

Thermal Regeneration Method of A Respirator Cartridge for Organic Vapors

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ABSTRACT

The possibility of thermal regeneration of a respirator cartridge that adsorbed methanol vapor was studied experimentally. The vapor was introduced into a respirator cartridge (Shigematsu Works, CA-104NII), and the breakthrough curve was obtained by a gas chromatograph equipped with a flame ionization detector (GC-FID). After the cartridge was saturated with methanol, it was heated and the desorption curve was obtained by supplying clean dry air continuously at the temperatures of 25, 45 and 65°C and the flow rate of 20 L/min. This adsorption-desorption cycle was repeated up to 26 times, and the effect of the number of adsorption – desorption cycles on the breakthrough time was investigated. The desorption rate increased with the increasing desorption temperature. When the desorption temperatures were 45 and 65°C, and the flow rate was 20 L/min, the desorption of methanol was almost completed within one hour, and there was no significant change in the breakthrough time even when the adsorption and desorption cycle was repeated. When the temperature was 25°C, a part of the adsorbed vapor could not be desorbed from the cartridge. Thus thermal regeneration of respirator cartridges for organic vapors is technically possible.

Keywords: thermal regeneration, respirator cartridge, methanol

INTRODUCTION

Activated carbon is widely used for cartridges and canisters for organic vapor respirators. These devices cannot be used beyond their service life, that is, the breakthrough time. Activated carbon has generally strong adsorption affinity to organic compounds, but the breakthrough time or the breakthrough volume depends on the vapors. There are many studies available for estimating the breakthrough times of organic vapors for respirator cartridges (Nelson *et al.*, 1976, Yoon *et al.*, 1992, Moyer, 1987, Tanaka *et al.*, 1999). In general, organic compounds with higher boiling points, such as toluene and xylene, have strong adsorption affinities to activated carbon, but for polar and high volatile compounds, the adsorption affinity is weak. In particular, the breakthrough volume for methanol is extremely small (Nelson *et al.*, 1974, Tanaka *et al.*, 1999).

Methanol is widely used in many industries (Seedorff *et al.*, 1990). Because of its high volatility (boiling point: 64.7°C, saturated vapor pressure: 127 mmHg at 25°C), the vapor concentration in the work environments is easy to exceed the Threshold Limit Values recommended by ACGIH (2003) or the Occupational Exposure Limits recommended by the Japan Society for Occupational Health (2002) (200 ppm). In such workplace, a worker who wears a respirator must exchange the cartridge several times in a day during one work shift in order to avoid methanol exposure.

In general, a compound that has low adsorption affinity to activated carbon can easily be desorbed by heating. If the adsorbed vapor in the cartridges or canisters can be desorbed, their repeated uses may be possible. In this study, desorption characteristics of methanol vapors adsorbed on a respirator

cartridge were investigated to explore the possibility of a thermal regeneration method of the cartridges by introducing air under heated conditions into a cartridge which adsorbed methanol vapor.

MATERIALS AND METHODS

Figure 1 shows a schematic diagram of the experimental apparatus. Methanol vapor was obtained by bubbling air in a reservoir containing liquid methanol (2). The generated vapor was diluted with clean dry air and introduced into a respirator cartridge for organic vapor (CA-104NII, Shigematsu Works, Japan) (4) inserted in a cartridge holder made of Teflon at flow rates of 20 L/min. Air was sampled from a sampling port (5) located downstream of the respirator with an auto gas sampler (GS-5000A, GL Science, Japan) (10) equipped with an auto gas sample selector (9) and the breakthrough curves were obtained by measuring the vapor concentration by a gas chromatograph equipped with a flame ionization detector (GC-17A, Shimadzu, Japan) (GC) (11), continually. The influent vapor concentration was also monitored periodically by sampling upstream air by changing sampling path with the auto gas sample selector. When the cartridge was almost saturated with the vapor, the vapor supply was stopped, and then the adsorbed vapor was desorbed by heating the cartridge holder using a ribbon heater under a constant air flow. The desorption curve was also obtained by measuring the outlet vapor concentration continually. The temperature was measured at the center of the holder by a thermocouple inserted in the cartridge holder. When desorption was almost completed, that is, the desorbed vapor concentration became below the detection limit, the holder was cooled to room temperature, and the adsorption – desorption cycle was repeated.

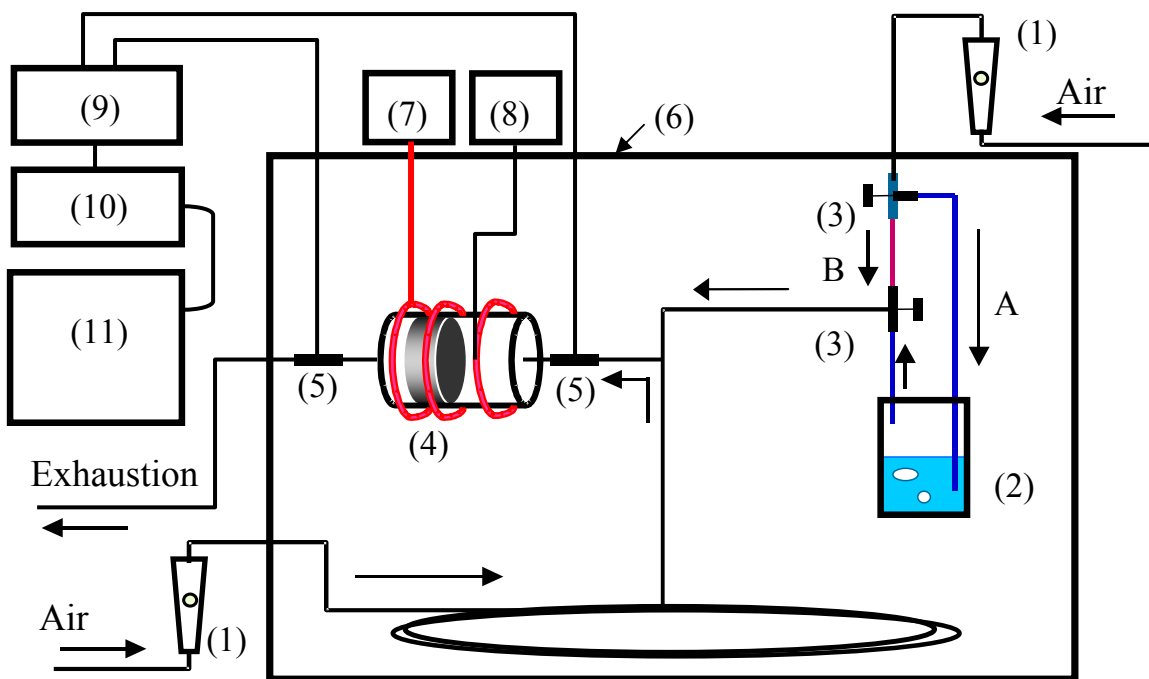


Figure 1. Schematic diagram of experimental apparatus: (1) Rota meter, (2) Vapor generator, (3) Three way cock, (4) cartridge, (5) Sampling port, (6) Thermostatic bath, (7) Ribbon heater, (8) Temperature controller with thermocouple, (9) Auto gas sample selector, (10) Auto gas sampler, and (11) FID-Gas chromatograph, (A) Flow path at adsorption, and (B) Flow path at desorption.

The challenge concentration of methanol vapor was 1500 ppm. Breakthrough time was defined as time when the cartridge outlet vapor concentration reached 200 ppm, which is Occupational Exposure Limit of methanol in Japan (The Japan Society for Occupational Health, 2002). The desorption temperatures were 25, 45 and 65°C. Methanol used in this study was of reagent grade (Wako Pure Chemical Industries Ltd., Japan).

Student's t-test was applied for statistical analysis of the data.

RESULTS

Characteristics of breakthrough and desorption curves

Figure 2 shows a typical example of the breakthrough curve and the desorption curve of methanol using a new cartridge. The methanol vapor become detectable about 30 minutes after the adsorption started. The vapor concentration reached the breakthrough level at 32 minutes, and then it was almost saturated within 90 minutes. Desorption was started at 90 minutes after the beginning of the experiment. The desorption temperature was 65°C. The outlet vapor concentration rose quickly, then it began to decrease from 8 minutes after the beginning of desorption. The vapor concentration at the outlet dropped under the detection limit within 1 hour.

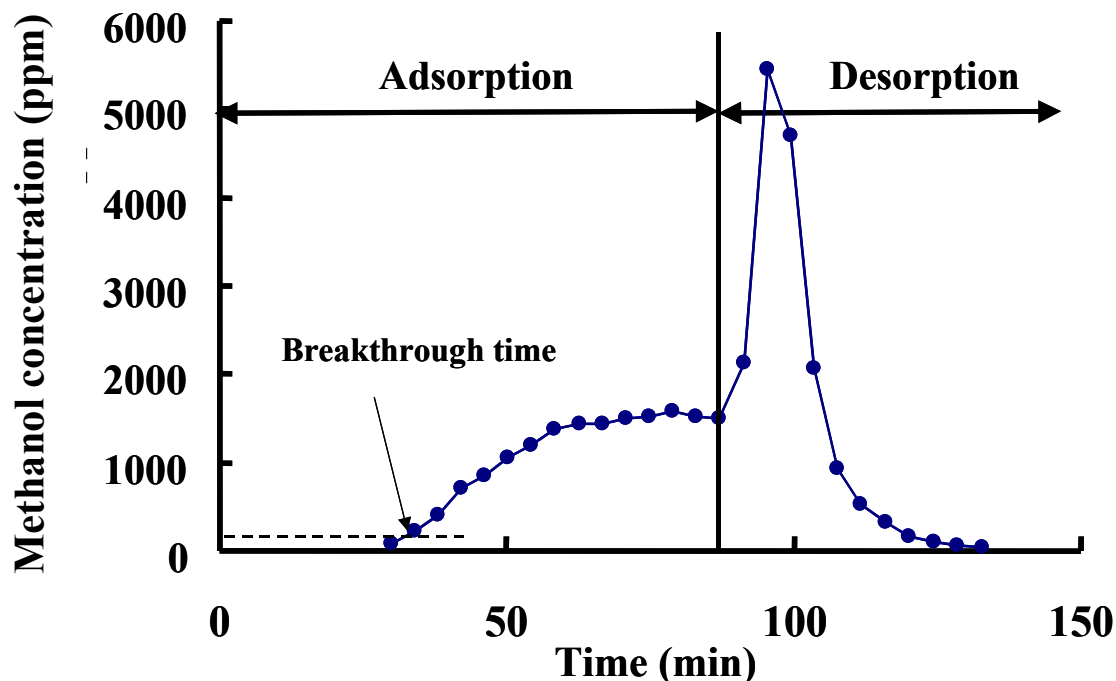


Figure 2. Examples of the breakthrough curves and the desorption curves when adsorption temperature was 25°C and desorption temperature was 65°C for vapor concentration of 1500 ppm.

Effect of desorption temperature on breakthrough and desorption curves

Figure 3 illustrates the effect of the desorption temperature on the breakthrough and the desorption curves for 2nd adsorption - desorption cycle. The breakthrough time of a cartridge after regeneration at

25°C was shorter than at higher regeneration temperatures. The peak concentration of the desorption curve increased with increasing temperature, and the vapor concentration decreased quickly in that case. The desorption was completed within one hour at all temperatures but the desorption time required was slightly longer time when the desorption temperature was 25°C.

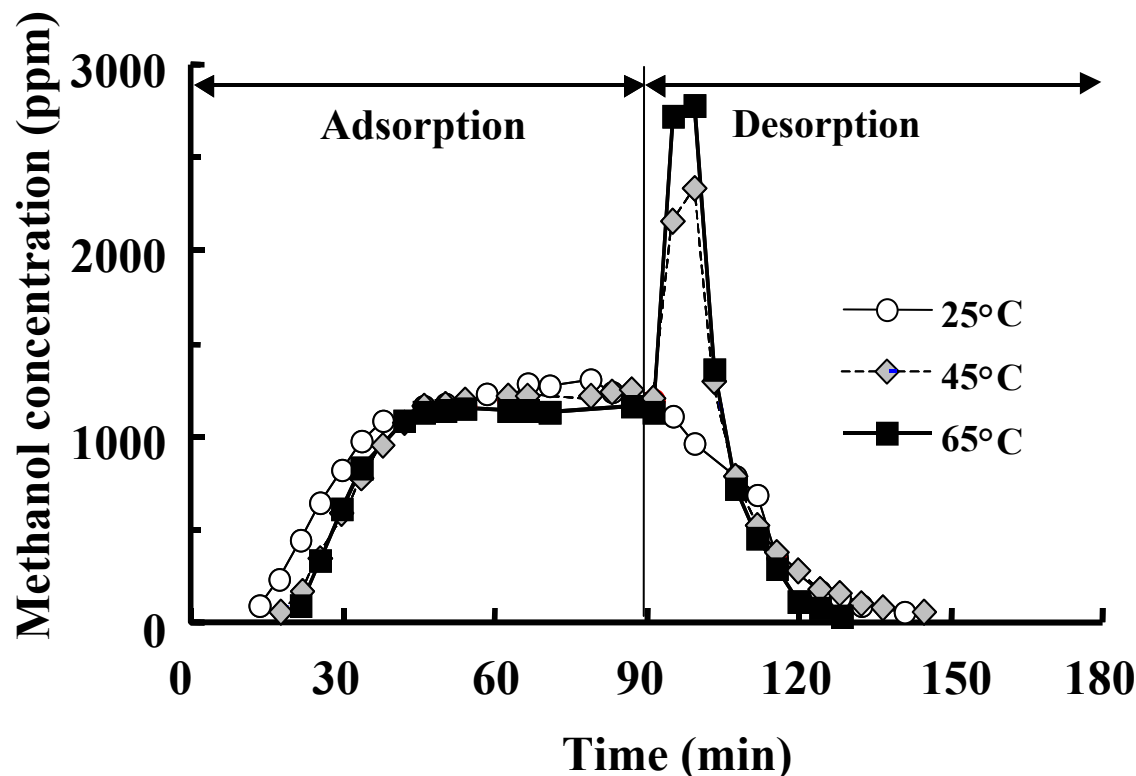


Figure 3. Effect of the desorption temperature on the desorption time after 1st adsorption-desorption cycle (Vapor concentration: 1500 ppm, adsorption temperature: 25°C, and air flow rate: 20 L/min).

Effect of repeated regeneration on the breakthrough time

Examples of the breakthrough times for new and regenerated cartridges when the desorption temperatures were 25 and 65°C are shown in Figure 4. The adsorption – desorption cycle was repeated up to 5 times in each temperature using the same cartridges. The breakthrough time of a regenerated cartridge tended to be shorter than that of a new one. In particular, the breakthrough time of the regenerated one was 17 to 20 minutes, while that of the new one was 32 minutes when the desorption temperature was 25°C (Figure 4(a)). This difference became smaller when the desorption temperature was 65°C (Figure 4(b)).

Because the breakthrough time was not always the same for all cartridges even if the experimental conditions are the same, we repeated the above experiment four times at 25°C and 65°C to quantify the reduction of the breakthrough time. Table I summarizes the average breakthrough times and its standard deviations (SD) when the desorption temperature was 25°C and 65°C. In both cases, the breakthrough time of regenerated ones was significantly shorter than that of new ones.

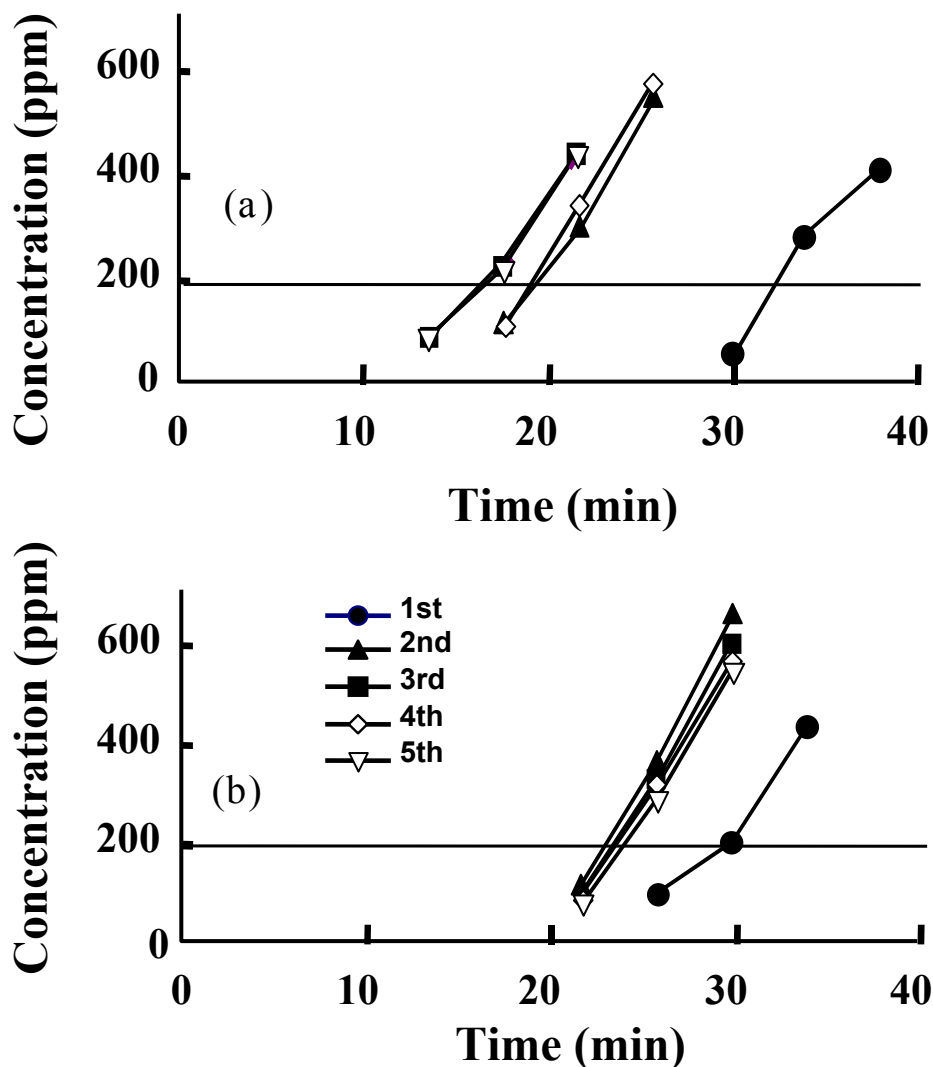


Figure 4. Examples of the effect of desorption temperature on the breakthrough time (Vapor concentration: 1500 ppm, adsorption temperature: 25°C, air flow rate: 20 L/min, and desorption temperature: (a) 25°C, (b) 65°C).

Table I. Breakthrough Time of Methanol Vapor for New and Regenerated Cartridges

Temperature (°C)	Breakthrough time $\pm$ SD (min)				
	1st (New)	2nd	3rd	4th	5th
25	37.7 $\pm$ 3.8	22.7 $\pm$ 2.1**	20.0 $\pm$ 2.0**	21.7 $\pm$ 2.5**	19.3 $\pm$ 3.1**
65	36.7 $\pm$ 4.9	30.8 $\pm$ 4.3*	30.5 $\pm$ 4.0*	30.3 $\pm$ 3.8*	30.5 $\pm$ 5.3*

n = 4 for each temperature

**p < 0.05, *p < 0.01 compared with 1st breakthrough time

Figure 5 shows the breakthrough times when the adsorption-desorption cycle was repeated up to 26 times using the same cartridge. The desorption temperature was 65°C. The breakthrough time was the longest when a new cartridge was used (42 min), and it decreased down to about 30 min in the following adsorption cycles. The breakthrough time of a regenerated cartridge varied but it did not change remarkably even when the adsorption – desorption cycle was repeated.

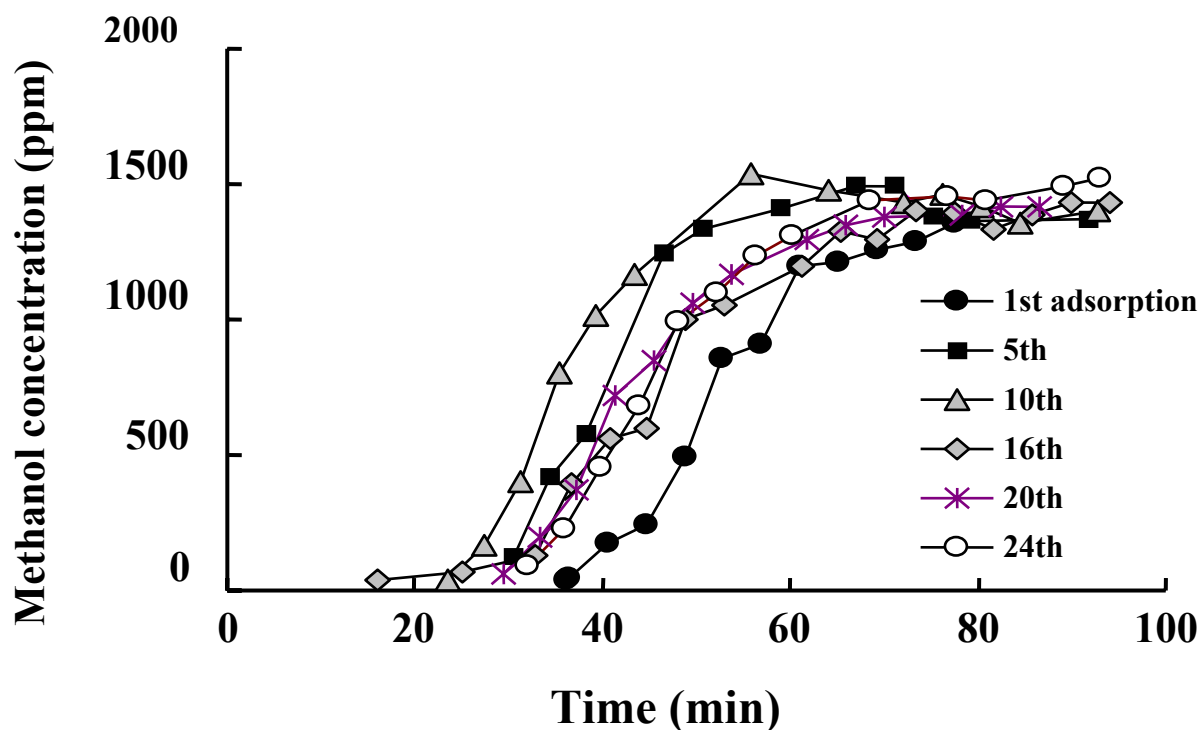


Figure 5. Change in the breakthrough curves when adsorption-desorption cycle was repeated up to 26 times (Vapor concentration: 1500 ppm, adsorption temperature: 25°C, and desorption temperature: 65°C).

DISCUSSION

The amount of chemical adsorbed on activated carbon at a certain vapor concentration depends on the adsorption isotherm. Because the major adsorption mechanism of organic vapors on activated carbon is physical adsorption, the adsorbed amount decreases with increasing temperature, and the adsorbed vapor can be desorbed by heating. We have studied the adsorption equilibria of organic vapors on activated carbon at high temperatures (Hori *et al.*, 1989a) and thermal desorption efficiencies of organic vapors from activated carbon bed (Hori *et al.*, 1989b). However, there are no reports for thermal desorption method in order to regenerate respirator cartridges.

In this study, desorption temperature was 25 - 65°C, which are low temperatures for desorption of organic vapors from activated carbon in comparison to the cases of industrial uses of activated carbon adsorption beds. The reason of the low desorption temperature is that it is possible for the vapors to react with activated carbon under the presence of oxygen and new compounds may be synthesized at higher temperature, and that cartridges possibly include parts other than activated carbon which may be susceptible to the thermal degradation. If this is the case, the respirator cartridge cannot be re-used even

if the entire adsorbed vapor is desorbed. The adsorption affinities of methanol to activated carbon are weak, so that we were readily able to select this temperature range.

As shown in Figure 4 and Table I, the breakthrough time of a regenerated cartridge was significantly shorter than that of a new one especially when the desorption temperature was 25°C. On the other hand, the breakthrough time was also shorter but it was not so remarkable when the desorption temperature was 65°C. Possible explanation for this difference might be that at 25°C not the entire vapor could be desorbed from the cartridge and remained in the activated carbon. From above results, we found that desorption is insufficient at room temperature (25°C), and heating is necessary for regeneration of the respirator cartridges. In this study, therefore, most desorption experiments were carried out at 65°C. Even under this condition, however, the breakthrough time of a regenerated cartridge was shorter than that of a new one. One reason for such shorter service life of the regenerated cartridge could be caused by the pore structure of the carbon being occupied by high boiling compounds that have been formed before or during the desorption process.

When the adsorption and desorption cycle was repeated up to 26 times, the breakthrough time did not change significantly except for the first adsorption (Fig.5). This suggests that a cartridge that adsorbed methanol vapor can be regenerated without reducing its adsorption capacity so much except of the reduction associated with the first cycle (Table I).

For practical use, however, there are some problems that have to be considered. One is that the breakthrough time of a regenerated cartridge is shorter than that of a new one (Figure 4). This indicates that a worker who uses a regenerated cartridge has higher risk of exposure to vapors than when he or she uses a new one. In particular, a risk could be from desorption of compounds during inactive use periods, then dosing the respirator user when respirator is reused. If the worker uses a respirator with a breakthrough detector (Hori *et al.*, 2003), such risks could be avoided. The other problem is that most organic solvents used in the work environments are not single component but mixtures of several components. For example, typical components of thinners are toluene, xylene, isopropyl alcohol, and so on (Seedorff *et al.*, 1990). These solvents have stronger adsorption affinities to activated carbon than methanol. The adsorption mechanism of mixtures on activated carbon is not simple, but in general, a component with weaker adsorption affinity is replaced by stronger affinity components and such component is easily desorbed from activated carbon. On the other hand, desorption of the stronger affinity components by weaker one is few (Hori *et al.*, 1987). To regenerate such cartridge containing strong adsorption affinity components, a higher desorption temperature may be needed. In such a case, because possibilities of thermal decomposition of solvents and generation of bi-products by chemical reactions are not eliminated, the desorption temperature may become important. The desorption efficiency for such solvents should be investigated in future studies.

CONCLUSIONS

We studied thermal regeneration characteristics of a respirator cartridge that adsorbed methanol vapor by measuring the breakthrough time of new and used respirator cartridge that was regenerated by heated air. The desorption rate increased with increasing desorption temperature, and when the desorption temperature was 65°C, the desorption of methanol was almost completed within one hour. The breakthrough time of a regenerated cartridge was significantly shorter than that of a new one, but for regenerated cartridge, there was no significant change in the breakthrough time even when the adsorption and desorption cycle was repeated up to 26 times. These results suggest that the organic vapor respirator cartridges that adsorb methanol vapor can be regenerated by the thermal desorption method.

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