Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1411-1414

Separation of Some Halogenated Phenols by GC-MS¶

A. HAKAN AKTAS
Department of Chemistry, Faculty of Science and Art, Süleyman Demirel University
32260 Isparta, Turkey
Tel: (90)(246)2114080; E-mail: ahakan@fef.sdu.edu.tr

Phenolic compounds are common pollutants in aquatic environments. These pollutants are required to be detected at trace levels by most environment protection authorities. In present studies the GC and MS chromatograms of the solution of 4-chlorophenol, 3-bromophenol, 4-fluorophenol, 4-iodophenol and 3-chlorophenol in MeOH of 50 ppm have been taken. The peaks due to each sample in the GC chromatography is determined and corrected with MS chromatogram. The mixture of the halogenated phenols in MeOH is done and taken the GC chromatogram. As seen from this figure in these condition the halogenated phenols are determined to be well separate by suggest GC-MS method. After this determination, this condition is determined to be applying for a very kind of natural sample. The aim of this study is certain the separation of the synthetic sample with halogenated phenols found to be pollution in the nature.

Key Words: Halogenated phenols, Pollutant, GC-MS.

INTRODUCTION

Phenolic compounds are common pollutants in aquatic environments as a result of industrial outfalls and degradation of pesticides. These pollutants are required to be detected at trace levels by most environment protection authorities. In addition to the requirement for the sensitive determination technique an effective preconcentration step is required to reach the sub ppb detection level necessary for the these compounds in water[1].

Phenols are generated by a number of processes including the petroleum industry, the paper industry and the synthesis of plastics and pharmaceuticals[2]. Halogenated phenols such as 3-chlorophenol or 4-chlorophenol have been used as insecticides and are found in drinking waters as a result of chlorination. Due to their toxicity, the United State Environmental Protection Agency has included some of them in the list of high priority pollutants[3]. Their determination in waste and drinking waters is, therefore,

¶This paper has been presented at 3rd BBCAC (3rd Black Sea Basin Conference on Analytical Chemistry) 12-14 September 2005 Constanta, Romania.

of great importance and many analytical methods have been developed. Chromatographic methods are suitable for the selective determination of individual phenolic compounds, while spectrophotometric methods are employed for the determination of the sum of phenolic compounds[4,5].

The chromatographic studies are often concerned with the separation of complex mixtures with a variable behaviour of their components, which makes good resolution sometimes extremely difficult. Several optimization strategies have been proposed to solve this problem[6]. The most reliable and less time-consuming strategies apply resolution criteria based on empirical or mechanistic models to describe the retention of solutes[7].

In gas chromatography, the elution order of analytes is governed by several factors such as latent vapour pressures, solubility's in stationary phase and propensities for molecular interaction in the stationary phase. All of these effect changes with temperature and their concerned effect ultimately determine the equilibrium distribution of solute molecules between the mobile and stationary phase[8].

The simultaneous detection and identification of a wide range phenol in a single analysis is now commonly encountered problems in the environmental screening works as well as in the controlling of their overuses. In the literature, high-resolution capillary gas chromatography (GC) combined with mass spectrometry (MS) has been preferentially employed for the multi component profiling analyses in screening works because of its inherent high resolving power, high sensitivity and positive peak confirmation as well[9].

Many analytical approaches have been used for the trace-level analysis of phenols, mainly using high performance liquid chromatography (HPLC)[10-15] or capillary gas chromatography is often preferred, offering unrivalled high resolution and easy coupling with sensitive and selective detectors. Actually, HPLC detection was reported to be prone to interferences from matrix compounds, such as humic substances naturally occurring in environmental samples[16]. In general, phenols are amenable to gas chromatography without derivatization[17,18]. But at lower concentrations, peak tailing and discrimination in the injector or capillary column might occur[19], especially when environmental samples are analyzed.

The aim of this study involves certain the separation of the synthetic sample with halogenated phenols found to be pollution in the nature. The determination of these separation conditions will be helper to separate the other same type phenols.

EXPERIMENTAL

The following phenols were studied 3-bromophenol (Aldrich, Steinheim, Germany), 3-chlorophenol (Fluka, Buchs, Switzerland), 4-

fluorophenol (Merck, Darmstadt, Germany), 4-chlorophenol (Fluka, Buchs, Switzerland) and 4-iodophenol (Aldrich, Steinheim, Germany).

Stock Solution: A stock standard solution of halogenated phenols were prepared by dissolving 0.025 g of pure crystalline halogenated phenols such as 3-bromophenol, 3-chlorophenol, 4-fluorophenol, 4-chlorophenol and 4-iodophenol in MeOH and made up to 25 mL with the MeOH. Stock solution (with concentrations of 1000 mg/L) was kept in a deep freezer (at -18ºC).

An Agilent 6890 GC System 5973 MSD with Chemstation software (Agilent Technologies, Burwood, Australia) was used with a flame ionization detector at 310ºC. Samples (*ca.* 1.0 µL) were injected in the splitless mode and analyzed on an Agilent 19091S-433 HP-5MS capillary column (30 m × 0.25 I.D., 0.25 µm film thicknesses; Hewlett-Packard, Avondale, PA, USA). The GC oven was operated using different analytical conditions depending on the objective of the particular study. Both isothermal and temperature program conditions were employed as required. The initial temperature was set at 40ºC with a column head pressure of 13.31 psi (1 psi = 68794.76 Pa). Helium (99.999%) at a flow rate of 20.0 mL/min was utilized as the carrier gas.

RESULTS AND DISCUSSION

The GC and MS chromatograms of the solution of 4-chlorophenol, 3-bromophenol, 4-fluorophenol, 4-iodophenol and 3-chlorophenol in MeOH of 50 ppm have been taken. The peaks due to of each sample in the GC chromatography is determined and corrected with MS chromatogram. Table-1 lists the retention times, selected masses and the start scan times for each compound studied by GC-MS. The mass spectrum of each compound was already obtained by the direct injection of a standard solution of each analyte into the GC-MS.

TABLE-1
RETENTION TIMES, SELECTED IONS AND SCAN START TIME OF COMPOUNDS STUDIED BY GC-MS

Compound	Retention time (min)	Selected ion (m/z)	Scan start time (min)
4-Fluorophenol	5.86	64,83,112	1.34
3-Chlorophenol	7.57	65,100,128	4.25
4- Chlorophenol	7.58	65,100,128	4.27
3-Bromophenol	8.29	65,93,172	5.48
4-Iodophenol	9.12	65,93,220	6.88

Then the mixture of the halogenated phenols in MeOH is done and taken the GC chromatogram. This chromatogram is shown in Fig. 1.

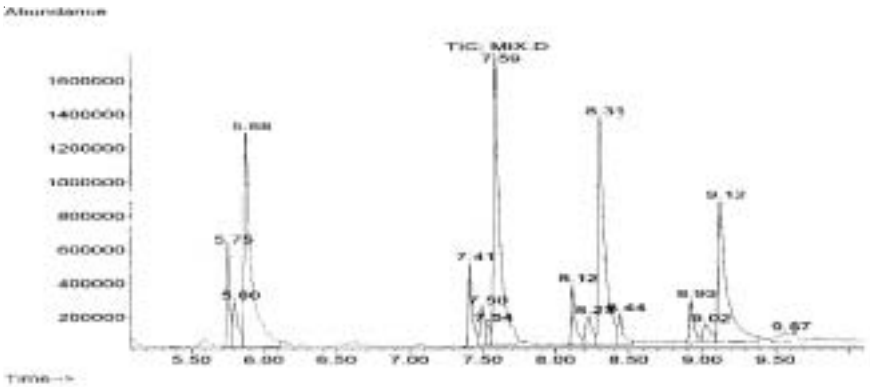

Fig. 1. GC chromatogram of mixture halogenated phenols in MeOH. Peak identification: 5.88: 4-fluorophenol; 7.41: 3-chlorophenol; 7.59: 4-chlorophenol; 8.31: 3-bromophenol; 9.12: 4-iodophenol

As seen from these Fig. 1 in these condition the halogenated phenols are determined to be well separate by suggest GC-MS method. After this determination, this can be applied for natural sample.

REFERENCES

1. J. Cheung and R.J. Wells, *J. Chromatogr. A*, **771**, 203 (1997).
2. W. Frenzel, J. Frenzel and J. Moeller, *Anal. Chim. Acta*, **261**, 253 (1992).
3. USEPA, Toxic Substance, Control Act, Washington, DC (1979).
4. F.P. Bigley and R.L. Grob, *J. Chromatogr.*, **350**, 407 (1985).
5. C.P. Ong, H.K. Lee and S.F.Y. Li, *J.Chromatogr.*, **464**, 405 (1989).
6. J.R.T. Lapasia, M. Roses, E. Bosch and M.C. Garcia, *J. Chromatogr. A*, **886**, 31 (2000).
7. C.H.Lochmuller, C.Reese, A.J.Aschman and S.J.Breiner, *J. Chromatogr. A*, **656**, 3 (1993).
8. R. Ong, P. Marriott, P. Morrison and P. Haglund, *J. Chromatogr. A*, **962**, 135 (2002).
9. T. Herberer and H.J. Stan, *Anal. Chim. Acta*, **341**, 21 (1997).
10. E. Pocurull, M. Calull, R.M. Marce and F. Borull, *Chromatographia*, **719**, 105 (1996).
11. C. Baiocchi, M.A. Roggero, D. Giacosa and E. Morengo, *J. Chromatogr. Sci.*, **33**, 338 (1995).
12. G. Achii, G.P. Cellerino, G.M. Deril and S. Bird, *J. Chromatogr. A*, **697**, 357 (1995).
13. M.T. Galceran and O. Jauregui, *Anal. Chim. Acta*, **304**, 75 (1995).
14. W.J. Landzettel, K.J. Hargis, J.B. Caboot, K.L. Adkins, T.G. Strein, H. Veening and H.D. Becker, *J. Chromatogr. A*, **718**, 45 (1995).
15. E. Pocurull, R.M. Marce and F. Borull, *Chromatographia*, **41**, 521 (1995).
16. E. Pocurull, G. Sanchez, F. Borull and R.M. Marce, *J. Chromatogr. A*, **696**, 31 (1995).
17. M.I. Turnes, I. Rodriguez, M.C. Mejuto and R. Cela, *J. Chromatogr. A*, **683**, 21 (1994).
18. L. Wennrich, J. Efer and W. Engewald, *Chromatographia*, **41**, 361 (1995).
19. K.D. Buchholz and J. Pawlizyn, *Anal. Chem.*, **66**, 160 (1994).

(*Received*: 5 January 2006; *Accepted*: 18 September 2006) AJC-5108