

NON-PURGEABLE VOLATILE ORGANIC COMPOUNDS RAPIDLY DETERMINED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING DIRECT AQUEOUS INJECTION

Steven M. Pyle and Alvin B. Marcus*, U.S. Environmental Protection Agency, EMSL-LV, Las Vegas, NV 89193-3478; Linda S. Johnson, U.S. Environmental Protection Agency, NEIC, Denver, CO 80225

ABSTRACT

A direct aqueous injection (DAI) method was developed for the determination of 18 non-purgeable volatile organic compounds of which 9 have no EPA-approved method. These polar liquids were spiked into distilled water at 1- to 100-ppm levels and analyzed in triplicate at 7 concentration levels using a fused-silica capillary column interfaced to an ion trap mass spectrometer. Using internal standardization, the relative response factors and relative retention times for the 18 compounds were determined. Duplicate data were collected using on-column and splitless injectors. Accuracy and method detection limits (MDLs) were calculated from 10 replicate injections of 2-ppm standards. For splitless injection, the average relative standard deviation for the compounds was 19% and the average MDL was 800 ppb; for on-column injection, the respective values were 13% and 800 ppb. Agreement with EPA-established criteria for 4-bromofluorobenzene will also be shown. Data from the EMSL-LV Analytical Sciences Division will be presented to show conditions and limitations involving method parameters, such as column type, injection volume, and spectral quality. Attempts to optimize method precision and peak shape will also be discussed.

INTRODUCTION

The ion trap mass spectrometer, a recent commercial innovation, has made possible the detection of organic compounds at the picogram level in the full-scan mode. Using μL sample injection volumes, this translates into potential parts-per-billion sensitivity for the direct injection and analysis of aqueous environmental samples. Direct aqueous injection (DAI) is rapid, simple, and sensitive. It also eliminates the need for waste-solvent disposal and is compatible with EPA pollution prevention policy. Compared with solvent extraction and purge-and-trap preparatory methods, DAI is particularly suited to analyzing aqueous samples for non-purgeable, poorly purgeable, or non-extractable, volatile organic pollutants.

*Senior Environmental Employee Program Enrollee hosted by the National Association for Hispanic Elderly

EXPERIMENTAL

Standard Solutions

Stock solutions were prepared by using a 10- μ L syringe to add the neat liquid to distilled water in a 100-mL volumetric flask. The density (Table 1) and volume added were used to calculate the concentration in parts-per-million (ppm). Serial dilutions were prepared in 10-mL volumetric flasks. Triplicate injections at 7 concentrations over a 2-decade range were used to calculate the relative response factors (RRF). MDLs¹ were determined at the 2-ppm level and 10 replicate injections.

Conditions

After some initial experimentation, the following conditions were used to collect the data for method development. Two different gas chromatographic columns were used.

GC Conditions

initial temperature	35 °C
initial time	5 min
temperature rate	10 °C/min
final temperature	165 °C
final hold time	2 min
total run time	20 min
transfer line	200 °C

On-column Injection

initial temperature	100 °C
initial time	0.1 min
temperature rate	200 °C/min
final temperature	260 °C
final hold time	1 min
total run time	1.9 min

Splitless Injection

temperature	200 °C
splitless time	30 sec
split ratio	20:1

Mass Spectrometer

scan range	29 to 180 amu
scan time	0.6 sec/scan
mass defect	30 mmu/100 amu
acquire time	17 min

Column #1

dimensions	30 m \times 0.53 mm id \times 1.5 μ m film
liquid phase	5% diphenyl-95% dimethyl polysiloxane
head pressure	12 psig
linear velocity	37.5 cm/sec of helium carrier gas

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liquid phase	5% diphenyl-95% dimethyl polysiloxane
head pressure	12 psig
linear velocity	37.5 cm/sec of helium carrier gas

Column #2

dimensions	30 m × 0.32 mm id × 0.25 μm film
liquid phase	Carbowax PEG
head pressure	20 psig
linear velocity	50 cm/sec of helium carrier gas

In order to match the flow from a wide-bore column to the ion trap vacuum manifold and to facilitate changing columns, a post-column splitter was used (Fig. 1). This configuration resulted in 35% of the 0.53 mm id column effluent (50 % of the 0.32 mm id column effluent) going into the mass spectrometer manifold.

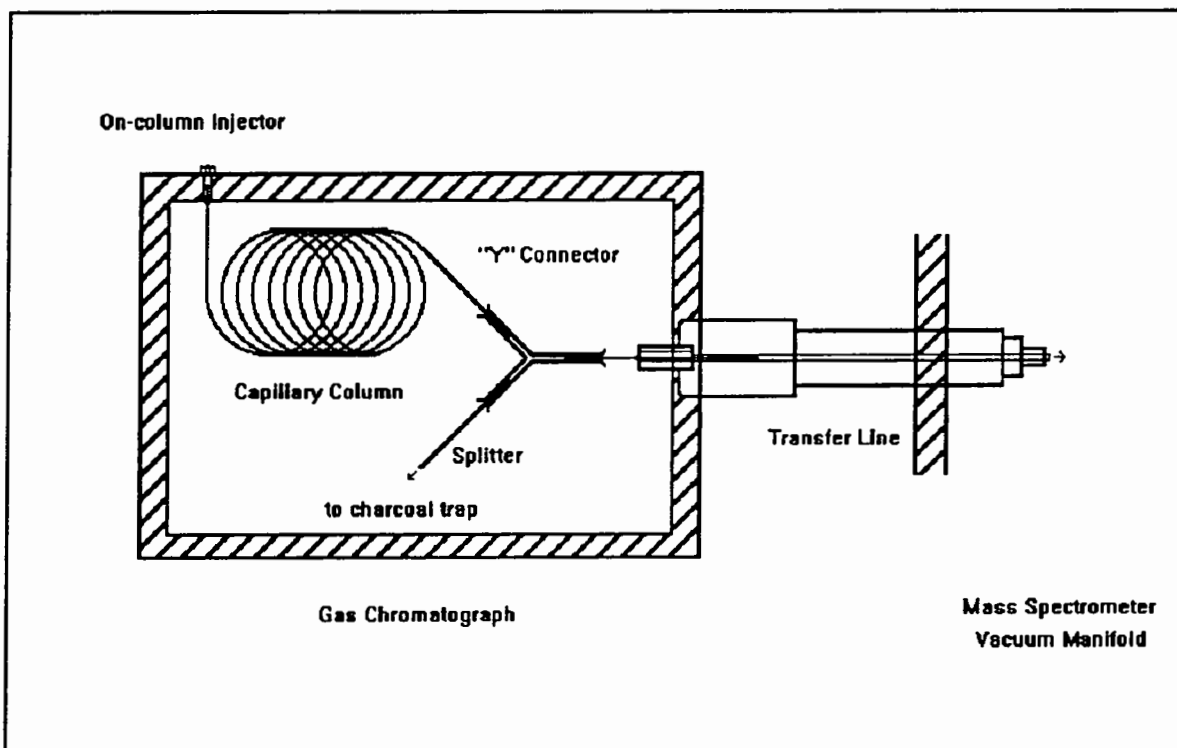


Figure 1. Post-column split diagram.

RESULTS AND DISCUSSION

Table 1 shows the compound number, quantitation ion, density, retention times, relative response factor, and MDL for each of the 18 analytes and internal standard. Figure 2 shows the column #1 chromatogram of the separation of the 18 analytes and internal standard.

The method showed adequate MDLs and good separation on both columns. However, the mass spectra generated on the ion trap were somewhat different from the NIST library spectra. This is due to the low-molecular-weight nature of these compounds. The oxygen and nitrogen background interfered with ions in the 28 to 33 amu range. Also there were inherent differences in ion trap spectra compared to conventional quadrupole mass spectrometers.

purgeable volatiles², these problems were not encountered because of the higher molecular weights of these halogenated compounds.

CONCLUSIONS

- 1) DAI method showed good chromatographic separation on two columns of different dimensions and liquid phases.
- 2) Adequate sensitivity was obtained for non-purgeable volatiles.
- 3) DAI is rapid, easily applied, and generates no waste solvent.
- 4) This research and previous work³ show that direct aqueous injection is feasible for these compounds with a variety of columns, injectors, injection volumes, and instruments.

Table 1. Compound versus quantitation ion, density, retention time, relative response factor, and method detection limit.

no.	compound	ion m/z	density g/mL	RT1 ^a min.	RT2 ^b min.	RRF ^c	MDL ppm
IS ^d	d5-Nitrobenzene	82	1.253	15:45	16:13	1.000	--
1	Ethanol	45	0.785	1:45	2:16	0.106	0.88
2	Acetonitrile	41	0.786	1:55	3:15	0.090	0.66
3	2-Propanone	43	0.791	1:56	1:26	0.425	0.67
4	Diethyl ether	59	0.714	2:03	1:02	0.031	1.16
5	Acrylonitrile	53	0.806	2:12	3:03	0.084	0.59
6	1-Propanol	59	0.804	2:38	4:02	0.062	1.36
7	Propionitrile	54	0.772	2:53	3:41	0.159	1.36
8	2-Butanone	43	0.805	3:13	1:55	0.540	0.58
9	Ethyl acetate	43	0.902	3:38	1:50	0.764	0.58
10	1-Butanol	56	0.805	5:07	7:37	0.201	0.89
11	3-Pentanone	56	0.814	6:13	2:46	0.488	0.65
12	p-Dioxane	88	1.034	6:35	4:27	0.189	0.54
13	Methyl methacrylate	69	0.936	6:46	3:15	0.297	0.55
14	4-Methyl-2-pentanone	43	0.800	7:40	3:15	0.874	0.68
15	Ethyl methacrylate	69	1.100	9:03	4:13	0.554	0.39
16	2-Hexanone	43	0.812	9:07	5:06	1.052	0.76
17	3-Picoline	93	0.957	11:01	10:02	0.745	1.04
18	1,3-Dichloro-2-propanol	79	1.351	11:47	16:26	0.351	1.18

a retention time on Column #1

b retention time on Column #2

c relative response factor

d internal standard

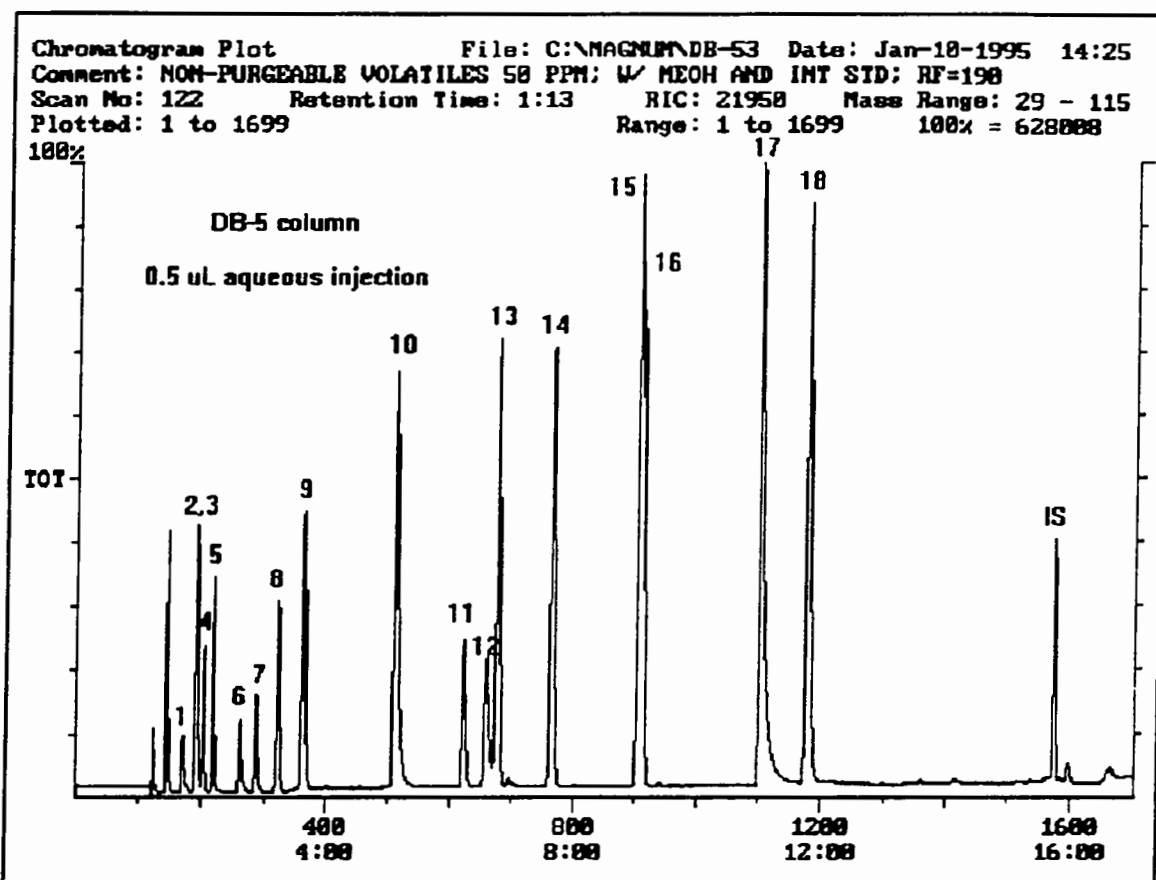


Figure 2. DB-5 chromatogram of 18 compounds and IS. See Table 1 for peak IDs.

Table 2. 4-Bromofluorobenzene tune criteria.

4-BFB mass	Method 524	Method 8240b	DAI average	%rsd*
50	8 to 40% of mass 95	15 to 40% of mass 95	22	4
75	30 to 66% of mass 95	30 to 65% of mass 95	56	2
95	base peak, 100%	base peak, 100%	100	30
96	5 to 9% of mass 95	5 to 9% of mass 95	6	2
173	< 2% of mass 174	< 2% of mass 174	0	-
174	50 to 120% of mass 95	> 50% of mass 95	70	3
175	4 to 9% of mass 174	5 to 9% of mass 174	8	1
176	93 to 101% of mass 174	95 to <101% of mass 174	101	1
177	5 to 9% of mass 176	5 to 9% of mass 176	6	3

*n=5

1. Glaser, J. A.; Forest, D. L.; McKee, G. D.; Quave, S. A.; Budde, W. L., *Envir. Sci. and Tech.*, 1981, **16**, 1426.
2. Pyle, S. M.; Gurka, D. F., *Talanta*, 1994, **41**, 1845-1852.
3. Gurka, D. F.; Pyle, S. M.; Titus, R., *Anal. Chem.*, 1992, **64**, 1749-1754.

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