
Selective Water Removal In Purge/GC Analysis of Volatile Aromatics in Aqueous Samples

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1 Introduction

The trace levels of volatile organics found in ground water and drinking water have placed an increased demand on the laboratory's ability to analyze at concentrations in the ppb and ppt range [1,2]. Purge-and-trap (PT)/packed column gas chromatography is a commonly used method of analysis but the poor efficiency of the packed column and associated lengthy analysis times make PT/capillary GC an attractive alternative.

External cryoloops with subsequent flash injection [3] and on-column cold traps [4] have been employed in PT/capillary GC. Both rely on short lengths of capillary tubing at liquid nitrogen temperatures to trap and focus volatile analytes. However, significant breakthroughs of volatile organics can occur in these systems [5]. The introduction of purge-and-trap/whole column cryotrapping (PT/WCC) by Pankow and Rosen [6] involved maintaining the entire capillary column at cryogenic temperatures during the focussing step thus creating a 30 m long cold trap and eliminating breakthrough problems.

Recently Pankow [7] and Pankow and Rosen [8] have removed the adsorbent trap from PT/WCC and purge directly onto a cryogeni-

cally cooled capillary column. In attempting to maximize simplicity of their method they have not incorporated a procedure for removal of water from the purge stream prior to its introduction to the GC column. Their purge/whole column cryotrapping (P/WCC) method is dependent upon using a column with a moderately polar stationary phase such as DB-624 (J & W Scientific). With this phase, the water transferred to the column during the sample purge does not appreciably degrade the chromatography.

This paper expands the P/WCC method through the use of a Nafion tube drier that selectively removes water from the analyte-containing purge stream. Advantages include a wider choice of stationary phases and the possibility of using 0.25 mm or 0.32 mm i.d. columns without ice traps.

2 Experimental

A 30 m long, Megabore (0.53 mm i.d.) DB-5 column with a 1.5 μ m film thickness (J & W Scientific) connected to a flame ionization detector (FID) at 175°C in a Hewlett-Packard 5880 Gas Chromatograph was used for all analyses. Standards were from Chem Service, Inc.

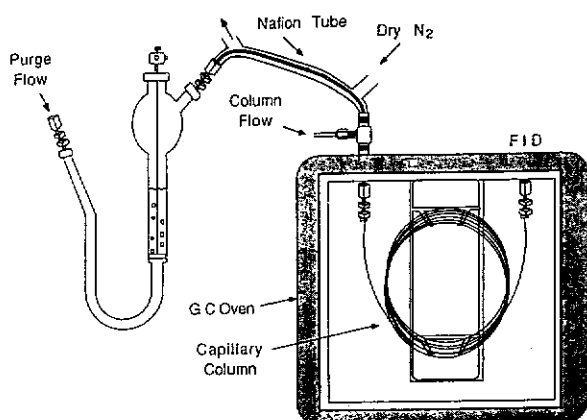


Figure 1

Apparatus with Nafion tube drier for water removal during purge sampling.

The purge system is similar to that described by Pankow and Rosen [8]. A 5 ml purge sampler was mounted with a Hamilton Miniature Inert Valve for sample introduction.

A tube drier (Perma-Pure) was attached between the purge vessel and the GC column. The drier shown in Figure 1 consists of a 24 inch length of Nafion, a desiccant tube, surrounded by a shell of polypropylene. Dry nitrogen at 200 ml/min was provided as a countercurrent gas through the polypropylene shell to sweep away water that diffuses through the wall of the Nafion during the purging process.

The 5 ml sample was purged for 10 minutes while the GC oven was at -80°C . After selecting carrier flow the oven was warmed to 25°C ballistically and the GC run started.

3 Results and Discussion

Initial attempts in our lab to employ P/WCC with the Megabore DB-5 column failed because water transferred to the column during sample purge either extinguished the flame of the FID or severely distorted the chromatography. The addition of the tube drier reduced the water background and resulted in excellent chromatographic peak shape.

Quality control standards were obtained from EPA to test the precision and accuracy of the P/WCC-with-Nafion method for EPA Method 602 compounds [9]. Table 1 illustrates the excellent reproducibility. All determined values are well within EPA's acceptance limits for Performance Evaluation samples. A representative chromatogram is illustrated in Figure 2.

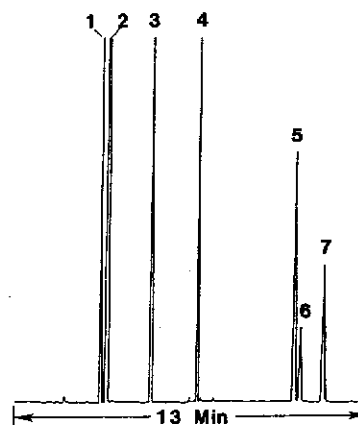


Figure 2

Chromatogram of EPA method 602 compounds. Peak identification: 1, benzene; 2, fluorobenzene (ISTD); 3, toluene; 4, ethylbenzene; 5, *m*-dichlorobenzene; 6, *p*-dichlorobenzene; 7, *o*-dichlorobenzene.

Table 1

EPA Method 602 compounds by P/WCC with Nafion.

	Concentrations are reported in ppb						
	Concentrate 1				\bar{x}	SD	True
	1	2	3				
Benzene	7.86	7.94	7.85		7.88	0.05	7.78
Toluene	18.8	19.1	18.9		18.9	0.15	18.2
Ethylbenzene	10.7	10.8	10.7		10.7	0.06	10.5
<i>m</i> -Dichlorobenzene	20.6	20.8	20.6		20.7	0.12	20.6
<i>p</i> -Dichlorobenzene	6.42	6.22	6.11		6.25	0.16	5.46
<i>o</i> -Dichlorobenzene	14.7	14.8	14.7		14.7	0.06	14.0
	Concentrate 2				\bar{x}	SD	True
	1	2	3	4			
Benzene	53.9	51.8	51.0	51.2	52.0	1.33	51.8
Toluene	104	99.6	98.4	98.7	100	2.60	99.0
Ethylbenzene	80.3	77.6	76.6	76.8	77.8	1.71	78.6
<i>m</i> -Dichlorobenzene	77.9	74.7	74.8	74.8	75.6	1.57	77.4
<i>p</i> -Dichlorobenzene	58.3	55.8	56.1	56.1	56.6	1.16	54.6
<i>o</i> -Dichlorobenzene	77.1	73.3	74.4	74.1	74.7	1.65	72.9

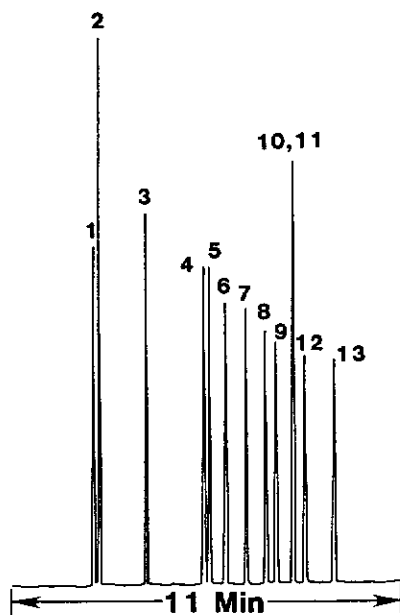


Figure 3

Chromatogram of volatile aromatics in water. Concentrations are 5 ppb per compound. The sample size is 5 ml. Peak identification: 1, benzene; 2, fluorobenzene (ISTD); 3, toluene; 4, ethylbenzene; 5, *m*-xylene; 6, *o*-xylene; 7, cumene; 8, propylbenzene; 9, mesitylene; 10 + 11, pseudocumene, *t*-butylbenzene; 12, *s*-butylbenzene; 13, *n*-butylbenzene.

The Nafion tube drier is an efficient water removal device that performs without apparent loss of analytes of interest. Indeed, Baker [10] has reported that hydrocarbons, including chlorinated and fluorinated hydrocarbons, are not removed when passed through Nafion tubing. Therefore this method will be applicable to many of the halovolatiles and purgeable aromatics (Figure 3) found in contaminated aqueous samples. The ability to selectively remove water has enhanced the P/WCC method by allowing a

wider selection of column stationary phases. Ice-plugging that results from increasing purge gas volume can be avoided. When the greater sensitivity and resolution of 0.25 mm and 0.32 mm i.d. columns are necessary the Nafion tube drier would eliminate the need for ice traps.

Disclaimer

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References

- [1] J. Barbash and P. V. Roberts, *J. Water Pollut. Control Fed.* **58** (1986) 343.
- [2] W. G. Leseman, *J. Am. Water Works Assoc.* **78** (1986) 39.
- [3] T. H. Noij, A. van Es, C. Cramers, and J. Rijks, *HRC & CC* **10** (1987) 60.
- [4] D. Kalman, R. Dills, C. Perera, and F. DeWalte, *Anal. Chem.* **52** (1980) 1993.
- [5] J. W. Graydon and K. Grob, *J. Chromatogr.* **254** (1983) 265.
- [6] J. F. Pankow and M. E. Rosen, *HRC & CC* **7** (1984) 504.
- [7] J. F. Pankow, *HRC & CC* **10** (1987) 409.
- [8] J. F. Pankow and M. E. Rosen, in preparation.
- [9] U.S. EPA, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", J. E. Longbottom and J. J. Lichtenberg (eds.), EPA-600/4-82-057 (1982) 602-1.
- [10] B. B. Baker, *Am. Ind. Hyg. Assoc. J.* (1974) 735.

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