Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Poly(Trimethylsilylpropyne) Utility as a Polymeric Absorbent for Removal of Trace Organics from Air and Water Sources

Lloyd M. Robeson[a]; Michael Langsam[a]
[a] AIR PRODUCTS AND CHEMICALS INC., ALLENTOWN, PENNYSLVANIA

To cite this Article Robeson, Lloyd M. and Langsam, Michael(1992) 'Poly(Trimethylsilylpropyne) Utility as a Polymeric Absorbent for Removal of Trace Organics from Air and Water Sources', Separation Science and Technology, 27: 10, 1245 — 1258

To link to this Article: DOI: 10.1080/01496399208019423

URL: http://dx.doi.org/10.1080/01496399208019423

SEPARATION SCIENCE AND TECHNOLOGY, 27(10), pp. 1245–1258, 1992

Poly(Trimethylsilylpropyne) Utility as a Polymeric Absorbent for Removal of Trace Organics from Air and Water Sources

LLOYD M. ROBESON and MICHAEL LANGSAM
AIR PRODUCTS AND CHEMICALS, INC.
7201 HAMILTON BLVD., ALLENTOWN, PENNYSLVANIA 18195

Abstract

Poly(trimethylsilylpropyne), PTMSP, is well known to exhibit the highest permeability for gas and vapors of all dense polymeric systems. The high free volume observed yields extremely high diffusion coefficients for penetrating species. These properties have yielded interest for various gas and pervaporation membrane separation processes. It has been found that PTMSP also exhibits unique characteristics as a polymeric absorbent for removal of trace organics from air and water sources. The distribution coefficient for organics between the PTMSP phase and the water phase is extremely high for aliphatic, aromatic, and chlorinated hydrocarbons. In fact, PTMSP approaches activated carbon adsorbents in efficiency (much closer than other polymeric species). The removal of organics from PTMSP proceeds easier than activated carbon, and applications involving simple regeneration of a fixed bed may indeed be possible.

INTRODUCTION

The need to investigate new approaches toward materials which offer the ability to remove trace organics from oil and water continues to increase. The primary methods utilize aeration and adsorption of the organic moieties in porous activated carbon particles (*1–3*). This method is quite efficient and activated carbon is inexpensive. Once the activated carbon bed reaches breakthrough, the activated carbon is either disposed of or regenerated (primarily off-site) using steam treatment to drive off adsorbed organics. In specialty applications, easier on-site regeneration may be preferred. In addition to activated carbon, various polymeric adsorbents are also utilized for water purification for removal of specific functional organics (e.g., phenol). These materials (*4*, *5*) include macroreticular ion-exchange-type materials such as crosslinked polystyrene, often functionalized to provide specific surface properties. Particulate vulcanized rubber has been noted to be useful to remove organic vapors from air (*6*) as well as to absorb toxic chemicals (*7*) for collection and incineration.

Poly(trimethylsilylpropyne), PTMSP, has been noted to exhibit the highest gas and vapor permeability of any known polymer (*8–11*). In fact, the common gas permeabilities of PTMSP are an order of magnitude higher than silicone rubber which previously held the distinction of having the highest gas permeability. PTMSP offers high solubility to organic compounds which are not highly polar and have only limited solubility in water. PTMSP has also been noted to have utility as a pervaporation membrane (*12*, *13*). These properties suggest that PTMSP could offer unique characteristics as a bulk absorbent for trace removal of organic compounds from water or air sources and prompted the investigation reported in this paper.

In pervaporation applications, the more permeable component of a liquid mixture passes through the membrane at a faster rate relative to the feed concentration. The permeability rate is a function of the diffusion coefficient and the solubility constant. For nonpolar organics, the high solubility ratio of organic/water is a favorable separation factor versus water; however, it will be diminished by the organic/water diffusion coefficient ratio which will be expected to be less than unity. For absorption, the separation factor will essentially be equal to the solubility ratio, assuming equilibrium conditions. This favors absorption over pervaporation when PTMSP is employed for separation.

PTMSP has been noted in several papers (*11*, *14*, *15*) to exhibit permeability decline with aging. A close review of the literature data as well as detailed studies (*16*) in our own laboratories revealed contamination with hydrocarbon sources (e.g., vacuum pump oil) was the major reason for permeability decline. In fact, PTMSP gains weight when kept under vacuum due to sorption of vacuum pump oil (aerosol). This ability to remove organics suggested utility in purification of air-borne organics.

EXPERIMENTAL

The poly(trimethylsilylpropyne) utilized in this study was prepared according to the procedure that follows. 1-(Trimethyl)silylpropyne (TMSP) was purchased from Petrarch and was distilled from CaH_2 under a nitrogen stream prior to polymerization. All distillations were performed under Schlenk line conditions.

Toluene (from Aldrich, HPLC Grade) was refluxed over CaH_2 for 24 h and then distilled under nitrogen stream using Schlenk line conditions.

$TaCl_5$ (from Jolinson-Mattey, Puratronic grade) was provided in a sealed glass capsule and used without further purification.

All manipulations were performed in a VAC dry box at an O_2 content <5 ppm.

A typical polymerization was as follows: $TaCl_5$ (0.175, 0.49 mmol) was dissolved in 45 mL toluene. The mixture was stirred for ~1 at room temperature. The $TaCl_5$ completely dissolved in the toluene to form a deep yellow-colored solution. TMSP (10 mL, 7.5 g, 67 mmol) was added rapidly to the stirring $TaCl_5$/toluene solution. This ternary mixture immediately turned dark brown. Within 15 min the solution became too viscous to stir with the magnetic stirrer. After 24 h the polymerized TMSP was worked up by precipitation in ~300 mL methanol in a Waring blender. The slightly off-white polymer was dried overnight in a vacuum oven. Typical yields were 95%. Typical IV was 5–8 dL/g (toluene, 30°C).

The PTMSP was dissolved in toluene (~5 wt%) and cast into a thick slab. After devolatilization, the sample was ground into particles of 2 to 5 mm. The larger particles were chosen over coagulated particles to eliminate any pressure drop in the columns employed.

Analysis of the organic content of water samples was conducted using a Hewlett-Packard 5890 gas chromatography system equipped with flame ionization detection for the first series of experiments. Later experiments employed an electron capture detector which was believed to yield improved results over the entire concentration range tested. External standard calibration was conducted to quantify the results.

The distribution coefficient (determined in static experiments) noted in this study is defined as

$$\frac{\text{weight of organic in PTMSP}}{\text{weight of PTMSP}} \bigg/ \frac{\text{weight of organic in water phase}}{\text{weight of water}}$$

Distilled water was employed for the water phase, and organic(s) were added, followed by agitation, until solubility was complete.

EXPERIMENTAL RESULTS

The initial experiment involved static experiments to determine the distribution of chloroform between PTMSP and the water phase. A 100-mL buret was packed with 15.5 g PTMSP, and a $CHCl_3$/water solution was added. Samples (30 mL) were taken after various times. Another static experiment involved exposure of 200 mL of the $CHCl_3$/water solution to 20 PTMSP. The results of the $CHCl_3$ concentration remaining in the water phase are noted in Table 1. The sealed jar static experiment clearly shows the ability of PTMSP to remove $CHCl_3$ from water. The calculated distribution coefficient is 943. The buret experiment is a combination of dynamic

TABLE 1
Analysis of $CHCl_3$ Content of Water Sources

Sample description	$CHCl_3$ content (ppm)
Control	1744
After 30 min in buret	1.7
After 2 h in buret	1.1
After 5 h in buret	2.6
Sample of 200 mL water (control) after 3 h exposure to 20 g PTMSP	18.3
Analysis using flame ionization detector	

and static conditions and well demonstrates the ability of PTMSP to remove $CHCl_3$ from water.

The next experiment was designed to evaluate the removal of $CHCl_3$ from water in a dynamic mode of operation. Two burets were employed in series. The first buret was the same as that employed in the initial experiment and was evacuated with vacuum to regenerate the column. The second buret was packed with 15.1 granulated PTMSP. The control solution contained 3917 ppm $CHCl_3$ and was continuously added to the system at an average rate of 11.9 g/min. Samples were taken from the second column at various time intervals as noted in Table 2. A sample was taken from the first column after 4 h to determine if breakthrough had occurred. The

TABLE 2
Analysis of $CHCl_3$ Content of Water Samples

Time of running	$CHCl_3$ content (ppm)	Total water eluted (g)
0 (control)	3917.4	0
8 min	4.4	95.2
32 min	4.1	380.8
1 h, 15 min	2.3	892.5
1 h, 45 min	1.6	1250
2 h, 10 min	1.5	1547
2 h, 30 min	1.6	1785
3 h	1.3	2142
3 h, 20 min	1.4	2380
4 h	1.9	2856
4 h, 20 min	0.9	3094
4 h (out of first buret)	740	2856
Analysis using flame ionization detector		

results clearly demonstrate the ability of PTMSP to remove $CHCl_3$ from water. It is interesting to note that at the end of the test, the water out of the second buret had been reduced to <1 ppm whereas a material balance showed 12.1 g $CHCl_3$ had been absorbed by 30.6 g PTMSP (39.5 wt% sorption). The PTMSP column was quite saturated with $CHCl_3$, however, and retained the ability to remove $CHCl_3$. Even at this level of sorption, blockage or sintering of the PTMSP particles was not observed. Breakthrough at the end of 4 h occurred for the first buret. The decreasing $CHCl_3$ content in the water eluting the column is believed to be due to decreasing channeling in the columns due to the swelling of PTMSP particles by sorbed $CHCl_3$.

The next experiment involved trichloroethylene removal from water. The two burets from the previous experiment were regenerated via vacuum applied with a slow air leak at the end of the columns. A control solution of 728 ppm trichloroethylene in distilled water was slowly added to the top of the first column, and samples were removed from the first and second columns at various time intervals. The results are listed in Table 3. The trichloroethylene concentration at the end of the second column was below the limit of the analytical determination (<0.5 ppm) whereas low values were measured at the end of the first column.

The next experiment involved the evaluation of PTMSP as a bulk absorbent to remove toluene from water. A solution of ~1.6 mL toluene was added to 3200 mL distilled water and agitated until solution had occurred.

TABLE 3
Analysis of Trichloroethylene in Various Water Samples

Time of running	Source	TCE content (ppm)	Water eluted (g)
0 (control)	Control	728	0
30 min	2nd buret	<0.5	449
1 h	2nd buret	<0.5	897
1 h	1st buret	1.2	897
2 h	2nd buret	<0.5	1794
2 h	1st buret	1.26	1794
3 h	2nd buret	<0.5	2691
3 h	1st buret	2.02	2691
4 h	2nd buret	<0.5	3588
4 h	1st buret	2.05	3588

Analysis utilizing Hewlett-Packard 5890 gas chromatography system with flame ionization detection. External standard calibration was employed to quantify the results

Using the vacuum regenerated columns from the previous experiment, the columns were connected in series as before. The water samples were obtained at various time intervals and tested for toluene content as listed in Table 4. A static experiment was also conducted where the control solution was exposed to PTMSP granules. All samples contained lower than the limit of determination of the analytical procedure utilized.

In order to compare PTMSP with activated carbon, a column of activated carbon (49.2 g Fischer Brand activated carbon, 6–14 mesh, Catalog No. 05-685A) was assembled. The PTMSP columns employed were from the previous experiments after regeneration with vacuum. The control water source was prepared by utilizing ~15.0 $CHCl_3$ in 3000 mL distilled water. The results of the $CHCl_3$ content on the eluted water samples are illustrated in Fig. 1. It is interesting to note that the breakthrough position for both materials occurred at similar values of grams of water eluted/grams of column packing. The results clearly show that activated carbon is more efficient in lowering the $CHCl_3$ content than PTMSP. The pressure drop in the activated carbon column was observed to be significantly higher than the PTMSP columns. The possibility of channeling thus may have been part of the reason for the poorer performance of PTMSP. Static experiments noted later, however, indicate the distribution coefficient is also better for activated carbon versus PTMSP. The results are believed valid at low ppm levels where external standards were employed. At high ppm levels, the calibration did not properly account for the initial concentration. This problem was addressed and corrected in future examples.

TABLE 4
Analytical Results on Toluene Content in Various Water Samples

Time of running	Source	Toluene content (ppm)	Water eluted (g)
0 (control)	Control	405	0
30 min	2nd buret	<1	419
1 h	2nd buret	<1	860
2 h	2nd buret	<1	1649
2 h	1st buret	<1	1649
3 h	2nd buret	<1	2540
3 h	1st buret	<1	2540
4 h	2nd buret	<1	3365
4 h	1st buret	<1	3365
Water sample taken from sealed jar containing 150 mL toluene/water mixture and 15 g PTMSP; after 1 h, 30 min exposure		<1	

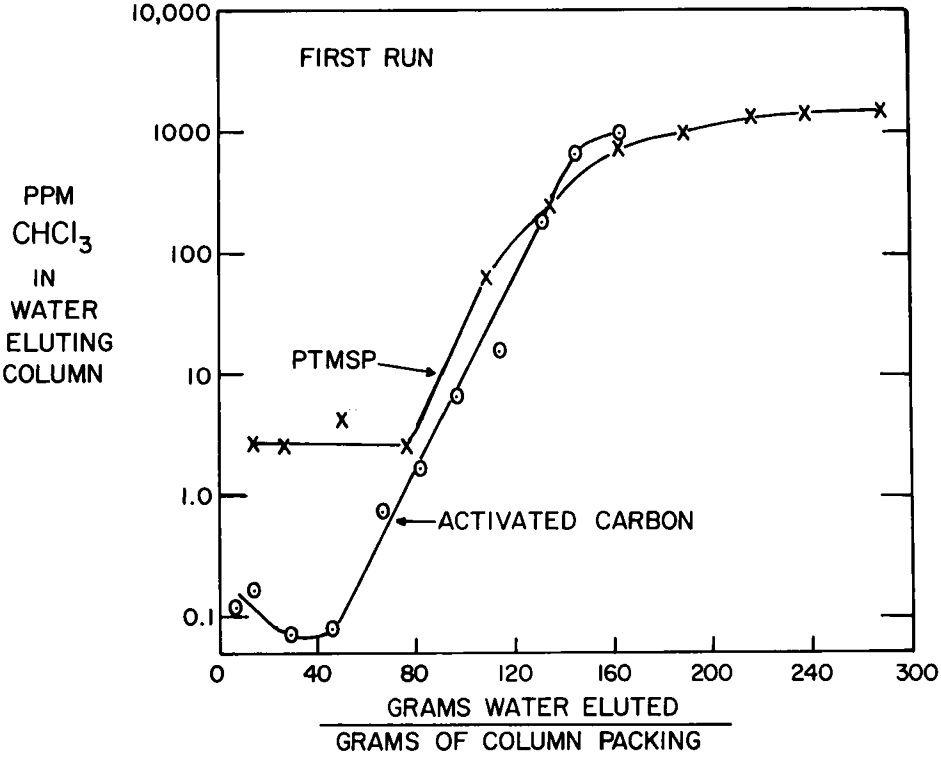

FIG. 1. Comparison of activated carbon versus PTMSP in removing $CHCl_3$ from water (~5000 ppm $CHCl_3$).

As activated carbon outperformed PTMSP in the initial test results as shown in Fig. 1, a comparison of the ability to regenerate the materials was evaluated. The PTMSP columns were connected to a vacuum source with a slow leak allowed at the end of the column (8 h duration). The activated carbon column was likewise exposed to equivalent conditions. The columns were then reassembled, and the experimental procedure employing the $CHCl_3$/water solution was repeated. The results are shown in Fig. 2 and clearly demonstrate the improved ability of regeneration of the PTMSP columns as compared to activated carbon. As both materials were taken to breakthrough conditions, another regeneration procedure was applied. In this case, an air sweep was applied to both columns. Note that the difference of the air sweep versus the prior regeneration procedure was primarily not having vacuum applied to the column. The results are noted in Fig. 3. The air sweep regeneration procedure also favors PTMSP

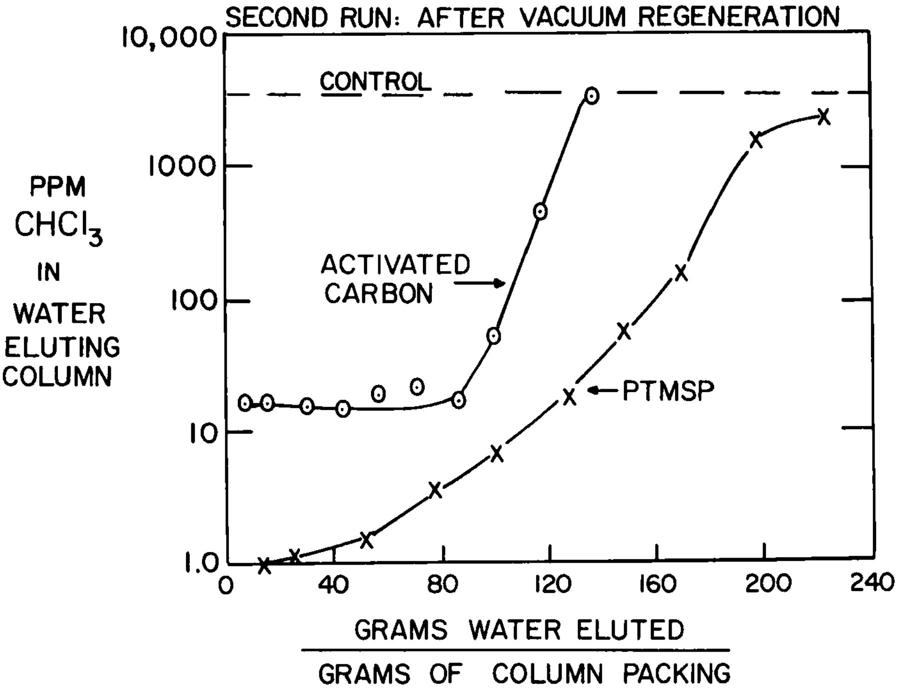

FIG. 2. Comparison of regenerated columns of activated carbon versus PTMSP in removing $CHCl_3$ from water (vacuum regeneration).

over activated carbon although the vacuum procedure (Fig. 2) appears more efficient.

The PTMSP employed for the next experiment involved a finer particle PTMSP (~0.5 to 2 mm particle dimensions). New columns of PTMSP (23.1 and 21.3 g) were assembled. An electron capture detector was employed to yield improved sensitivity for $CHCl_3$ detection over the previously utilized flame ionization detector. A solution of $CHCl_3$ in distilled water was prepared at ~6550 ppm. The $CHCl_3$ contents of the water eluting the columns are shown in Fig. 4.

The next comparison of PTMSP with activated carbon involved multicomponent hydrocarbon solutions in distilled water. Static experiments were also employed to determine distribution coefficients. The columns of PTMSP (23.1 and 21.3 g) from the previous experiments were regenerated and connected in series. A new column of activated carbon (44.4 g) was also prepared. A 3000-mL sample of distilled water containing ~3 g trichloroethylene, ~2 g toluene, and ~15 g chloroform was prepared. The

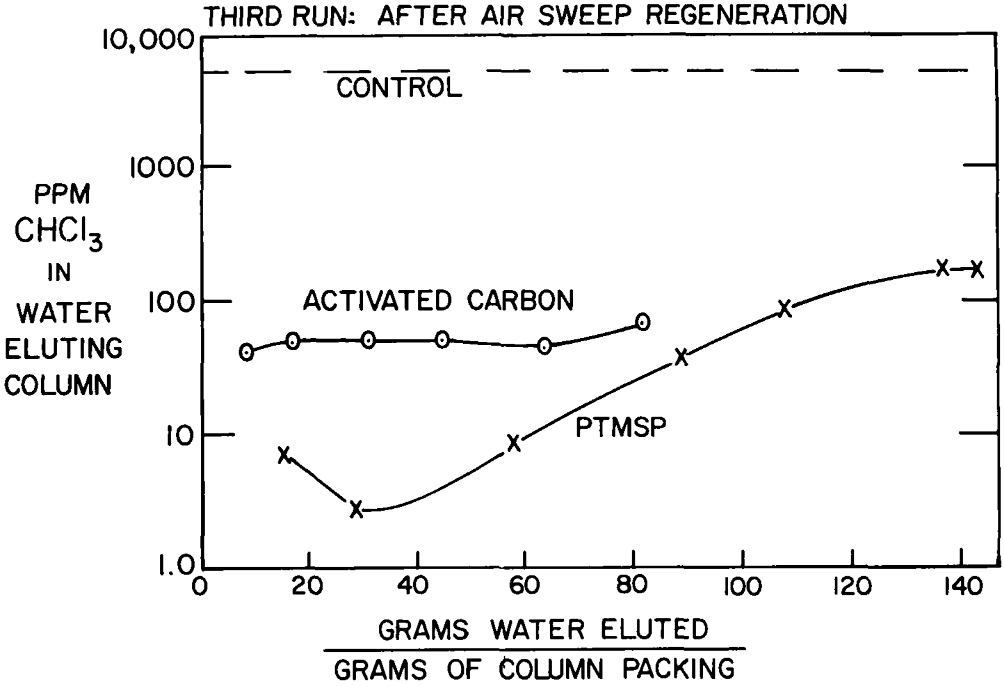

FIG. 3. Comparison of regenerated columns of activated carbon versus PTMSP in removing $CHCl_3$ from water (air sweep regeneration).

solution was added to the columns continuously, and the water eluted was collected at various times. The results are noted in Table 5. The rate of water elution from PTMSP was higher due to pressure drop problems with activated carbon. In comparison, at equal levels of water elution, activated carbon shows better efficiency than PTMSP in the removal of trace organics. The static experiments show higher distribution coefficients for activated carbon for each of the hydrocarbons tested. While activated carbon shows better performance for multicomponent hydrocarbon sorption, regeneration experiments (not conducted) would be expected to favor PTMSP.

In comparison to the ability of PTMSP to remove hydrocarbons from water versus other polymeric materials, a control solution of $CHCl_3$ in water was prepared and 200 mL of this solution was exposed to various levels of PTMSP (1.2 to 20 g). Also, the same solution was exposed to 20 g each of linear low density polyethylene (Exxon) and very low density polyethylene (Union Carbide). The water samples were taken after 20 h

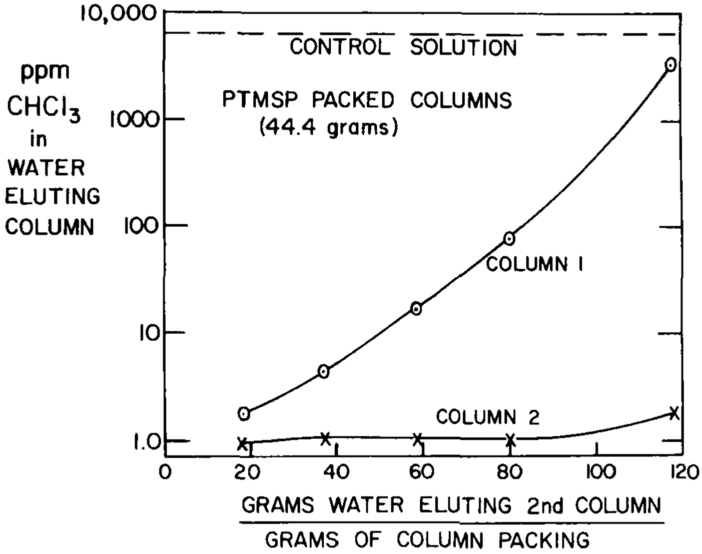

FIG. 4. Results of PTMSP packed columns in removing $CHCl_3$ from water (6550 ppm $CHCl_3$). Electron capture detector employed.

TABLE 5
Multicomponent Sorption Comparison of Activated Carbon and PTMSP

Sample description	Time	Trichloroethylene concentration (ppm)	Toluene concentration (ppm)	Chloroform concentration (ppm)	Water eluting column (H_2O)
Control solution		972	417	4609	—
Activated carbon	1 h	0.1	0	0	1035
PTMSP	1 h	1.8	0	1.6	1671
Activated carbon	2 h	0	0	0.17	2403
PTMSP	2 h	3.8	0	4.4	3135
Activated carbon	3 h	0	0	6.8	3465
PTMSP	3 h	4.4	0	11.1	4806
Activated carbon	4 h	0	0	3.9	4479
PTMSP	4 h	2.7	0	14.9	6063
Activated carbon[a]	Static	2.3	1.3	83.1	—
PTMSP[a]	Static	17.0	6.5	112.9	—

[a] Ten grams activated carbon or PTMSP in contact with 200 g control solution.

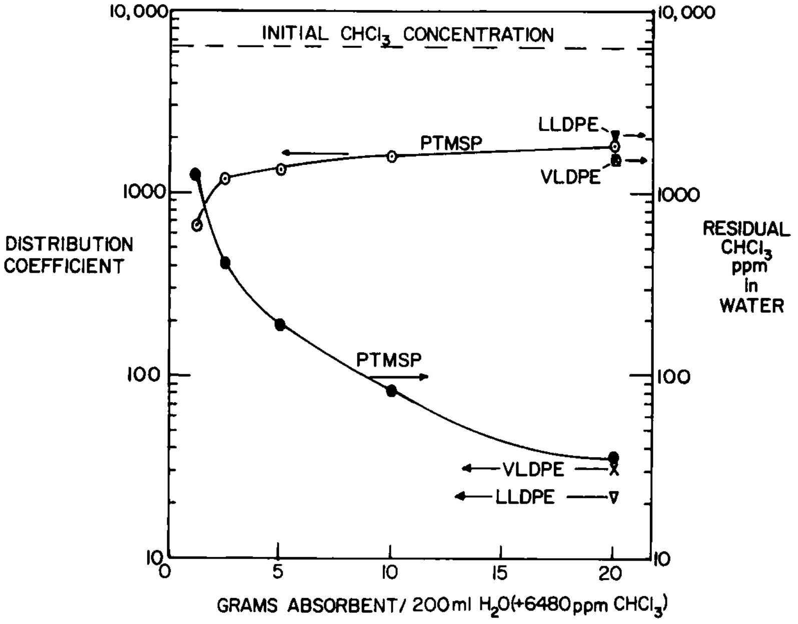

FIG. 5. Distribution coefficient data for $CHCl_3$ in PTMSP/water static experiment: Comparison with polyethylene.

exposure. The distribution coefficient results are illustrated in Fig. 5. The results show that PTMSP exhibits an increase in distribution coefficient with the quantity employed. The results also show that PTMSP is vastly superior to the polyethylene samples tested. Additional experiments utilizing porous PVC and various granulated rubber samples also demonstrated the superior performance of PTMSP. The results for the granulated rubber particles are listed in Table 6. For the experiment involving dynamic flow, a 100-mL buret was filled with 47.6 g of 8130 Carlisle Baker rubber particles.

In order to demonstrate the ability of PTMSP to remove hydrocarbons from contaminated air sources, a 1 cm diameter, 70 cm length column was packed with 16 g of 0.5–2.0 mm particles. Toluene vapor in a N_2 stream was utilized as the hydrocarbon source. The nitrogen stream of 50 cm^3/min was bubbled through a container of toluene held at 0°C. The analysis of the control nitrogen stream and the stream exiting the PTMSP packed column was conducted using a Hewlett-Packard J890 gas chromatography with a flame ionization detector and a Propak Q-type column.

TABLE 6
Multicomponent Sorption Data for Crosslinked Rubber Samples

Sample description	Trichloroethylene concentration (ppm)	Toluene concentration (ppm)	Chloroform concentration (ppm)	Water eluting column (H_2O)
Control solution	741	289	3285	—
8130 Carlisle Baker rubber column (1 h)	3.6	0	256	1158
8130 Carlisle Baker rubber column (2 h)	2.1	0.1	1105	2307
Static sample[a] Carlisle Baker rubber	41	13.7	747	—
Static sample[a] TR-20 Baker rubber	42	15.7	712	—
Static sample[a] WM-40 Baker rubber	47	16.2	792	—

[a] Sample of 10 g rubber in contact (24 h) with control solution.

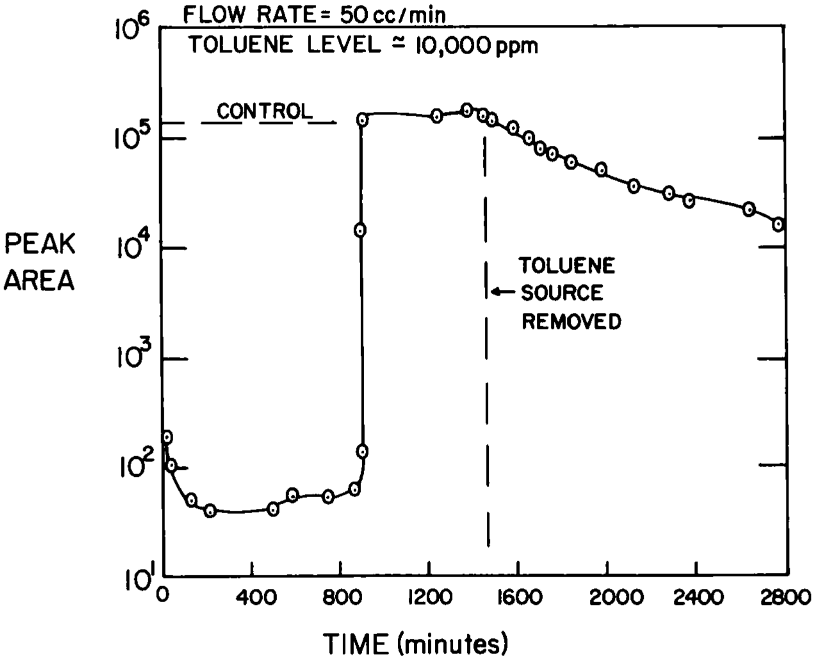

FIG. 6. Sorption of toluene from a N_2 gas stream (10,000 ppm toluene) by a column of PTMSP.

The control stream contained a toluene concentration in the range of 10,000 ppm. The peak areas of the samples were determined at various time intervals as illustrated in Fig. 6. The minimum value of toluene exiting the PTMSP column was ~3 ppm, thus demonstrating the effective removal from the inlet stream of ~10,000 ppm. The test was conducted for 24 h with toluene in the inlet stream. Column breakthrough was observed after ~15 h. After 24 h, pure N_2 at the same rate was continued to monitor the desorption of toluene from the column. These results well demonstrate the effectiveness of PTMSP to remove toluene from a contaminated N_2 stream.

CONCLUSIONS

The ability of PTMSP to remove trace organics from air and water sources has been well demonstrated. While PTMSP is significantly more efficient than the other polymeric samples investigated, it is not as effective as activated carbon (when compared on an equal weight basis). PTMSP does exhibit the ability to be regenerated more effectively than activated carbon by using a vacuum source or an air sweep on the fixed packed columns. Regeneration after many cycles appears feasible. These results indicate PTMSP could offer utility in specialty purification applications where regeneration of fixed columns is desired. These results also indicate that PTMSP could offer promise for personnel protection equipment where exposure to air-borne toxic organic vapors is possible. The ability to be fabricated in fibers, films, and porous sheets offers an added dimension over that possible with activated carbon. Hybrid combinations with activated carbon systems could offer bulk removal and regeneration of major organic contaminants while utilizing activated carbon for clean-up of the residual stream. This would offer the advantage of significantly lengthening the time required before it would be necessary to replace the activated carbon.

Acknowledgments

The authors wish to acknowledge the gas chromatography analysis of the trace organics in water by C. Shoop. The toluene sorption experiment was conducted with the assistance of P. J. Clark.

REFERENCES

1. F. E. Bernardin Jr., in *Adsorption Technology* (F. L. Slejko, ed.), Dekker, New York, 1985, p. 37.
2. W. A. Beverlov, G. M. Pierik, and K. Ch. A. M. Luyben, in *Fundamentals of Adsorption* (A. L. Myers and G. Belfont, eds.), Engineering Foundation, New York, 1984, p. 95.
3. T. H. Chung, *Water Supply, 4,* 451 (1986).

4. *Amberlite XAD Macroreticular Adsorbents,* product literature of Rohm & Haas Co.
5. C. Costa and A. Rodrigues, in *Fundamentals of Adsorption* (A. L. Myers and G. Belton, eds.), Engineering Foundation, New York, 1984, p. 163.
6. R. H. Synder, U.S. Patent 4,728,343 (March 1, 1988), assigned to The Uniroyal Goodrich Tire Co.
7. R. H. Synder, U.S. Patent 4,764,282 (August 16, 1988) assigned to The Uniroyal Goodrich Tire Co.
8. T. Masuda and T. Higashimura, *Adv. Polym. Sci., 81,* 121 (1987).
9. T. Masuda, E. Isobe, and T. Higashimura, *Macromolecules, 18,* 841 (1985).
10. E. Isobe, T. Masuda, T. Higashimum, and A. Yamamoto, *J. Polym. Sci., Part A, Polym. Chem., 24,* 1839 (1986).
11. K. Takada, H. Matsuya, T. Masuda, and T. Higashimura, *J. Appl. Polym. Sci., 30,* 1605 (1985).
12. T. Masuda, B.-Z. Tang, and T. Higashimura, *Polym. J., 18,* 565 (1986).
13. T. Higashimura and T. Masuda, U.S. Patent 4,591,440 (May 27, 1986), assigned to Toray Industries, Inc.
14. H. Shimomura, K. Nakanishi, H. Odani, M. Kurata, T. Masuda, and T. Higashimura, *Kobunshi Ronbunshu, 43,* 747 (1986).
15. S. Asakawa, Y. Saitoh, K. Waragai, and T. Nakagawa, *Gas Sep. Purif., 3,* 119 (1989).
16. M. Langsam and L. M. Robeson, *Polym. Eng. Sci., 29,* 44 (1989).

Received by editor August 30, 1991