Thermo-Responsive Polymer-Mediated Extraction Followed by Flotation for the Removal of Poly(aromatic hydrocarbons) from Gases

Tohru Saitoh,* Koji Mizutani, and Masataka Hiraide

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603

Received June 3, 2005; E-mail: saitoh@numse.nagoya-u.ac.jp

A simple and efficient gas decontamination system has been developed. The method is based on the aeration of an aqueous solution of a thermo-responsive polymer and polymer-mediated extraction followed by flotation. Polyaromatic hydrocarbons (PAHs) in gas phase were dissolved by aeration through the aqueous solution of a water-soluble polymer, poly(*N*-isopropylacrylamide) [PNIPAAm], containing 0.1 mol dm^{-3} sodium nitrate and 1% (v/v) ethanol. The efficiency of the dissolution increased with increasing PNIPAAm concentration. PAHs consisting of more than 3 aromatic rings were quantitatively collected in the polymer solution, while the collection of volatile naphthalene was insufficient. Subsequently, on heating the polymer solution to 50 °C, the polymer media incorporating PAHs formed precipitates. The precipitates were floated to the surface of water by bubbling. Hydrophobic PAHs, such as pyrene and benzo[*a*]pyrene, were highly concentrated into the polymer phase having a very small volume.

Poly(aromatic hydrocarbons) (PAHs) are ubiquitous environmental pollutants resulting from the combustion of fossil fuels and the cremation of waste products.[1,2] Because of their toxic, carcinogenic, mutagenic, and bioaccumulative properties, PAHs in exhaust gases or contaminated air must be removed effectively. A simple and efficient method for collecting organic pollutants may be the aeration of aqueous solutions with contaminated gas. Gas or air bubbles containing pollutants are introduced into the bottom of a cylinder-type tank (column) filled with the aqueous washing solution, in which gas bubbles are generated by passing the gas through filters or nozzles. In order to achieve sufficient mass transfer from the gas to the aqueous solution, a considerable amount of aqueous solution is necessary. Thus, an important problem remains in reducing the large volume of highly contaminated washing solution.

An attractive method for separating the pollutants from bulk aqueous solution is an extraction method based on the thermo-responsive precipitation of some water-soluble polymers, poly(vinylmethyl ether) [PVME] and poly(*N*-isopropylacrylamide) [PNIPAAm], in the aqueous solution. Above the lower critical solution temperature (LCST, ca. 32 °C), these polymers are water-insoluble and form precipitates (polymer phase).[3–5] We have designed polymer-mediated extraction as an efficient separation method for concentrating hydrophobic organic compounds, metal chelates, and ion pairs.[6–12] In aqueous polymer solution, any hydrophobic solutes present were solubilized and incorporated into the hydrated polymer assembly. They were efficiently concentrated into the polymer phase by means of the thermo-responsive polymer precipitation.

An important advantage of polymer-mediated extraction is the ability to concentrate a variety of hydrophobic pollutants by very simple and rapid procedures. The hydrated polymer media involving the pollutants precipitates by warming the solution. Subsequent vigorous shaking of the solution induces the condensation of the precipitates to a very small gum-like droplet that can float on water, and thus can easily be separated from the bulk aqueous solution. The volume of the pollutants can be extremely reduced. However, difficulty and potential hazard lie in vigorously shaking a large volume of warmed aqueous solution. Handling of heavy containers containing the solutions is also tiresome.

The flotation technique seems to be useful for conducting the coagulation of polymer precipitates. In the present study, the feasibility of the application of polymer-mediated extraction to gas decontamination was studied in laboratory scale. The concept includes the dissolution of PAHs from contaminated gas to aqueous polymer solution and the subsequent polymer recovery by flotation. The potential usefulness of the present system was demonstrated with the use of model combustion gases and tobacco smoke.

Experimental

Reagents. A thermo-responsive polymer, poly(*N*-isopropylacrylamide) [PNIPAAm], was synthesized by aqueous radical polymerization of *N*-isopropylacrylamide with an ammonium peroxosulfate–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine redox initiator under a nitrogen atmosphere.[5,11] After repeated polymer precipitation in an aqueous-ethanol solution and dialysis against Milli-Q water, the aqueous polymer solution was passed through a solid-phase extraction cartridge (C18, Environmental, Waters, Milford, MA, U.S.A.) to remove trace organic impurities. White cotton-like PNIPAAm {average molecular weight, 2.9×10^4 obtained by GPC (polystyrene standard)} was obtained by freeze-drying the aqueous polymer solution. Poly(aromatic hydrocarbons) (PAHs), including naphthalene, fluoranthene, phenanthrene, benz[*a*]anthracene, pyrene, and benzo[*a*]pyrene (Sigma, St. Lous, MO, U.S.A.), were used as 1.0 mmol dm^{-3} ethanol solutions. Other reagents used were of analytical grade. The water employed was prepared with a Milli-Q Gradient System (Millipore, Billerica, MA, U.S.A.).

Published on the web January 13, 2006; DOI 10.1246/bcsj.79.95

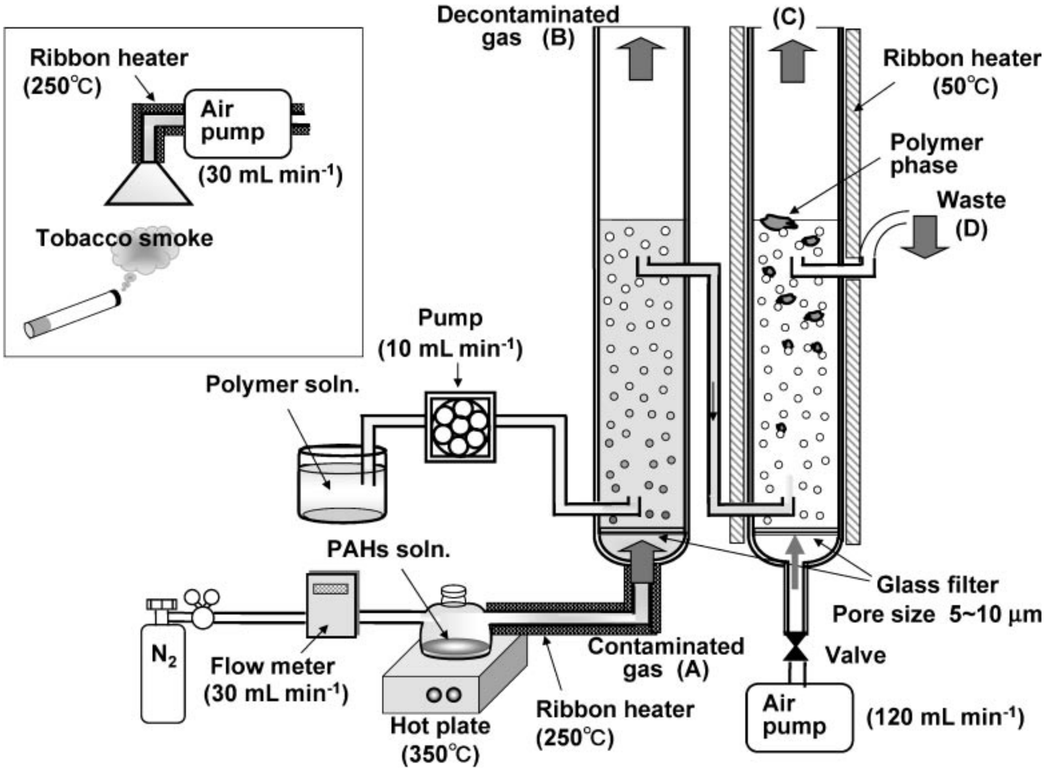

Fig. 1. Illustration of the present gas decontamination apparatus.

Preparation of Model Combustion Gas. Model combustion gas was prepared by passing nitrogen at a flow rate of 30 $cm^3\,min^{-1}$ (at 25 °C) through a vessel in which PAHs were vaporized by heating on a hot plate thermostated at 350 °C. The flow rate was regulated with an Aera (Tokyo, Japan) FC-260E digital flow meter. The contaminated gas was introduced from the bottom of a chromatographic column (30 mm i.d. × 500 mm length), having a sintered glass disk (5–10 μm pore), via a glass tube (6 mm i.d.). The glass tube was heated at 250 °C with a ribbon heater to prevent condensation of PAHs (Fig. 1).

Gas Decontamination. A laboratory scale apparatus for gas decontamination was composed of two separation columns. The first column (Column 1) was used for collecting PAHs in the aqueous polymer solution, while the second column (Column 2) was employed to recover the polymer phase containing highly concentrated PAHs by flotation (Fig. 1). The two columns were connected by a glass tube (6 mm i.d.).

To Column 1 was added 35–210 cm^3 of a 0.1 $mol\,dm^{-3}$ sodium nitrate aqueous solute ion containing 0.1–1.5% (w/v) of PNIPAAm and 1% (v/v) of ethanol to obtain fine bubbles. Contaminated gas was introduced in the form of bubbles from the bottom of the column to dissolute PAHs in the aqueous polymer solution. The polymer solution, containing 0.1% (w/v) of PNIPAAm (flow rate: 10 $cm^3\,min^{-1}$), was fed to Column 1.

Column 2 was warmed to 50 °C with a ribbon heater to conduct polymer precipitation. Air was introduced at a flow rate of 120 $cm^3\,min^{-1}$ from the bottom of the column. The polymer phase floated to the surface of the water was collected with a Teflon®-coated spatula, and then dissolved in acetonitrile to prepare 1 cm^3 of sample solution. A 20-mm^3 aliquot of the sample was taken using a 1700 Hamilton gastight microsyringe and injected into an HPLC system composing of a Jasco (Tokyo, Japan) PU-980 intelligent pump, an FP-2020 Plus intelligent fluorescence detector (excitation: 295 nm, emission: 400 nm), and an 807-IT integrator.

Measurement of Polymer Recovery. The recovery of polymer was measured based on the solubility of a water-insoluble dyestuff, Sudan III, as previously reported.[9,11] To 200 cm^3 of a 0.1 $mol\,dm^{-3}$ sodium nitrate aqueous solution containing 1% (w/v) PNIPAAm was added 2 cm^3 of ethanol solution containing 0.5 $mmol\,dm^{-3}$ of Sudan III. After collecting the polymer phase by flotation at 50 °C, the absorbance at 520 nm of the residue aqueous solution was measured.

Observation of Air Bubbles. Gas bubbles were observed with an SMZ-1000 Nikon stereomicroscope (Tokyo, Japan) with a DS-5M digital camera. The number and size of the air bubbles in the photographs were manually measured.

Results and Discussion

Dissolution of PAHs to Aqueous PNIPAAm Solution. The effect of liquid height on the transfer of PAHs from gas to liquid phase was studied. As shown in Fig. 2, the extent of the dissolution of pyrene and benzo[*a*]pyrene increased with increasing the liquid height of the polymer solution. PAHs were insufficiently collected by the aqueous solution containing no PNIPAAm. In contrast, they were effectively collected into the aqueous polymer solution. Furthermore, the liquid height required for quantitative collection of PAHs decreased with the use of a higher concentration of PNIPAAm. Hydrated PNIPAAm in the aqueous solution allows for solute incorporation of the hydrophobic media.[13] The collection of PAHs can be explained by their dissolution into the hydrated polymer media.

Another reason for the improvement of the recovery seems to be attributed to the formation of smaller bubbles. As illustrated in Fig. 3, the size distribution of air bubbles shifted to the smaller side in the presence of PNIPAAm. It is reported

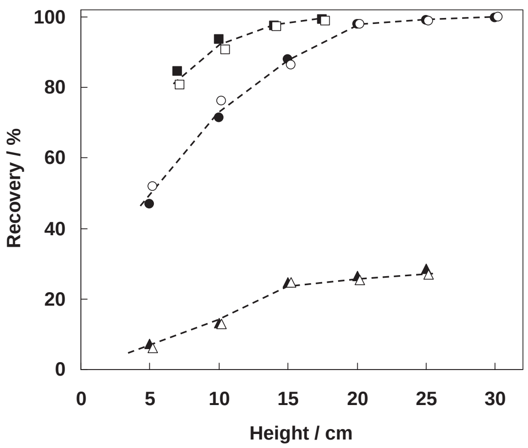

Fig. 2. Effect of liquid height on the dissolution of pyrene (△, ○, □) and benzo[*a*]pyrene (▲, ●, ■) to the aqueous polymer solution containing 0.1 M sodium nitrate and 1% (v/v) ethanol. Concentration of PNIPAAm, % (w/v): (△, ▲) 0, (○, ●) 0.1, (□, ■) 1.

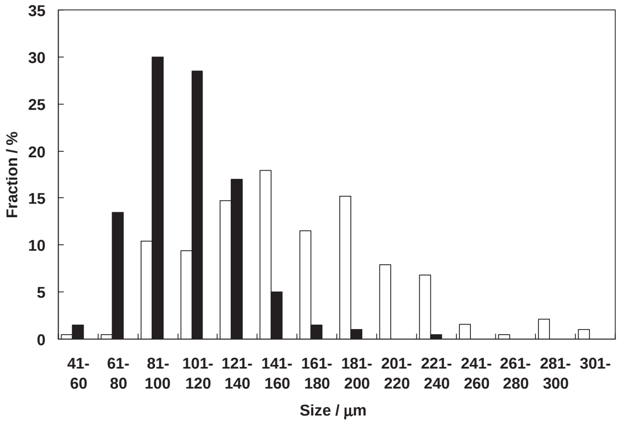

Fig. 3. Size distribution of air bubbles introduced in pure water (□) and aqueous solution of 1% (w/v) PNIPAAm (■).

that PNIPAAm sorbs to air–water interfaces.[14] PNIPAAm at the air–water interface could play an important role in preventing the union of gas bubbles. The decrease in bubble size resulted in an increase in area of the gas–water interfaced, which enhances the mass-transfer efficiency at the interfaces.

However, PAHs dissolved in the aqueous polymer solution may volatilize during aeration. For evaluating the extent of vaporization, pure nitrogen gas was introduced from the bottom of the column to the aqueous polymer solution to which 1 μmol dm^{-3} of each naphthalene, phenanthrene, and pyrene had been precedently added. Approximately 30% of the naphthalene was lost during 30 min of feeding the gas due to its relatively high volatility (bp 218 °C).[15] In contrast, the losses of less volatile phenanthrene (bp 338 °C)[15] and pyrene (bp 393 °C),[15] having 3- or 4-aromatic rings, were negligible (<1%). Thus, the present method is useful for collecting less volatile PAHs.

Another problem is the capacity or the maximum amount of PAHs that can be solubilized in the aqueous PNIPAAm solution. Insoluble fractions of solutes formed precipitates and were barely incorporated into the hydrated polymer media. Figure 4 illustrates the effects of the amounts of pyrene and benzo[*a*]pyrene on their recovery in the polymer phase. Approximately 2 mg of them were dissolved in 200 cm^3 of an aqueous solution containing 0.1% (w/v) of PNIPAAm. The recovery increased with increasing polymer concentration.

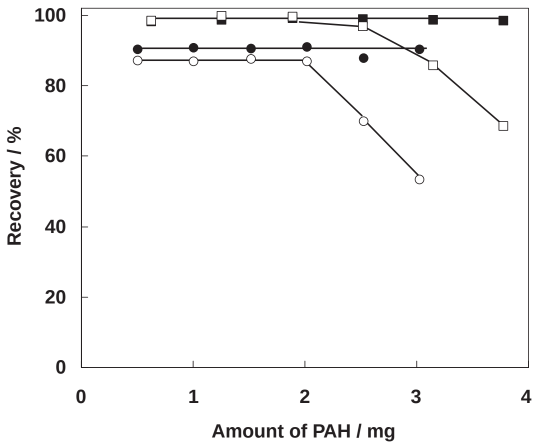

Fig. 4. Effect of the concentration of pyrene (○, ●) and benzo[*a*]pyrene (□, ■) on their recoveries to the polymer phase separated from the aqueous washing solution containing 0.1% (w/v) (○, □) or 0.2% (w/v) (●, ■) of PNIPAAm.

Recovery of Polymer Phase. In the present experimental conditions, the LCST of PNIPAAm based on the turbidity measurement was approximately 30 °C. The slightly lower LCST than the values in the literature (32–34 °C)[3–5] can be explained by the salting-out effect of sodium nitrate and ethanol. Another role of the salt is in the induction of the agglutination of the polymer precipitates. The precipitates were quite dispersive with the absence of salts or buffer components. In contrast, the precipitates in the aqueous solution of sodium nitrate condensed to a gum-like droplet, which could easily be removed from the water surface. Quantitative recovery (>98%) of the polymer phase was obtained in the presence of 0.05 mol dm^{-3} of sodium nitrate. In the present study, 0.1 mol dm^{-3} of sodium nitrate was added to the polymer solution. The recovery of the polymer phase was quantitative (>98%) at 40 °C. Thus, the temperature was set to 50 °C.

When the solution including the polymer precipitate was shaken, air bubbles seemed to play an important role in adhering the precipitates to form a condensed droplet and in floating it to the surface of the water. In the present study, flotation was found to be an excellent method for continuously generating air bubbles. This fact is quite advantageous for collecting the polymer phase. Under the above described conditions, sufficient recovery (>98%) of the polymer phase was obtained within 1 min.

Concentration of PAHs to Polymer Phase. The recoveries of naphthalene, phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, and benzo[*a*]pyrene increased with increasing the concentration of PNIPAAm (Fig. 5). The extents of the recoveries were almost the same as the values previously obtained by batch extraction[11] and were negligibly influenced

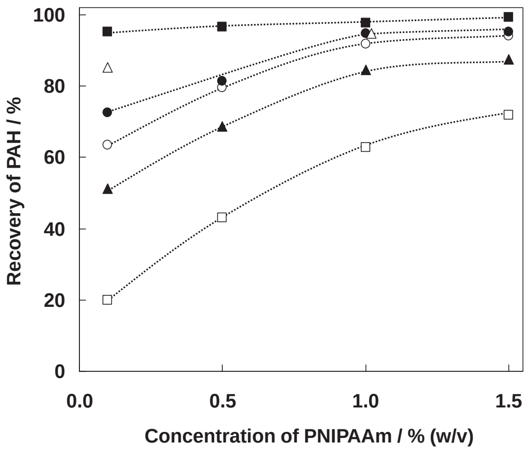

Fig. 5. Recovery of PAHs to the polymer phase as a function of the concentration of PNIPAAm. (□) Naphthalene, (▲) phenanthrene, (○) fluoranthene, (●) pyrene, (△) benz[*a*]anthracene, and (■) benzo[*a*]pyrene.

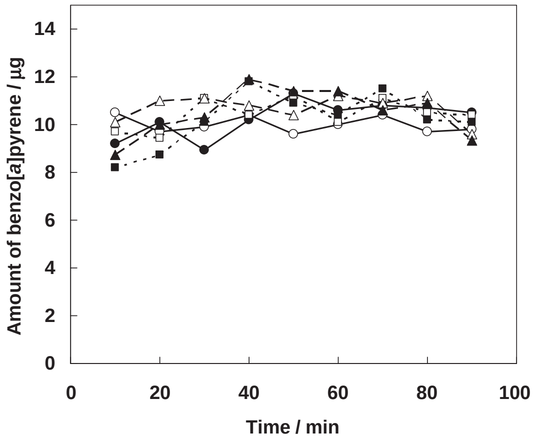

Fig. 6. Time course of the total amount of benzo[*a*]pyrene existing in Columns 1 (○, △, □) and 2 (●, ▲, ■) in the respective experiments performed in different days.

by the small amount of ethanol. Highly hydrophobic pyrene, benz[*a*]anthracene, and benzo[*a*]pyrene were well collected in the polymer phase.

Gas Decontamination. A model combustion gas involving benzo[*a*]pyrene was introduced into Column 1 to test the stability of the system running continuously. Once the system was in steady state, which usually took around 30 min after starting decontamination under the present experimental conditions, the quantities of these pollutants in the respective columns became constant (Fig. 6). In Column 1, the dissolution of the pollutants from the gas-phase counterbalances the drain to Column 2 due to the constant feed of fresh aqueous polymer solution. In Column 2, constant quantities of pollutants were maintained by the removal of the polymer phase at 10-min intervals. The amounts of benzo[*a*]pyrene in the respective column were almost constant during a 90 min run. Since no apparent change was observed in the situation, the present system could be continuously operated as long as further aqueous polymer solution is supplied.

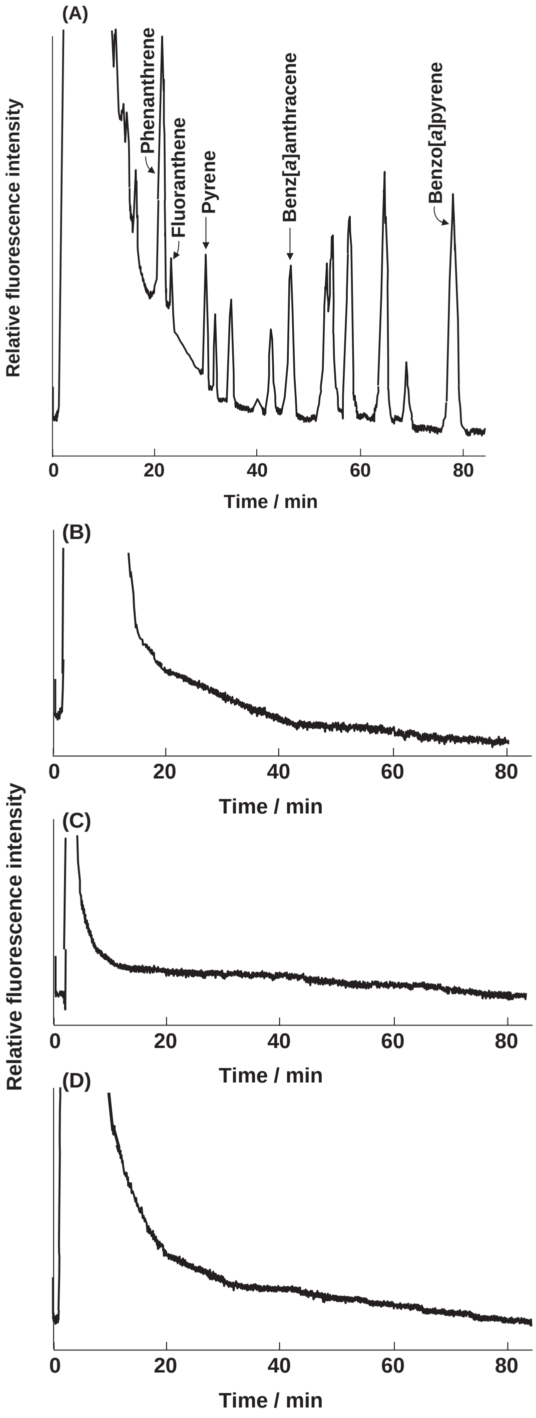

Fig. 7. Chromatograms of organic pollutants sampled at the points of (A)–(D) in Fig. 1. Column: Mightysil RP-18 150 mm × 4.6 mm i.d., Mobile phase: 60% (v/v) aqueous acetonitrile, Flow rate: 1.0 $cm^3 min^{-1}$, Detection wavelengths/nm: excitation 295, emission 400.

Another problem for the steady-state run may be the rise in solution temperature due to the passing of heated gas. If the temperature in Column 1 became higher than LCST, hydrated polymer media would precipitate and as a result lose the solubilization ability. However, the rise in temperature of the aqueous polymer solution was within 2 °C, even after the introduction of heated gas for 90 min. This is explained by the greater heat capacity of the aqueous solution than that of the gas.

A successful demonstration of gas decontamination was performed with the use of tobacco smoke. The extents of contamination were determined at the inlet of the system (A), the outlet for decontaminated gas (B), the exit of the air used for flotation (C), and the effluent from the flotation column (D, waste) (see Fig. 1). Figure 7 shows the chromatograms. The peaks in Figs. 7A–C indicate the pollutants collected by the activated carbon cartridge for 30 min, while Figure 7D was obtained by direct injection of the waste. Numerous peaks in Fig. 7A could not be observed in Fig. 7B, indicating efficient decontamination of tobacco smoke. Furthermore, no apparent peaks in Figs. 7C and D mean a very small leakage of pollutants from the system and the sufficient recovery of pollutants to the polymer phase.

Finally, reuse of the polymer was examined. At room temperature, the polymer precipitates could be re-dissolved in water. An aqueous solution containing 2% (w/v) PNIPAAm and concentrated PAHs was passed through a short cartridge column filled with activated carbon. Fluoranthene, pyrene, and benzo[*a*]pyrene were sufficiently removed from the aqueous polymer solution, while almost all of the PNIPAAm remained in the effluent. Fresh polymer solution could be prepared by mixing the decontaminated aqueous polymer solution and the solution overflowed from Column 2. The reuse of thermo-responsive polymer would save on cost and resources.

In conclusion, the aeration of an aqueous thermo-responsive polymer solution with contaminated gas and the subsequent polymer-mediated extraction is a hopeful concept for a gas decontamination system. Further studies about the apparatus will be fruitful for developing the present system into a practical process.

This study was supported by a Grant-in-Aid for Scientific Research Japan (B) (No. 16310059).

References

1 N. E. L. Hall, E. L. Wynder, *Environ. Res.* **1984**, *34*, 77.

2 S. Hayano, L. J.-H. Furuya, T. Kikuchi, T. Someya, C. Oikawa, Y. Iida, H. Matsushita, T. Kinouchi, Y. Manabe, Y. Ohnishi, *Atmos. Environ.* **1985**, *19*, 1009.

3 M. Heskins, J. E. Guillet, *J. Macromol. Sci., Chem.* **1968**, *2*, 1141.

4 R. F. S. Freitas, E. L. Cussler, *Chem. Eng. Sci.* **1987**, *42*, 97.

5 H. G. Schild, D. A. Tirrell, *J. Phys. Chem.* **1990**, *94*, 4352.

6 C. Matsubara, S. Izumi, K. Takamura, H. Yoshioka, Y. Mori, *Analyst* **1993**, *118*, 553.

7 T. Saitoh, T. Ohyama, K. Takamura, T. Sakurai, T. Kaise, C. Matsubara, *Anal. Sci.* **1997**, *13*, 1.

8 M. Hiraide, A. Morishima, *Anal. Sci.* **1997**, *13*, 829.

9 T. Saitoh, T. Ohyama, T. Sakurai, T. Kaise, K. Takamura, Y. Suzuki, C. Matsubara, *Talanta* **1998**, *46*, 541.

10 T. Saitoh, M. Haga, T. Sakurai, T. Kaise, C. Matsubara, *Anal. Sci.* **1998**, *14*, 929.

11 T. Saitoh, Y. Yoshida, T. Matsudo, S. Fujiwara, A. Dobashi, K. Iwaki, Y. Suzuki, C. Matsubara, *Anal. Chem.* **1999**, *71*, 4506.

12 T. Saitoh, C. Matsubara, H. Hiraide, *Bunseki Kagaku* **2003**, *52*, 221.

13 T. Saitoh, T. Sakurai, T. Kaise, C. Matsubara, *Anal. Sci.* **1997**, *13*, Suppl., 181.

14 J. Zhang, R. Pelton, *Colloids Surf., A* **1999**, *156*, 111.

15 F. A. L. Ribairo, M. M. C. Ferreira, *THEOCHEM* **2003**, *663*, 109.