Int. J. Environ. Res., 4(2):341-346,Spring 2010
ISSN: 1735-6865

Determination of Toxic Toluene, Xylene and Cumene in Different Lake Waters

Amzad Hossain, M.*, **Kabir, M. J. and Salehuddin, S.M.**

Chemistry Division, Atomic Energy Centre, GPO Box No. 164, Ramna, Dhaka-1000,
Bangladesh

Received 17 April 2009; Revised 15 Nov. 2009; Accepted 25 Nov. 2009

ABSTRACT: A rapid and reproducible method is described that employs solid phase extraction (SPE) using dichloromethane, followed by gas chromatograph-mass spectrometry for the determination of toxic toluene, xylene and cumene (TXC) from different lake water of Dhaka mega city of Bangladesh. The method was applied to detect and quantify TXC in water samples collected from surface and 30 cm depth of water. Fifty milliliters of pretreated methanol and filtered water samples were applied directly to a C_{18} SPE column. TXC were extracted with dichloromethane and the TXC concentration was obtained to be 2.34 to 52.12 ppm. The factors influencing SPE *e.g.*, absorbent types, sample load volume, eluting solvent and temperature, were investigated. A cartridge containing a C_{18} absorbent and using solvent gave a better performance for the extraction of TXC from the lake water samples. Average recoveries exceeding 90% could be achieved for toluene at 24°C with a 2.8% RSD.

Key words: Toxic volatile organic compound, TXC, Analysis, Lake water, GC-MS

INTRODUCTION

Volatile organic compounds (VOC), *e.g.*, benzene, toluene, ethylbenzene, xylene and cumene (BTEXC), are important environmental contaminants because of their high toxicity and widespread occurrences. They are present in aviation fuel (gasoline) and are widely used as industrial solvents and raw materials for the production of different commodities (Klist, 1993). Benzene, toluene and ethylbenzene are among compounds designated as "priority pollutants" by the US EPA and the action and risk levels of benzene, toluene ethylbenzene and xylene are described in the Dutch Government Quality Standards for the assessment of soil and water contaminations (EQSS, 1991). The determination of BTEXC in environment matrices is difficult because of their trace level presence and losses incurred during sample handling, extraction etc. Recently there has been considerable interest in the development of SPE column for the clean-up, extraction and pre-concentration of liquid samples (Berrueta *et al*, 1995). SPE applications are found in different environmental areas, such as soils and sediments (Loconto, 1991; Zhang and Pawliszyn, 1995; Chambers *et al.*, 2006), industrial effluents (Deans *et al.*, 1993) and water samples (Saner *et al.*, 2007; Auther *et al.*, 1992). SPE has been used for the extraction of BTEXC (Mency *et al.*, 1998; Redondo *et al.*, 1993; Montero e*t al.*, 2005) and pesticides (Murry, 2001) from soils and sediments. A few SPE applications have also appeared for VOC components in the BTEXC analysis of water samples; a cartridge containing C_{18} absorbent was used to extract BTEX from industrial effluents (Deans *et al.*, 1993) and benzene and toluene from seawater (Saner *et al.*, 2007). Although solid phase micro extraction (SPME) was also applied to isolate BTEX from water samples either by direct absorption from the liquid (Auther *et al.*, 1992; Saraji and Bakhshi, 2005) or *via* headspace sampling (Mency *et al.*, 1998), the limitation of SPME for the quantitation of sulfur based VOC has been reported (Tan *et al.*, 2000). The VOCs analysis from air and water samples by open-tubular, wall coated columns

---

*Corresponding author E-mail: dramzadh@yahoo.com

(Stone and Taylor, 2000), solvent trapping (Charles *et al*, 2001) and semi-VOC from air by atmospheric pressure chemical ionization mass spectrometry (Hossain *et al.*, 1999) were also described.

Lakes are of importance because of their presence in the Dhaka mega city, the capital of Bangladesh, and have an enormous impact on socio-economic activities of the country. Household, workshop and road washing as well as oil spillage are the common features of the lakes at different places. As a result, the water of these lakes is being polluted awesomely by various organic compounds, especially hydrocarbons. In addition, aromatic solvents are increasingly used in industry (Klist, 1993) and the wastes are sometimes disposed of in the aquatic environment, which becomes increasingly contaminated. To monitor contaminants, we recently determined the concentrations of various normal and polycyclic aromatic hydrocarbons in Buriganga river water (Motaleb and Abedin, 1999) and pesticides in soils (Saner *et al.*, 2007) by GC, using liquid - liquid extraction and SPE methods, respectively. We had also reported on the development of a chromatography method for the determination and characterization of anionic detergents in river water (Motaleb, 1999).

The present paper describes the concentration levels of toluene, xylene and cumene in lake water sas amples collected at two depths from the five biggest lakes of Dhaka mega city. The biggies are: Ramna lake, Dhanmondi lake, Gulshan lake, Gabtoli lake and Rupnagar lake. Also discussed are the recoveries of BTEXC using different absorbents for SPE columns and factors influencing SPE absorption, such as the sample load volume, eluting solvent and temperature.

MATERIALS & METHODS

Toluene, xylene and cumene standards were purchased from Sigma-Aldrich Company with purity 99.9%. Dichloromethane (DCM) (BDH, UK), methanol and water (Merck, Germany) were of HPLC grade. Anhydrous sodium sulphate (Merck, Germany) was cleaned by heating at 200°C before use. Silica gel (60-120 mesh, Loba, India) was activated at 400°C for 12 hr. prior to use. The C_{18}, C_8 and PH SPE cartridge were obtained from Supelco Ltd. GC-MS was carried out using total ion monitoring mode on a Varian 3800 gas chromatograph interfaced to a Varian Saturn ion trap 2200 GC-MS. The temperatures of transfer line and ion source were 280°C and 275°C respectively. Ions were obtained by electron ionization mode. The VF-5 capillary column (30 m length, 0.25 mm I.D., 0.25 µm film thickness) was used. A 20% split injection mode was selected with a solvent delay time of 3 min. with injection volume 1µl. The initial column temperature was started at 50°C for 1 min, programmed at 8°C min^{-1} to 200 °C and heated until 300°C at 10°C min^{-1}. Injection port was set at 250°C. Helium was used as carrier gas with a flow-rate of 1.0 mL/ min. Molecular ions were monitored for identification. Mass range: 40-500 m/z. Calibration curves for the samples, treated according to the described analytical procedure, were made using the SIM mode. The reference compounds, toluene, xylene and cumene were used as markers. The markers were accurately weighed and dissolved in dichloromethane to produce a series of concentrations. Standard calibration curves were established by plotting the peak areas against different concentrations of the reference compound (varying from 1.25 to 10 µg/mL). The external standard method was used for quantification of the markers in the lake water extract.

Contaminated lake water samples were collected in 1-1 dark amber - color glass bottles on May 21, 2009 from the five biggest lakes, the names of which are mentioned as above, of Dhaka mega city. Cleaned bottles were rinsed with simple water prior to sample collection. The locations of the sampling points of the lakes are shown in Fig. 1.Ten samples at the surface and ten at a depth of 30cm were collected. The distance of the sample collection point from the lake bank was about 2 meter. At first, the bottle was lowered slowly into the water and its cork was opened by hand, marked accordingly in cm at the desired depth. When the bottle was filled with water, it was closed and drawn up carefully. Then 100 mL of water was discharged from the glass bottle. At the same time 10% $CuSO_4$ was added as a stabilizing agent [8] into the water samples, closed by the cork and shaken vigorously by the hand.

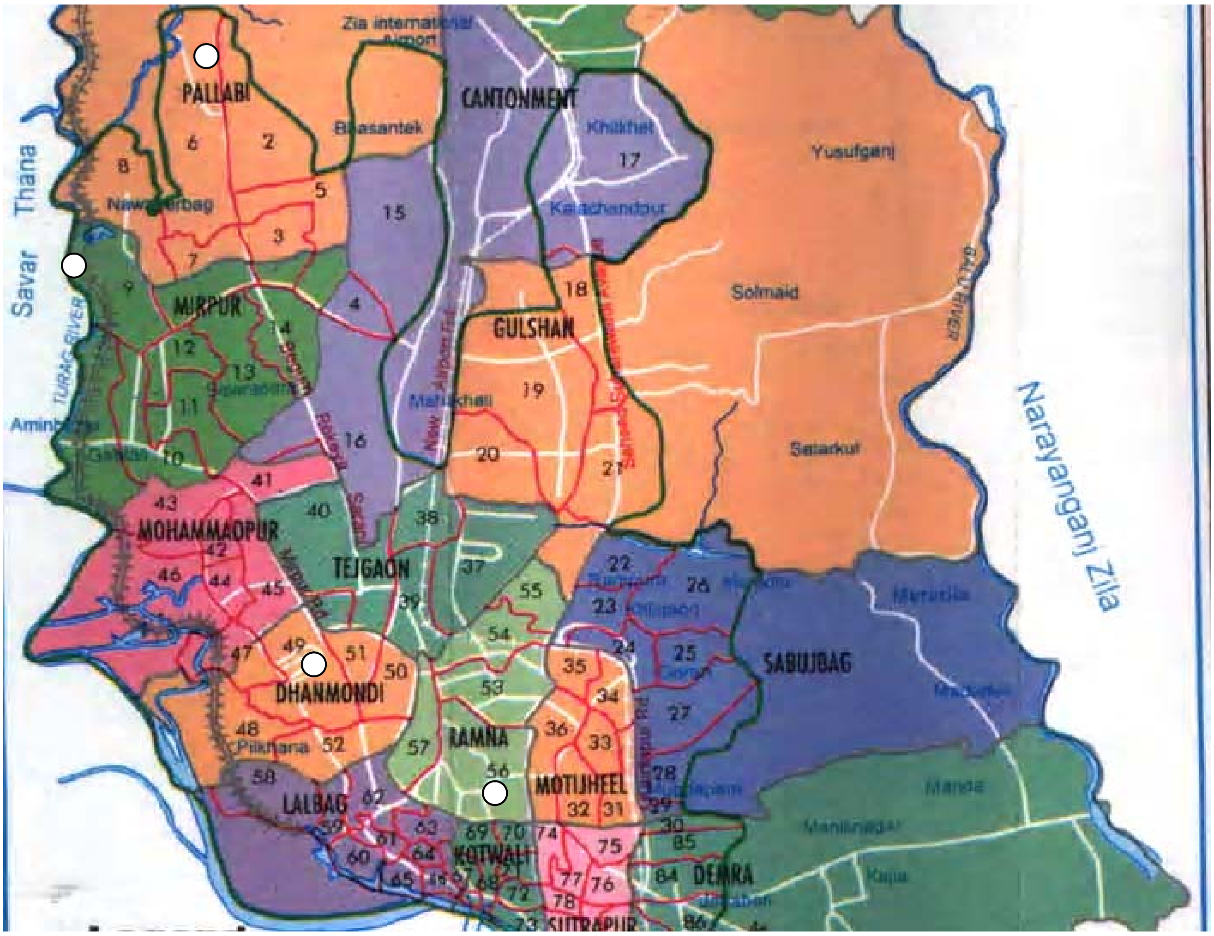

Fig. 1. Map of different lakes showing the locations of the sampling stations and collection points of water samples (○ S sampling collection points)

The column was activated with 3 mL of methanol and pre-equilibrated with 3 mL of de-ionized water. The lake water sample (10 mL) was loaded on the column at 3 mL/min. Elution was carried out with two portions of 2 mL aqueous 1% methanol. Finally, solutes were eluted with two aliquots of 2 mL of dichloromethane. Similar elution profiles were obtained for recovery experiments. Dichloromethane (5%) was added as an internal standard prior to a GC-MS analysis. Passing samples through a dryer containing sodium sulphate only eliminates trace amount of water.

The relative response factor of a component (R_F) to the internal standard of DCM is given by

$$R_F = C_{DCM}/A_{DCM} \ x \ A_C/C_C$$

Where C_{DCM} and C_C represent the concentrations of DCM and the component analyte, respectively, in terms of µg/mL. The term A_{DCM} and A_C indicate the peak area for DCM and the component analyte, respectively.The response factors for all components were calculated as mentioned above, and the concentration of each component (C_C) was calculated as follows:

$$C_C = C_{DCM}/A_{DCM} \ x \ A_C/ \ R_F$$

RESULTS & DISCUSSION

The GC-MS system used was optimized before the VOC measurement. Separations were achieved with different temperature programs. A good separation of TXC constituents, including dichloromethane (DMC), was obtained under the following conditions: Injector temperature, 250°C; Column oven temperature, 50°C for 1 min, programmed at 8°C min^{-1} to 200°C and heated until 300°C at 10°C min^{-1}. Helium was used as carrier gas with a flow-rate of 1.0 mL/min^{-1}. The linearity of the GC-MS response was also demonstrated by injecting the working standard solutions into the GC-MS instrument. Table 1. depicts the calibration graph of the peak area versus the concentration. The GC-MS gave the good linearity of the response for the detection of TXC constituents. Hence, it was decided that the above conditions could be used for the determination of toluene from the lake water samples.

Table 2 summarizes the concentration of toluene, predominantly present in the lake water samples, analysed by SPE-GC-MS. The presence of ethylbenzene, xylene and cumene was not detected using the experimental conditions described previously, although trace levels of toluene was found. To detect the other constituents of the BTEXC family, an increased volume of 10 mL of water samples was directly applied to the SPE at 4°C. An appreciable amount of toluene was obtained in the lake water samples. While the other constituents, except xylene present in a tiny amount, were not found. Fig. 2 shows a representative GC-MS chromatogram of the standard solution and lake water samples. The chromatograms in Fig. 2 also correspond to the surface and 30 cm depth of water, collected from the different lakes of Dhaka mega city of Bangladesh. These were obtained when 2 µL SPE eluted samples were injected into the GC-MS and showed a similar chromatographic elution pattern with different magnitudes of the toluene compound peak. Blank experiments were performed prior to sample injection.

To select the suitability of adsorbents and eluting solvents, the percentage of recovery of BTEXC constituents was investigated using C_{18}, C_{18} and pH cartridges with dichloromethane and chloroform solvents. The recoveries obtained when 2 mL portions of standard toluene solution were passed through different SPE columns and eluted with two portions of 2 mL of dichloromethane or chloroform at 4°C. The recovery results are presented in Table 3. The extractions were performed simultaneously for each solvent.

Table 1. Analytical characteristics of calibration curves for the standard markers

Constituet	Ret. Time (min)	Range ((µg/mL)	Regression Equation	Detection Limit (µg/mL)	R^2	Precision (%) (SD[a]) (n=5, 10ng/µl)	
						Inter-day	Intra-day
Toluene	3.873	2 -1000	0.1917x-0.3250	2.3	0.9997	0.78	0.37
Xylene	6.594	2.5 -1000	0.0698x-0.0243	2.0	0.9994	0.83	0.42
Cumene	6.861	2 – 1000	0.1950x+0.3032	2.5	0.9998	1.52	1.21

[a] **SD = standard deviation**

Table 2. SPE of lake water samples at 4°C (C_{18} column, sample volume 10mL)

Lake	Concentration of components in lake water					
	Surface water			30 cm depth		
	Cone. of toluene (µg/mL)	Cone. of xylene (µg/mL)	Cone. of cumene (µg/mL)	Cone. of toluen (µg/mL)e	Cone. of xylene (µg/mL)	Cone. of cumen (µg/mL)e
Gulshan lake	52.12	2.287	ND*	33.09	2.113	ND
Dhanmodi lake	23.777	2.919	ND	16.98	2.684	ND
Gabtoli lake	28.74	3.129	ND	21.34	2.769	ND
Ramna lake	16.87	2.998	ND	13.78	2.739	ND
Rupnagar lake	24.024	2.148	ND	19.33	2.0861	ND

*** ND = Not detectable**

Table 3. Recovery of toluene from different SPE columns eluted with dichloromethane and chloroform at a temperature of 4°C

Recoveries (%) ± standard deviation (SD)[a]		
Solvent	**SPE Column**	**Toluene**
Dichloromethane	C_{18}	75.5 ± 2.5
	C_8	68.3 ± 2.1
	pH	65.8 ± 3.1
Chloroform	C_{18}	71.2 ± 2.9
	C_8	62.9 ± 2.8
	pH	63.7 ± 3.6

Regardless of the solvents used, higher recoveries were obtained for xylene and cumene. This may have been due to a less evaporative loss of the two components because of their higher boiling point. Moreover, in comparison between dichloromethane and chloroform solvents, it was observed that slightly better recoveries were obtained when dichloromethane was used as the eluting solvent (Table 3). This is probably due to a more non - polar interaction between a bonded phase and the dichloromethane system.

The effect of the sample volume on the SPE recovery is one of the most important factors, because the SPE performance is affected by the amount of sample loaded on a particular column. The break through volume of a C_{18} column (500 mg, 3 mL capacity) was determined by passing a number of VOC standard solutions to a volume of up to 10 mL. Known masses of the analytes were introduced. There were no appreciable changes in the recovery rates up to a sample volume of 8 mL. The percentage of recovery of benzene and toluene decreases more rapidly than other EXC. This observation confirms the fact that ethylbenzene, xylene and cumene possess higher breakthrough volumes than benzene and toluene. Similar break through volume were obtained for C_8 and phenyl substituted SPE columns. These are not shown.

To investigate the effect of the temperature on SPE performance, a cartridge containing C_{18} material was employed with dichloromethane solvent at temperature of 20°C and 4°C. An effect of temperature on the SPE recovery of BTEXC constituents was found to occur as shown in Table 3. It has been observed that both liquid-liquid and solid-phase extractions provided slightly recoveries when experiments were carried out at a temperature of 4°C. The relative standard deviations (RSD) were calculated for each of the BTEXC constituents and temperature. At 20°C, the RSD of recoveries were between 3.3 and 4.0%, however, at 4°C, improved recoveries of the constituents were achieved with RSD values of 2.7 to 3.7%.

CONCLUSION

Toxic organic pollutants such as toluene, xylene and cumene (TXC) are important priority pollutants in most countries in the world, and many related analytical techniques have been developed for the detection of those pollutants. Present work has been done by us with new extraction and separation method for TXC determination based on without any derivative process. In conclusion, the concentrations of TXC in water samples at the lake were determined. Samples were collected from surface and 30 cm depths of water from each of the sampling stations. The collected samples were extracted, pre-concentrated and analyzed by GC-MS. Almost similar pattern results were obtained from the lakes. From our experimental findings, we can aware the respective authority of the Government of Bangladesh and also the mass people of the Dhaka mega city about the level of toxicity of the different lake water. The experimental results demonstrated that this GC-MS method had offered excellent recoveries and could be employed for environmental sample analysis. In view of the rapidity, sensitivity, simplicity, environment-friendly nature and so on, the proposed method will be an excellent alternative detection technology for TXC analysis, and will be widely employed in environmental and other related fields.

ACKNOWLEDGEMENT

We are grateful to M. Ali, Chief Scientific Officer and Head, Chemistry Division, Atomic Energy Centre, Ramna, Dhaka for his continuous encouragement and logistic support during the work. We also thank to Mr. Zahidul Islam and Mr. Ayub Ali for their help to collection and preparation of the water samples.

REFERENCES

Auther, C. L., Pawliszyn, J. and Belardi, P. R. (1992). Solid-phase microextraction in biomedical analysis. Journal of High Research Chromatography,**15**, 741-744.

Berrueta, L. A., Gallo, B. and Vicente, F. (1995). A review of solid phase extraction: basic principles and new developments. Chromatographia, **40**, 474-476.

Chambers, D. M., McElprang, D. O., Waterhouse, M. G. and Blount, B. C. (2006). An Improved Approach for Accurate Quantitation of Benzene, Toluene, Ethylbenzene, Xylene, and Styrene in Blood. Analytical Chemistry, **78**, 5375-5383.

Charles, L., Riter, L. S. and Cooks, R. G. (2001). Direct Analysis of Semivolatile Organic Compounds in Air by Atmospheric Pressure Chemical Ionization Mass Spectrometry. Analytical Chemistry, **73**, 5061-5065.

Deans, I. S., Davidson, C. M., Littlejohn, D. and Brown, L. (1993). Determination of pesticides in environmental waters by solid-phase extraction and gas chromatography with electron-capture and mass spectrometry detection. Analyst, **118**, 1375-1379.

Environmental Quality Standards for Soil and Water, (1991). Netherlands Ministry of Housing, Physical Planning and Environment, Leidschendam.

Klist, J. J. G. (1993). Chemistry and Analysis of VOCs in the Environment. Ed. H. J. T. Bloemen and J. Burn, Glasgow.

Loconto, P. (1991). Disks versus columns in the solid-phase extraction of pesticides from water. *LC-GC Int.*, **4**, 10-14.

Mency, K. M., Davidson, C. M. and Littlejohn, D. (1998). *Solid phase microextraction for quantitative analysis in nonequilibrium situations.* Analyst, **123**, 195-199.

Motaleb, M. A., Ferdous, M., Islam, M. A. and Hossain, M. A. (1999).Determination of Normal Saturated Hydrocarbons in the Buriganga River Water of Bangladesh By Gas Liquid Chromatography. Analytical Science, **15**, 995-1000.

Motaleb, M. A. and Abedin, M. Z. (1999). Determination of Chlorinated Pesticides in Soil by Solid Phase Extraction-Gas Chromatography. Analytical Science, **15,** 283-287.

Motaleb, M. A. (1999). Development of a HPLC Method for Analysis of Linear Alkylbenzene Sulphonates and Detection by UV and FTIR Spectroscopy Using Thermospray Interface. Mikrochemica Acta, **132,** 31-39.

Montero L. A., Conradi S. A. H., Weiss B. and Poppa, P. (2005). Determination of phenols in lake and ground water samples by stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry. Journal of Chromatography A, **1071,** 163–169.

Murry, R. A. (2001). Imitations to the Use of Solid-Phase Microextraction for Quantitation of Mixtures of Volatile Organic Sulfur Compounds. Analytical Chemistry, **73,** 1646-1649.

Redondo, M. J., Ruiz, M. J., Boluda, B. and Font, G. (1993). Solid Phase Extraction Technique – Trends, Opportunities and Applications. Chromatographia, **36**, 147-151.

Tan, B. C. D., Marriott, P. J., Lee, H. K. and Morrison, P. D. (2000). Sorption of volatile organics from water using an open-tubular, wall-coated capillary column. Analyst, **125**, 469-475.

Saner, W. A., Djadamec, J. R., Sagar, R. W. and Kleen, T. J. (2007). Use Of Solid-Phase Extraction in the Determination of Benzene, Toluene, Ethylbenzene, Xylene And Cumene in Spiked Soil And Investigation Of Soil Spiking Methods. Analytical Chemistry, **51**, 2180-2185.

Saraji, M. and Bakhshi, M. (2005). Determination of phenols in water samples by single-drop microextraction followed by in-syringe derivatization and gas chromatography–mass spectrometric detection. Journal of Chromatography A, **1098**, 30-36.

Stone, M. A. and Taylor, L. T. (2000), Quantitative coupling of supercritical fluid extraction and high-performance liquid chromatography by means of a coated open-tubular interface. Analytical Chemistry, **72**, 1268-1274.

Zhang, Z. and Pawliszyn, J. (1995). Solid Phase Microextraction for Quantitative Analysis in Nonequilibrium Situations. Analytical Chemistry, **67,** 34-43.