As. J. Energy Env. **2009**, 10(02), 91-98

Asian Journal on Energy and Environment
ISSN 1513-4121
Available online at www.asian-energy-journal.info

Research Article

Quantification of phenol in surface water by gas chromatography and mass spectroscopy

M. Amzad Hossain* and S. M. Salehuddin

Chemistry Division, Atomic Energy Centre, GPO Box 164, Ramna, Dhaka-1000, Bangladesh.

*Author to whom correspondence should be addressed, email: dramzadh@gmail.com

Abstract

Phenol was analyzed by both gas chromatography–flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS) to compare the techniques and to find out if GC-FID is a suitable tool for the analysis of phenol extracted from environmentally important phenol in water. After the treatment of water with $CuSO_4$ and H_3PO_4, phenol in the water was extracted with dichloromethane. The extract was cleaned up by silica gel column chromatography. The analytical results obtained by GC-FID and GC-MS were generally of similar magnitude. Limits of detection and determination were between 0.01 and >0.05 ng/l and <0.01 and 0.05 ng/l, respectively. And the recovery of phenol was above 45%.

Keywords: Toxic Phenol, quantification, Surface water, GC-MS, Bangladesh

Introduction

Phenolic compounds are gaining great popularity due to their widespread application to produce pharmaceutical fragrance, polymeric materials, dyes, paper, pesticides and petrochemical products etc. Therefore, it is not difficult to understand their presence in the manufacturing waters and in industrial waste from relative industries and in some of the natural waters. Due to its toxicity, they could have significant detrimental effects on water quality or animals as well as some plants even at very low level. For these reasons, some of them have been included in the lists of priority pollutants. A number of analytical techniques have been established for phenols analysis in recent years. High performance liquid chromatography is presently the most popular and reliable technique for the analysis of phenolic compounds. Often used detectors usually are the UV, electrochemical detector and colorimetric detector [1-5]. Recently, LC-MS has been developed to be a robust and valuable instrumental analytical method for the determination of

many compounds including phenolic compounds, which possess the merit that they do not require the analytes must be volatile and has been considered as an ideal tool in analytical, medical and environmental and other fields. However, it is very expensive and needs high requirement for the operator. Up to now, it cannot be employed as common instrument for routine analysis [6]. Capillary electrophoresis (CE), another alternative analytical technique, has also been utilized for the analysis of these compounds [7-9]. It can provide many strong points such as high separation efficiency, small sample and electrolyte consumption and rapid analysis. These merits make CE of great utility in routine analysis and monitoring processes in a number of industrial fields. Moreover, CE is relatively well suited to analysis of complex samples, and it allows in-capillary concentration such as electrokinetic stacking [10], sweeping, dynamic pH junction, and anion or cation selective exhaust injection-sweeping-MEKC, and dynamic pH junction-sweeping etc. More Recently, CE has been shown to be a powerful and efficient technique and also applied to separate the EPA 11 priority phenols successfully [11-13].

In addition to instrumental methods, biological methods have been improved to be very useful in the analysis of phenols in food and environmental samples etc. Among these, biosensors are the popular and gaining more attention in recent years. A great number of biosensors have been developed for the determination of phenols, which are on the basis of tyrosinase and perodidase [14-20]. However, these enzymes require strict conditions for keeping and using as well as transporting to make it inconvenient to establish and apply these bio-methods. Gas chromatography, a very sensitive and reliable analytical tool, especially in combination with mass selective detector, has been applied in separation and identification of the phenolic compounds [21]. In this paper, we describe the identification and quantification of phenol in surface water samples supplied by Environmental Conservation Management Consultants (ECMC) by both GC-FID and GC-MS in the way previously established in our laboratory.

Experimental

General experimental procedures

Chemicals

Phenol crystal, E. Merck (Germany), purity 99.0%; anhydrous Na_2SO_4, BDH Laboratories (England), purity 99.5%; dichloromethane, HPLC grade, E. Merck; H_3PO_4, E. Merck, purity 88.0% and $CuSO_4$, BDH Laboratories, purity 99.0% were used in this work.

Instrument and operating conditions

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/MS mass spectrometer. 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 0.2 μl. The initial column temperature was started at 40°C for 1 min, programmed at 8°C min^{-1} to 200°C and heated until 280°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^{-1}. Molecular ions were monitored for identification. Mass range: 40-500 m/z.

Sample collection

Three water samples were supplied to our laboratory for analysis by the Environmental Conservation Management Consultants (ECMC) on 3rd October 2007. They might have collected the surface water from the industrial area or gas field area. Each sample was collected in a one-liter amber color glass bottle with 10 ml of 10% $CuSO_4$ stabilizing agent. The water samples were stored at 4°C before analysis.

Extraction procedure

The water samples were collected from the sampling spot and instantly stabilized by stabilizing agent of 10% $CuSO_4$ solution. 100 ml of water sample was extracted twice with dichloromethane (30 and 20 ml) in 30 minute by shaking with hand at pH 2, adjusted with H_3PO_4 (Hossain *et al*. 1999). Finally both the extracts were combined and dried with anhydrous Na_2SO_4. Then the dried extract was pre-concentrated (1-2 ml) using Kuderna-Danish (K-D) evaporative concentrator. From this concentrated samples, certain volume was injected into the Gas liquid chromatography and mass spectroscopy (GC-MS/MS).

Clean-up procedure

The cleanup column (i. d. = 1 cm) was filled with cotton in the bottom. Activated silica gel (17 gm) was soaked with dichloromethane and loaded into the cleanup column (5 cm), which was then topped with 1.5 cm of anhydrous sodium sulfate. 5 ml of dichloromethane was added to wash the sodium sulfate and the silica gel. The dried sample was then transferred into the column. The vessel was rinsed twice with 2 ml dichloromethane to add to the column. Another 60 ml of dichloromethane was added to the column and allowed to flow through the column at a rate of 3–5 ml/min, and the eluent was collected. The collected eluent from the cleanup procedure was reconcentrated to 0.5 ml with K-D concentrator.

Preparation of standard

Calibration graphs for the samples, treated according to the described analytical procedure, were made using the SIM mode. Different concentrations of phenols (1ng/ml, 100 ng/ml, 250 ng/ml, 500 ng/ml and 1000 ng/ml) were used to establish the calibration curve. They were linear with the concentration range 1-1000 ng/ml of the phenols target.

Results and Discussion

In our previous study [22-23] done in our laboratory, it was observed that the –OH group of phenols is stable in aqueous medium at pH 2. The dissociation is suppressed at lower pH and it increases at higher pH values [24]. In our present study, the extraction of phenolic compounds has been carried out at pH 2, too. Phenol is less stable in aqueous medium because of its biological action [25]. So, during sampling for phenol and its derivatives from water matrices, some authors [22-23] used $CuSO_4$ as a stabilizing agent. In our laboratory, one author [25] used $CuSO_4$ as stabilizing agent and produced average recovery results of phenols derivatives. He also showed that in the absence of any stabilizing agent such as $CuSO_4$, the presence of phenol and its

derivatives could not be detected after 72 hours i.e. it was completely dissociated with water matrices.

The quantitative determination of phenol was done by external calibration curve method. The calibration curve (Fig. 1) was already prepared with known concentrations of phenol as detailed below.

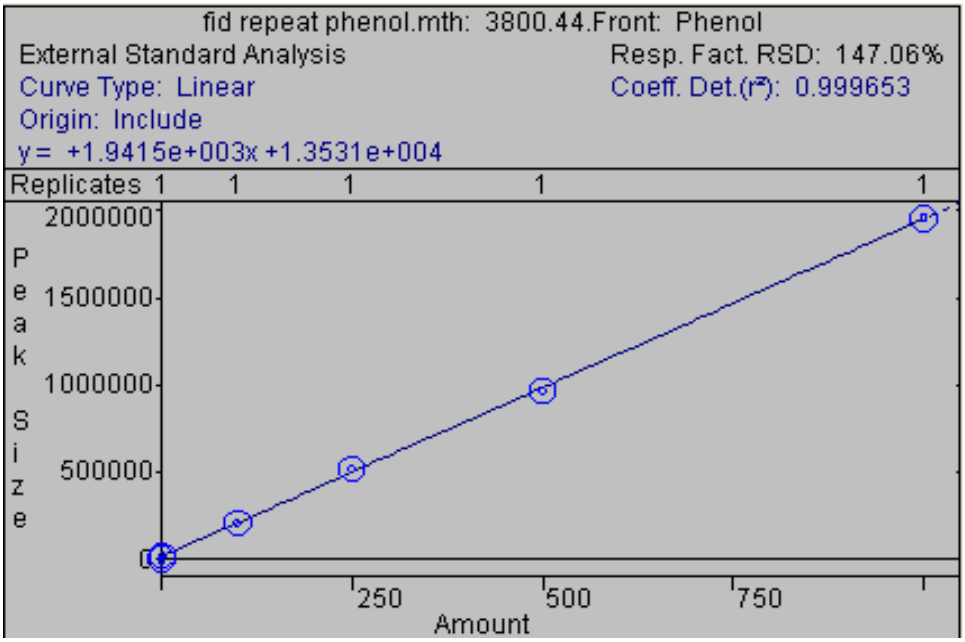

Figure 1. Standard Calibration Curve of Phenol.

Standard curve for phenol generated by plotting the area of five spots vs. the concentration, gave high correlation coefficients. The concentration of phenol in three water samples (Fig. 2, Fig. 3 and Fig. 4) was calculated from the external curve method by GC-FID. Linear responses were achieved for phenol in the concentration range for water samples with the values 9.16 mg/l, 9.71mg/l and 10.37 mg/l respectively. Over this concentration range, the linear regression analysis of peak areas (y) in function of concentration (x), calculated by least square method, leads to the following equations: $y = +1.9415e^{+003x} +1.3531e^{+004}$ ($r^2 = 0.999653$) for phenol. The results obtained with this method were found to be in agreement with the confirmatory determinations done on MS.

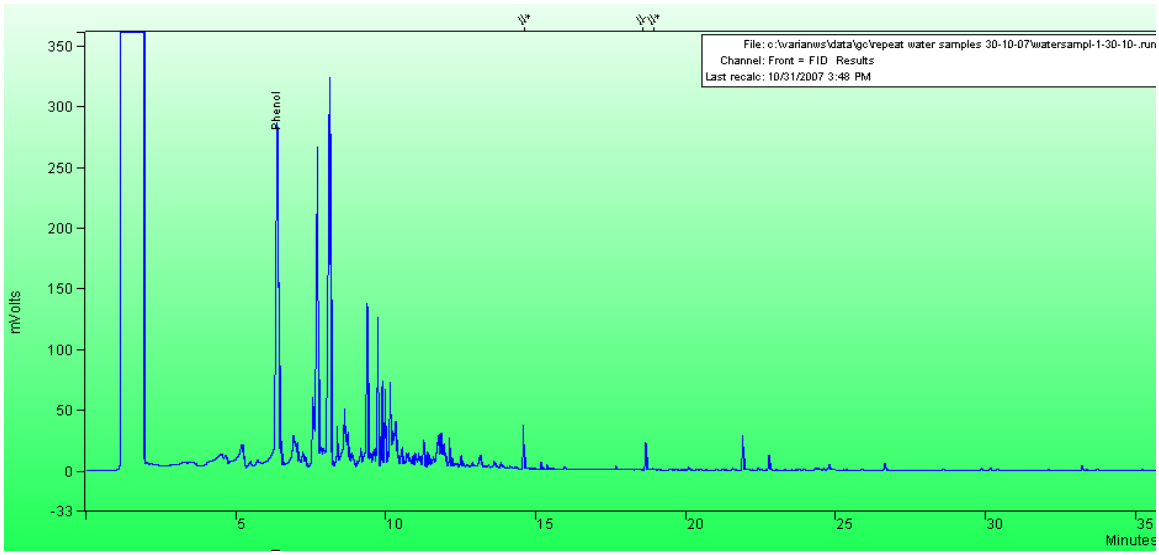

Figure 2. Chromatogram of phenol compound from surface water sample 1.

Column: VF-5 (l. 30m, i.d. 0.25, film thickness 0.25 µm); delay: 3min; Temperature Program: 40°C(1)—›200°C (8°C)—›280°C (10°C); Injector Temperature: 250°C; Split: 20%; Carrier gas: He; Flow rate: 1ml/min.

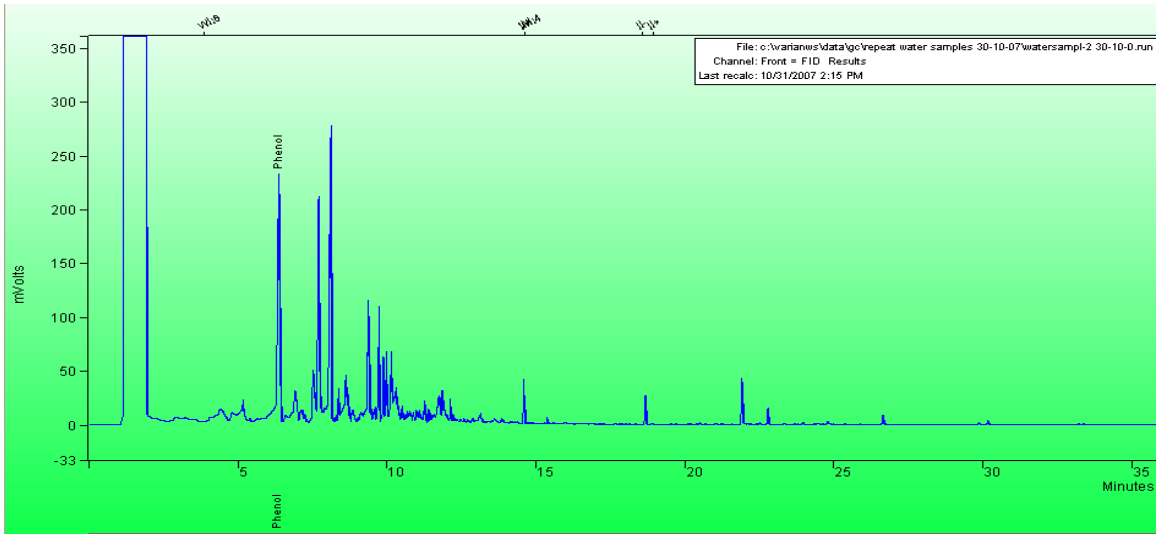

Figure 3. Chromatogram of phenol compound from surface water sample 2.

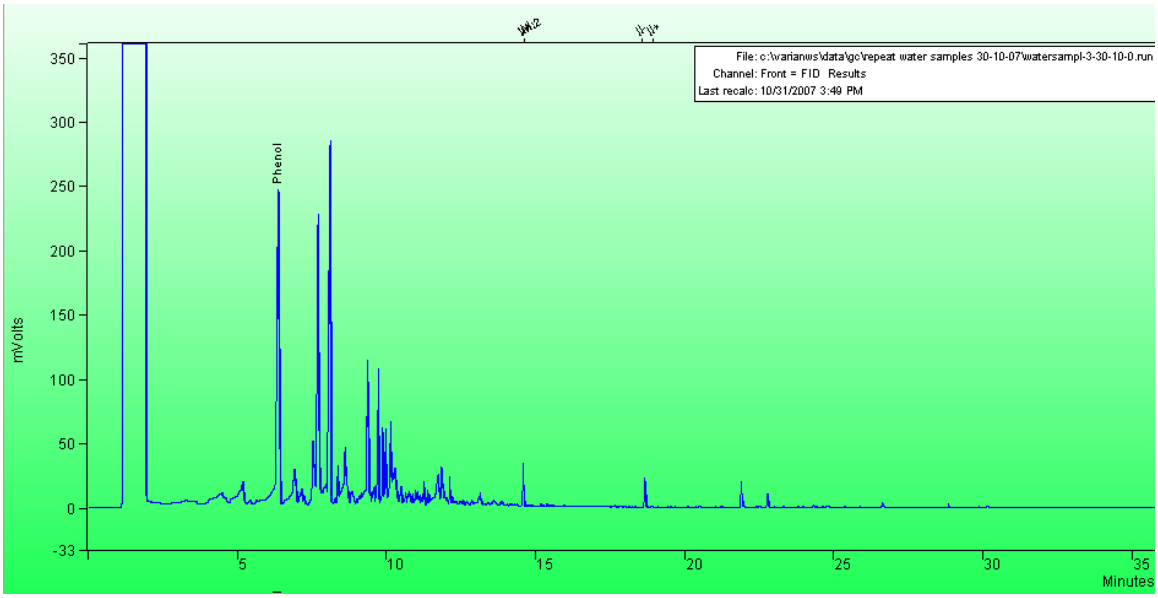

Figure 4. Chromatogram of phenol compound from surface water sample 3.

Column: VF-5 (l. 30m, i.d. 0.25, film thickness 0.25 µm); delay: 3min; Temperature Program: 40°C(1)—›200°C (8°C)—›280°C (10°C); Injector Temperature: 250°C; Split: 20%; Carrier gas: He; Flow rate: 1ml/min.

Table 1. Concentration of Phenol obtained from three water samples.

Sl. No	Sample	GC-FID (Phenol)	GC-MS (Phenol)
1	Sample 1	9.16± 0.015 mg/L	9.22± 0.045 mg/L
2	Sample 2	9.71± 0.065 mg/L	9.88± 0.070 mg/L
3	Sample 3	10.37± 0.080 mg/L	10.43± 0.051 mg/L

From Table 1, it is clear that the concentrations of phenol in three water samples are different, although not by much. The highest concentration of phenol was found in sample 3 and the lowest in sample 1. The similarity in results obtained from both the instruments means that they are almost identical in terms of sensitivity. So, we can use the comparatively cheaper GC-FID for the quantification of phenol in water for routine analysis.

Conclusion

Phenolic compounds are important priority pollutants in most countries in the world, and many related analytical techniques have been developed for detection of phenols. Present work has been done by our previously established method (Hossain *et al*., 1999) for phenols determination based on without any derivative process. Comparable results were obtained by GC-FID and GC–

MS methods. GC-FID was chosen as an analytical tool for the analysis of phenol in water because of its reliability and low-cost compared to the other. The experimental results demonstrated that this GC-FID 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 phenol analysis, and will be widely employed in environmental and other related fields.

Acknowledgement

The authors are grateful to Sohela Akhtar, Head, Chemistry Division, Atomic Energy Centre, Dhaka, Bangladesh for her constant encouragement and helpful suggestions. They are also grateful to Mr. Zahidul Islam and Mr. Abbas Ali for their help to preparation the water samples.

References

1. Akasbi, M., Schoeman, D. W., and Csallany, A. S. (1993). **Journal of American Oil Chemistry Society.**, 70**,** 367–370.

2. Angerosa, F., d'Alessandro, N., Konstantinou, P. (1995). **Journal of Agriculture and Food Chemistry.,** 43**,** 1802–1807.

3. Bendini, A., Bonoli, M., Cerretani, L. (2003). **Journal of Chromatography**, 985**,** 425–433.

4. Bonnely, S., Peyrat-Maillard, M. N., Berset, C. (2000). **Talanta**, 51**,** 709–716.

5. Bonoli, M., Montanucci, M., Toschi, T. G., 2003, **Journal of Chromatography *A*,** 1011**,** 163–172.

6. Campuzano, S., Serra, B., Pedrero, M. (2003). **Analytica Chimica Acta.** 494**,** 187–197.

7. Demianova, Z., Siren, H., Kuldvee, R. (2003). **Electrophoresis**, 24**,** 4264–4271.

8. Ferapontova, E., Puganova, E. (2002). **Journal of Electroanalytical Chemistry**, 518**,** 20–26.

9. Gaspar, S., Habermuller, K., Csoregi, E. (2001). **Sens Actuators** *B*, 72**,** 63–68.

10. Groom, C. A., Luong, J. H. (1997). **Electrophoresis**, 18**,** 1166–1172.

11. Hossain**,** M. A., Salehuddin, S. M., Abedin, Z., 1999, **Nuclear Science Applications***,* 8(1-2), 95-97.

12. Huang, R., Hu, N. (2001). **Bioelectrochemistry**, 54**,** 75–81.

13. Kuban, P., Kuban, P., Kuban, V. (2002). **Electrophoresis,** 23**,** 3725–3734.

14. Liu, S. Q., Ju, H. Z. (2002). **Analytical Biochemistry**, 307**,** 110–116.

15. Mai Anh, T., Dzyadevych, S. V., Soldatkin, A. P. (2002). **Talanta**, 56, 627–634.

16. Martinez, D. Pocurrull, E. Marce, R. M. (1996). **Journal of Chromatography,** 734**,** 367–373.

17. Mottaleb, M. A. Ferdous, M. Islam, M. S. Salehuddin S. M. Hossain, M. A. (1999). **Analytical Sciences** (Japan), 15**,** 995-1000.

18. Salehuddin, S. M. Mottaleb, M. A. Khan, A. H. (1992). **Journal of Bangladesh Academy of Sciences***,* 1 **,** 69-74.

19. Serra, B. Jimenez, S. Mena, M. L. (2002). **Biosensors and Bioelectronics,** 17, 217–226.

20. Tasioula-Margari, M. Okogeri, O. (2001). **Food Chemistry,** 74**,** 377– 383.

21. Vaher, M. Koel, M. (2003). **Journal of Chromatography A,** 990**,** 225–230.

22. Watanabe, T. Terabe, S. (2000). **Journal of Chromatography A,** 880**,** 311–322.

23. Wilkinson, A. P. Wahala, K, Williamson, G. (2002). **Journal of Chromatography A,** 777**,** 93–109.

24. Zemann, A. Volgger, D. (1997). **Analytical Chemistry,** 69**,** 3243–3250.

25. Zhang, S. Zhao, H. John, R. (2001). **Analytica Chimica Acta***,* 441**,** 95–105.