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**REMOVAL OF IRRITANT VAPOURS FROM ENCLOSURES
BY VENTILATION (U)**

by

J.M. McAndless, M.E. Galloway and C.L. Chenier

PCN No. 13E30

July 1983



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ABSTRACT

A small test chamber was used as a model enclosed space to study the removal of irritant vapours by ventilation. Quantitative data was obtained on the relative rates of removal of CH and CN and their adsorption/desorption rates from selected materials. Triethyl phosphate, a liquid of intermediate volatility, was included in the study for comparison purposes. Ventilation removal rate data for the chamber was compared to data for ventilation trials carried out using a one-room building. Under the given experimental conditions, results obtained from experiments with the model enclosure allow qualitative predictions to be made of vapour removal rates for other enclosures based on air exchange rates, vapour concentration decay half-lives, mixing factors and relative volatility of the vapour source.

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INTRODUCTION

The dissemination of irritant chemicals (e.g., riot control agents) into buildings or enclosed spaces creates the need for subsequent removal of the agent to render the space habitable. In some cases, the only practical way to remove the agent is to ventilate the enclosed space. However, standard irritants such as CS and CR are solids of low volatility which are not rapidly removed by ventilation. Methods such as vacuum cleaning or application of decontaminating solution may be required in order to remove these agents.

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A newer liquid irritant, CH, and the solid irritant CN have sufficient volatility to suggest that their removal from an enclosed space by ventilation may be a practical method of decontamination. For example (1), CH vapour could be reduced to a low concentration level ($< 0.5 \text{ mg m}^{-3}$) in an unfurnished room in a few hours by ventilation at 20°C . For furnished rooms, a longer period of ventilation was necessary but the removal of CH required a much shorter time than would be expected for removal of CN, CS or CR.

As described herein, a small instrumented test chamber was used to provide quantitative data on the relative rates of removal of CH and CN from enclosed spaces by ventilation and to determine their relative adsorption/desorption rates from selected materials. Triethyl phosphate (TEP), an organophosphorus liquid of intermediate volatility was also included in the experiments for comparison purposes. As a practical example, a few ventilation trials were carried out using a one-room building purposely contaminated with either CH or TEP.

THEORY

For an enclosed space, the removal of an ideal vapour strictly by ventilation may be described by a mass balance equation, that is:

$$V \frac{dC}{dt} = - C Q \quad [1]$$

where

- V = enclosure volume
- C = vapour concentration
- Q = air flow rate

The solution to Equation 1 is the so-called Turk equation (2, 3):

$$C(t) = C_0 \exp(-k_2 t) \quad [2]$$

where C_0 = initial vapour concentration and
 $k_2 = QV^{-1}$, the ventilation rate constant which is numerically equal to the number of air changes in the enclosure per unit time.

Equations 1 and 2 assume perfect mixing of the enclosure air and, in reality, this is not always the case. Therefore, Equation 2 is usually modified to include a mixing factor, m , which is defined as

$$m = (t_i k_2)^{-1} \quad [3]$$

where t_i = time required for an ideal gas to be removed from the enclosure at the given air flow rate. Therefore, Equation 2 becomes

$$C(t) = C_0 \exp(-m k_2 t) \quad [4]$$

For perfect mixing $m = 1$. Normally, $0.1 < m < 0.6$ for large rooms (3, 4, 5).

When adsorbent surfaces are present in the enclosure, the overall rate of vapour removal is affected by adsorption/desorption rates from these surfaces as well as the rate of air flow through the enclosure and mixing efficiency. To account for these other processes, the Turk equation may be modified in the following manner:

a) Vapour losses from adsorption and ventilation

$$C(t) = C_0 [\exp(-m k_2 t - m k_1 t)]$$

or

$$C(t) = C_0 \exp(-m k_0 t) \quad [5]$$

where

k_2 = ventilation removal rate constant determined for a particular compound;

k_1 = adsorption rate constant = APV^{-1} ;

A = surface area of adsorbent materials;

P = permeation velocity of vapour from air to adsorbent surfaces;

V = volume of enclosure;

m = mixing factor;

t = time; and

$k_0 = k_1 + k_2$

b) Vapour build-up from desorption and loss by ventilation

Vapour evolution from adsorbed liquids is usually described by an exponential decay equation, i.e.,

$$\frac{dM}{dt} = k_3 M_0 \exp(-k_3 t) \quad [6]$$

where k_3 = first-order desorption rate constant, and
 M_0 = amount (mass) of liquid available for evaporation.

In a ventilated enclosure, the concurrent vapour generation by desorption and the removal of this vapour by ventilation may be described by the equation:

$$C(t) = \frac{k_3 M_0}{V(k_0 - k_3)} [\exp(-k_3 t) - \exp(-mk_0 t)] \quad [7]$$

Combining Equation 7 with Equation 5 yields an expression which defines the overall vapour concentration at any given time as governed by the adsorption, desorption and ventilation processes:

$$C(t) = C_0 [\exp(-mk_0 t)] + \frac{k_3 M_0}{V(k_0 - k_3)} [\exp(-k_3 t) - \exp(-mk_0 t)] \quad [8]$$

At time $t = 0$, $C = C_0$. For $t \rightarrow \infty$ (i.e., a relatively long period of time), $C(\infty) \rightarrow 0$.

For a constant rate of desorption (i.e., k_3 is zero order), usually valid under equilibrium conditions, Equation 8 reduces to:

$$C(t) = C_0 [\exp(-mk_0 t)] + \frac{G}{Vk_0} [1 - \exp(-mk_0 t)] \quad [9]$$

where G is the constant rate of vapour generation from the enclosure surfaces of a given area A .

Equation 9 is the standard expression (6) normally used to characterize contaminant concentrations in enclosed spaces. It should be noted that Equations 8 and 9 imply that, under steady state conditions, the vapour concentration at any place in the enclosure will be the same regardless of the mixing factor (6). This is not valid if

e.g., there is a point source of vapour generation within the enclosure since vapour concentration will obviously be higher close to the source compared to some location further away. However, if point source vapour generation ceases while the air is continuously stirred and any further generation (e.g., from desorption processes) is steady and non-localized, then a uniform vapour concentration will essentially be established in the enclosure. The equations are then suitable for describing vapour concentration decay under ventilating conditions. Under non-ventilating conditions, an equilibrium vapour concentration will also be established in the enclosure, given a constant rate of desorption and stirring. That is, $k_2 = 0$ and

$$C(t) = C_0 [\exp(-mk_1 t)] + \frac{G}{Vk_1} [1 - \exp(-mk_1 t)] \quad [10]$$

Initially, $C = C_0$ for $t = 0$. As $t \rightarrow \infty$, $C(\infty) \rightarrow \frac{G}{Vk_1} = C_e$, an equilibrium concen-

tration which depends on the relative magnitudes of the desorption and adsorption rates, and the surface area to volume ratio of the enclosure. The enclosure surfaces, containing adsorbed liquid, can be considered a liquid reservoir from which vapour diffuses into the air. By analogy to a liquid-filled diffusion tube, the generation rate G will depend in part on the vapour pressure of the liquid source (7).

APPARATUS AND MATERIALS

1. Test Chamber

Figures 1 and 2 show end- and side-views respectively of the test chamber as well as ancillary equipment used in the ventilation studies. The chamber itself was a galvanized steel box 2.44 m long and 0.46×0.46 m square (external dimensions) equipped on one side with two small lexan windows and a support shelf for the vapour analyzer. The ends of the chamber could be sealed by special lexan windows which were pressure-fitted to a teflon gasket (Gore Industries Teflon Joint Sealant Gasket) by means of spring-loaded metal collars. The chamber could be opened for ventilation purposes by releasing the collars and sliding the windows on the gasket material.

One end of the chamber was connected to a large ventilation fan and filter system which was ducted to the exterior of the laboratory building. The fan speed could be

carefully controlled so as to draw air through the chamber at a selected flow rate. The flow rate was monitored with a hot-wire anemometer probe sealed inside the chamber.

Vapour concentration in the chamber was measured using a Miran 1A Infrared Gas Analyzer equipped with a 20 m pathlength gas cell. The analyzer air pump was used to continuously circulate chamber air through the instrument. The fixed volume of the gas cell (5.6 L) was less than 2% of the total internal volume of the chamber and was not included in calculations involving the system air volume. Using an electric heating jacket, the gas cell was thermostatted to $50^{\circ} \pm 0.1^{\circ}\text{C}$ for all experiments to prevent condensation of vapour inside the analyzer. The sampling inlet consisted of a 1.25 cm O.D. copper pipe located in the center of the chamber and connected directly to the analyzer inlet through a seal in the chamber wall. The exhaust from the analyzer was connected in similar fashion to a second pipe located downstream of the sample inlet. It was found that the particulate filter normally attached to the air sampling inlet of the infrared analyzer retained a "memory" of vapour sampled at relatively high initial concentrations. Therefore, the particulate filter was removed from the chamber sampling inlet for the ventilation experiments.

It should be noted that the time required to complete one air change in the analyzer gas cell at the sampling rate used was approximately 0.2 min (12 seconds), or $k_2 = 5$ air changes per minute. This was the same rate of air exchange selected for the chamber ventilation studies (see Table I).

The inside walls of the chamber could be modified by inserting four lengths of 1.25 cm thick plywood support sheets grooved on the edges to overlap one another. One sheet was cut out so as to leave the small lexan windows uncovered to permit viewing inside the chamber. The support sheets could be individually covered as required with e.g., carpet material or inserted pre-treated with other construction materials, e.g., stippled gyproc. Table I describes the types of surfaces employed and also lists the various physical dimensions (internal) of the chamber and other experimental parameters associated with the ventilation studies.

Two small electric fans (Rotron MU2A-1 muffin fans) were positioned at opposite ends of the chamber to provide continuous mixing of the air.

Vapour from either solid or liquid sources was disseminated into the chamber by rapidly heating a small petri dish containing the sample using a Glas-col heating mantle

switched into an external 110 VAC circuit.

The laboratory in which experiments were carried out was maintained at $25^{\circ} \pm 2^{\circ}\text{C}$ by means of an air conditioning system.

2. One-Room Building

A small, one-room building ($V = 72.6 \text{ m}^3$) was purposely contaminated with CH or TEP vapour and then ventilated in order to compare data with the test chamber experiments. The interior surfaces of the building were constructed of unpainted fir plywood (similar to chamber type II surfaces) and air mixing was provided by four floor-mounted 20-inch diameter electric fans (Torcan fans) located mid-point on the diagonals from the room corners to the center. The fans were positioned so as to circulate the air outwards from the center of the building towards the corners. Ventilation was provided by an external wall-mounted 20-inch fan over which a cover could be placed and by opening a door opposite to the wall-mounted fan. Air sampling was accomplished by means of a length of 1.25 cm O.D. nylon tubing which extended through the wall to the inlet port of a Miran 1A Infrared Gas Analyzer located externally to the building. The sample inlet of the tube was positioned approximately 1 m from the wall at the mid-point between two of the circulating fans. Air flow rates were measured at several points in the building, at the entrance door and at the ventilation fan duct with a portable hot-wire anemometer.

3. Vapour Sources and Calibration Procedures

The three compounds listed in Table II were used as vapour sources for ventilation experiments. These compounds were purified to constant melting point or boiling point range and were stored in sealed glass containers in a desiccator. The irritant CH was stored in a glass container under dry nitrogen atmosphere and shielded from direct room light to minimize oxidative degradation of the liquid.

For CH and TEP, the infrared analyzer was calibrated by injecting (and vaporizing) known volumes of liquid into the closed calibration loop system supplied with the instrument. For CN, a 10% W/V stock solution in carbon tetrachloride was made up and known volume aliquots of this solution were injected into the calibration loop. Very little interference from carbon tetrachloride was found at the analytical wavelength selected for CN. The calibration data for CN, TEP and CH is summarized

in Table III, along with that for Freon 12, the tracer gas used to determine the chamber mixing factor m . In all cases, the gas cell of the analyzer was thermostatted at $T = 50^\circ \pm 0.1^\circ\text{C}$ as described previously.

PROCEDURE

1. Test Chamber

The procedure for a typical experiment was as follows:

- a. The appropriate internal surfaces and mixing fans were installed in the chamber;
- b. The chamber end windows were slid open and air was drawn through the chamber at a flow rate of $12.2 \pm 0.1 \text{ m min}^{-1}$. The mixing fans were operated continuously throughout the experiment;
- c. Chamber air was circulated through the infrared analyzer gas cell and stable baseline absorbance readings were established at the appropriate analytical wavelength;
- d. The chamber end windows were closed and the circulated chamber air was monitored to check for residual revaporization from previous experiments. The chamber was ventilated for a further period of time, if necessary, to remove any residual vapours;
- e. The chamber window furthest from the ventilation fan was opened momentarily while the petri dish of the vaporizer unit was charged with liquid (500 – 800 μL) or solid agent (250 – 500 mg) as appropriate. The window was then resealed;
- f. Electrical power was supplied to the heating mantle of the vaporizer until all agent had vaporized and was mixed thoroughly with the chamber air;
- g. Absorbance readings were recorded while the vaporized agent adsorbed onto the interior surface of the chamber. Approximately 1 hour was usually sufficient to acquire enough data for determining adsorption rates;

- h. While continuing to record, both chamber windows were opened simultaneously and the chamber was ventilated at the pre-set flow rate (12.2 m min^{-1}) until little or no vapour could be detected;
- i. The chamber was then resealed, and the desorption of residual agent from the materials inside the chamber was monitored until an approximate equilibrium concentration of agent vapour was established in the chamber air;
- j. The chamber was then ventilated, usually overnight, to remove traces of residual agent. In some cases, the interior surfaces of the chamber were removed and allowed to stand outdoors (weather permitting) in fresh air and sunlight to assist in decontaminating the surface materials.

2. One-Room Building

For each experiment, 110 mL of TEP or 30 mL of CH were sprayed as a fine mist into the building using a small pressurized nozzle and siphon system. After a few minutes of circulating the air, the building door was opened and the ventilation fan was uncovered and started. Recordings were made of vapour concentration decay and other relevant parameters in the usual manner.

MIXING FACTOR

The mixing factor, m , for the chamber was determined using Freon 12 (dichlorodifluoromethane) as a tracer gas. The tracer was sprayed into the chamber using a pressurized aerosol container (Quixpray Instant Aerosol, Pierce Chemical Company, Rockford, Illinois), followed immediately by sealing the chamber. After stable infrared absorbance readings were obtained (usually after a few minutes), the chamber was ventilated at a known rate while the decay in Freon 12 concentration was monitored. The concentration decay was exponential and no adsorption of the gas onto the metal surfaces of the chamber occurred. This latter observation also confirmed that the chamber was leakproof.

It was found that with an air flow of 12.2 m min^{-1} , the time required to remove Freon 12 from the chamber corresponded to the analyzer sample dwell time

(approximately 12 seconds). Therefore, a much slower ventilation rate was employed to ensure that the analyzer dwell time would not constitute a rate limiting factor. Table IV summarizes the experimental parameters and test results carried out with the tracer gas. These results indicate that the chamber air is thoroughly mixed ($m = 0.99$) at the sampling point under the given conditions. Figure 3 shows a semi-log plot of Freon 12 concentration versus time which yields the ventilation rate constant from the line slope.

DATA INTERPRETATION

For all chamber experiments, a mixing factor $m = 1$ was assumed based on the tracer gas ventilation experiment described above.

The vapour concentration versus time profile for a typical experiment is shown schematically in Figure 4. The three portions of the profile from which rate data was derived are indicated in this figure.

1. Adsorption rate constant (k_1)

This constant was determined by monitoring changes in vapour concentration with time under non-ventilating conditions.

Referring to Equation 10, initially $C_0 \gg \frac{G}{Vk_1}$ so that this equation reduces

to

$$C(t) \approx C_0 \exp(-k_1 t) \quad (m = 1) \quad [11]$$

Taking logarithms yields

$$\ln C(t) = \ln C_0 - k_1 t \quad [12]$$

or

$$\ln [C_0/C(t)] = k_1 t \quad [13]$$

from which the adsorption rate constant k_1 is obtained from the line slope of a plot of logarithm of concentration ratio versus time. Figure 5 shows a plot for a typical CH adsorption experiment.

Vapour concentration decay due to adsorption losses followed Equation 13 for approximately the first 10% of a given experiment before deviation from linearity occurred due to establishment of equilibrium between adsorption and desorption processes.

The initial concentration, C_0 , was taken as the highest recorded value following the dissemination process (see Figure 4). In general, $C_0 < C_0'$ (the theoretical concentration which is equal to the vaporized mass divided by the enclosure volume) due to adsorption which occurs during vaporization.

The amount of liquid vaporized was less than the saturated vapour concentration in each case, whereas CN was disseminated to a saturated vapour condition. In this latter case, a deposit of small CN particles covered all inner surfaces of the chamber after dissemination.

2. Ventilation Rate Constant (k_2)

The chamber was ventilated after the adsorption/desorption processes approached an approximate equilibrium (i.e., change in vapour concentration with time became relatively small). The vapour concentration at the time the chamber was opened, C_0'' , was taken as the initial concentration for ventilation experiments.

Initially, vapour concentration decayed exponentially due to the combined absorption losses and ventilation removal, as described by Equation 5. That is, a plot of $\ln[C_0''/C(t)]$ versus time was linear, yielding the rate constant $k_0 = k_2 + k_1$ from the line slope. However, for CH and TEP, the plots rapidly became non-linear as $C(t)$ approached C_e' , the equilibrium concentration characteristic of the concurrent ventilation and desorption processes. A modified expression

$$\ln \left[\frac{C_0'' - C_e'}{C(t) - C_e'} \right] = k_0 t \quad [14]$$

was therefore employed for all ventilation experiments to extend the linear range of the data. Equation 14 is essentially the same as the logarithm of Equation 5 for the conditions C_0'' , $C(t) \gg C_e'$. As C_e' was sometimes difficult to establish accurately, an arbitrary value $C_e' = 0.01 C_0''$ was employed in Equation 14. This choice provided data which was rectilinear to approximately a 60% decrease in C_0'' .

A typical plot for a TEP ventilation experiment is shown in Figure 6.

3. Generation Rate (G) and Desorption Rate Constant (k_3)

Vapour evolution from the chamber under non-equilibrium conditions may be described by an equation similar to Equation 6, i.e.,

$$\frac{dM}{dt} = k_3 M' \exp(-k_3 t) \quad [15]$$

where

$$\frac{dM}{dt} = \begin{array}{l} \text{rate of vapour evolution in terms of mass increase with} \\ \text{time} = \text{vapour generation rate G} \end{array}$$

and

$$M' = \text{mass of material available for desorption.}$$

Since $C = MV^{-1}$, an equivalent expression in terms of concentration is

$$\frac{dC}{dt} = \frac{dM}{V dt} = \frac{k_3 M'}{V} \exp(-k_3 t) \quad [16]$$

Since a) M' was not readily accessible experimentally and b) ventilation times for experiments were not identical in all cases prior to commencing desorption (i.e., the amount of adsorbed vapour source M' is different for each run), the data was analyzed using the expression

$$C(t) = \frac{k_3 M'}{V} (1 - \exp(k_3 \Delta t)) + C(t + \Delta t) [\exp(k_3 \Delta t)] \quad [17]$$

where

$$C(t) = \text{vapour concentration at time } t;$$

$$\Delta t = \text{time interval between measurements of } C(t).$$

A $C(t)$ versus $C(t + \Delta t)$ plot yields a straight line with slope $\exp(k_3 \Delta t)$ from which the value of k_3 can be calculated. A typical plot is shown in Figure 7, using the desorption of CH from the plywood surfaces as the example.

RESULTS AND DISCUSSION

1. Comparison of Removal Rates By Adsorption, Ventilation

a. Effect of Different Initial Vapour Concentrations

Several preliminary experiments were carried out to determine whether the rate constants e.g., k_1 and k_0 varied with different initial vapour concentrations in the chamber. Using examples for each compound, the data in Table V shows that, under the given conditions, observed adsorption and ventilation rate constants are not affected by changes in initial vapour concentration. Therefore, all chamber experiments were performed using a 500 μ L or 500 mg charge of liquid or solid, respectively.

b. Comparison of Adsorption Rate Constants (k_1)

The surface area to volume ratio of the chamber varied from 10.68 to 11.82 depending on the type of adsorbent surface present (see Table I). Therefore, all rate constants were normalized to values which corresponded to a surface area to volume ratio of 10.68. (i.e., a Type I surface). This was required since vapour loss rate depends upon both the surface area of adsorbent material present and the volume of the enclosure. Normalization was accomplished by multiplying the observed rate constant by an appropriate factor, as given by the examples in Table VI, footnote a.

As shown by the adsorption rate constants summarized in Table VI, the vapour from CN, TEP and CH adsorbed most rapidly into the porous stippled gyproc ceiling insert. This is indicated by the relatively large increases in k_1 which occur when this material forms one of the chamber surfaces.

c. Comparison of Ventilation Rate Constants (k_2 , k_0)

As indicated by the data in Table VII, overall rates of vapour removal (k_0) exceed adsorptive removal (k_1) by approximately an order of magnitude under the given high air flow rate. Thus, within experimental error, the type of enclosure surface present has little effect on the overall removal rate constant (k_0) since k_1 , which depends strongly on the type of surface present, is relatively small compared to k_0 . CN is a possible exception to the above since this compound is removed more rapidly by ventilation in the presence of the gyproc surface as compared to the other surfaces.

It should be noted that, for buildings and rooms where the air exchange rate is relatively slow compared to the test chamber, rates of vapour loss may be governed more by adsorption into the types of surfaces present rather than by removal through ventilation.

The data in Table VII also shows that the vapour of the source compounds is removed at rates which are slower than the enclosure ventilation rate, k_v (5 air changes min^{-1}) except for CH which is removed at approximately the rate k_v . When the relative volatilities and ventilation removal rate constants (k_0 or k_2) of the compounds are compared, an approximate correlation between these parameters is found, as indicated by the data in Table VIII. Again, the exception appears to be CN for the case where a highly adsorptive surface is present. It has been shown (12), that the rate of drying of a wetted solid surface (e.g., the chamber surfaces) under constant air flow, surface geometry and other external parameters is proportional to the volatility of the wetting liquid.

To explore this further, tests were carried out in which the chamber was ventilated at a constant rate but the ambient temperature of the incoming air was varied. TEP was used as the vapour source in all cases. The ambient air temperature in the room could be varied over approximately an 8°C range ($22 - 30^\circ\text{C}$) depending upon the air conditioner settings used for room temperature control and the external air temperature. The data for these tests is summarized in Table IX, and indicates that there is a trend towards faster rates of vapour removal (i.e., larger ventilation removal rate constants) at higher temperatures.

2. Vapour Generation Rates

The desorption rate constants (k_3) under non-ventilating conditions for CN, TEP and CH are summarized in Table X for the various chamber surfaces. For the liquids, desorption is more rapid from the porous surfaces as a consequence of the increased mass of adsorbed material available for evaporation. The "desorption" rate of CN is approximately the same for all surfaces (except perhaps the porous Type IV surface) and k_3 in this case is more likely related to the rate of sublimation of discrete solid particles resting on the interior surfaces of the chamber.

It should be noted that under the given conditions the mass of liquid available for desorption will vary according to the length of time the experiment proceeds prior to

acquiring the desorption data. That is, there will be less adsorbed liquid after prolonged ventilation compared to the case where ventilation is carried out for only a short period. For example, desorption data could be acquired after only a few minutes of ventilation with CH, whereas TEP required up to an hour or two and CN several hours of ventilation before commencing desorption measurements. Thus, there is little obvious correlation with comparative physical properties of the compounds, although the desorption rate constants are generally larger than the corresponding adsorption rate constants.

When adsorbed liquid evaporates from surfaces into a ventilated enclosed volume, a small, constant vapour concentration will result, the magnitude of which depends on the relative magnitude of the desorption and ventilation rate constants. In general, a higher air flow rate (larger k_v) will produce a lower equilibrium vapour concentration for a constant vapour generation rate. By analogy to drying of a wetted solid (13), vapour generation remains constant until liquid no longer covers the exposed surfaces. The rate of vapour generation then falls off and is governed by the diffusion rate of liquid/vapour through the solid matrix to the surface. Eventually, the entire mass of adsorbed liquid will diffuse to the surface, evaporate and be removed by the air flow. Thus, the time required to completely decontaminate an enclosure by ventilation cannot be fully predicted strictly from knowledge of the air flow rate and mixing factor alone. Decontamination time will also depend on the mass of liquid adsorbed into the surfaces, liquid volatility and diffusion rate through the solid matrix to the exposed surfaces.

In the case of desorption from the metal surface (Type I), the rate constants shown in Table X for CH and TEP probably pertain to desorption from other materials in the chamber, such as the lexan windows, plastic casings for the circulating fans, glass-col heating mantle material, etc. Desorption from these materials is common to experiments carried out with the other types of chamber surfaces.

3. Ventilation of a One-Room Building

The air mixing factor for the building was assumed to be close to unity ($m = 1$) because of the use of the relatively large circulating fans.

Under ventilation the air flow through the building approached a rate of one air change per minute (or half this value if the fan was run at approximately one-half

speed). Under the given conditions, CH was removed at the air change rate (i.e., $k_0 = k_v$). Because the building was not airtight, adsorption rates were not determined since leakage could significantly affect the rate of vapour loss under non-ventilating conditions. However, for Trial 4, a value of $k_1 = 0.032 \text{ min}^{-1}$ (combined adsorption, leakage rate) was obtained by monitoring decay of CH vapour concentration prior to commencing ventilation of the building. This value is small relative to the overall rate of vapour removal by ventilation in the case of CH; a similar k_1 for TEP would be of the same order as the overall removal rate for the compound. The data for ventilation trials of the one-room building is summarized in Table XI.

By comparing the TEP and CH vapour decay half-lives ($t_{1/2}$) for the building and chamber experiments, a reasonable correlation between the two structures is found with respect to the number of air changes required to remove vapour under the given conditions, even though the absolute values of k_0 differ because of the different air flow rates employed. That is, the chamber may be useful in predicting ventilation rate constants for other enclosures from vapour decay half-life data when sets of experimental conditions such as temperature, surface types and mixing factors are similar. Poorer correlation of data for other enclosures will occur if these and other factors including enclosure geometry and sampling location (if $m < 1$), leakage and adsorption rates, etc. differ greatly from the chamber.

4. Practical Considerations

Intuitively, higher air flow rates through an enclosure would be expected to remove vapour (irritant or otherwise) more quickly. This is the case for the present experiments as shown by comparing k_0 values obtained for trials carried out in the one-room building versus those associated with the chamber experiments. That is, the building air exchange rate was 5 or 10 times slower than that for the chamber and k_0 values for the CH and TEP building ventilation trials are correspondingly smaller by roughly the same magnitude.

The results of the chamber experiment also show that by raising the ambient air temperature (and hence the volatility of the vapour source), the rate of vapour removal by ventilation may be correspondingly increased. At normal ambient temperature, the more volatile vapour sources can be advantageously removed from an enclosure by ventilation in a practical period of time (e.g., a few hours or a day). Based on the

approximate correlation between volatility and ventilation removal rate under a constant set of ambient conditions, a prediction of the time required to remove different irritants from an enclosure is possible. An example of such a prediction is given by the data in Table XII for a hypothetical case. In this example, an arbitrary ventilation rate constant is assigned to CN for a typical set of external conditions, from which the rate constants for other irritants may be calculated based on their relative volatility to CN. From the rate constants, the time required to reduce vapour concentration to near zero levels may be calculated, assuming vapour concentration decays in an exponential fashion as described by e.g., Equation 4.

This hypothetical example points out the advantage of using a volatile liquid irritant such as CH with respect to decontaminating an enclosure by ventilation. Under the typical set of conditions described, CH is essentially removed from the enclosure in an hour whereas removal of the non-volatile solid irritants CS and CR would require more than a year under the same conditions. That is, completely removing CS and CR strictly by ventilation is not practical under the given conditions, although the vapour concentration may be reduced to non-sensory levels well before this time depending on the initial vapour concentration.

The ventilation data obtained from experiments carried out in the chamber and one-room building indicate that CH vapour behaves approximately as an ideal gas. That is, for CH, $k_0 \approx k_v$, the air change rate for the enclosure. This would further suggest that compounds more volatile than CH should also be removed by ventilation at the air exchange rate provided $k_v \gg k_1$, as was generally the case in the present series of experiments.

In general, measurement of ventilation rates using the infrared analyzer creates a rate limiting factor due to the sampling rate of the analyzer itself (i.e., 5 air changes per minute). This normally does not create a problem since the air exchange rate of buildings and other enclosures such as aircraft cockpits is much slower than this. In the chamber studies described herein, the enclosure air exchange rate and sampler rate were essentially identical; thus, an increase in flow rate through the chamber above the sampling rate would not be reflected as an increase in ventilation rate constants for the three compounds since the analyzer sampling rate would then constitute a rate limiting factor for the concentration decay data.

CONCLUSIONS

1. The overall rate at which vapour (irritant or otherwise) is removed from an enclosure by ventilation depends on several factors, some of which are interrelated, including:
 - a. rate of air movement or air exchange rate in the enclosure;
 - b. speed and efficiency of air mixing;
 - c. ambient temperature;
 - d. volatility of the vapour source;
 - e. rates of adsorption and desorption into and from adsorbent surfaces and mass of adsorbed material available for desorption;
 - f. surface area of exposed adsorbent surfaces; and,
 - g. internal volume of the enclosure.
2. CN, TEP and CH vapour adsorb more rapidly into porous surfaces such as gyproc and carpet compared to materials such as wood and metal.
3. As expected, higher air temperatures and higher air flow rates produce a corresponding increase in vapour removal rate by ventilation (and a decrease in time required to remove a given amount of vapour).
4. Under the given experimental conditions, an approximate correlation exists between vapour removal rate and volatility of the vapour source. At constant air flow rates and temperatures, CH is removed more rapidly than TEP or CN in accordance with differences in their respective volatilities.
5. For a given vapour source, results obtained from experiments using a small model enclosure allow qualitative predictions to be made of vapour removal rates for other enclosures with similar surface types based on air exchange rates, vapour concentration decay half-lives and mixing factors.
6. Under constant external conditions, qualitative predictions can be made of the differences in time required to decontaminate an enclosure by ventilation for different vapour sources based on their relative volatilities.
7. For perfect mixing ($m = 1$) CH behaves approximately as an ideal gas, the vapour being removed at a rate which is close to the air exchange rate for the enclosure.

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ANNEX A
TABLES

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TABLE I
TEST CHAMBER PARAMETERS

SURFACE TYPE	MATERIAL ^a	VOLUME ^b (m ³)	SURFACE AREA (m ²)	AREA/VOLUME RATIO (m ⁻¹)
I	metal ^c	0.402	4.29	10.68
II	wood	0.354	4.01	11.32
III	II + carpet (floor)	0.336	3.90	11.61
IV	III + stippled gyproc (ceiling)	0.324	3.83	11.82
	air flow velocity	= 12.2 m min ⁻¹	(40 feet min ⁻¹)	
	chamber length	= 2.44 m		
	air change rate	= 5 min ⁻¹		
	analyzer sampling rate	= 5 min ⁻¹		

- a. For all experiments, the lexan windows, fans and electrical cords located inside the chamber constitute a small, constant surface area for adsorption of vapour.
- b. Does not include the volume associated with the infrared gas analyzer and connecting sampling tubes (approximately .006 m³).
- c. That is, the interior walls of the chamber itself without inserts.

TABLE II
DATA FOR TEST COMPOUNDS

COMPOUND	CHEMICAL NAME	PHYSICAL STATE	VOLATILITY @ T = 25°C (mg m ⁻³)	ANALYTICAL WAVELENGTH (μm)
CN	α-Chloroacetophenone	solid	65 ^b	7.85
TEP	Triethyl Phosphate	liquid	2140 ^c	9.45
CH	1-Methoxy-1, 3, 5-cycloheptatriene ^a	liquid	9478 ^d	8.60

- a. CH is usually a mixture of the 1-, 2- and 3-methoxy cycloheptatriene isomers in an approximate isomer ratio of 90, 2 and 8%, respectively.
- b. From Reference 8.
- c. Reference 9 data.
- d. Reference 10a reports the volatility of CH as approximately 8400 mg m⁻³ at T = 20°C. Using vapour pressure data supplied under Reference 10b, a value of 9478 mg m⁻³ is found for T = 25°C.

TABLE III
INFRARED ANALYZER CALIBRATION DATA SUMMARY

Slit Width: 1 mm
Cell Temperature: 50°C

COMPOUND	WAVELENGTH (μm)	PATHLENGTH (m)	PROPORTIONALITY CONSTANT (k)²
CN	7.85	20.25	655.2
TEP	9.45	0.75	1018.0
CH	8.60	11.25	1227.6
FREON-12	9.10	20.25	252.3

a. $\text{Concentration} = \text{Absorbance} \times k$

TABLE IV
CHAMBER AIR MIXING FACTOR

Air Flow Rate:	$28 \pm 2 \text{ L min}^{-1}$
Chamber Volume:	$0.402 \text{ m}^3 = 402 \text{ L}$
Surface:	Type I (metal)
Air Change Rate:	$k_v = 6.97 \times 10^{-2} \text{ min}^{-1}$ (14.4 minutes per change)
Observed Freon 12 ventilation rate constant:	$k_{obs} = 6.90 \pm 0.39 \times 10^{-2} \text{ min}^{-1}$
Mixing Factor:	$m = k_{obs}/k_v = 0.99 \pm 0.06$

TABLE V
EFFECT OF INITIAL VAPOUR CONCENTRATION ON RATE CONSTANTS^a

SURFACE TYPE	COMPOUND	AMOUNT VAPORIZED	C_0^b (mg m^{-3})	$k_1 \times 10^{-2}$ (min^{-1})	$k_0 \times 10^{-1}$ (min^{-1})
I	CN	250 mg	49.6	0.61	0.32
		500 mg	62.1	0.66	0.34
II	TEP	500 μL	256.7	3.37	6.97
		800 μL	347.2	3.25	6.85
III	CH	500 μL	757.8	4.01	45.87
		800 μL	1028.6	3.96	45.22

- a. Data reported for single runs only. $T = 25^\circ \pm 2^\circ\text{C}$.
- b. C_0 is the vapour concentration at which concentration versus time measurements commenced. C_0 was less than the theoretical (or saturated) vapour concentration (C_0') which could be produced in the chamber due to concurrent adsorption of vapour during the vaporization process.

TABLE VI
ADSORPTION RATE DATA SUMMARY

T = 25° ± 2°C

Source: 500 μL or 500 mg of liquid or solid as appropriate

SURFACE TYPE	COMPOUND	ADSORPTION RATE CONSTANT ^{a,c} $k_1 \times 10^{-2}$ (min ⁻¹)	ADSORPTION HALF-LIFE ^b $t_{1/2}$ (min)
I	CN	0.65 ± 0.05	107
	TEP	2.85 ± 0.13	25
	CH	0.73 ± 0.05	95
II	CN	0.50 ± 0.05	143
	TEP	3.24 ± 0.25	21
	CH	1.24 ± 0.06	56
III	CN	0.58 ± 0.04	119
	TEP	3.78 ± 0.16	18
	CH	3.68 ± 0.37	19
IV	CN	1.57 ± 0.25	44
	TEP	6.56 ± 0.61	11
	CH	7.72 ± 0.27	9

- a. For direct comparison, the adsorption rate constants and half-life constants have been normalized to correspond to a chamber surface to volume ratio of 10.68. For example, for a Type III chamber surface, normalized k_1 = observed $k_1 \times (10.68/11.61)$. For a Type I surface, normalized k_1 = observed k_1 .
- b. Time required to reduce vapour concentration to one-half of any given concentration value, $t_{1/2} = \ln 2 / k_1$ under non-equilibrium conditions.
- c. Results are reported as mean ± standard deviation for three replicate runs.

TABLE VII
VENTILATION RATE DATA SUMMARY

Air Flow Rate: 12.2 m min⁻¹
Temperature: 25° ± 2°C
Source: 500 μL or 500 mg of liquid or solid as appropriate

SURFACE TYPE	COMPOUND	VENTILATION RATE CONSTANT ^{a, b}		HALF-LIFE ^c	
		k ₀ × 10 ⁻¹ (min ⁻¹)	k ₂ × 10 ⁻¹ (min ⁻¹)	t _{1/2} (min)	(air change)
I	CN	0.36 ± 0.03	0.30	19.3	97
	TEP	5.85 ± 0.27	5.57	1.2	6
	CH	46.00 ± 0.62	45.93	0.15	0.9
II	CN	0.44 ± 0.03	0.39	15.8	79
	TEP	6.73 ± 0.28	6.41	1.0	5
	CH	46.02 ± 0.41	45.90	0.15	0.9
III	CN	0.33 ± 0.04	0.27	21.0	105
	TEP	6.17 ± 0.60	5.79	1.1	6
	CH	46.52 ± 0.96	46.15	0.15	0.9
IV	CN	0.78 ± 0.06	0.62	8.9	45
	TEP	5.74 ± 0.39	5.08	1.2	6
	CH	46.11 ± 0.84	45.34	0.15	0.9

- a. Rate constants k₀, k₁ are normalized to a chamber surface area to volume ratio of 10.68 (Type I surface).
- b. k₂ = k₀ - k₁
- c. Time required to reduce vapour concentration to one-half of any given concentration value under non-equilibrium conditions.

$$t_{1/2} = \ln 2 / k_0$$

The corresponding numbers of air changes under the given conditions is t_{1/2} × 5.

TABLE VIII
CORRELATION BETWEEN VOLATILITY AND
VENTILATION REMOVAL RATE

COMPOUND	RELATIVE VOLATILITY ^a	RELATIVE k_2 ^b				AVERAGE	
		Surface:	I	II	III		IV
CN	1		1	1	1	1	1
TEP	33		19	16	21	8	16
CH	146		153	118	171	73	129

- a. Relative volatility = volatility of compound divided by CN volatility. Volatilities for $T = 25^\circ\text{C}$.
- b. Relative k_2 = normalized ventilation decay constant k_2 divided by k_2 for CN.

TABLE IX
EFFECT OF TEMPERATURE ON VENTILATION REMOVAL RATES

Vapour Source: TEP
Charge: 500 μ L
Chamber Ventilation Rate: 5 air changes min^{-1}
Air Flow Rate: 12.2 m min^{-1}

SURFACE TYPE	AIR TEMPERATURE ($^{\circ}\text{C}$)	VOLATILITY TEP @ T (mg m^{-3})	VENTILATION RATE CONSTANT $k_0 \times 10^{-1}$ (min^{-1})
I	23.0	1900	4.82
	25.0	2140	$5.85 \pm 0.27^{\text{a}}$
	29.0	2850	7.43
II	23.0	1900	4.17
	25.0	2140	$6.73 \pm 0.28^{\text{a}}$
	29.0	2850	7.79
	31.0	3200	8.46

- a. Data reported as mean \pm standard deviation for three replicate runs. Otherwise, data is for a single run only.

TABLE X
DESORPTION RATE DATA SUMMARY

T = 25° ± 2°C

SURFACE TYPE	COMPOUND	DESORPTION RATE CONSTANT ^a $k_3 \times 10^{-2} \text{ (min}^{-1}\text{)}$	k_3/k_1	DESORPTION HALF-LIFE ^b $t_{1/2} \text{ (min)}$
I	CN	2.9 ± 0.4	4.5	24
	TEP	7.8 ± 2.7	2.7	9
	CH	6.7 ± 1.0	9.2	10
II	CN	3.2 ± 0.7	6.4	22
	TEP	18.2 ± 3.0	5.6	4
	CH	8.6 ± 1.5	6.9	8
III	CN	3.2 ± 0.6	5.5	22
	TEP	20.4 ± 1.5	5.4	3
	CH	11.7 ± 0.3	3.2	6
IV	CN	4.1 ± 0.5	2.6	17
	TEP	31.9 ± 1.6	4.9	2
	CH	28.3 ± 2.2	3.7	2

- a. Constants are normalized to correspond to a chamber surface to volume ratio of 10.68 (Type I surface).
- b. Time required for a given vapour concentration to increase $2 \times$ (non-equilibrium state)

$$t_{1/2} = \ln 2 / k_3$$

TABLE XI
VAPOUR REMOVAL FROM ONE-ROOM BUILDING

$$V = 72.6 \text{ m}^3$$

$$A = 111.7 \text{ m}^2$$

Surface Type: Plywood

$$\text{Surface Area/Volume Ratio} = 1.54 \text{ m}^{-1}$$

$$T = 15^\circ\text{C} \pm 2^\circ\text{C}$$

TRIAL NO.	COMPOUND	VOLUMETRIC FLOW RATE ($\text{m}^3 \text{ min}^{-1}$)	AIR CHANGES k_v (min^{-1})	RATE CONSTANT $k_o \times 10^{-1}$ (min^{-1})	HALF-LIFE $t_{1/2}$	
					(min)	(air changes)
1	TEP	36.7	0.5	0.38	18	9
2	TEP	76.5	1.1	0.72	10	10
3	CH	36.7	0.5	5.93	1.2	0.6
4	CH	76.5	1.1	10.66	0.7	0.7

TABLE XII
PREDICTION OF REMOVAL RATES AND TIMES BASED ON
RELATIVE VOLATILITY

External Conditions

Air Change Rate: 0.2 min^{-1} (5 minutes for one complete air change)

Temperature: 25°C

Mixing Factor: $m = 0.8$ ($k_v = 0.8 (0.2) = 0.16 \text{ min}^{-1}$)

Measured CN $k_o = 1.0 \times 10^{-3} \text{ min}^{-1}$

COMPOUND	VOLATILITY @ T (mg m^{-3})	RELATIVE ^a VOLATILITY	k_o ^b (min^{-1})	$t_{0.001}$ ^c	
				(h)	(air changes)
CS	0.45	0.007	7.0×10^{-6}	2.0×10^4	2.5×10^5
CR	0.75	0.012	1.2×10^{-5}	1.2×10^4	1.4×10^5
CN	65	1	1.0×10^{-3}	144	1728
CH	9478	146	1.5×10^{-1}	1	12

- a. Relative Volatility = volatility of compound/CN volatility.
- b. Compound $k_o = 1.0 \times 10^{-3}$ (CN k_o) \times relative volatility.
- c. $t_{0.001}$ = time required for vapour concentration to decay to 0.1% of the initial vapour concentration. That is, $C(t)/C_o = 0.001$. The decay equation $\ln(C_o/C_t) = -mk_o t$ then yields
 $t_{0.001} = -6.908 / -0.8k_o = 8.64/k_o$.

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ANNEX B
FIGURES

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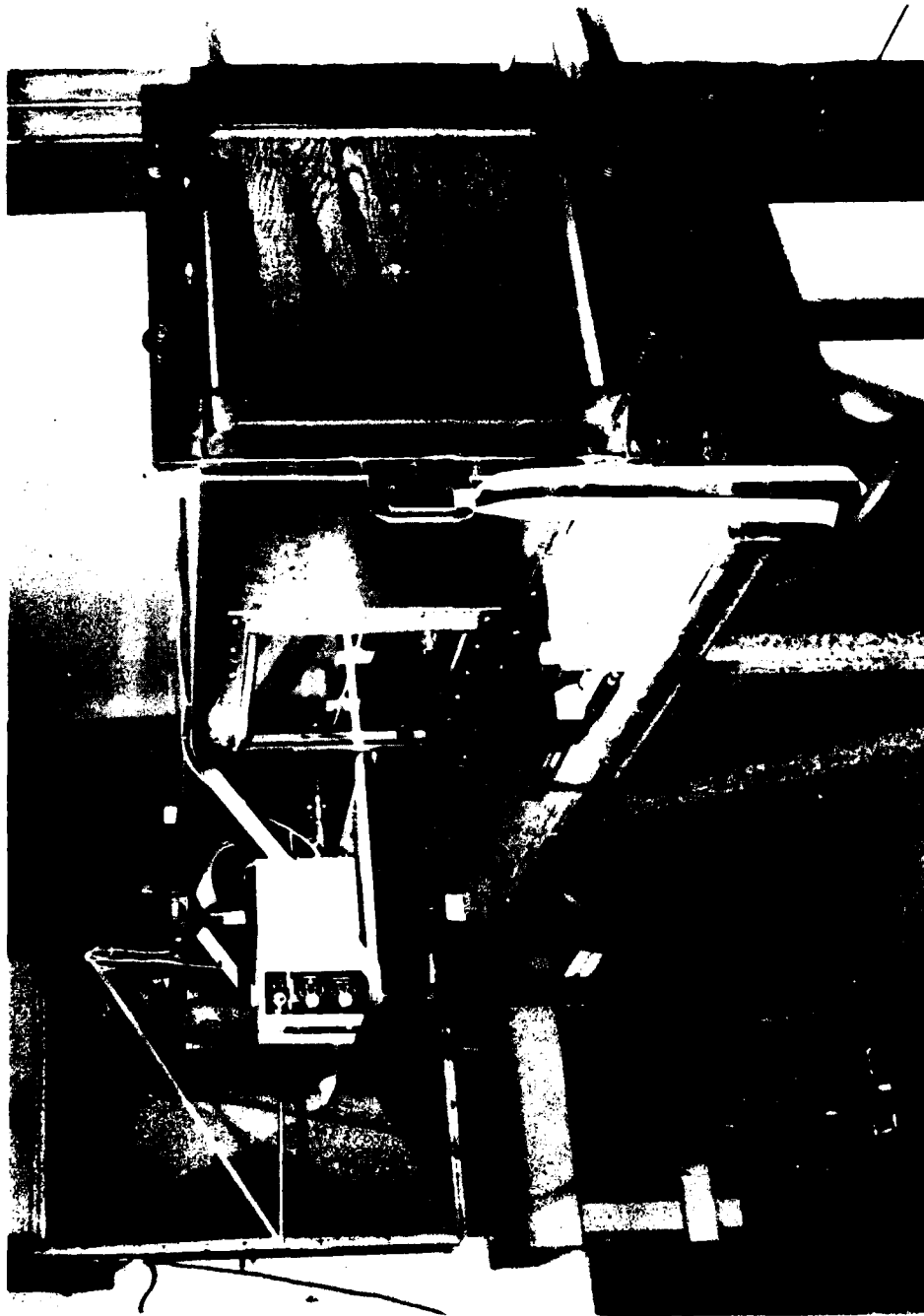


Figure 1
INSTRUMENTED TEST CHAMBER – END VIEW

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Figure 2
INSTRUMENTED TEST CHAMBER - SIDE VIEW

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AIR CHANGE RATE = 1 per 14.4 minutes
 $k_v = 6.97 \times 10^{-2} \text{ min}^{-1}$
CHAMBER SURFACES = TYPE I
 $C_0 = 270.5 \text{ mg m}^{-3}$

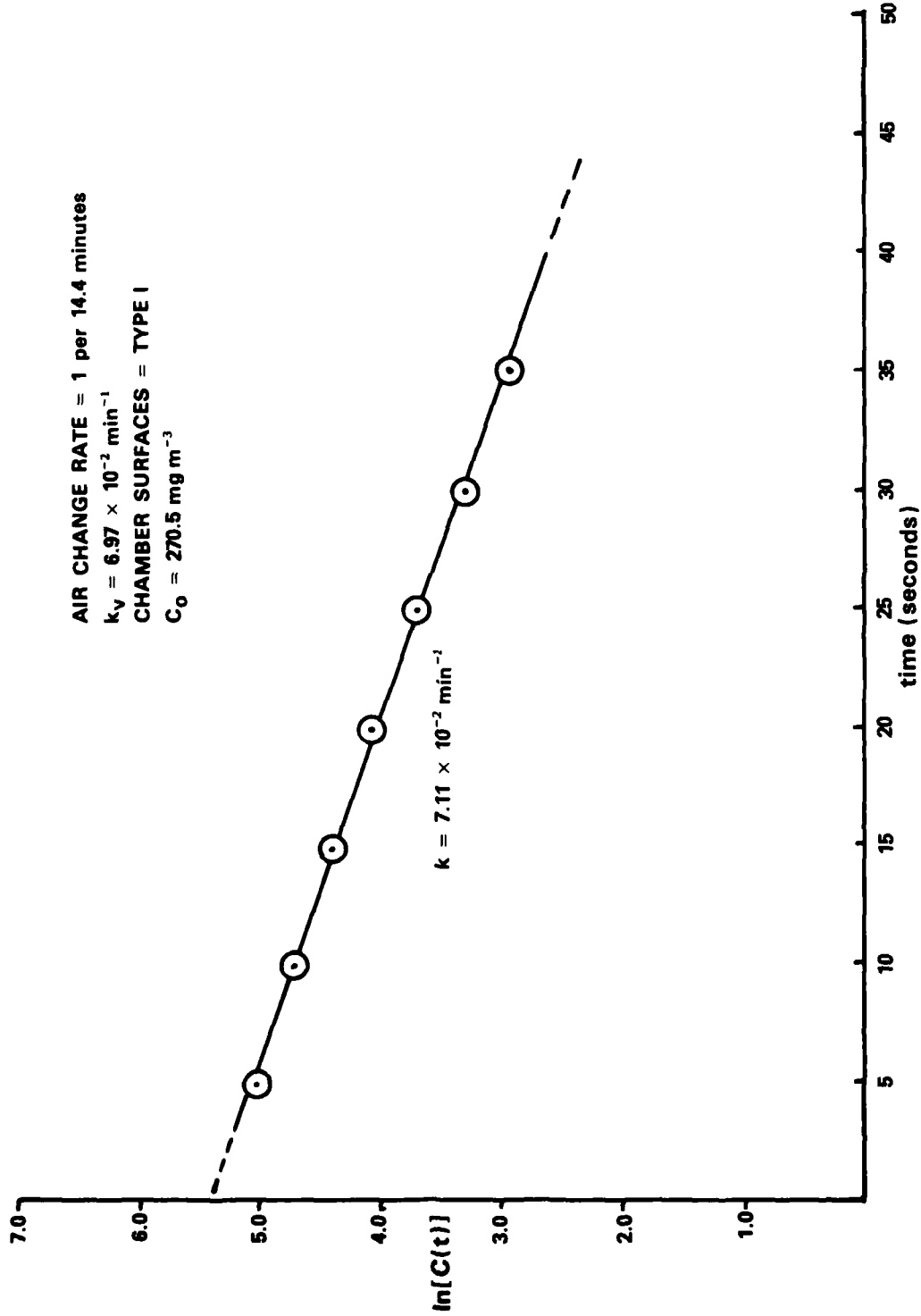


Figure 3

REMOVAL OF FREON 12 TRACER FROM CHAMBER BY VENTILATION

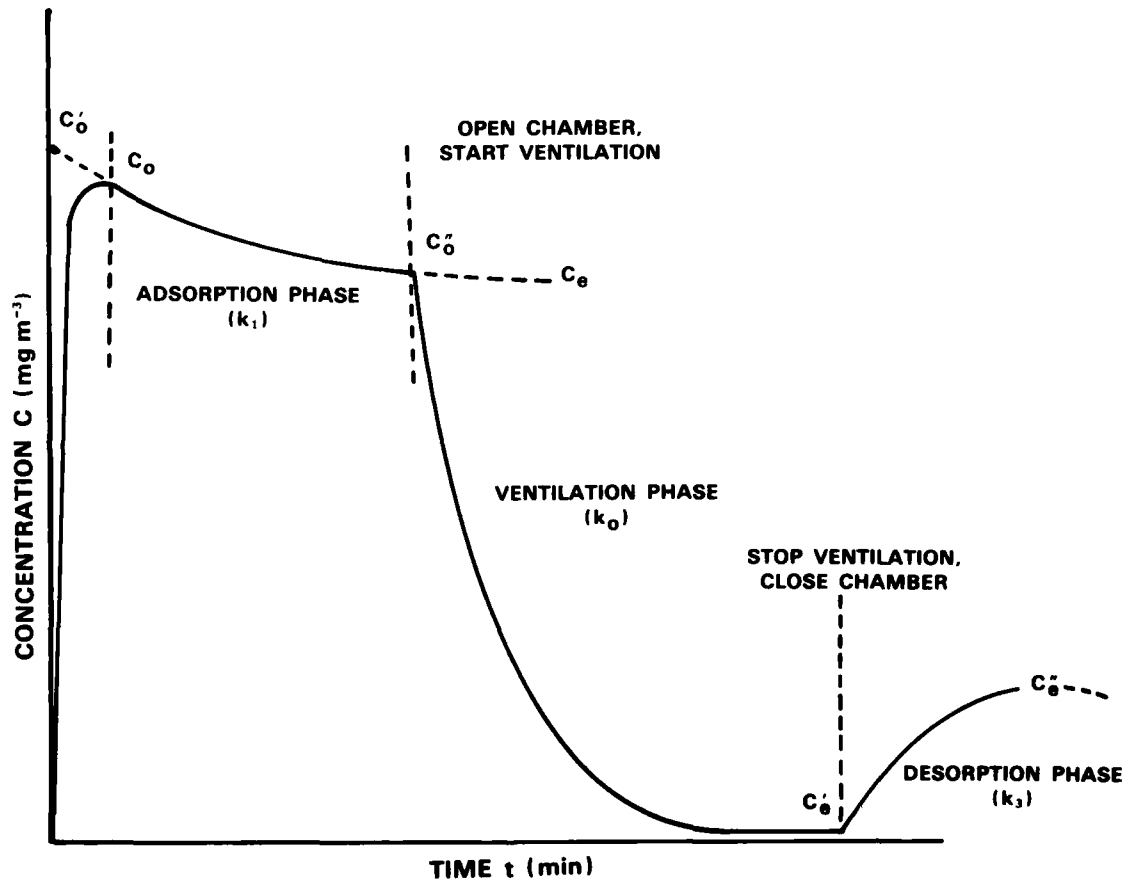


Figure 4
CONCENTRATION VS TIME PROFILE FOR A TYPICAL VENTILATION EXPERIMENT

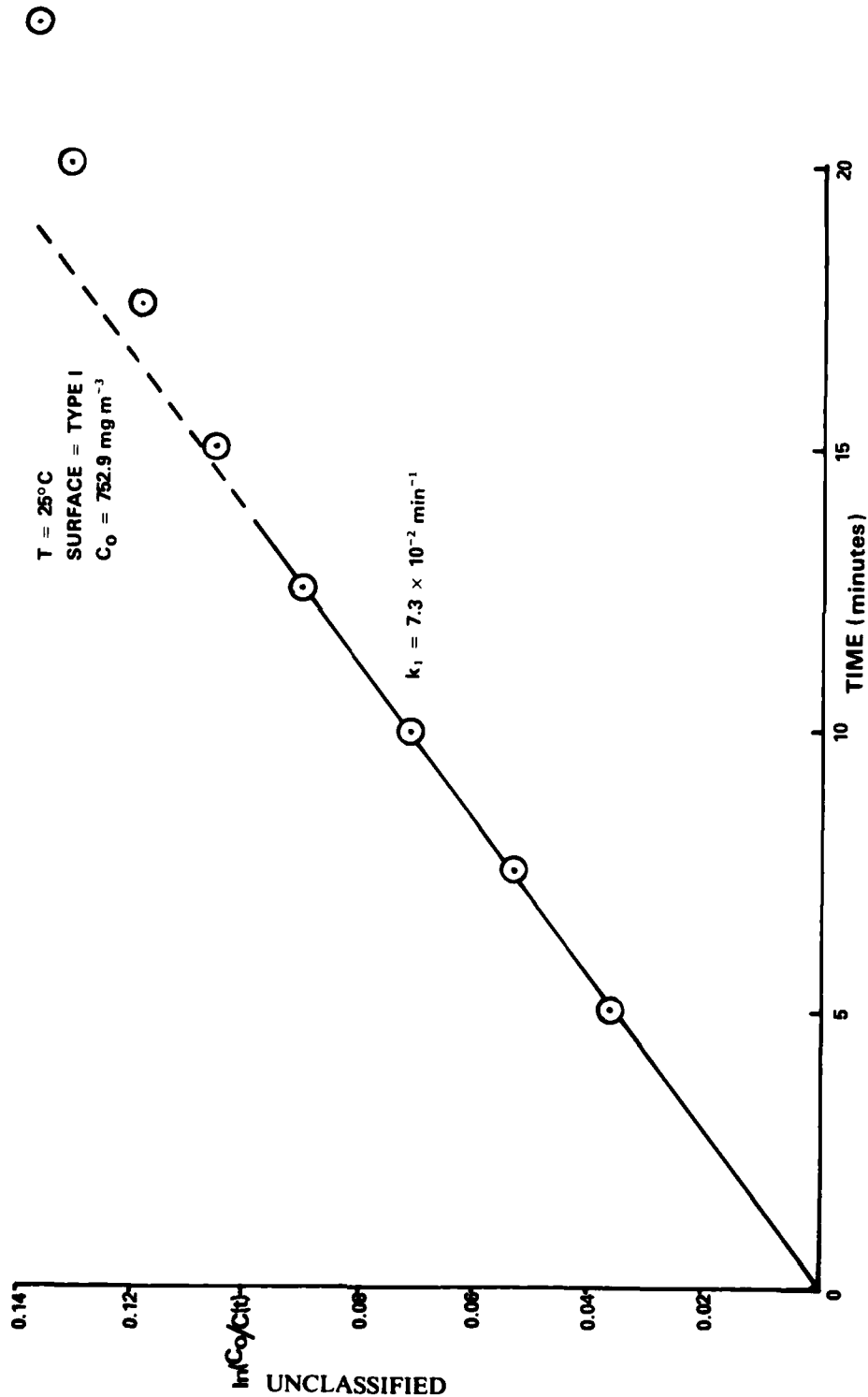


Figure 5
TYPICAL CH ADSORPTION RATE CURVE
 $\ln [C_0/C(t)]$ vs time

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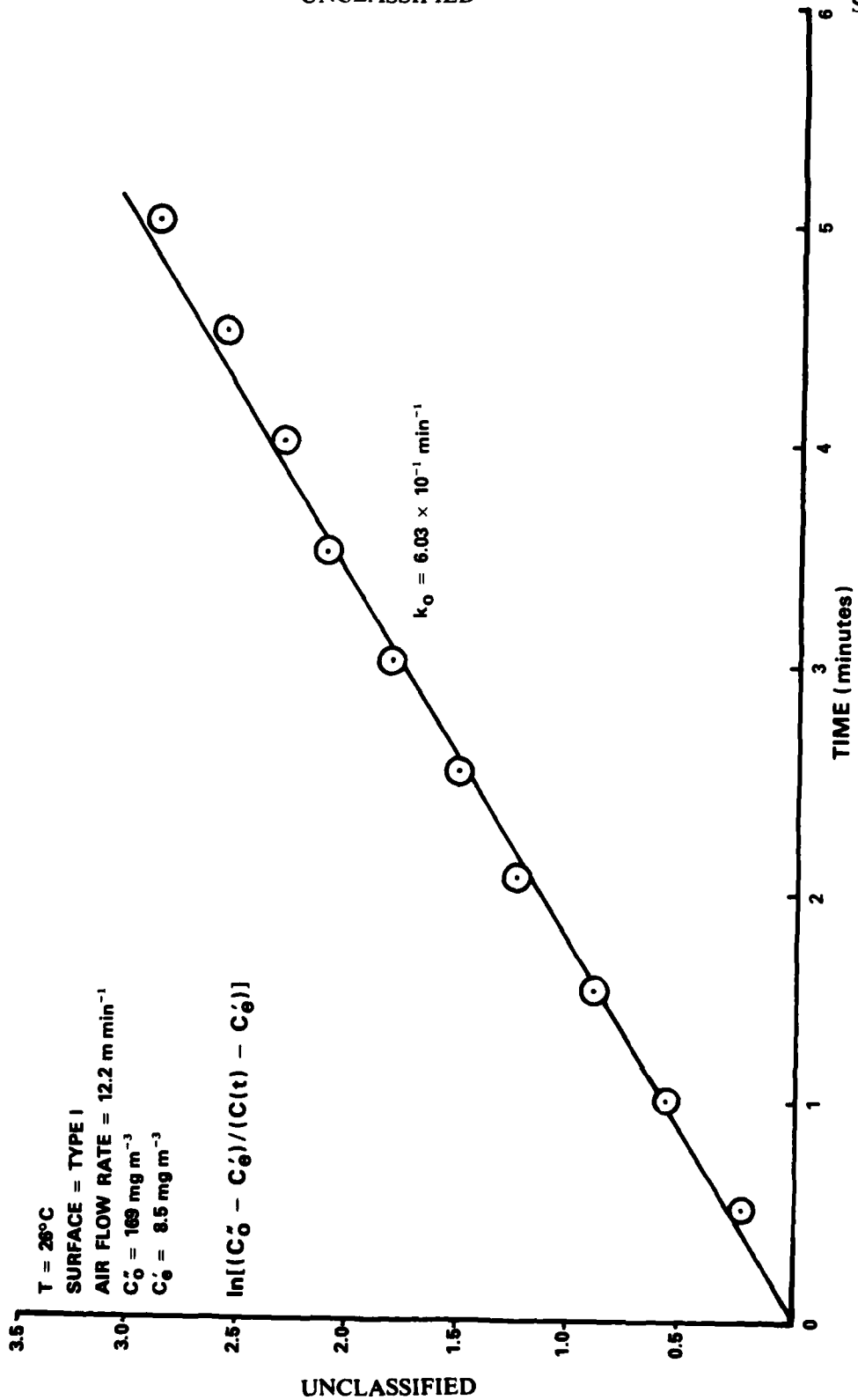
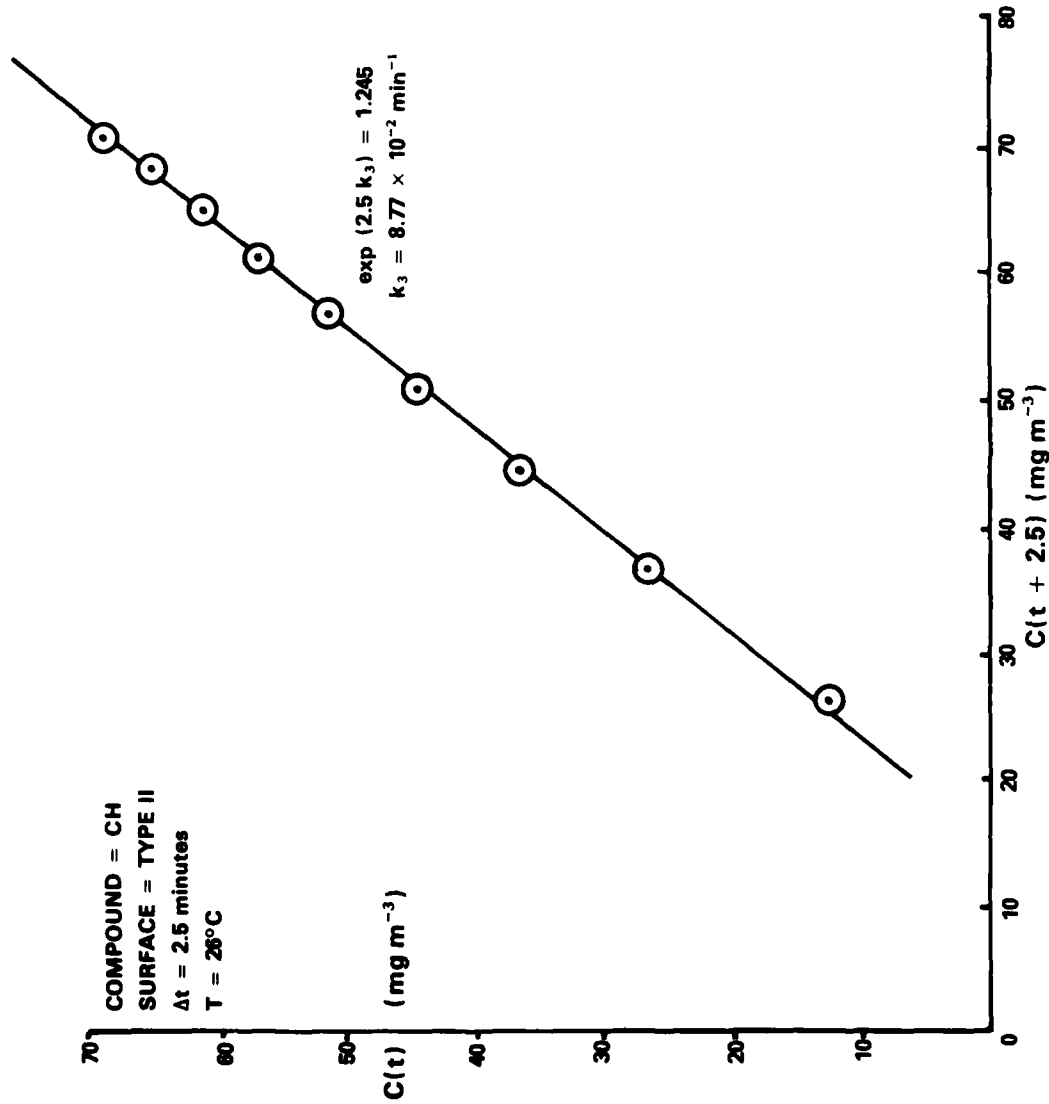


Figure 6

TYPICAL TEP VENTILATION RATE CURVE



TYPICAL $C(t)$ VS $C(t + \Delta t)$ PLOT FOR DETERMINING DESORPTION RATE CONSTANTS

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1. ORIGINATING ACTIVITY DEFENCE RESEARCH ESTABLISHMENT SUFFIELD	2a. DOCUMENT SECURITY CLASSIFICATION UNCLASSIFIED	
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3. DOCUMENT TITLE REMOVAL OF IRRITANT VAPOURS FROM ENCLOSURES BY VENTILATION		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) SUFFIELD REPORT		
5. AUTHOR(S) (Last name, first name, middle initial) McANDLESS, John M., GALLOWAY, Milton E., CHENIER, Claude L.		
6. DOCUMENT DATE July 1983	7a. TOTAL NO. OF PAGES 26	7b. NO. OF REFS 13
8a. PROJECT OR GRANT NO. PCN 210-13E30	9a. ORIGINATOR'S DOCUMENT NUMBER(S) Suffield Report 360	
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13. ABSTRACT A small test chamber was used as a model enclosed space to study the removal of irritant vapours by ventilation. Quantitative data was obtained on the relative rates of removal of CH and CN and their adsorption/desorption rates from selected materials. Triethyl phosphate, a liquid of intermediate volatility, was included in the study for comparison purposes. Ventilation removal rate data for the chamber was compared to data for ventilation trials carried out using a one-room building. Under the given experimental conditions, results obtained from experiments with the model enclosure allow qualitative predictions to be made of vapour removal rates for other enclosures based on air exchange rates, vapour concentration decay half-lives, mixing factors and relative volatility of the vapour source.		

KEY WORDS

Ventilation
 Incapacitating agents
 Enclosures
 CS
 CR
 CH
 CN
 Triethyl Phosphate
 Volatility

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