are given in Table V and plotted as logarithm of break time against reciprocal of absolute temperature in Fig. 2. There was considerable scatter of the points but a straight line relationship

$$\log t_B = b_0 + \frac{b_1}{T} \quad (4)$$

was significant at the 5% level for group A and at the 1% level for the other two (Table VI). The slopes of the three lines were not significantly different, so a pooled slope was calculated and used to correct all break times to a constant temperature of 25°C by means of the equation

$$\log t_{25} = \log t_B + 3.4860 - \frac{1039.37}{T} \quad (5)$$

TABLE V

Break Times for Tests at Different Temperatures

Set	Temp, °C	Relative humidity, %	Inlet concn, ppm	Flow velocity, ft/min	Bed depth, in	Break time, min	Time corrected to 25°C
A	5	30	130	64.6	0.73	57.2	32.1
	5					59.3	33.3
	15					24.2	18.3
	15					31.8	24.1
	25					33.0	
	25					33.3	
B	5	55	97	64.6	1.10	107.3	60.3
	10					86.0	56.2
	15					58.7	44.5
	20					65.3	57.0
	25					57.6	
	25					68.7	
	25					45.6	
	29					51.7	57.4
	29					46.8	52.0
C	5	30	97	64.6	1.10	180.0	101.1
	15					123.0	93.2
	25					102.2	
	25					101.0	

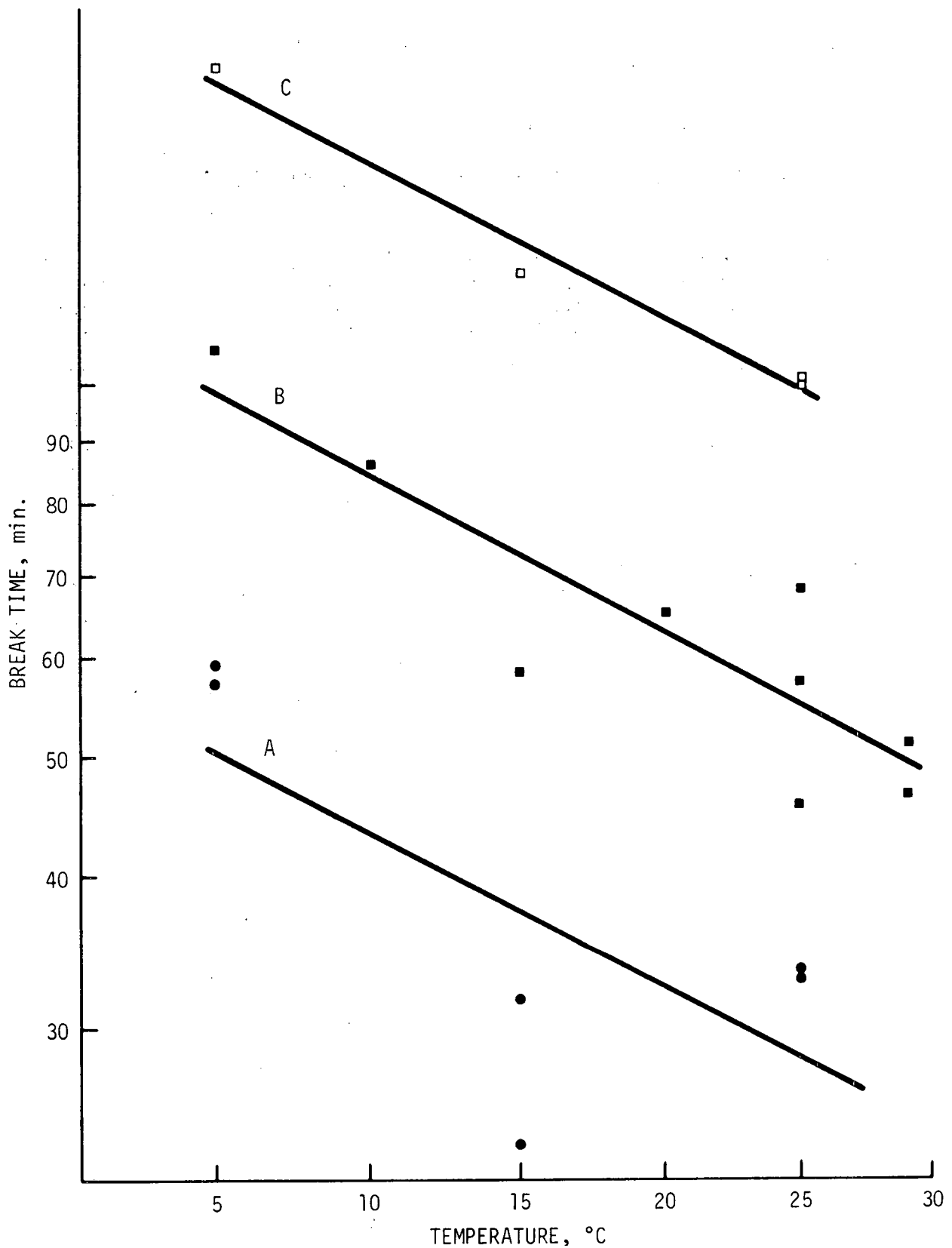


Fig. 2. Plot of logarithm of break time vs reciprocal of absolute temperature (Conditions for sets A, B, and C are given in Table V).

TABLE VI
Correlation of Temperature Data

$$\log t_B = b_0 + \frac{b_1}{T}$$

Set	Regression line slope, b_1	Standard deviation of slope	Correlation coefficient	Number of points
A	1035.9	347.0 (33.5%)	0.7200*	6
B	1056.1	220.2 (20.9%)	0.8758**	9
C	1006.1	111.8 (11.11%)	0.9879**	4

* Significant at the 5% level.

** Significant at the 1% level.

CORRELATION OF LOW RELATIVE HUMIDITY RESULTS

The results of 47 runs carried out at a relative humidity of 30% or below are listed in the first portion of Table IV. Break times measured at temperatures other than 25°C were corrected to this temperature by means of equation (5). Average break times of replicate runs of this portion of Table IV are given in Table VII. In a preliminary examination of the data, it appeared that concentration of test gas and flow velocity could be combined into a single parameter, F, defined by

$$F = \frac{1,000,000}{CV} \quad (6)$$

TABLE VII

Experimental Results for Relative Humidity of 30% and Below

Inlet concn, ppm	Flow velocity, ft/sec	Bed depth, inches	F = $\frac{1,000,000}{CV}$	No. of runs	Break time (t_{25}), min	Calcd break time \hat{t}_{25} Eqn (16), min	Difference $t_{25} - \hat{t}_{25}$, min
97	48.5	0.51	212.6	2	20.0	21.5	-1.5
		0.73		2	70.6	65.1	5.5
		1.10		1	139.0	138.5	0.5
	64.6	0.51	159.6	2	10.4	10.2	0.2
		0.73		2	33.4	42.9	-9.5
		1.10		4	99.4	98.0	1.4
	80.8	0.51	127.6	1	10.7	3.3	7.4
		0.73		1	27.1	29.5	-2.4
		1.10		1	73.2	73.6	-0.4
130	48.5	0.44	158.6	1	10.0	5.0	5.0
		0.51		3	12.3	15.4	-3.1
		0.73		2	55.7	47.9	7.8
		1.10		1	98.2	102.7	-4.5
	64.6	0.51	119.1	3	7.9	6.9	1.0
		0.58		1	11.0	14.7	-3.7
		0.73		12	28.7	31.4	-2.7
		1.10		1	75.0	72.5	2.5
	80.8	0.44	95.2	1	4.1	-4.4	8.5
		0.51		2	5.2	1.9	3.3
		0.58		1	13.2	8.1	5.1
		0.73		2	19.5	21.4	-1.9
1.10		1		62.1	54.3	7.8	

The product, CV, is a measure of the rate of flow of test gas to the filter. The reciprocal of CV and the constant of 1,000,000 were used to simplify the resulting equations.

The 47 individual data points of the first section of Table IV were fitted to several empirical equations using a computer to carry out the calculations. The equations used were as follows

$$t_{25} = B_0 + B_1 LF + B_2 F \quad (7)$$

$$t_{25} = B_0 + B_1 LF + B_2 F + B_3 L \quad (8)$$

$$t_{25} = B_0 + B_1 LF + B_2 F + B_3 C \quad (9)$$

$$\ln t_{25} = B_0 + B_1 \ln F + B_2 \ln L \quad (10)$$

$$\ln t_{25} = B_0 + B_1 \ln L + B_2 \ln V + B_3 \ln C \quad (11)$$

Equations (8) and (9) are the same as (7) with one additional parameter for each. The two logarithmic equations are respectively equivalent to

$$t_{25} = \beta_0 F^{B_1} L^{B_2} \quad (12)$$

$$\text{and } t_{25} = \beta_0 L^{B_1} V^{B_2} C^{B_3} \quad (13)$$

where $\log \beta_0 = B_0/2.303$.

Coefficients for the five equations are given in Table VIII along with the correlation coefficients and the average value of the absolute difference between experimental break time and break time calculated from each equation. All but two of the regression coefficients were significant at the 1% level. The coefficient B_3 of equation (8) was not significant so the $B_3 L$ term could be omitted making this equation the same as equation (7). The coefficient B_3 of equation (9) was significant to only the 5% level but including it gave a worthwhile reduction in average error. The two logarithmic equations tested were not as successful in correlating the experimental data as the arithmetic equations. Equation (13) is interesting

though because the coefficients are nearly whole numbers or even fractions so that it could be closely approximated by

$$t_{25} = \frac{KL^3}{CV^{1.5}} \quad (14)$$

Similarly, equation (12) is closely approximated by

$$t_{25} = KL^3 F^{1.5} = \frac{KL^3}{C^{1.5} V^{1.5}} \quad (15)$$

From equation (14) it is seen that C and V are not present to the same exponent so equations (7) and (10), which contain concentration and velocity only as the product CV, are improved by including a concentration term, B_3C , in equation (9) or by separating the two parameters as in equation (11).

TABLE VIII

Comparison of Equations for Break Time at Low Relative Humidity

Equation	(7)	(8)	(9)	(10, 12)	(11, 13)
B_0	-13.4213	-5.6923	-39.8088	-2.23367	15.2030
B_1	0.91635	0.98851	0.93338	1.32724	2.89896
B_2	-0.29995	-0.3502	-0.26282	2.83868	-1.58959
B_3		-11.1346	0.16434		-0.90593
correlation coefficient	0.98540	0.98553	0.98700	0.96869	0.97173
Average error, %	11.74	11.41	10.96	18.78	17.66

All of the five equations tested had a significant mean square for lack of fit, equation (9) at the 5% level and the other four at the 1% level. This was determined by subtracting the pure error sum of squares which was calculated from replicate determinations, from the residual sum of squares as shown in Table IX for equation (9) only. This means that improved equations could be found by using additional or different terms. The improvement however would not be large and the effort was not warranted at this stage.

TABLE IX
Analysis of Variance for Correlation of Break Time
Using Equation (9)

Source of variation	Sum of squares	D.F.	Mean square	Standard deviation, minutes	% of mean
Total	50234.8256	46			
Coefficient B ₁	45987.5	1			
Coefficient B ₂	2791.0	1			
Coefficient B ₃	159.143	1			
Correlation	48937.7	3			
Residual	1297.16	43	30.1664	5.492	14.71
Pure error	489.72	25	19.589	4.426	12.94
Lack of fit	807.44	18	44.858	6.698	17.93

Equation (9) which was the best equation found can be expressed as follows using rounded values of the coefficients

$$\hat{t}_{25} = -39.81 + 0.9334LF - 0.2628F + 0.1643C \quad (16)$$

where \hat{t}_{25} indicates an estimated value of break time. Break times calculated from this equation are given in Table VII opposite the experimental break times. Also given are the differences between experimental and calculated break times. It can be seen that one disadvantage of the equation is that at low break times the calculated result can come out to be a negative number. The logarithmic equations, of course, do not give negative values for break time so they tended to be more accurate for break times below 10 min and the arithmetic equations tended to be more accurate for high break times. Since an equation would be used to estimate the break time of fresh charcoal beds, which would be expected to have a reasonably large break time, the arithmetic equation is preferred.

EFFECT OF RELATIVE HUMIDITY

Table X and Fig. 3 show the effect of relative humidity on the break time of 0.73 in. deep beds tested at an inlet concentration of 130 ppm and a flow velocity of 64.6 ft/min. The twelve data points for relative humidity of 30% and below are also listed in Table IV and the average (28.7 min) is given in Table VII. This average is indicated in Fig. 3 by a horizontal line. The standard deviation of these 12 points is 5.24 min or 18.3% of the mean which is somewhat higher than the standard deviation of 4.43 min for all replicate data (Table IX). At higher relative humidity, break times seemed to be more consistent and to fall on a straight line decreasing to a break time of zero at about 70% RH. The line shown for this region is the least squares line for the six points at 30% RH and the eight higher humidity points. Thus the data can be fitted by using two straight lines meeting at 30% relative humidity. It would also be possible to fit the data with a single curved line or possibly a single straight line could have been obtained by transformation of one or both of the variables. However, for at least a preliminary correlation of break time and relative humidity, it was decided to assume that two straight lines, as in Fig. 3, could be used to fit the data for all the combinations of inlet concentration, flow velocity and bed depth that were used. Thus, it was assumed that above 30% RH, break time could be expressed by

$$t_{25, RH} = \hat{t}_{25, 30} + H(RH - 30) \quad (17)$$

where $t_{25, RH}$ is the break time at a relative humidity of RH and H is a relative humidity coefficient for each set of test conditions.

TABLE X

Effect of Relative Humidity on Freon Break Time

(Concentration = 130 ppm, Velocity = 64.6 ft/sec, Bed depth = 0.73 in)

Temperature, °C	Relative humidity, %	Break time t_{25} , min
25	0	24.2
	5	25.3
	10	34.4
	15	29.5
	20	24.0
	25	32.4
	30	33.0
	30	33.3
15	30	18.3
	30	24.1
5	30	32.1
	30	33.3
25	35	28.8
	40	24.6
	45	19.1
	45	20.1
	50	15.6
	55	9.8
	60	8.8
65	2.4	

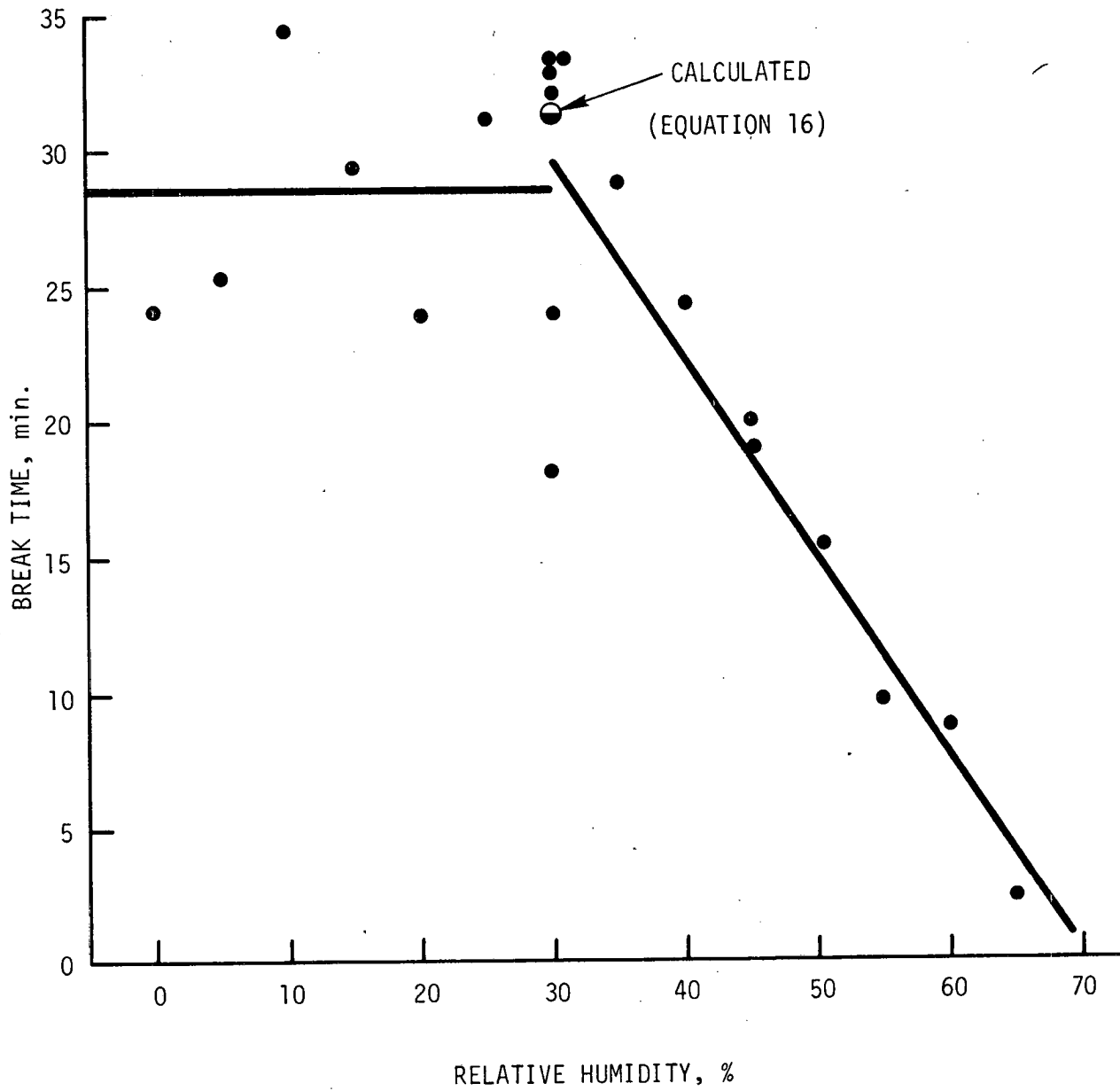


Fig. 3. Effect of relative humidity on Freon-113 break time (Data of Table X).

Break times measured at 55% RH are given in the last portion of Table IV. Measurements were not made at all of the combinations of concentration, velocity and depth used at 30%. Averages for the results are given in Table XI alongside the experimental and calculated (equation 16) values of break time at 30% RH for the same test conditions. The coefficient H was calculated by substituting the 55% RH values into equation (17). The calculated break time for 30% RH was used instead of experimental values to make the results consistent with equation (16). The resulting values of H are plotted against the calculated 30% RH break time ($\hat{t}_{25,30}$) in Fig. 4. The least squares equation for the line shown, using the 22 individual values of H is

$$\hat{H} = 0.04781 - 0.033376 \hat{t}_{25,30} + 0.0001588 (\hat{t}_{25,30})^2 \quad (18)$$

It would seem at first that the magnitude of H should continue to increase instead of showing a maximum and then decreasing. However, if the straight lines of Fig. 3 were replaced by a series of curved lines, it is apparent that the magnitude of the slope of the lines joining the 30% and 55% RH points could show a maximum and eventually decrease again to zero. Nevertheless, it was thought better to use equation (18) to the inflection point at $\hat{t}_{25,30} = 105.1$ min where $\hat{H} = -1.705$ and to use this value of H for all higher values of break time. Calculated values of \hat{H} and break time at 55% RH ($\hat{t}_{25,55}$) calculated from

$$\hat{t}_{25,RH} = \hat{t}_{25,30} + \hat{H}(RH - 30) \quad (19)$$

are given in Table XI. The average error (absolute value) was 1.6 min and the average absolute percentage error was 8.5%.

TABLE XI

Estimation of Break Time at 55% Relative Humidity
From Results at 30%

Break time, min		H		\hat{H}		Break time	Difference	
30% RH		55% RH				55% RH	$t_{25,55} - \hat{t}_{25,55}$	
Exptl	Calcd	Exptl	Exptl	Calcd	Calcd		minutes	% of $t_{25,55}$
$t_{25,30}$	$\hat{t}_{25,30}$	$t_{25,55}$	Eqn (17)	Eqn (18)	$\hat{t}_{25,55}$			
7.9 (3)*	6.9	2.4 (2)	-0.180	-0.175	2.5	-0.1	-4.2	
11.0 (1)	14.7	4.5 (1)	-0.408	-0.408	4.5	0.0	0.0	
19.5 (2)	21.4	8.5 (1)	-0.516	-0.594	6.6	1.9	22.4	
28.7 (12)	31.4	9.2 (6)	-0.888	-0.844	10.3	-1.1	-12.0	
	48.1	22.0 (1)	-1.044	-1.190	18.4	3.6	16.4	
99.4 (4)	98.0	55.5 (9)	-1.700	-1.698	55.6	-0.1	-0.2	
139.0 (1)	138.5	100.5 (1)	-1.520	-1.705	95.9	4.6	4.6	

* Number of tests made is shown in parentheses.

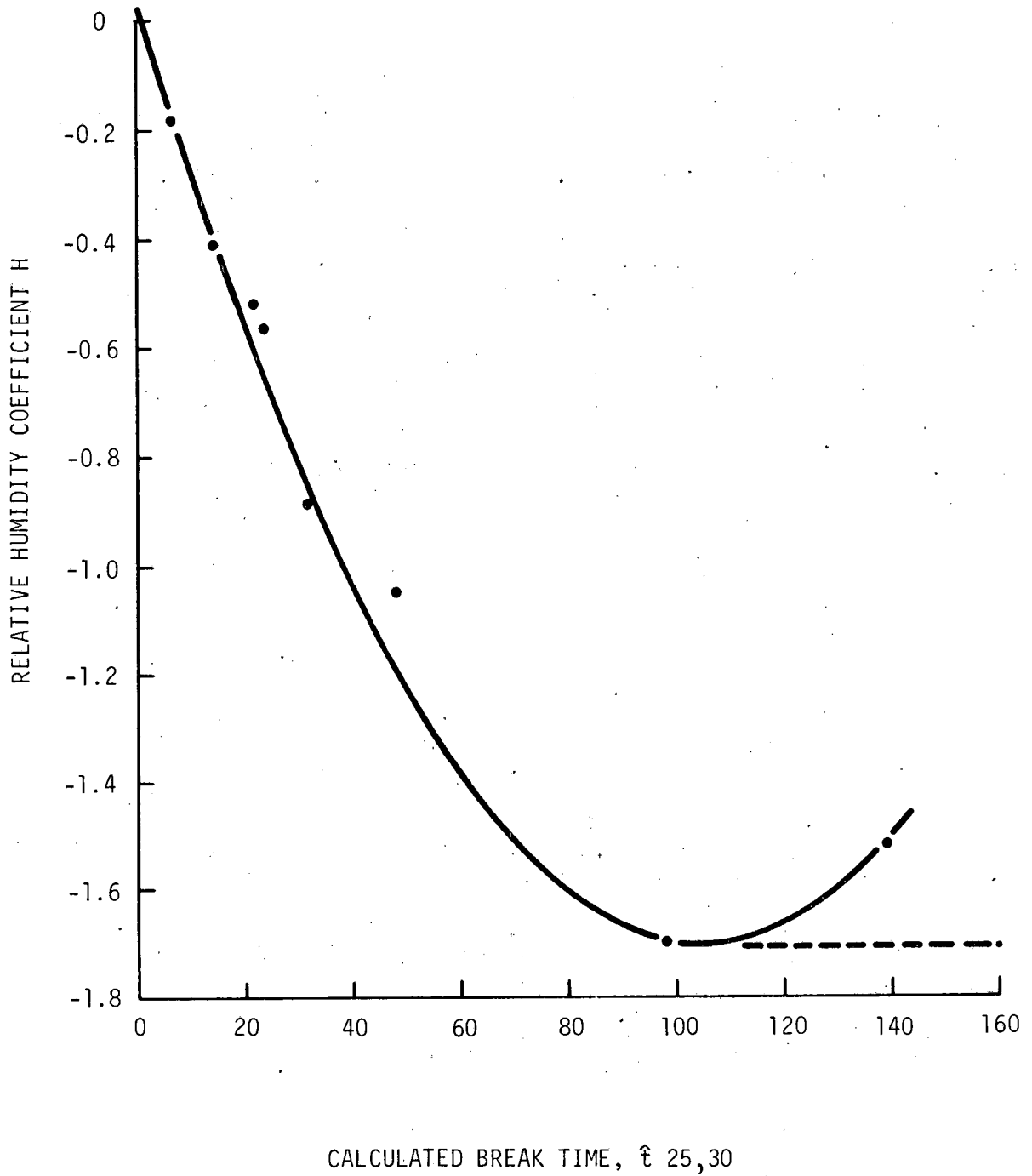


Fig. 4. Variation of the coefficient H (equation 17)).

APPLICATION OF RESULTS

The procedure for estimating the residual adsorption capacity of a charcoal filter would be to measure the break time of Freon-113 gas at known conditions of inlet concentration, flow velocity, temperature, relative humidity and bed depth. The measured break time would be corrected to a temperature of 25°C using equation (5) and the corrected value compared with the estimated break time for a bed of fresh charcoal of the same depth calculated from equations (16), (18) and (19) in sequence. The temperature correction can be made graphically by means of Fig. 5 and Fig. 6 presents a graphical solution of the other three equations for estimating $\hat{t}_{25, RH}$.

Fig. 6 is used by entering the left hand horizontal axis at the flow velocity used, for example 76 ft/min, and proceeding down as indicated to the value of the inlet concentration (107 ppm). The construction line is then drawn across the lower vertical axis, which gives the value of F (123), to the bed depth (1.5 in.) up to the concentration value (107 ppm), and then left across the vertical axis following the relative humidity lines to the test relative humidity (41%). Calculated break time (96 min) is then shown on the upper vertical scale across from this point.

Test conditions should be within the limits used for the laboratory experiments from which the relationships were derived. These limits are

Temperature	-	5 to 30°C or 41 to 97°F
Flow velocity	-	50 to 80 ft/min
Inlet concentration	-	97 to 130 ppm
Relative humidity	-	not over 55% - preferably at 30%.

It is apparent from Fig. 6 that for very shallow beds, a low flow velocity and low inlet concentration should be used to get as high a value for break time as possible. Facilities for accomplishing adequate mixing of the test gas with the upstream air are essential and the downstream air should also be mixed or samples should be taken immediately downstream from specific areas of the filter bed. The charcoal bed should be in equilibrium with the air temperature and humidity before starting the test.

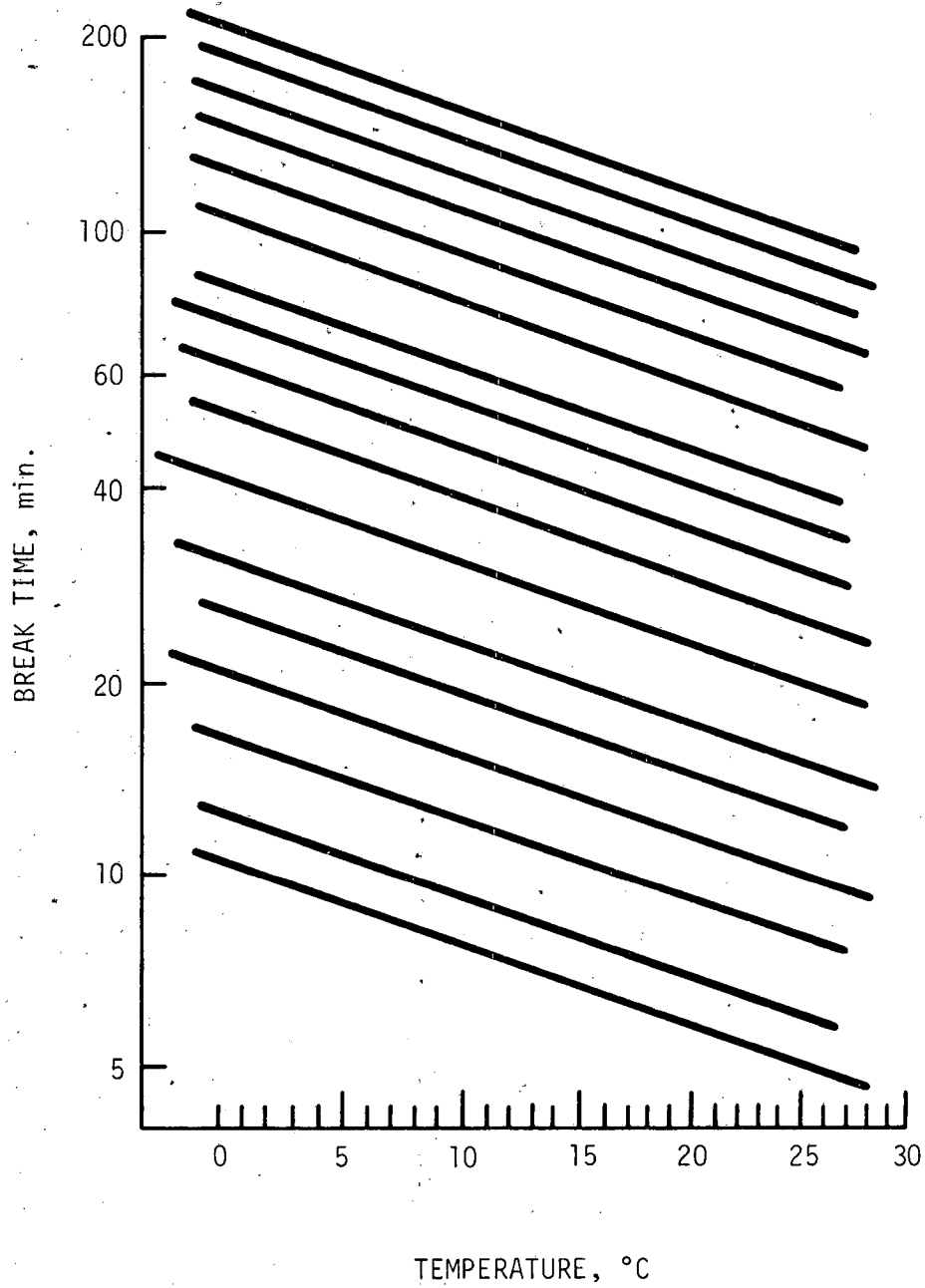


Fig. 5. Chart for correcting break times to a standard temperature of 25°C.

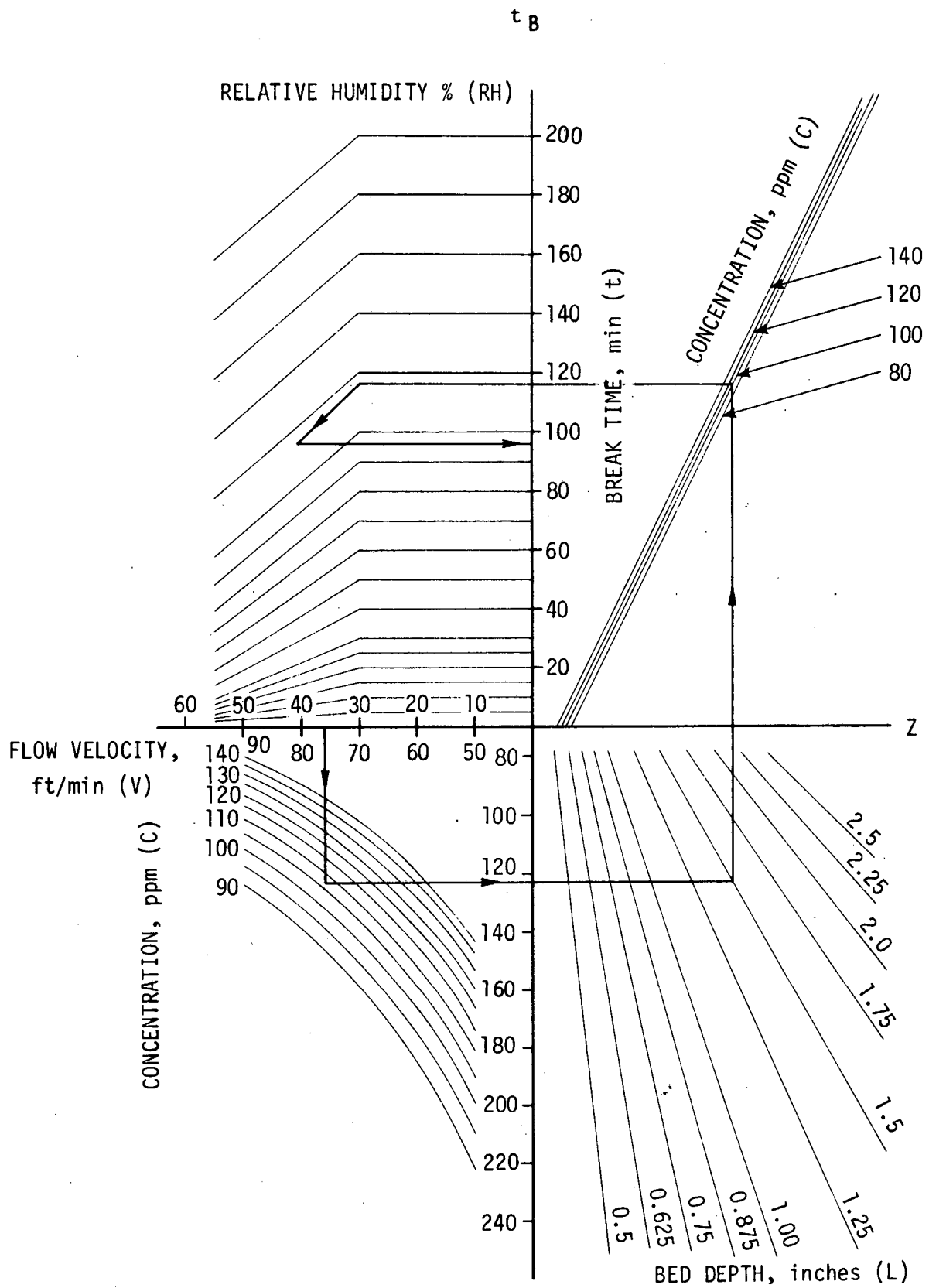


Fig. 6. Chart for estimating the break time of beds of fresh charcoal.

To determine the relationship between time in service and the measured break time of charcoal filters, a number of protective mask canisters were attached to a manifold and inside air was drawn through them. The air flow rate, which was measured at the discharge from the blower, decreased quite quickly in the first two weeks and then remained constant at 5.8 cfm. The time in service was therefore corrected to the time that would have given the same total volume of air at a rate of 5.8 cfm. Canisters were removed at intervals over a period of 160 days and break time was measured at a temperature of 25°C and a relative humidity of 30%. When a canister was removed from the manifold for testing it was replaced with another canister so as not to alter the distribution of air flow among the canisters. The results are shown in Fig. 7 in which break time expressed as a percentage of the initial break time of 39.2 min is plotted against corrected time in service. The relationship was found to be equivalent to that for a first order chemical reaction so that

$$\frac{dR}{dS} = kR \quad (20)$$

in which S is the number of days in service and R is the ratio, t/t_0 , of break time at S days to the initial break time. Integration of (20) and substitution of the boundary condition $R = 1.0$ at $S = 0$ gives

$$\log R = kS \quad (21)$$

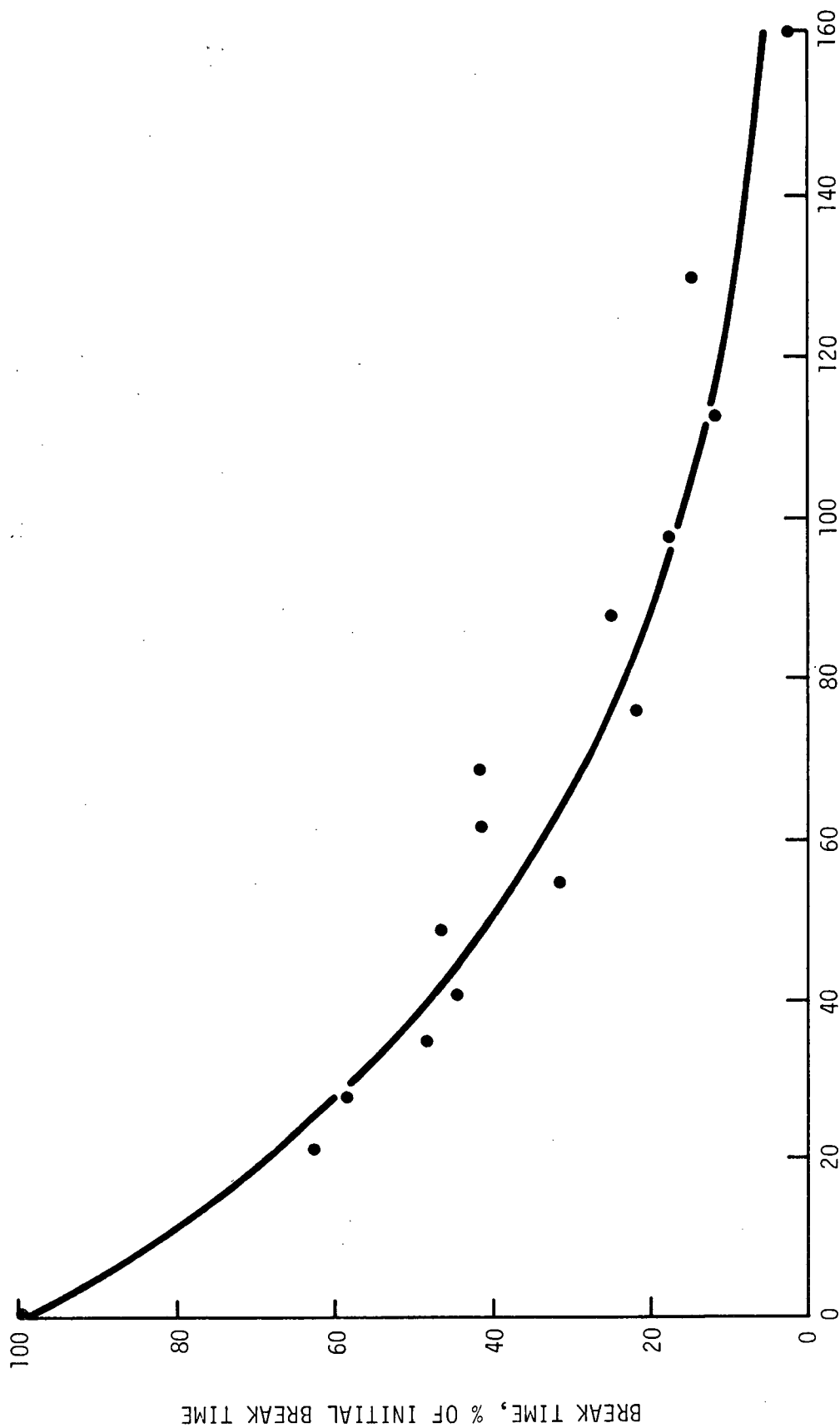
To confirm that equation (21) was valid, the experimental data were fitted to the regression equation

$$\log R = b_0 + b_1 S \quad (22)$$

The value of b_0 was found to be not significantly different from zero. The line in Fig. 7 is equation (21) with k calculated from the mean of S and the mean of $\log R$.

If it is assumed that a filter can be used until its break time is some specific fraction of the initial break time, R_L , the time at which this ratio will be reached, S_L , can be estimated from one measurement of R and S during the lifetime of the filter provided that the kind of contamination and the rate of accumulation has not changed. Thus, from equation (21)

$$S_L = \frac{S \log R_L}{\log R} \quad (23)$$



LENGTH OF TIME IN SERVICE, days

Fig. 7. Decrease for break time of respirator canisters with length of time in service.

For example, if a value of 75% were found for R after 6 months service, the filter could be used another 8.5 months before R would reach 50% and another 22.9 months before R would reach 25%. (In equations (20) to (23) R must be expressed as a fraction, not a percentage, but S may be in any time unit.)

Ideally, break time should be measured when a charcoal filter is first installed and break times determined after the filter has been in use could then be compared to this value instead of to a break time calculated from the relationships given in this report. If test conditions differed for the initial measurement, and that after use, the relationships could be used to correct them to the same conditions, possibly by using the initial measurement to calculate an "effective" bed depth from equation (16) which could then be employed for used bed tests.

DISCUSSION

It is believed that the proposed method of measuring the residual adsorption capacity of charcoal filters is basically a sound one. Freon-113 is easy to use and to inject into the upstream air. Measurement of downstream concentrations is straight forward once the necessary apparatus has been procured. Sampling ports and velocity measuring instruments are usually available at large filtering installations.

The maximum bed depth that was tested was 1.10 inches but break time would be expected to be linear with bed depth and this is confirmed by equation (16) so perhaps this equation could be extrapolated to a bed depth of 1.5 inches or possibly to 2.0 inches.

It was pointed out that no allowance was made for variation of charcoal properties. The results in this report could probably still be used, however, by measuring the break time when a filter is first installed and calculating an effective bed depth to be used in subsequent tests. It has already been suggested that this be done whenever it is possible to do so.

The main deficiency in correlating the experimental data is in the method used to allow for the effects of relative humidity. The method used is valid for the one set of conditions for which tests were made over the complete range of relative humidity but extrapolation to other conditions probably is not valid. Thus, in Fig. 6, the series of horizontal and sloped straight lines for the relative humidity correction should be a family of curves. Experimental data over the whole range of flow conditions and bed depth might be required to properly determine these curves.

It is apparent, therefore, that more accurate testing would be obtained at low relative humidities. Thus, tests should be made in winter time using outside air heated to approximately room temperature. In summer months, testing on warm, humid days would not be feasible because of uncertainties in the humidity correction and because of the low break times likely to be obtained.

The problems of allowing for relative humidity and, indeed, all allowances for variations in test conditions disappear if small filters which can be installed in a test set up or samples of charcoal which can be put into a special test bed are to be tested. Air for the test can then be conditioned to a constant temperature and relative humidity (preferably low) and constant flow velocity and inlet concentration can be used.

While it would be possible to use the method as a non-destructive test for protective mask canisters it would not be practical to test every canister during production because of the long break time involved. It would be feasible to test samples of production lots or samples of stored canisters or specific canisters for which an estimate of residual capacity was desired.

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13. ABSTRACT <p>A method has been developed for estimating the residual adsorption capacity of charcoal filters. Since the method is non-destructive and uses a low concentration of a non-toxic test gas, it can be applied to installed collective protectors. It can also be used as a non-destructive laboratory test method for protective mask canisters or other small charcoal filters.</p> <p>In laboratory experiments, beds of charcoal were challenged with Freon-113 and the time required for the exit concentration to reach 0.005% of the inlet concentration was determined. It was demonstrated that break time was related to the amount of material adsorbed on the charcoal and also to the length of time in service.</p> <p>Break time also depended upon flow rate, inlet concentration, temperature relative humidity and bed depth. Equations were developed to relate the break time of beds of fresh charcoal with these five variables. To estimate the residual capacity of a filter, its measured break time would be compared with the break time calculated for a bed of fresh charcoal. A graphical method of carrying out the calculations is given.</p>		

KEY WORDS

Activated carbon
 Adsorption
 Air cleaners
 Air conditioning
 Charcoal
 Leak detectors
 Military chemical operations
 Non-destructive tests
 Nuclear reactor containment
 Protective mask canisters
 Shelters
 Test equipment

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