

# Cyclohexane as an Alternative Vapor of Carbon Tetrachloride for the Assessment of Gas Removing Capacities of Gas Masks

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**Abstract:** An alternative vapor was explored to replace carbon tetrachloride (CCl<sub>4</sub>) for testing breakthrough times of cartridges and canisters of gas masks in the National Approval Test of Respirators. Cyclohexane was single out as a candidate for the alternative vapor out of six vapors: trichloroethylene, n-pentane, n-hexane, n-heptane, toluene and cyclohexane from the viewpoints of similarity of vapor pressure and water-solubility to CCl<sub>4</sub>, lower toxicity than CCl<sub>4</sub>, and technical feasibility in generating an airflow of 30 L/min containing the vapor ranging from 300 to 5000 ppm. Breakthrough times of cartridges and canisters were examined by generating cyclohexane vapor in a test airflow of 30 L/min in comparison with CCl<sub>4</sub> vapor under various test conditions with different vapor concentrations and relative humidities (RH). As the results, the breakthrough times of the cartridges and canisters for cyclohexane were found to almost coincide with those for CCl<sub>4</sub> under all examined range of concentrations and RH. By an increase of humidity from 50%RH to 80%RH, the cartridges showed significant shortening of breakthrough times for both of CCl<sub>4</sub> and cyclohexane, but the susceptibility of the breakthrough time of cyclohexane to humidity was also similar to that of CCl<sub>4</sub>. It was, therefore, concluded that cyclohexane can be recommended as the alternative vapor of CCl<sub>4</sub> for testing the breakthrough times of gas mask cartridges and canisters in the National Approval Test.

**Key words:** Gas mask, Cartridge, Canister, Carbon tetrachloride, Cyclohexane, Breakthrough time, Respirator

## Introduction

Carbon tetrachloride (CCl<sub>4</sub>) vapor has long been used as a representative organic vapor for testing breakthrough times of gas mask cartridges and canisters in the National Approval Test of Respirators as well as in respirator tests in manufactures. However, the production and use of CCl<sub>4</sub> in industries are now phased out, because of its potentially significant depleting effect on stratospheric ozone<sup>1,2)</sup>, and because of its suspected human carcinogenicity<sup>3)</sup>. This study was funded by the Ministry of Labour to establish a new

test method of gas masks without the use of CCl<sub>4</sub>. To keep the continuity of the quality criteria of gas masks through the change of the test method was the requirement of the National Approval Test System. Besides, the deterioration of the gas removing capacities of cartridges and canisters by the airborne moisture should be detected similarly by the new method as by the CCl<sub>4</sub> method. Similarity of vapor pressure and water-insolubility to CCl<sub>4</sub>, technical feasibility in generating a test airflow containing the vapor ranging from 300 to 5000 ppm (v/v), and the lower risk in toxicity, carcinogenicity and flammability are the primary requirement to single out a CCl<sub>4</sub> replacement vapor. At first, the six candidates of alternatives were chosen within these scopes.

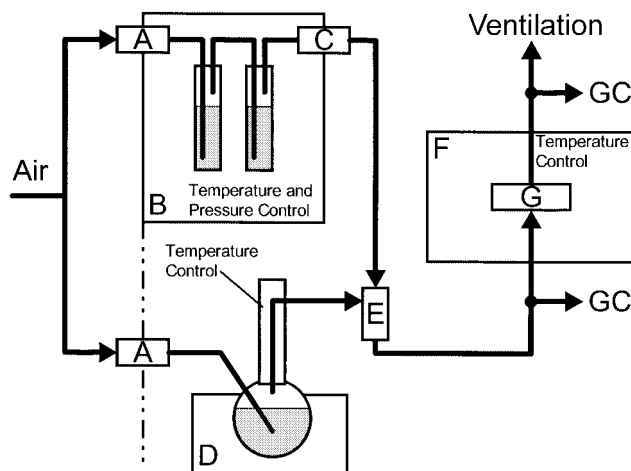
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They were trichloroethylene, n-pentane, n-hexane, cyclohexane, n-heptane and toluene. Among the candidates, n-pentane has very low boiling point of 36.06°C which is close to the climatic temperature in the summer in Japan and its handling in laboratory is difficult. To obtain 5000 ppm vapor concentration of toluene in the test airflow of 30 L/min needs the higher evaporation temperature than the laboratory ambient temperature and consequently, the vapor tends to condense in the downstream pipes kept at 20°C. By these reasons relating their volatility, n-pentane and toluene were excluded from the candidates. Trichloroethylene and n-hexane were taken as the second candidates due to their higher toxicity. Cyclohexane and n-heptane were experimentally examined for the test of breakthrough times of gas masks in comparison with CCl<sub>4</sub>. The Notification of The Ministry of Labour on Standards of Gas Masks for the National Approval Test stipulated in 1990<sup>4)</sup> requires that the breakthrough time of CCl<sub>4</sub> be longer than 50 minutes for cartridges with the CCl<sub>4</sub> concentration of 300 ppm in a test airflow, longer than 30 min for chin-style canisters with 3000 ppm CCl<sub>4</sub>, and longer than 100 min for front-mounted or back-mounted (FM/BM) canisters with 5000 ppm CCl<sub>4</sub>, at the airflow of 30 L/min. In the present experiment, cyclohexane was examined for breakthrough times of commercially available gas mask cartridges and canisters in comparison to CCl<sub>4</sub> at certain concentration ranges of vapors and coexistent moisture. n-Heptane was also applied for the test, but finally it was excluded from the candidate due to the technical difficulty in generating vapor at high concentration.

## Materials and Methods

### *Apparatus for measuring breakthrough times of respirator cartridges and canisters*

Figure 1 illustrates a schematic diagram of a testing apparatus for measuring breakthrough times of respirator cartridges and canisters. The apparatus is consisted of two parts; one for generating an airflow containing an organic vapor at a constant concentration with constant RH, and the other for testing breakthrough time of a cartridge or canister by passing the organic vapor-containing airflow through a test piece mounted in a thermostatic air box and by monitoring the exit vapor concentration by a gas chromatograph (GC) (Type 5890 Series II, Hewlett-Packard, USA). A test airflow with a certain vapor concentration and a constant RH was obtained by the former part of the apparatus by mixing two controlled airflows; one airflow was saturated with water vapor at 20°C and at a certain pressure up to 338 kPa and then reduced to the atmospheric



**Fig. 1. A schematic diagram of the apparatus for generating test airflow.**

A: Airflow controllers, B: Two pressurized humidifier containing distilled water (20°C, 127~337 kPa), C: Back pressure regulator, D: Reflux condenser, E: Gas mixing tube, F: Thermostatic air box (20°C), G: Test piece of gas mask cartridge or canister.

pressure, and the other airflow was saturated with the test vapor at a certain temperature below the ambient temperature. These two flows were mixed in a gas mixing tube to get a test airflow. The concentration of an organic vapor in the test airflow was measured every 3 minutes at the downstream of the mixing tube with a GC equipped with an automatic gas sampling device and a hydrogen flame ionization detector (FID). Then, the test airflow was introduced into the latter part of the apparatus for testing breakthrough times of cartridges and canisters. In this study, the test airflow entering the thermostatic air box was regulated at a temperature of 20°C and a flow rate of 30 L/min with constant RH of 30, 50, 70 or 80%. CCl<sub>4</sub> and cyclohexane vapors in the airflow were regulated precisely at the suitable concentrations required for the classes of cartridges and canisters, i.e., cartridges were tested in the concentration range from 100 to 600 ppm, chin-style canisters in the range from 1000 to 5000 ppm and FM/BM canisters in the range from 3000 to 8000 ppm. CCl<sub>4</sub>, cyclohexane and n-heptane used in the present study were of reagent grade (Wako Pure Chemical, Japan). However, n-heptane vapor could not be generated enough to prepare 5000 ppm test airflow due to its lower volatility, though it could be generated within the concentration range from 150 to 620 ppm in the test airflow. By this reason, we did not examine n-heptane further.

### *Measurement of breakthrough time*

After a test piece of cartridge or canister was mounted to

**Table 1. Classes and sizes of respirator cartridges and canisters tested in the present study**

Classes of cartridge or canister	Manufacturer	Number of cartridges or canisters used	Size of activated carbon container	Content of activated carbon
Cartridge	A	28	75.2 mm ( $\phi$ ) 15 mm (Thickness)	23 g
Cartridge	B	42	77 mm ( $\phi$ ) 20 mm (Thickness)	41 g
Chin-style canister	C	16	85 mm ( $\phi$ ) 35 mm (Thickness)	80 g
FM/BM canister	B	12	135 mm (Length) 75 mm (Width) 114 mm (Thickness)	312 g
FM/BM canister	C	16	145 mm (Length) 76 mm (Width) 68 mm (Thickness)	270 g

FM/BM canister: front-mounted or back-mounted canister.

the test line in the thermostatic air box, the airflow containing an organic vapor of a constant concentration with constant RH was introduced through it. The concentration of the organic vapor was measured every 3 minutes at a sampling port located at the exit of the test piece with the same GC used for the test airflow monitoring. The breakthrough limit concentration at the exit of the cartridge and canister to determine the breakthrough times for both of CCl<sub>4</sub> and cyclohexane were set at 10 ppm in this study. The breakthrough times were measured in relation to the concentration of the vapor and humidity in the test airflow.

#### *Respirator cartridges and canisters tested*

Table 1 shows classes, sizes, activated carbon contents and number of respirator cartridges and canisters tested in the present study, which were commercially purchased in the market. We used three classes of cartridges and canisters manufactured by Japanese companies A, B and C, i.e., two kinds of cartridges, a kind of chin-style canister and two kinds of FM/BM canisters. The cartridges and canisters were submitted to the test “as purchased”.

## **Results**

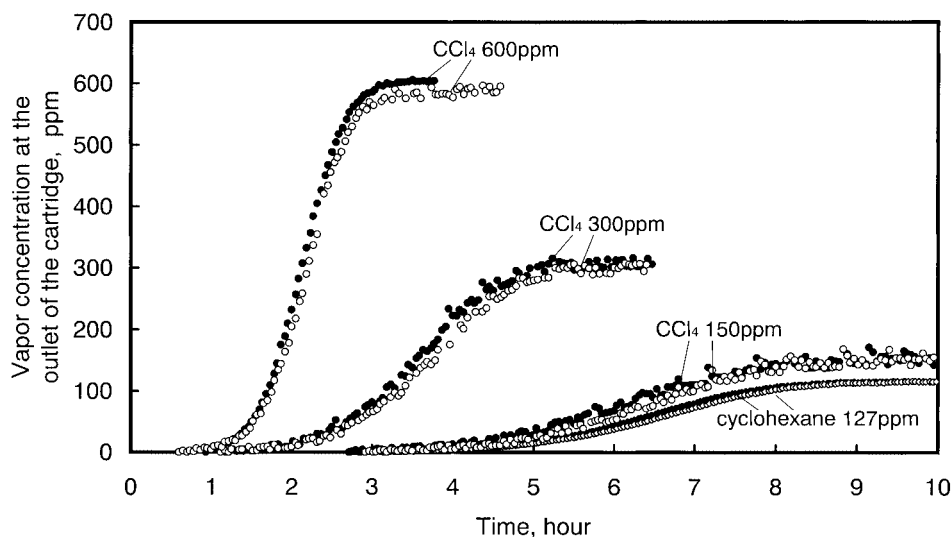
#### *Stability and reproducibility of concentrations of organic vapors in the test airflow*

Stability of the vapor concentration in the test airflow was monitored as the variation coefficient (CV). Taking the air sample every 3 minutes during 2 or 3 hours of constant running of the test airflow generating apparatus, the CV of the vapor concentration was found to be 1.22% for time-averaged concentration of 285 ppm for intended

concentration of 300 ppm cyclohexane vapor in the test airflow. The CVs of cyclohexane vapor at different concentrations as well as those of CCl<sub>4</sub> and n-heptane were also found to be within the same range from 1 to 3%. As to reproducibility in generating the test airflow, day-to-day variations of CCl<sub>4</sub> and cyclohexane concentrations in the airflow were found to be within the range from 1 to 4%. High reproducibility of the vapor concentration in the test airflow was also indicated by the breakthrough curves obtained by duplicated measurements in Fig. 2 which agreed well with each other. This means that the apparatus generated a stable and reproducible test airflow containing an organic vapor at a satisfactorily constant concentration.

#### *Breakthrough curves*

Figure 2 shows breakthrough curves of CCl<sub>4</sub> and cyclohexane as a function of time elapsed from the start of passing the test airflow through the cartridge manufactured by A. All the four breakthrough concentration-time relationships were found to follow sigmoidal curves, indicating three distinct stages in the breakthrough concentrations: The first stage is characterized by the beginning of the test vapor leakage into the exit airflow whose concentration increases slowly. In the practical uses of gas masks, cartridges or canisters should be replaced with a new one at this stage before the exit vapor concentration reaches to the noxious level to the users. After this first stage, the exit vapor concentration rapidly rises and then reached to a plateau level approximated to the inlet concentration. The breakthrough times of the cartridges or canisters are defined as those when the vapor begins to leak from the test piece at the maximum permissible concentrations for the wearers



**Fig. 2. Vapor concentrations of carbon tetrachloride and cyclohexane at the outlet of the cartridge A.** Temperature, relative humidity and the airflow rate: 20°C, 50% and 30 L/min, respectively.  $\circ$ : the first measurement,  $\bullet$ : the second measurement.

on principle, but conventionally at 10 ppm in this study.

#### *Breakthrough times for CCl<sub>4</sub> and cyclohexane*

Figure 3 shows relationships between the breakthrough times of cartridge A and the vapor concentrations of CCl<sub>4</sub> and cyclohexane in the test airflow. The breakthrough times of cartridge A for cyclohexane under two different RH conditions were found to agree well with those for CCl<sub>4</sub>. As shown in Fig. 4, it was also found with the cartridge manufactured by B that the breakthrough times for cyclohexane also agreed well with those for CCl<sub>4</sub> under two different RH conditions. The comparison of Figs. 3 and 4 reveals that the breakthrough times of cartridge B were longer than those of cartridge A. This difference can be attributed mainly to larger contents of activated carbon in the cartridge B, as indicated in Table 1. Figure 5 shows relationship between the breakthrough times of chin-style canister C and the vapor concentrations of CCl<sub>4</sub> and cyclohexane in the test airflow under two different RH conditions. The breakthrough times of the chin-style canister for these two vapors were found to agree well with each other. Figure 6 shows the breakthrough times of FM/BM canisters B and C as a function of vapor concentrations of CCl<sub>4</sub> and cyclohexane under two different RH conditions. It was also confirmed that the breakthrough times of FM/BM canisters for cyclohexane were almost identical to those for CCl<sub>4</sub>.

#### *Effect of humidity*

Figures 3 and 4 show that the breakthrough times of

cartridge A and cartridge B obtained by cyclohexane and CCl<sub>4</sub> were shortened by an increase of RH from 50% to 80% in the airflow. These two figures reveal that the breakthrough times of cartridges and canisters for the test vapor in the lower concentration range are shortened significantly by the high humidity to the similar extents. Figures 5 and 6 indicate no apparent difference in the breakthrough times of chin-style and FM/BM canisters at 50% and 80% RH, in which the breakthrough times were observed at the higher vapor concentration ranges, and not susceptible to the effect of coexisting moisture. However, in Fig. 5, the breakthrough times for cyclohexane of 1000 ppm was slightly reduced at 80% RH for chin-style canister C. RH effect was further examined with cartridge B passing through the airflow containing cyclohexane with different RH ranging from 30 to 80%. The result is shown in Fig. 7. The significantly shortened breakthrough times were found only at a relative humidity higher than 50% RH of the test airflow containing cyclohexane vapor lower than 400 ppm. In this result again, the effect of humidity at 70% and 80% RH to shorten the breakthrough time was diminished according to the cyclohexane vapor concentration increase in the test airflow, and almost negligible at around 1000 ppm.

#### *Amounts of vapor adsorbed*

Figure 8 shows the amounts of CCl<sub>4</sub> and cyclohexane adsorbed by cartridges, chin-style and FM/BM canisters. The amounts of vapors adsorbed by the activated carbon were calculated by the following equation:

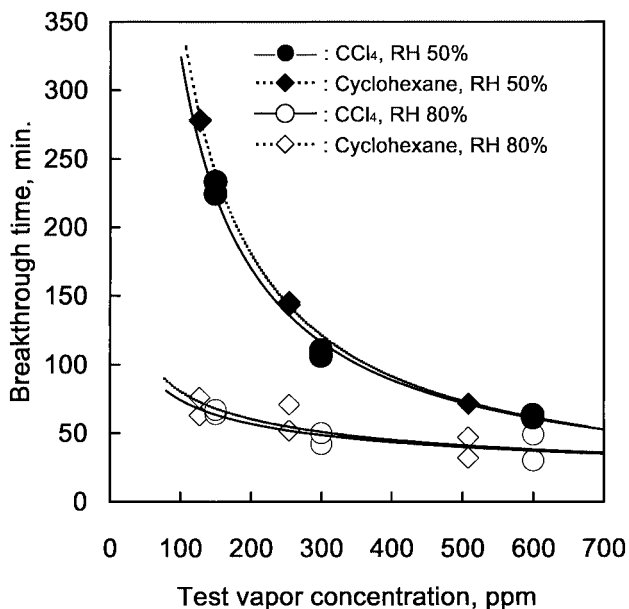


Fig. 3. Relationship between breakthrough times of cartridge A and concentrations of carbon tetrachloride and cyclohexane in the airflow.

Temperature and the airflow rate: 20°C and 30 L/min, respectively.

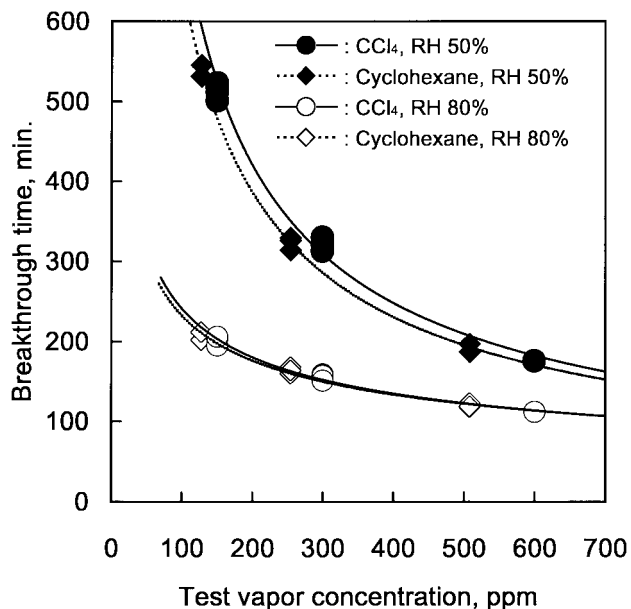


Fig. 4. Relationship between breakthrough times of cartridge B and concentrations of carbon tetrachloride and cyclohexane in the airflow.

Temperature and the airflow rate: the same as Fig. 3.

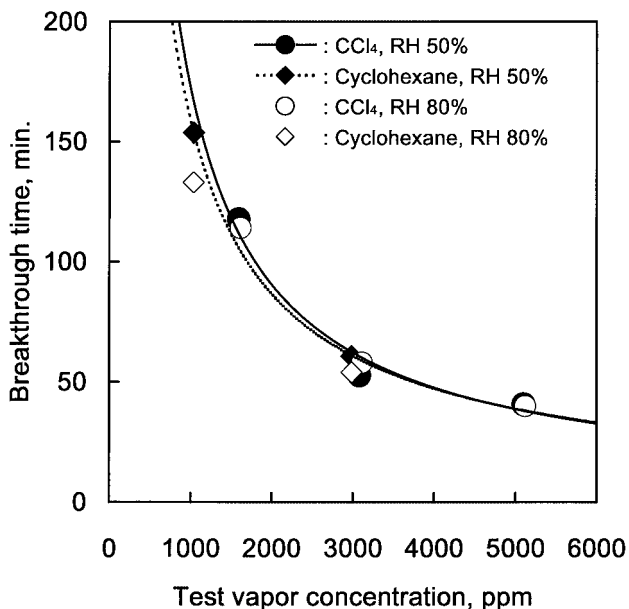


Fig. 5. Relationship between breakthrough times of chin-style canister C and concentrations of carbon tetrachloride and cyclohexane in the airflow.

Temperature and the airflow rate: the same as Fig. 3.

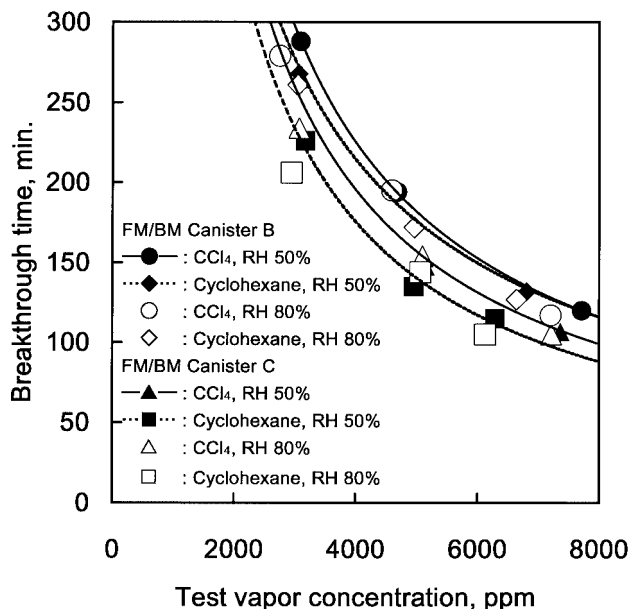


Fig. 6. Relationship between breakthrough times of front- or back-mounted (FM/BM) canisters B and C and concentrations of carbon tetrachloride and cyclohexane in the airflow.

Temperature and the airflow rate: the same as Fig. 3.

[adsorbed amount (L)] = [breakthrough time (min)]  
 × [airflow rate (L/min)]  
 × [vapor concentration (ppm)],  
 then expressed as adsorbed capacity in mol. The adsorbed

amounts were found to vary, depending upon the amounts of activated carbon packed in the containers and the vapor concentration in the test airflow. The results indicate that the amount of CCl<sub>4</sub> vapor adsorbed on each of the cartridges

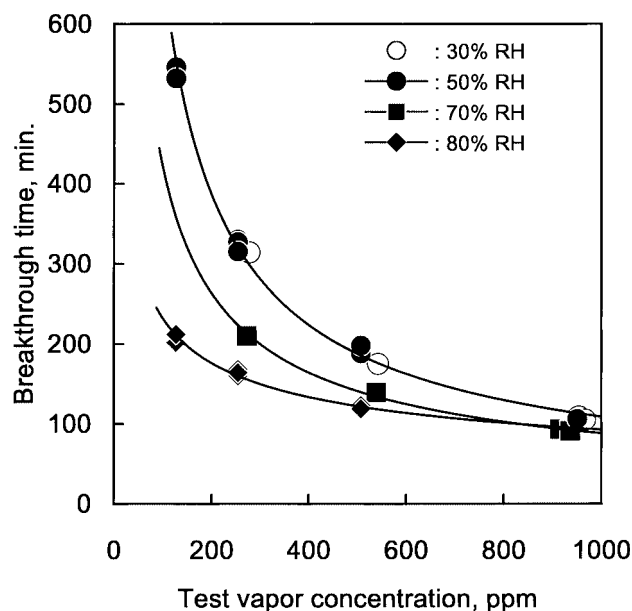


Fig. 7. Effect of relative humidity on breakthrough times of cartridge B for cyclohexane vapor.

and canisters until the breakthrough time was in essential agreement with that of cyclohexane vapor adsorbed, with only a small difference between the two.

## Discussion

In the present study, two steps of approaches were employed to single out a suitable  $\text{CCl}_4$  replacement vapor out of six candidate vapors: trichloroethylene, n-pentane, n-hexane, cyclohexane, n-heptane and toluene. The first step was based on reference to health and safety data of candidate vapors, similarity of physico-chemical properties of the candidate vapors to  $\text{CCl}_4$  which are related to the technical difficulty in generating an airflow containing an organic vapor by evaporation and refluxing method. Trichloroethylene and n-hexane were excluded due to their low exposure limit concentrations which were in the order of several tens ppm, lower than those of n-pentane, cyclohexane and n-heptane<sup>3, 6)</sup> by an order. Among cyclohexane, n-heptane and n-pentane which are flammable, n-pentane is the most difficult material among them to handle with due to the high volatility at room temperature. Physico-chemical properties such as water solubility and vapor pressure of cyclohexane are closer to those of  $\text{CCl}_4$  in comparison to those of n-pentane and n-heptane. Water-solubilities of cyclohexane, n-heptane and n-pentane at 25°C are 0.010%, 0.00036%, 0.0038% (w/w), respectively, in comparison to 0.077% of  $\text{CCl}_4$ <sup>8)</sup>; and the vapor pressures of

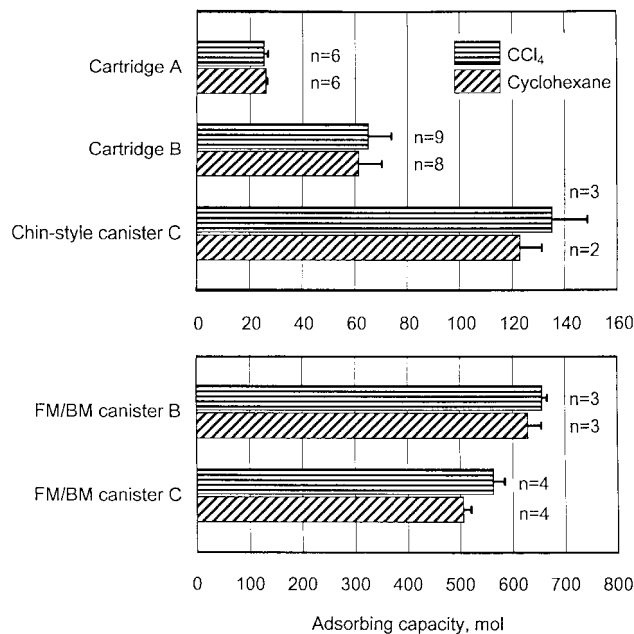


Fig. 8. Comparison of adsorbing capacities of  $\text{CCl}_4$  and cyclohexane vapor by cartridges, chin-style canisters and front-mounted or back-mounted (FM/BM) canisters.

The values are the mean  $\pm$  SD.

cyclohexane, n-heptane and n-pentane at 25°C are 13.0 kPa, 6.1 kPa and 68.3 kPa<sup>9)</sup>, respectively, in comparison to 15.2 kPa of  $\text{CCl}_4$ . The technical feasibility of generating an airflow of 30 L/min containing the test vapor in a wide range of concentration in use of evaporation and refluxing method is a basic requirement for the  $\text{CCl}_4$  replacement vapor with minimal changes in any other procedures and conditions for National Approval Test which should evaluate the same critical levels of the gas removing capacities of cartridges and canisters of gas masks. Therefore, referring to the health and safety data, the physico-chemical data as well as the technical feasibility, it was deduced that cyclohexane was taken as the most advantageous candidate and n-heptane as the second among the six candidates.

The second step was the experimental study to prove the applicability of the candidates for replacing  $\text{CCl}_4$  in the National Approval Test. The requirements are that the breakthrough times of all classes of commercially available and approved respirator cartridges and canisters for cyclohexane vapor should be close to, or kept in a certain ratio with those for  $\text{CCl}_4$  under various conditions of different concentrations and RH in the test airflow. Because n-heptane has low volatility, the evaporation method was proved to be not applicable to generate the airflow containing 5000 ppm vapor for the examination of FM/BM canisters. So, in

the present experiment, we examined breakthrough times of all classes of cartridges and canisters which had already been approved to be compliant to the Japanese standards by the National Approval Test for CCl<sub>4</sub> and cyclohexane. It was found that the breakthrough times for cyclohexane agreed well with those for CCl<sub>4</sub> under various conditions of different vapor concentrations ranging from 120 to 8000 ppm and different RH conditions ranging from 30 to 80%. The Notification<sup>4)</sup> for standards of gas masks in the National Approval Test stipulates that the breakthrough time of CCl<sub>4</sub> be longer than 50 minutes for cartridges when the test airflow of 300 ppm CCl<sub>4</sub> passes, longer than 30 min for chin-style canisters with the test airflow of 3000 ppm CCl<sub>4</sub>, and longer than 100 min for FM/BM canisters with the test airflow of 5000 ppm CCl<sub>4</sub> at the air flow rate of 30 L/min, 20°C and 50%RH. In the present experiment, breakthrough times of cartridges A and B were 120 min and 330 min for 300 ppm cyclohexane, respectively, that of chin-style canister C was 50 min for 3000 ppm cyclohexane, and those of FM/BM canisters B and C were 180 min and 160 min for 5000 ppm cyclohexane, respectively, which were almost the same as the breakthrough times measured for CCl<sub>4</sub> at the same concentrations. The present results mean that the amount of cyclohexane vapor adsorbed on each of the cartridges and canisters up to the breakthrough time was in essential agreement with that of CCl<sub>4</sub> vapor adsorbed, and that the affinity of cyclohexane to activated carbon is similar in magnitude to that of CCl<sub>4</sub>. This speculation can be consistent with the relationship between breakthrough times and adsorptivity of organic vapors by charcoal proposed by Nelson and Harder<sup>10)</sup>.

It is additionally required for the intended change in the testing vapor that the shortening of the breakthrough time for an alternative test vapor in the presence of the increased RH should be similar to that for CCl<sub>4</sub>, because it is important to detect the damage of cartridges and canisters due to the moisture accumulation during storage in the national approval test similarly by the examination with the vapor of CCl<sub>4</sub>. It was found in the present experiment that the breakthrough times of all classes of the commercially available cartridges and canisters observed for cyclohexane were similar to those for CCl<sub>4</sub> under all RH conditions. The present results on RH effect are consistent with those reported by Moyer and Peterson<sup>11)</sup>. It can be interpreted as that cyclohexane and water molecules adsorb competitively on activated carbon in the similar manner as CCl<sub>4</sub> and water molecules do. The breakthrough time was defined in this study as the elapsed time from the start of passing the test airflow through a

cartridge or canister to the time when the exit vapor concentration reached 10 ppm for both of CCl<sub>4</sub> and cyclohexane to compare the results at the same conditions for adsorption.

In conclusion, cyclohexane can be recommended as a CCl<sub>4</sub> replacement vapor in the National Approval Test of Gas Mask without changes in the test conditions for generating a test airflow and also without changes in the criteria of gas removing capacities of cartridges and canisters of gas masks.

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