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

Emission of Volatile Organic Compounds to the Atmosphere in the Solvent Sublation Process. I. Toluene

Victor Ososkov[a]; Barbara Kebbekus[a]; Mei Chen[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, CHEMISTRY, AND ENVIRONMENTAL SCIENCE, NEW JERSEY INSTITUTE OF TECHNOLOGY, NEWARK, NEW JERSEY

To cite this Article Ososkov, Victor , Kebbekus, Barbara and Chen, Mei(1996) 'Emission of Volatile Organic Compounds to the Atmosphere in the Solvent Sublation Process. I. Toluene', Separation Science and Technology, 31: 2, 213 — 227
To link to this Article: DOI: 10.1080/01496399608000691
URL: http://dx.doi.org/10.1080/01496399608000691

SEPARATION SCIENCE AND TECHNOLOGY, 31(2), pp. 213–227, 1996

Emission of Volatile Organic Compounds to the Atmosphere in the Solvent Sublation Process.
I. Toluene

VICTOR OSOSKOV, BARBARA KEBBEKUS, and MEI CHEN
DEPARTMENT OF CHEMICAL ENGINEERING, CHEMISTRY, AND ENVIRONMENTAL SCIENCE
NEW JERSEY INSTITUTE OF TECHNOLOGY
NEWARK, NEW JERSEY 07102

ABSTRACT

The mass of volatile organic compounds emitted to the atmosphere during solvent sublation was determined experimentally, using toluene as a test compound. It is shown that the emission of toluene to the atmosphere can be significantly reduced by using solvent sublation instead of air stripping under the same experimental conditions. The parameters which affect emission are the air flow rate, the nature and thickness of the organic layer, and the nature and concentrations of the co-solutes. Emissions are reduced as the thickness of the organic layer on the top of the column is increased. The use of decyl alcohol as the layer compound decreases emission to a greater extent than does paraffin oil. The emission of toluene during solvent sublation is further reduced as the air flow rate is lowered. The rate of toluene removal from water in solvent sublation is somewhat higher than in air stripping under the same experimental conditions. The effect of added anionic or cationic surfactants or alcohol was to improve the efficiency of water separation, but it also allowed more of the toluene to be emitted from the system.

INTRODUCTION

Solvent sublation, also called flotoextraction, is a surface physicochemical separation method which has been shown to be quite useful for the removal of certain types of organic compounds from aqueous solutions (1, 2). In this process, hydrophobic compounds dissolved in water are transported by fine air bubbles to the top of a water column where they are dissolved in a thin layer of an immiscible, nonvolatile organic liquid such as mineral oil or decyl alcohol.

Solvent sublation was originally applied by Sebba (3) to the extraction of ionic surfactant complexes. It was later used for removal of dissolved organic molecules from water (4, 5) and for the enhancement of the phase separation of oil emulsified in water (6). Valsaraj and coworkers further developed solvent sublation for removal of various chlorinated organic compounds from water in bench and continuous laboratory-scale processes (7–9). Solvent sublation combines the effectiveness of air stripping and solvent extraction, and has advantages over each. It is more efficient than air stripping, especially in the removal of less volatile hydrophobic organics (8, 9). Unlike solvent extraction, the efficiency of the solvent sublation process is not limited by equilibrium conditions, and the degree of dissolution or emulsification of the solvent in the aqueous phase is much less.

Investigations of the solvent sublation process have been focused on the enhancement of the removal of contaminants from water. Many published reports have mentioned that solvent sublation should reduce the emission of volatile and semivolatile organic compounds (VOC and SVOC) to the atmosphere in comparison with air stripping. However, there have been no systematic experimental studies which include the experimental determination of organic pollutants in both the aqueous and air phases. Limited data (unfortunately without a description of the analytical method used for air analysis) on the reduction of toluene and 1,4-dichlorobenzene (DCB) emission to the atmosphere in solvent sublation in comparison with air stripping have been published (10). However, some of these results are doubtful; for example, the absence of any emission to the atmosphere of 1,4-DCB in the experiment with a 2-octanol layer.

The objective of this research was to determine the efficiency of removal of VOC from an aqueous phase and its emission to the air using solvent sublation. The effect of the air flow rate, the nature and thickness of the immiscible organic layer, and the effect of cosolutes were studied. Both aqueous and gaseous phases in solvent sublation and air stripping were compared under the same experimental conditions.

Toluene was chosen as a test compound. It is a typical hydrophobic VOC and an important component of many industrial solvents and fuels. Toluene also is an EPA priority pollutant. It has a Henry's law constant of 0.0066 atm·m^3/mol·K at 20°C. Its solubility in water is 515 mg/L, and the logarithm of its octanol–water partition coefficient, log K_{ow}, is 2.69 at 25°C (11).

EXPERIMENTAL

Analytical grade toluene, hexadecyltrimethylammonium bromide (HTAB), sodium dodecylsulfate (DDS), and ethyl alcohol (all Fluka) were used in the experiments. Solvent-refined paraffin oil (Ivax Industries) and decyl alcohol (Fisher Scientific) were used as organic layers. The paraffin oil chosen is a high purity vacuum oil with negligible water solubility and vapor pressure. Decyl alcohol has a solubility in water of 37 mg/L at 20°C (12) and a boiling point of 233°C.

A saturated toluene solution in distilled water was prepared. Before each experiment, 120 mL of this solution was diluted 1:5 with distilled water, and a 600-mL sample was used for the solvent sublation or air stripping tests. The initial concentration of toluene in the aqueous phase for all experiments was 100 ± 4 mg/L.

A bench-scale laboratory apparatus was constructed, and a Varian 3700 gas chromatograph with FID detector was used for VOC determination in the liquid and gaseous phases, as shown in Fig. 1. The stripping column was constructed of glass reactor tubing and was 60 cm tall, with an internal diameter of 3.8 cm. Pure compressed air (zero grade, Matheson Gas Products) was introduced through a fine glass frit into the bottom of the column.

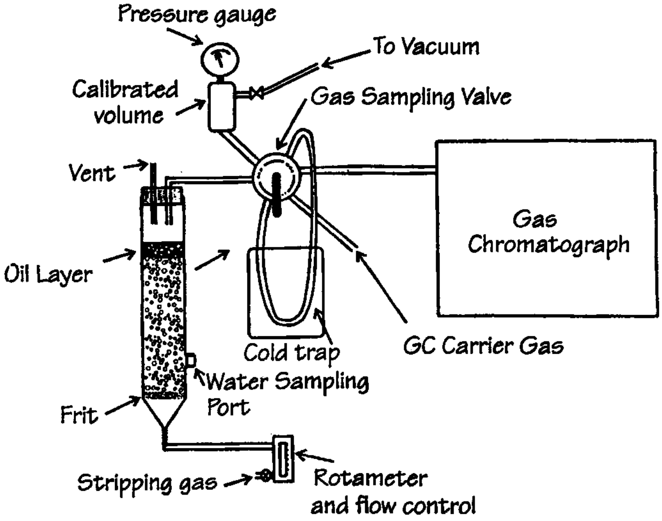

FIG. 1 Experimental apparatus.

The flow was controlled by a needle valve and monitored with a calibrated rotameter. The gas emerging from the top of the column was vented until a sample was needed.

For analysis of the effluent air, the gas from the top of the column was drawn through a trap chilled with isopropanol slush (−89°C). After passing through the trap, the gas flowed into a previously evacuated, calibrated volume, and its pressure was measured using an accurate vacuum gauge. From the pressure and the known volume, the sample size was calculated. Then the valve was turned to allow the carrier gas to sweep the sample into the GC column, and the trap was heated using a hot bath at 90°C. The column used was a 15-m, 0.54-mm ID capillary coated with a bonded methyl silicone stationary phase (Alltech). The separation was carried out at 130°C, using helium carrier at 2 mL/min.

Aqueous phase samples were drawn from the lower part of the column by using a syringe with a needle inserted through a rubber seal in a side port on the stripping column. The water samples were analyzed by direct injection into the GC. A 1/8-in. ID, 31-m Carbopack B 1% SP 1000 column was used at 170°C for the water analysis. The GC was calibrated against liquid standards made up in ether for the water analyses.

Both air and aqueous phases were analyzed in the air stripping and the solvent sublation experiments. In the case of air stripping, the total amount of toluene lost from the aqueous phase was equal to that found in the air, as there was no other mechanism for loss of toluene. By direct comparison of the peak area vs time curves obtained for toluene in air stripping and in solvent sublation, the emissions with and without the overlying layers were determined. It was, therefore, not necessary to do an absolute calibration for the gas-phase samples.

The sizes of the air bubbles under various conditions of flow and aqueous phase composition were estimated by comparing their diameter with the diameter of a calibrated glass capillary inserted in the column. A series of photos were made in approximately the middle of the column. The slides were projected, the diameters of about 100 bubbles were measured, and the average calculated.

RESULTS AND DISCUSSION

Bubble diameters for different air flows and with HTAB cationic surfactant added are shown in Table 1. Paraffin oil is very insoluble in water. Therefore, the bubble size for air stripping and for solvent sublation with an oil layer is identical at the same air flow rate and solute concentration. The range of air bubble diameters in our experiments was 0.1 to 0.8 mm. The average diameter of the bubbles increased with air flow. The addition

TABLE 1
Average Diameter of Air Bubbles in Air Stripping and Solvent Sublation with a Paraffin Oil Layer

Air flow rate, mL/min	32	60	94	32	60	94
HTAB concentration, ppm	—	—	—	5	5	5
Diameter, μm	410	440	460	260	280	310

of HTAB, even at a relatively low concentration of 5 ppm, reduced the size of bubbles. Moreover, the number of pores in the frit at which bubbles were generated increased when either surfactant or alcohol was added. At high concentrations of surfactants or ethanol, the swarm of fine bubbles was so dense that measurements of their size with our technique were not feasible.

In our experiments, as in previous solvent sublation investigations (8, 13), the rate of toluene removal from water by either air stripping or solvent sublation was found to follow first-order kinetics.

$$\ln C/C_0 = -Kt$$

where C_0 = initial concentration of toluene in water, ppm
C = current toluene concentration, ppm

The values of the rate constant K [min^{-1}] in both air stripping and solvent sublation at different air flows, using different thicknesses of the organic layer at the top of the column, are presented in Table 2.

Toluene removal from water by solvent sublation is somewhat faster than by air stripping at the same flow rate. The thickness of the organic layer does not significantly affect the rate of removal of VOC from the water. The rate of toluene removal by solvent sublation increases when decyl alcohol is used as the organic layer. The air flow rate is also an important factor for both stripping and sublation. The rate constants increase with flow almost linearly over the range of flow rates investigated.

To calculate the total emission of toluene to the atmosphere during solvent sublation, a plot of concentration of toluene in the emitted air vs time was prepared for both air stripping and solvent sublation experiments done under the same experimental conditions. The toluene peak areas from the chromatograms, which are proportional to concentration, were measured in arbitrary units and plotted against the elapsed time from the start of the air flow. Figure 2 shows, for example, the plots for experiments done at an air flow of 60 mL/min. The total amount of toluene emitted is calculated by integrating the area under the curve.

TABLE 2
Rate of Toluene Removal from the Aqueous Phase

Overlying layer	Flow (mL/min)	Layer thickness (mm)	Rate constant (10^{-4} min^{-1})
Air stripping (no layer)	32	0	218
Air stripping	60	0	422
Air stripping	94	0	637
Paraffin oil	32	10	258
Paraffin oil	60	10	474
Paraffin oil	94	10	703
Paraffin oil	60	5	436
Paraffin oil	60	20	475
Decyl alcohol	60	5	480
Decyl alcohol	60	10	515
Decyl alcohol	60	20	523

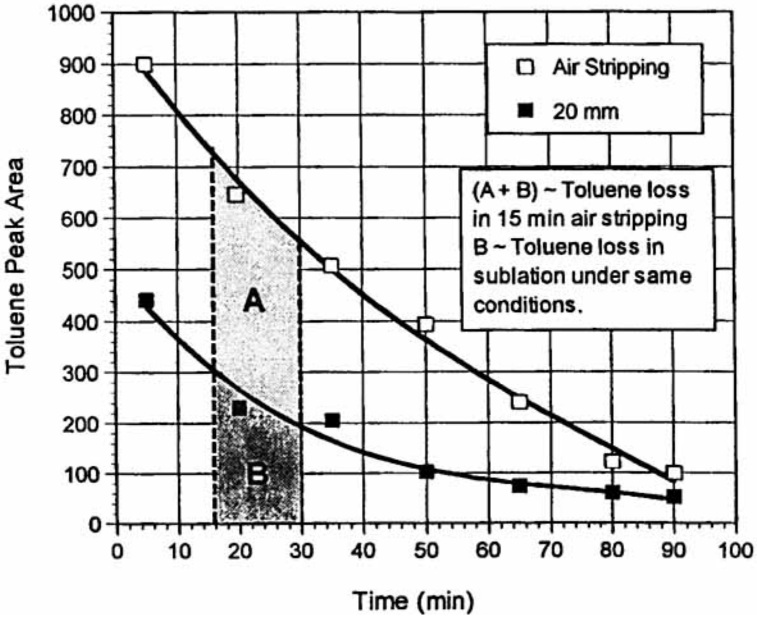

FIG. 2 Area of toluene GC peaks in emitted air sample, in air stripping, and in solvent sublation using a 20-mm layer of paraffin oil at air flow of 60 mL/min.

The integrated area of the peak vs time curve was divided into 15-minute time periods, and for each time period the amount emitted was calculated. In Fig. 2 the shaded area (A + B) is proportional to the amount of toluene emitted to the air during 15 minutes of air stripping. From the water concentration data obtained in the same experiment, the actual mass of toluene removed from water, corresponding to area A + B, was determined. This is necessarily equal to the amount found in the air. The shaded area marked B is proportional to the toluene emitted under the same experimental conditions, with a 20-mm paraffin oil layer present. From the ratio B/(A + B), the absolute amounts emitted in the solvent sublation experiments were calculated.

From the toluene emissions for each 15-minute period, the cumulative mass of toluene emitted was calculated and plotted vs time. From these plots the reduction of emissions when solvent sublation is used is evident. One can also calculate the amount of toluene in the oil layer at any point

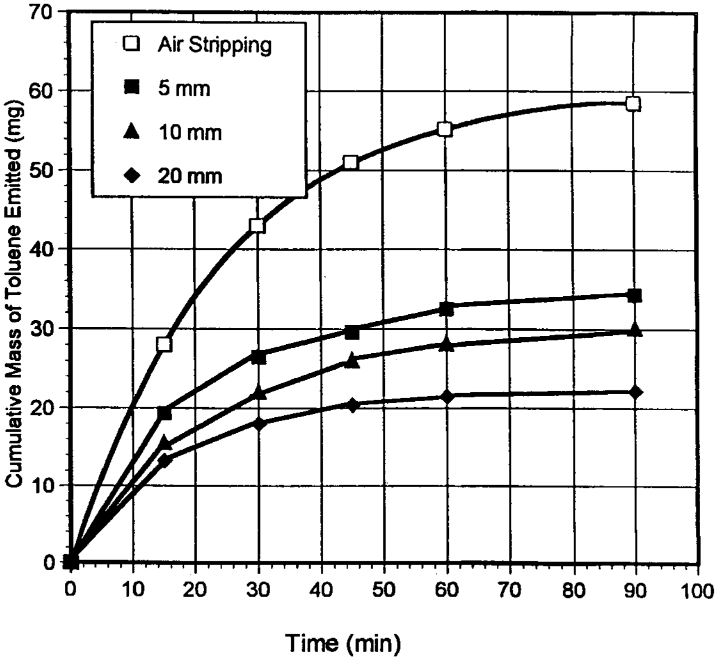

FIG. 3 Effect of paraffin oil layer thickness on the cumulative mass of toluene emitted in air stripping and in solvent sublation at air flow of 60 mL/min.

from the difference between the air and water amounts. The results of these measurements and calculations for different thicknesses of paraffin oil layer and for different air flows are shown in Figs. 3 and 4, respectively.

The oil layer on the top of the column significantly reduces toluene emission to the atmosphere. Less is emitted when a thicker layer is used (Fig. 3). The total amount emitted can be calculated from the graphs at any point in time during the solvent sublation process. Toluene emissions to the air in solvent sublation are higher at higher air flows (Fig. 4). As bubble size and velocity both increase with the air flow rate (Table 1), this lower efficiency of the mass transfer of toluene into the organic layer is expected.

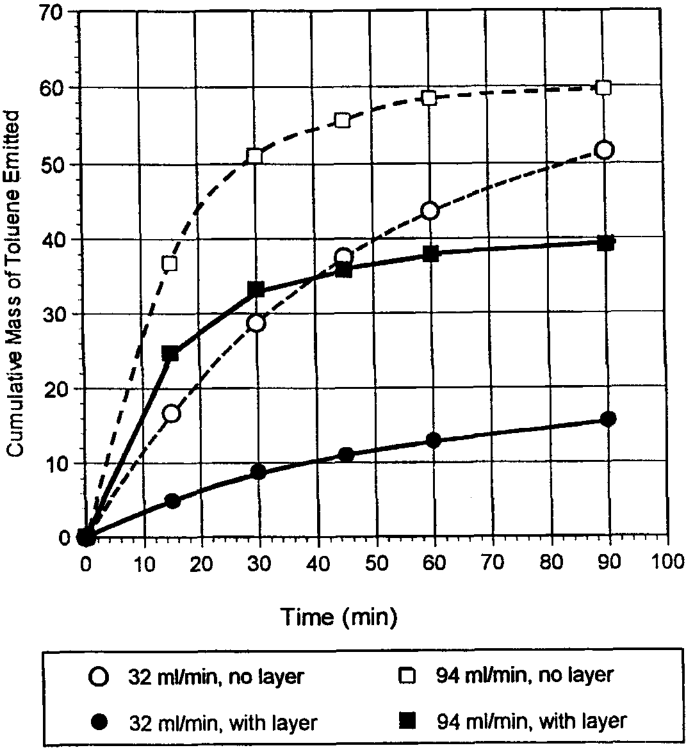

FIG. 4 Effect of air flow on the cumulative mass of toluene emitted to the atmosphere in air stripping (dashed lines) and solvent sublation (solid lines) using a 10-mm thick paraffin oil layer.

When the overlying layer is composed of decyl alcohol rather than paraffin oil, toluene emission is more efficiently reduced with the same thickness of layer (Fig. 5). This can be explained by two phenomena. First, the surface tension of the decyl alcohol/water interface is much lower than that of the oil–water interface. Bubbles penetrate easily into the decyl alcohol layer, while they are repelled by the oil/water interface, and tend to slide across the interface, coalesce, and exit between the oil and the wall of the column. Therefore, the bubbles are not in very good contact with the oil phase, and transfer of the toluene from the bubble surface or interior is less efficient. Second, when decyl alcohol is used, the air bubbles are smaller and slower rising because of the surface activity of the small amount of alcohol which dissolves in the water. Smaller bubbles enhance the mass transfer of toluene to the layer. However, paraffin oil also has some advantages. It is less soluble in water, so it does not contrib-

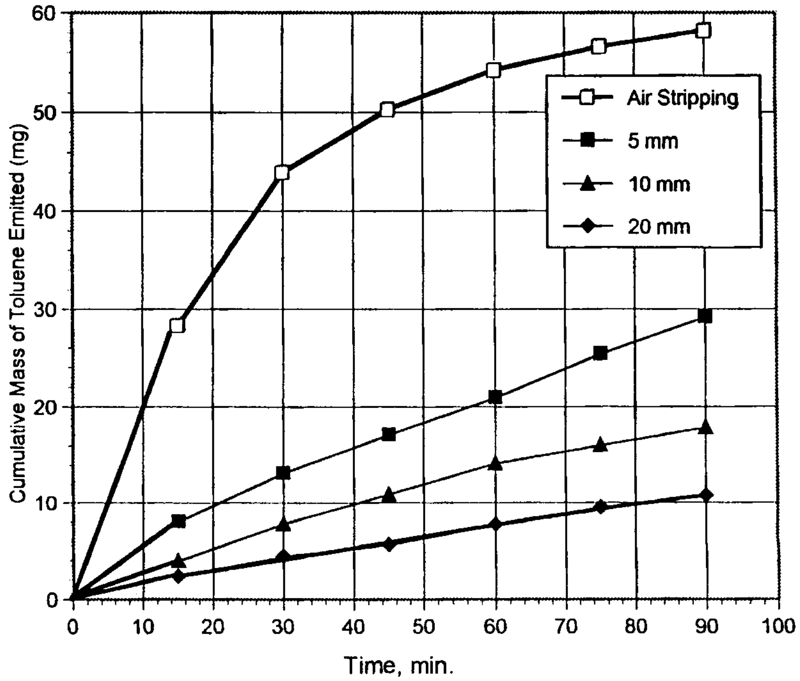

FIG. 5 Effect of decyl alcohol layer thickness on the cumulative mass of toluene emitted in air stripping and in solvent sublation at air flow of 60 mL/min.

ute to further organic pollution of the waste stream. Also, it is less expensive. Therefore, paraffin oil was chosen for further experiments with surfactants.

The effect of anionic (DDS) and cationic (HTAB) surfactants was investigated. Surfactants, even at relatively low concentrations, reduce the size and increase the number of bubbles generated at the porous frit. Addition of HTAB in concentrations as low as 5 ppm dramatically reduces the average bubble diameter in our experiments (Table 1). HTAB increased the rate of toluene removal from water both in the air stripping and the solvent sublation experiments (Table 3). HTAB is more surface active than DDS as shown by their critical micelle concentrations of 0.9 and 8 mM, respectively. HTAB was also more effective for removing toluene in both processes. However, the enhancement of toluene removal from water using either DDS or HTAB with solvent sublation is less than was reported for removal of less volatile compounds such as heptachlor and its metabolite, hydroxychlordene, using these surfactants (14).

Surfactants show several effects on the emission of toluene from the column. In air stripping, the presence of HTAB retards but does not reduce the overall emission of toluene by trapping it in the foam at the top of the column, and subsequently emitting it slowly (Fig. 6). This effect is more dramatic at higher HTAB concentration. Comparing the areas under the corresponding curves for air stripping and solvent sublation, the overall emission reduction can be calculated. These experiments were done under identical conditions of flow, initial concentration, and temperature. The curves for air stripping and solvent sublation in the presence of DDS are presented in Fig. 7. Less foam was generated with DDS, and the emission was retarded less than it was in the presence of HTAB at the same concentrations. When a paraffin oil layer is used on the top of the column, the toluene emission to the atmosphere is significantly higher in the presence of surfactants, especially DDS.

TABLE 3

Rate Constant (K) for Toluene Removal from Water in the Presence of Surface-Active Solutes at an Air Flow of 32 mL/min

	Air stripping					Solvent sublation				
	DDS		HTAB		Ethanol	DDS		HTAB		Ethanol
Concentration ppm	5	10	5	10	0.1% (v)	5	10	5	10	0.1% (v)
K (10^{-4})	228	237	236	248	260	238	243	241	259	302

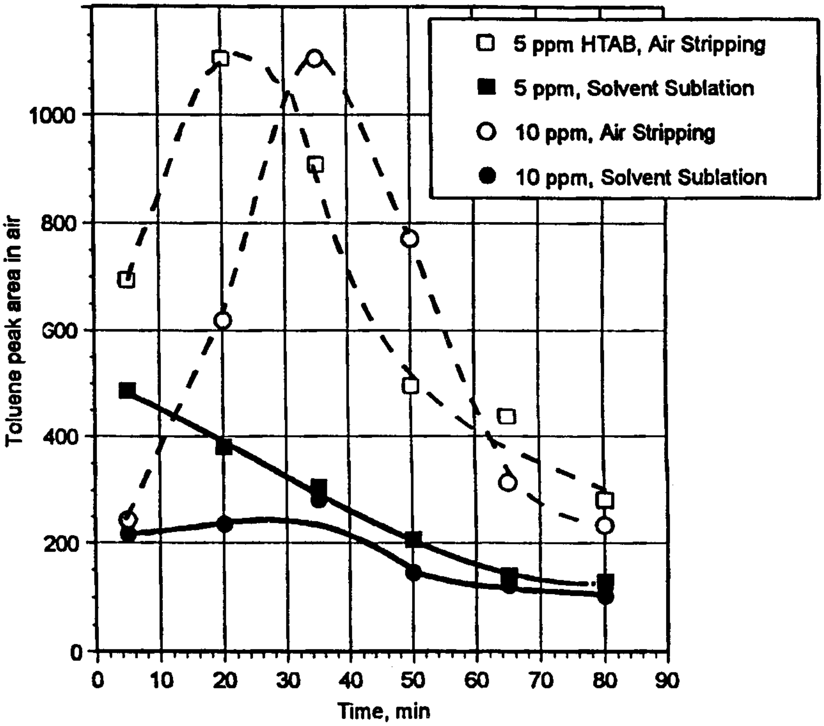

FIG. 6 Effect of added cationic surfactant (HTAB) on toluene concentration in emitted air.

The effect of adding ethanol on toluene removal from the aqueous phase was also investigated. It is known that ethanol at a concentration of 0.1% by volume enhances the rate of removal of VOC and SVOC in both air stripping and solvent sublation processes because of the dramatic decrease of bubble diameter and lowered surface tension at the air–water interface (8, 15).

This is confirmed by our results (Table 3). The difference between the rate constants for air stripping and solvent sublation is approximately the same with or without ethanol at the same air flow rate (Table 2). It was found that more toluene is emitted to the atmosphere during solvent sublation in the presence of ethanol (Fig. 8, Table 3). Some foam was formed under the paraffin oil layer during solvent sublation and on the top of the column during air stripping when ethanol was present.

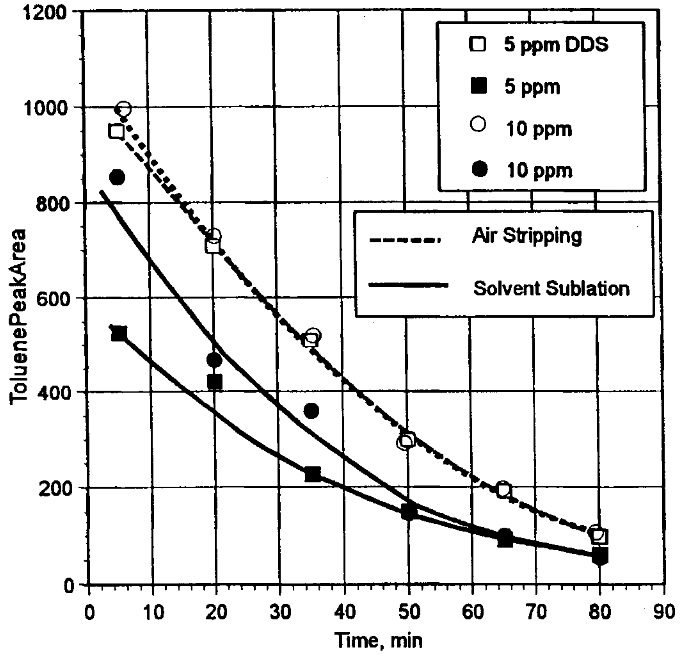

FIG. 7 Effect of added anionic surfactant (DDS) on toluene concentration in emitted air.

In spite of the smaller bubble size and the reduction in the surface tension of the oil–water interface, toluene emission to the atmosphere in the presence of these surfactants and ethanol is higher than without them. Surface-active substances change the properties of the films at the air–water interface and can reduce the diffusion of solutes through the surface of the air bubbles (16). For the compounds investigated, this effect was more important than the increased air–water interface and increased contact time between the bubbles and the oil layer. The presence of such cosolutes may also affect the value of the Henry's law constant for toluene (17), causing changes in rate for both air stripping and solvent sublation. The effect of different cosolutes on VOC emissions from the solvent sublation process requires further investigation, since in practice such compounds are likely to be present in the aqueous solutions for which this separation technique would be suitable.

The percent reduction in the amount of toluene emitted to the atmosphere during 90 minutes of solvent sublation, compared to an identical

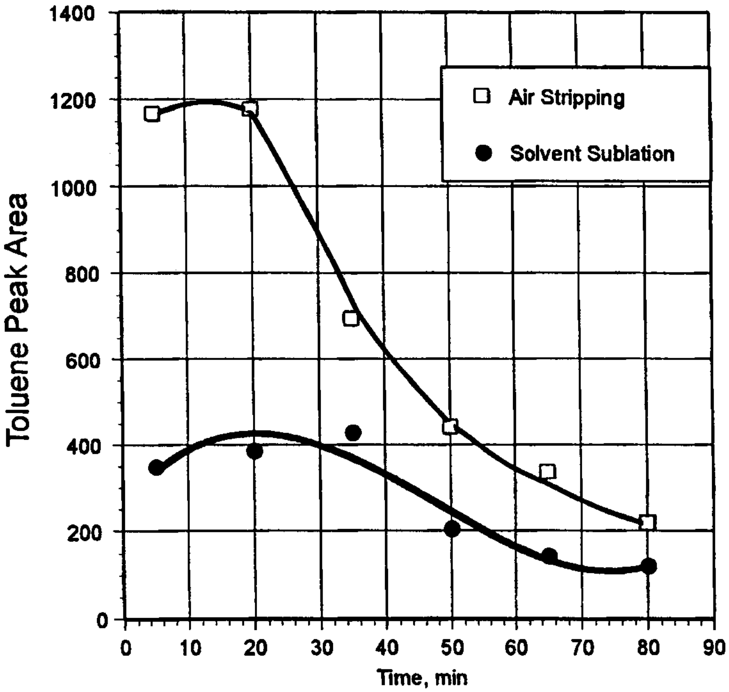

FIG. 8 Effect of added 0.1% (v) of ethanol on toluene concentration in emitted air.

air-stripping process for all the experiments carried out in this study, is shown in Table 4. Emission reductions ranging from 34 to 82% were achieved. Simultaneously, the presence of the paraffin oil or decyl alcohol layer increased the rate of removal of toluene from water to some extent, although this effect would be more important for less volatile contaminants (7, 8).

While the solvent sublation process cannot completely eliminate toluene emission to the atmosphere, it can significantly reduce the emission in comparison with air stripping. Our preliminary data show that the reduction is even better for less volatile hydrophobic compounds. Solvent sublation shows promise for practical application. It can be a quick and inexpensive way to reduce VOC and SVOC emissions in some air stripping and water flotation facilities currently operating. When carbon adsorption filters are needed to clean up the outflow air in these processes, adding an oil layer to the top of the column will extend the lifetime of the carbon

TABLE 4
Reduction in Emission of Toluene to the Atmosphere for Solvent Sublation in Comparison with Air Stripping under Identical Conditions

Air flow rate (mL/min)	Layer composition	Cosolute	% Reduction in emission
32	10 mm Paraffin oil	—	71
60	10 mm Paraffin oil	—	49
94	10 mm Paraffin oil	—	34
60	5 mm Paraffin oil	—	36
60	20 mm Paraffin oil	—	59
60	5 mm Decanol	—	50
60	10 mm Decanol	—	68
60	20 mm Decanol	—	82
32	10 mm Paraffin oil	DDS, 5 ppm	52
32	10 mm Paraffin oil	DDS, 10 ppm	35
32	10 mm Paraffin oil	HTAB, 5 ppm	61
32	10 mm Paraffin oil	HTAB, 10 ppm	66
32	10 mm Paraffin oil	Ethanol, 0.1%	59

bed by a factor of 2–4. In addition to emission reduction, solvent sublation also helps the removal of very nonvolatile hydrophobic substances from water. Compounds such as polycyclic aromatic compounds, pentachlorophenol, some pesticides, and emulsified motor oil, which are not amenable to air stripping, will be separated concurrently with the reduction of volatile emissions.

CONCLUSIONS

It was shown that the emission of toluene to the atmosphere in solvent sublation is 34–82% less than in air stripping under the same experimental conditions. The parameters which affect emission are the air flow rate, the nature and thickness of the organic layer, and the nature and concentrations of the cosolutes.

Emissions are further reduced as the thickness of organic layer on the top of the column is increased. The use of decyl alcohol as the layer compound decreases emission to a greater extent than does paraffin oil. The emission of toluene in the solvent sublation is reduced as the air flow rate is lowered. The rate of toluene removal from water in solvent sublation was always higher to some degree than in air stripping under the same experimental conditions. However, the improvements were not substantial.

Cosolutes which decrease the surface tension of the water and the water–oil interface (DDS, HTAB, ethanol) increase the rate of removal of toluene from water. However, these compounds also increase the amount of toluene emitted to the air. The effect of cosolutes on emission is specific to the individual compounds and depends on their effects on the air–water and oil–water interfaces.

ACKNOWLEDGMENTS

The authors are grateful for research funding for this project from the Hazardous Substance Management Research Center at the New Jersey Institute of Technology and the New Jersey Commission on Science and Technology.

REFERENCES

1. A. N. Clarke and D. J. Wilson, *Foam Flotation; Theory and Applications*, Dekker, New York, 1983.
2. K. T. Valsaraj, G. J. Thoma, and L. Thibodeaux, *Sep. Technol.*, *1*, 234 (1992).
3. F. Sebba, *Ion Flotation*, Elsevier, Amsterdam, 1962.
4. T. Lionel, D. J. Wilson, and D. E. Pearson, *Sep. Sci. Technol.*, *16*, 907 (1981).
5. S. D. Huang, K. T. Valsaraj, and D. J. Wilson, *Ibid.*, *18*, 941 (1983).
6. V. K. Ososkov, N. N. Ovsyannikova, and M. E. Kornelli, *Khim. Tekhnol. Vody*, *3*, 430 (1981).
7. K. T. Valsaraj and D. J. Wilson, *Colloids Surf.*, *8*, 203 (1983).
8. K. T. Valsaraj, J. L. Porter, K. Liljenfeldt, and C. Springer, *Water Res.*, *20*, 1161 (1985).
9. X. Y. Lu, K. T. Valsaraj, and L. Thibodeaux, *Sep. Sci. Technol.*, *26*, 977 (1991).
10. H. S. Shin and R. W. Coughlin, *Colloid Interface Sci.*, *138*, 105 (1990).
11. H. F. Hemond and E. J. Fechner, *Chemical Fate and Transport in the Environment*, Academic Press, San Diego, 1994.
12. K. Kinoshita, H. Tsikawa, and K. Shinoda, *Bull. Chem. Soc. Jpn.*, *31*, 1081 (1958).
13. W. K. Wang and S. D. Huang, *Sep. Sci. Technol.*, *23*, 375 (1988).
14. H. L. Chiu and S. D. Huang, *Ibid.*, *26*, 73 (1991).
15. K. Y. Shin, W. D. Han, and S. D. Huang, *Ibid.*, *25*, 477 (1990).
16. A. Yousef and B. J. McCoy, *J. Colloid Interface Sci.*, *94*, 497 (1983).
17. C. Yurteri, D. F. Ryan, J. J. Callow, and M. D. Gurol, *J. Water Pollut. Control Fed.*, *59*, 950 (1987).

Received by editor May 22, 1995