Headspace Analysis of Some Typical Organic Pollutants in Drinking Water Using Differential Detectors: Effects of Columns and Operational Parameters

M.F. Mehran*, N. Golkar, and W.J. Cooper
Drinking Water Research Center, Florida International University, Miami, Florida

A.K. Vickers
J&W Scientific, 91 Blue Ravine Road, Folsom, California

Abstract

Environmental analytical procedures in the United States are largely based on Environmental Protection Agency (EPA) methods. Different procedures have been adopted by the European Union (EU). In the United States, the determination of volatile organic compounds in drinking water employs purge and trap sampling followed by gas chromatography with photoionization and electrolytic conductivity detection. European analysts perform an "equivalent" priority pollutant analysis using static headspace injections and electron-capture detection. Some of the compounds included on the EPA list (1) do not appear on the EU lists (2) and vice versa. A distinctive difference is the use of megabore (greater than 0.45-mm i.d.) capillary columns in the EPA methods. European analysts are reluctant to adopt these columns in their methodologies. In this work, several open-tubular column dimensions are investigated and optimized with particular attention given to problems encountered when columns are interfaced to purge and trap or static headspace analyzers. Also, EPA and EU priority pollutant methods are contrasted according to the method of detection.

Introduction

A number of environmental analyses are closely tied to and influenced by United States Environmental Protection Agency (EPA) methodologies such as EPA Method 502.2, 524.2, and 502.1. These are purge and trap based techniques that seek to extend method sensitivity for drinking water analysis by preconcentrating target analytes from sample volumes too massive to be accommodated by direct injection onto a suitable adsorbent trap. The trapped analytes are subsequently thermally desorbed (i.e., injected) onto the column in a smaller volume of gas. Even so, the "injection" requires some time, which tends to increase band broadening at the head of the column and hence, chromatography suffers. The phenomenon is most noticeable with the more volatile solutes; even with longer injection times, higher boiling analytes exhibit a greater tendency to "cold trap" on the unheated column, and their starting bands are usually

much shorter than those of the more volatile analytes.

More rapid desorption from the trap (3), subambient cooling of the column (4–6), and volume reducing inlet adapters (7) have all been developed to help cope with these problems. A requirement for rapid trap desorption is that the column must be able to tolerate higher gas flow rates, and this led to widespread use of Megabore™ (0.53-mm i.d.) columns in these analyses. The use of subambient conditions is, in many ways, laborious and expensive. Most laboratories avoid implementing cryogenic techniques, opting instead to use longer columns (up to 105 m) and starting oven temperatures near ambient to help resolve the broader peaks that result from the longer starting bands. It has been demonstrated that under noncryogenic analysis conditions, improved resolution was due to the high pressure drop of the 105-m column rather than to the increased number of theoretical plates (8). Similar results were achieved when a restrictor (2 m × 50 µm) was attached to the outlet end of a 60-m column (M.F. Mehran, unpublished data). Discharging the trap into a higher pressure (and a higher density) area discourages expansion of the eluting vapors and shortens the band beginning the chromatographic process. Larger diameters and excessively long columns sacrifice chromatographic efficiency, but little effort has been directed toward exploration of whether slightly smaller diameters or slightly shorter columns might achieve the same results despite the high flow rates required while sacrificing less efficiency.

The large number of solutes to be resolved, plus the complicating factor of chromatographic parameters achieving lowered powers of resolution, led to the use of two semispecific sequential detectors for some of these EPA methods. The column effluent is discharged first through a photoionization detector (PID), the exit port of which is connected to an electrolytic conductivity detector (ELCD). The former detector gives enhanced response for olefinic and aromatic solutes, and the latter (in halogen mode) is specific for halogenated solutes.

The European Union (EU) has established methods for the analysis of water pollutants. Although the EU and EPA methods include many of the same solutes, other solutes are unique to either the EU or EPA lists. European analysts more commonly employ small sample static headspace injections (9) with elec-

tron capture detection (ECD) (10). Although it is unlikely that either of these two entities will completely accept or reject the other's methods, there is certainly a need for investigating the strengths and weaknesses of the methods. This will give a basis for relating environmental analyses performed in the different nations. This work was directed toward exploration of these considerations so that comparison can be made between the EPA and EU methodologies.

Experimental

Materials

Standard samples containing volatile aromatic and halogenated hydrocarbons in methanol at known concentrations were obtained from Supelco (Bellefonte, PA) and AccuStandard (New Haven, CT). The following compounds were investigated (numerals represent peak designations in the figures): 1, vinyl chloride; 2, trichlorofluoromethane; 3, 1,1-dichloroethene; 4, methylene chloride; 5, trans-1,2-dichloroethene; 6, 1,1-dichloroethane; 7, cis-1,2-dichloroethene; 8, chloroform; 9, 1,1,1-trichloroethane; 10, carbon tetrachloride; 11, benzene; 12, trichloroethene; 13, cis-1,3-dichloropropene; 14, trans-1,3-dichloropropene; 15, 1,1,2-trichloroethane; 16, toluene; 17, dibromochloromethane; 18, tetrachloroethylene; 19, chloroben-

zene; 20, ethylbenzene; 21, styrene; 22, 1,1,2,2-tetra-chloroethane; 23, 4-bromofluorobenzene; 24, 1,3-dichlorobenzene; 25, 1,2-dichlorobenzene. These compounds were added to deionized water at the concentrations indicated in Table I. Test solution 1 was used for determinations that employed PID–ELCD and contained 0.01–0.2 µg/µL. Test solution 2 was used for determinations that employed ECD and contained 0.001–1.0 µg/µL. An amount of the appropriate test solution was added to 15 mL deionized water to achieve the concentrations indicated in Table I. Test standards were formulated to compensate for the differential sensitivity and selectivity of the ECD relative to the PID–ELCD. Aliquots of 15 mL were placed into 22-mL glass vials and sealed with septa and aluminum crimp caps.

Instrumentation

The GC analyses were performed on a Model 5890 gas chromatograph equipped with a Model 19395A headspace sampler and the constant heating time (CHT) magazine (11) (Hewlett-Packard; Little Falls, MD). The GC was also equipped with an ECD (Hewlett-Packard) and a Model PI52-O2A PID (HNU Systems; Newton, MA) with a 10.2 eV lamp connected in series with a Model 4420 ELCD (OI Analytical; College Station, TX). An E-Lab™ chromatographic control and data acquisition system (OMS Tech; Miami, FL) was used to process the detector signals.

All columns were coated with DB-VRX (J&W Scientific; Folsom, CA). The following dimensions were used: column 1,

Table I. Comparison of Volatile Organic Pollutants Concentration on ECD and PID–ELCD

Analyte	ECD*	PID–ELCD*	ECD†	PID–ELCD†	ECD‡	PID–ELCD‡	ECD§	PID–ELCD§
Vinyl chloride	ND‖	133.3	ND	97.8	5000	53.3	5000	35.5
Trichlorofluoromethane	2.67	46.7	2.0	42.3	1.34	33.4	0.67	24.5
1,1-Dichloroethene	213.3	46.7	186.6	42.3	160	33.4	133.3	24.5
Methylene chloride	3570	46.7	3123.8	42.3	2677.5	33.4	2231.3	24.5
trans-1,2-Dichloroethene	2670	46.7	2336.3	42.3	2002.5	33.4	1668.8	24.5
1,1-Dichloroethane	5330	46.7	4663.8	42.3	3997.5	33.4	3331.3	24.5
cis-1,2-Dichloroethene	2670	68.9	2136	59.1	1602	39.4	1068	19.7
Chloroform	2.67	46.7	2.0	42.3	1.34	33.4	0.67	24.5
1,1,1-Trichloroethane	2.67	46.7	2.0	42.3	1.34	33.4	0.67	24.5
Carbon tetrachloride	2.67	46.7	2.0	42.3	1.34	33.4	0.67	24.5
Benzene	–	46.7	–	42.3	–	33.4	–	24.5
Trichloroethene	2.67	46.7	2.0	42.3	1.34	33.4	0.67	24.5
cis-1,3-dichloropropene	140.0	160	112	137.1	84	91.4	56	45.7
trans-1,3-dichloropropene	93.3	106.7	74.6	91.5	56	61.0	37.3	30.5
1,1,2-Trichloroethane	213.3	129.7	186.6	111.2	160	74.1	133.3	37.1
Toluene	–	46.7	–	42.3	–	33.4	–	24.5
Dibromochloromethane	3.3	668.3	2.64	572.8	1.98	381.9	1.32	190.9
Tetrachloroethylene	2.67	46.7	2.0	42.3	1.34	33.4	0.67	24.5
Chlorobenzene	ND	55	ND	47.1	5000	31.4	5000	15.7
Ethylbenzene	–	46.7	–	42.3	–	33.4	–	24.5
Styrene	–	66.7	–	57.2	–	38.1	–	19.1
1,1,2,2-Tetrachloroethane	33.3	166.7	26.6	142.9	19.98	95.3	13.32	47.6
4-Bromofluorobenzene	1330	183.3	1163.8	157.1	997.5	104.7	831.3	52.4
1,3-Dichlorobenzene	373.3	182.5	326.6	156.4	280	104.3	233.3	52.1
1,2-Dichlorobenzene	373.3	184.9	326.6	158.5	280	105.7	233.3	52.8

* Analyses performed with 30-m × 0.25-mm column.
† Analyses performed with 30-m × 0.32-mm column.
‡ Analyses performed with 75-m × 0.45-mm column.
§ Analyses performed with 75-m × 0.53-mm column.
‖ Not detected.

30 m × 0.25-mm i.d., 1.4 µm; column 2, 30 m × 0.32-mm i.d., 1.7 µm; column 3, 75 m × 0.45-mm i.d., 2.5 µm; and column 4, 75 m × 0.53-mm i.d., 3 µm.

Photoionization, electrolytic conductivity, and electron-capture detectors were used. The PID conditions were as follows: lamp, 10.2 eV; detector base temperature, 220°C; lamp intensity, 50% of scale; and makeup gas, helium (30 mL/min). The ELCD conditions were as follows: mode, halogen; hydrogen flow rate, 100 mL/min; 2-propanol flow rate, 30 µL/min; detector base temperature, 250°C; and reactor temperature, 850°C. For the ECD, the base temperature was 250°C and the makeup gas was nitrogen at 35 mL/min. For headspace, the temperature was 70°C and the valve and loop temperature was 75°C. The sample loop volume for the experiment was 1.0 mL. The typical injection sequence (minute:second) was as follows: probe down, 0:01; start pressurization, 0:03; stop pressurization, 0:13; start venting, 0:14; stop venting, 0:19; start injecting, 0:20; stop injecting, 0:30; probe up, 0:31. An auxiliary pressure of 1.4 bar was used. All capillary analyses were connected to the sampler's transfer line on the top of the GC oven.

Gas chromatography

Septum-sealed vials were first pressurized with helium carrier gas (approximately 22–23 psi). Each sample was placed in a vial by means of a sampling needle that pierced the septum to initiate the injection sequence. The pressurized headspace was then vented through the sampling needle and a 1.0-mL sample loop to atmospheric pressure. Once filled, the loop was placed in series with the normal carrier gas flow, and its contents were conducted through the heated transfer line to the GC injection port. To enhance detectability of low sample concentrations, the transfer line from the headspace unit was connected directly to the column with a zero dead volume union (Valco Instruments; Houston, TX).

Bath temperature

The temperature at which a sample is equilibrated strongly affects the concentration of analytes that partition into the headspace gas. In general, as the bath temperature increases, the amount of analyte delivered to the gas chromatograph, and thus the sensitivity of the method, both increase. However, at excessively high temperatures, highly volatile solutes are lost. The best results are obtained when the temperature of the bath is maintained at a level high enough to safely provide the desired analytical sensitivity. A bath temperature of 70°C gave the best results for the range of solutes investigated. All subsequent samples were held at 70°C for a minimum of three runs. The approximate times required for the three runs were as follows: column 1, 53 min; column 2, 55 min; column 3, 61 min; and column 4, 67 min.

Constant heating time magazine

The HP 19395A headspace sampler, when operated in the CHT mode, automatically drops a vial from the magazine to the carousel at a rate of one vial per injection cycle. Each sample vial is then heated for 1, 2, or 3 cycle times. In this case, each vial was heated 3 cycle times.

Column parameters

Comparison of the results obtained on this apparatus using columns that varied in length or internal diameter was complicated by several factors. Following the vial pressurization step, the headspace from the pressurized vial was directed through the valves, associated tubing, and sample loop to an atmospheric vent. During injection, the valve was switched, and the carrier gas flow was directed through the valve, the sample loop, and the associated tubing of the column. With a 1.0-mL sample loop, the path should be flushed with approximately 2 mL of carrier gas to quantitatively conduct the sample to the capillary column. Because the sample path was swept with the column carrier gas, an injection time of only a few seconds was required for larger diameter columns (i.e., higher flow rates) and up to a minute was necessary for smaller diameter columns (i.e., lower flow rates). Figure 1 illustrates how the flow rate requirements of the column can conflict with a chromatographically sound sample injection, particularly when narrow bore columns are used. Obviously, the amount of sample-laden gas conducted to the column is dependent on the injection time and the flow rate during the injection step. Conceivably, the injection time, the size of the sample loop, and the column head pressure could all be adjusted to ensure complete sample transfer. This would likely result in nonoptimum flow conditions for the column. In cases where the analytes of interest include low-potassium solutes, the length of the band beginning the chromatographic process is highly dependent on the injection time (i.e., sample sweep rate to the column). In addition, higher boiling solutes cold trap on the head of the column and commence the chromatographic process only later in the temperature program; this generates sharp peaks. The more volatile analytes begin chromatographic development at the onset of the injection process. The low potassium solute band will have proceeded (spread) some distance through the column by the time that the injection is completed and the last of that band has been introduced. These elongated starting bands produce broadened peaks of lowered intensity for the more volatile solutes (Figure 1C).

One solution to this problem would be to use the higher sweep flow rates offered by interfacing the headspace analyzer to the capillary column via a split interface. This technique has become common in volatile organic compound analysis where narrow bore capillary columns are used with mass selective detectors (12,13). Purge and trap analyzers are more amenable to the use of a split injector interface because target analytes are nearly completely extracted and concentrated onto a sorbent trap prior to injection. This process enriches the sample and provides good sensitivities even though a portion of the sample is split prior to entering the column. This is not the case in static headspace analysis where a much smaller mass amount of the analytes is injected. By comparison, the purge and trap analysis provided detection limits as much as 10 fold lower (14).

Owing to these considerations, it was decided that the best way to evaluate the effects of column parameters with the headspace analyzer was to optimize the carrier flow rate for each given column and hold the vial pressurization and the in-
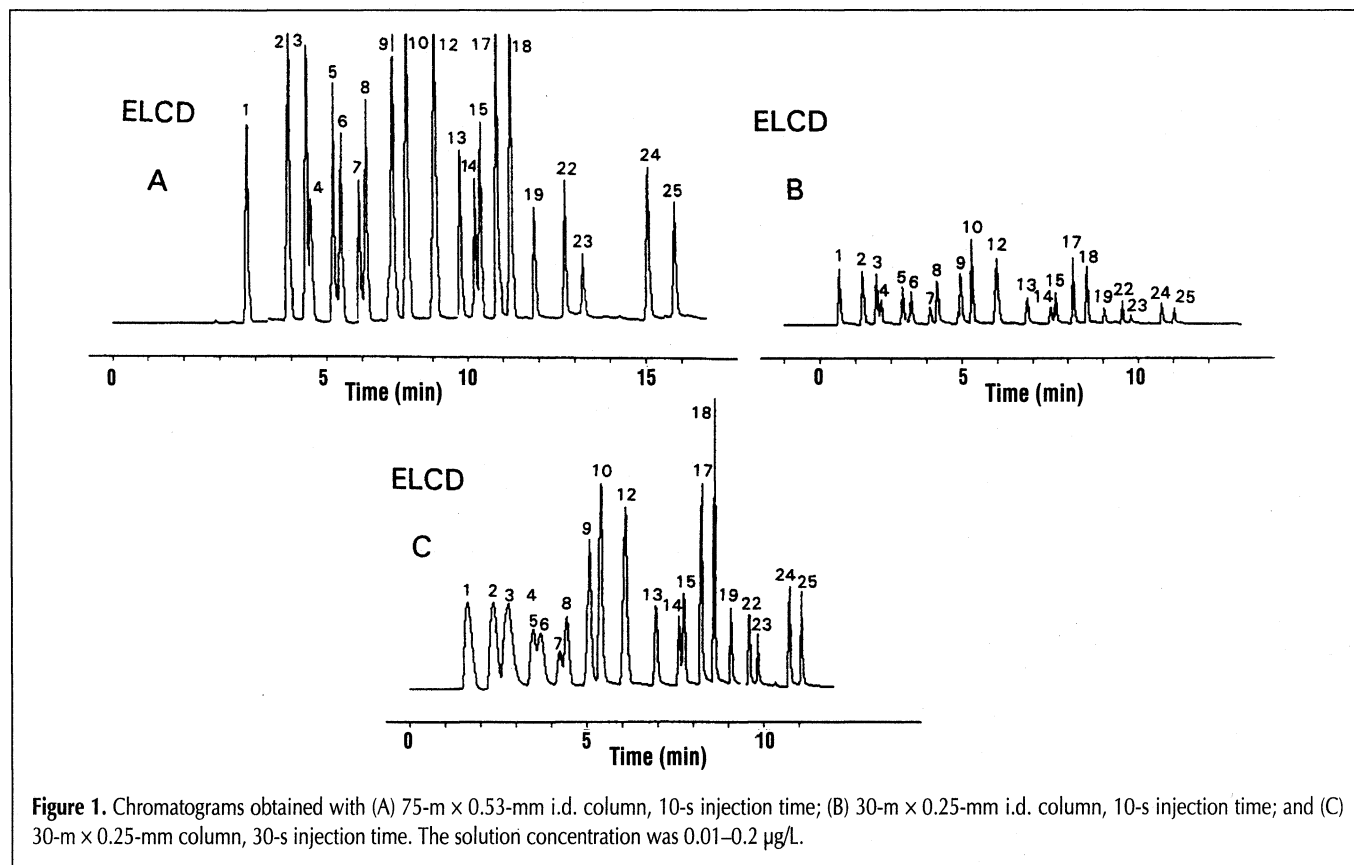
Figure 1. Chromatograms obtained with (A) 75-m × 0.53-mm i.d. column, 10-s injection time; (B) 30-m × 0.25-mm i.d. column, 10-s injection time; and (C) 30-m × 0.25-mm column, 30-s injection time. The solution concentration was 0.01–0.2 µg/L.

jection time constant at 10 s. The concentration of solutes was then varied in the appropriate sample vials to provide adequate detector response.

Results and Discussion

A full range of calibration standards was analyzed using the static headspace method. The standard ranged from 5 mg/L to 0.67 µg/L for the ECD analyses, and 190.9–15.7 µg/L for PID–ELCD analyses. The wide variation of ECD concentrations was necessary because the detector does not respond well to low levels of monohalogenated solutes, and the response to poly-halogenated analytes is much greater. Table II shows the method detection limits (MDL) for the test compounds where this divergent behavior is exemplified. MDLs were estimated based on the signal generated at the lowest detectable concentration in water matrix. The MDL for each analyte was at a signal-to-noise ratio of 3. The more electronegative the halogen, (F>Cl>Br>I), the greater the detector's response. The position of the heteroatom on the carbon chain also has an effect on the ECD response (e.g., 1,1,1-trichloroethane > chloroform > 1,1,2-trichloroethane). This is in contrast to the ELCD responses of the test analytes, which are roughly equivalent depending upon the degree of halogen substitution. The claimed linearity of the ELCD (approximately 10^5 from the detection limit) also gives a more predictable response for halogens in this case. The combined use of the PID–ELCD seems advantageous for these reasons. The PID is well-suited to the detection of

Table II. Comparsion of Method Detection Limits (MDL) for Volatile Organic Pollutants on PID, ELCD, and ECD

| Analyte	PID (µg/L)	ELCD (µg/L)	ECD (µg/L)
Vinyl chloride	1.06	0.89	5000
Trichlorofluoromethane	–	0.47	0.001
1,1-Dichloroethene	0.87	0.93	5.2
Methylene chloride	–	0.47	35.7
trans-1,2-Dichloroethene	0.47	0.93	24.2
1,1-Dichloroethane	–	0.93	53.3
cis-1,2-Dichloroethene	0.91	1.4	26.7
Chloroform	–	0.93	0.008
1,1,1-Trichloroethane	–	0.47	0.003
Carbon tetrachloride	–	0.47	0.001
Benzene	0.45	–	–
Trichloroethene	0.45	0.47	0.005
cis-1,3-dichloropropene	6.1	5.7	5.3
trans-1,3-dichloropropene	3.9	4.3	2.6
1,1,2-Trichloroethane	–	5.2	7.9
Toluene	0.40	–	–
Dibromochloromethane	–	8.9	0.007
Tetrachloroethylene	0.90	0.93	0.009
Chlorobenzene	0.37	2.2	5000
Ethylbenzene	0.36	–	–
Styrene	0.39	–	–
1,1,2,2-Tetrachloroethane	–	6.7	0.33
4-Bromofluorobenzene	3.05	15.3	19.3
1,3-Dichlorobenzene	1.5	3.7	4.1
1,2-Dichlorobenzene	1.9	3.7	4.1
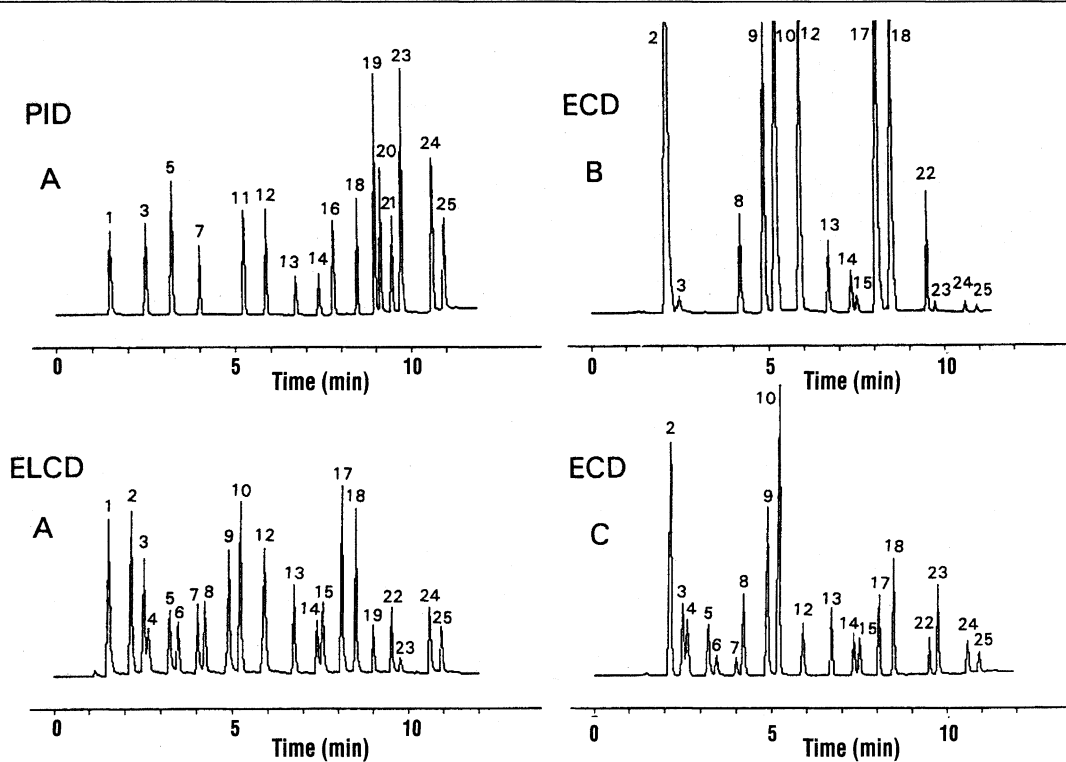
Figure 2. Chromatograms obtained with a DB-VRX column (column 4; 30-m x 0.25-mm i.d., 1.4-μm film thickness). The temperature program was as follows: 35°C held for 3 min then programmed to 70°C at 15°C/min, held 2 min, programmed to 150°C at 40°C/min, and held 3 min. The carrier gas was helium at 46.3 cm/s. For detection, a PID–ELCD (A), an ECD (solution concentration, 0.01–0.2 μg/L) (B), and an ECD (solution concentration, 0.001–1.0 μg/L) (C) were used.

Figure 3. Chromatograms obtained with a DB-VRX column (column 3; 30-m × 0.32-mm,1.8-μm film thickness). The temperature program was as follows: 35°C held for 3 min, then programmed to 80°C at 14°C/min, held 2 min, programmed to 150°C at 40°C/min, and held 3 min. The carrier gas was helium at 43.9 cm/s. For detection, a PID–ELCD (A), an ECD (solution concentration, 0.01–0.2 μg/L) (B), and an ECD (solution concentration, 0.001–1.0 μg/L) (C) were used.
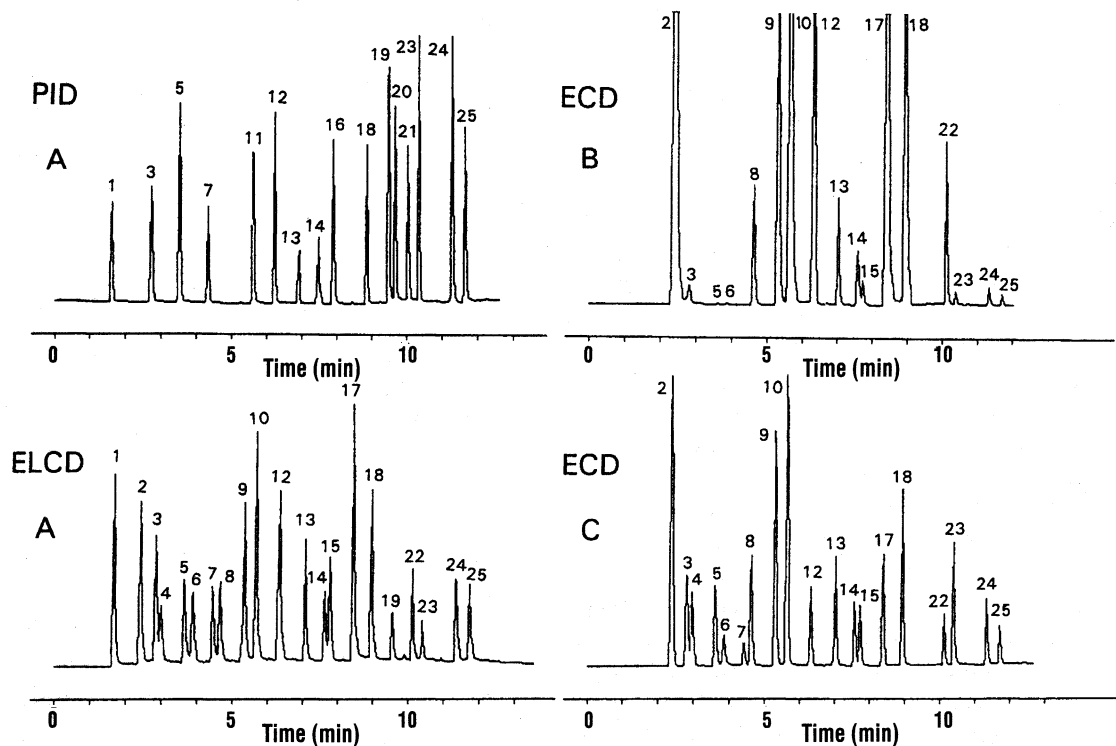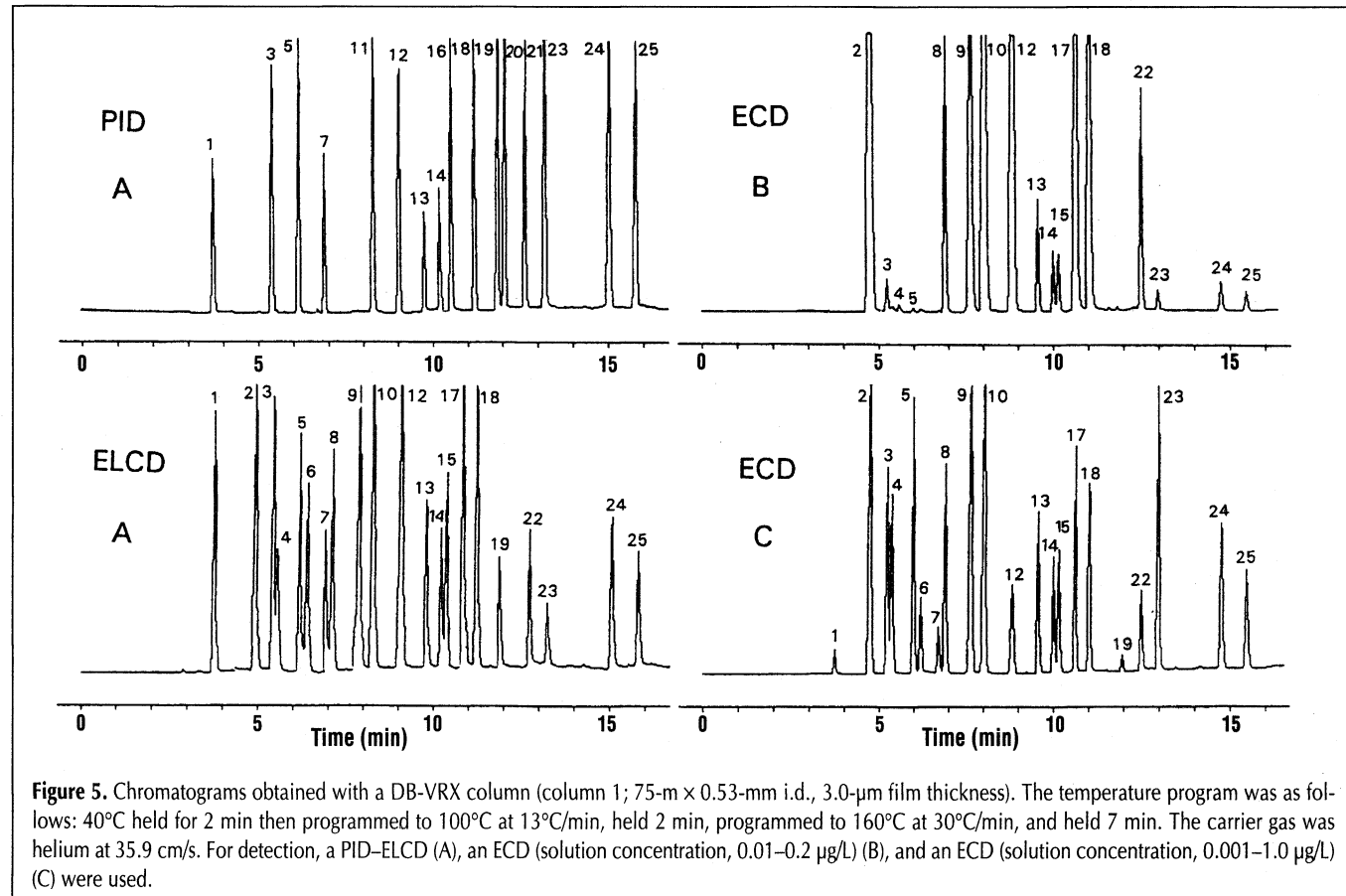
Figure 4. Chromatograms obtained with a DB-VRX column (column 2; 75-m × 0.45-mm i.d., 2.5-μm film thickness). The temperature program was as follows: 40°C held for 2 min then programmed to 100°C at 13°C/min, held 2 min, programmed to 160°C at 30°C/min, and held 5 min. The carrier gas was helium at 38 cm/s. For detection, a PID–ELCD (A), an ECD (solution concentration, 0.01–0.2 μg/L) (B), and an ECD (solution concentration, 0.001–1.0 μg/L) (C) were used.
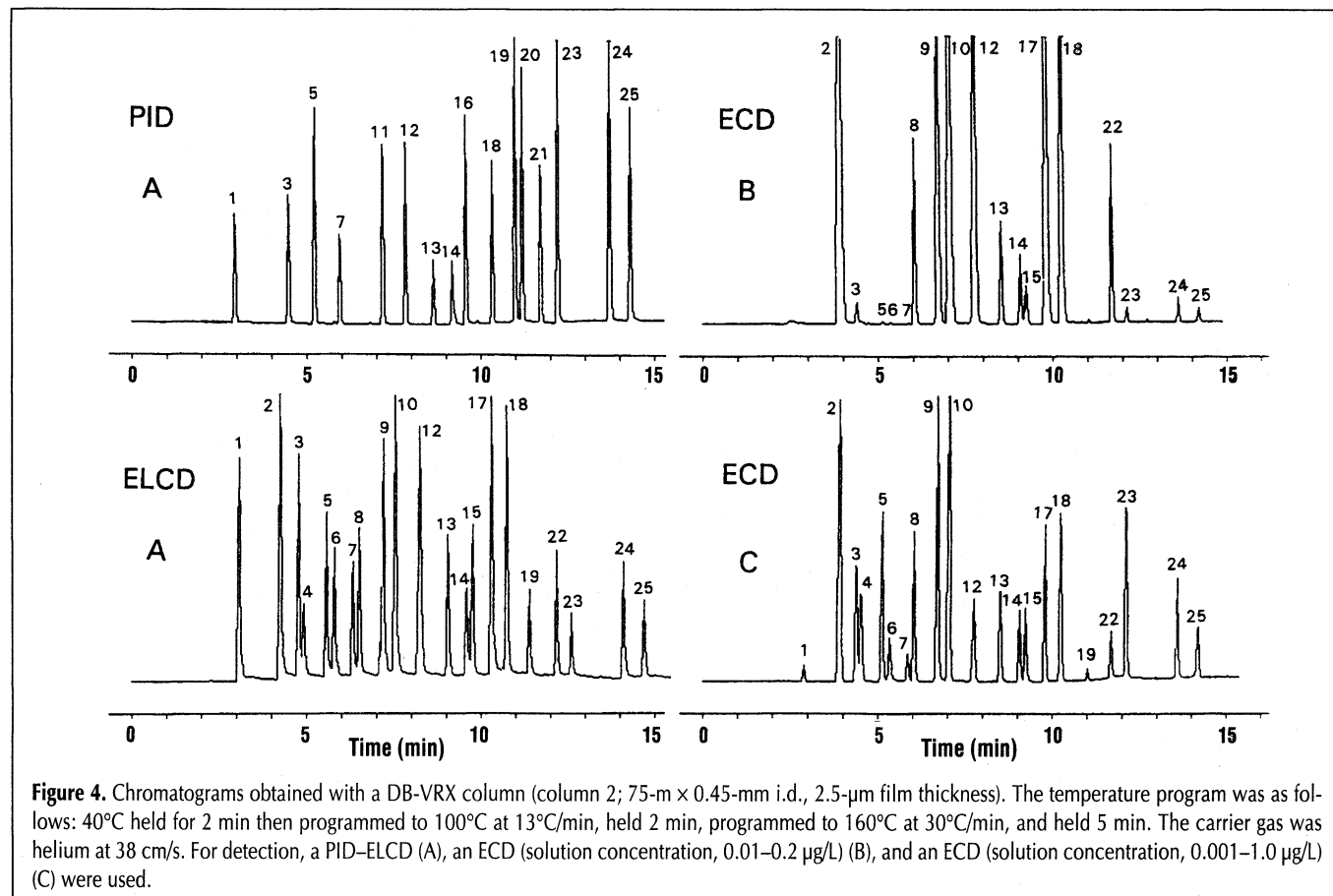

Figure 5. Chromatograms obtained with a DB-VRX column (column 1; 75-m × 0.53-mm i.d., 3.0-μm film thickness). The temperature program was as follows: 40°C held for 2 min then programmed to 100°C at 13°C/min, held 2 min, programmed to 160°C at 30°C/min, and held 7 min. The carrier gas was helium at 35.9 cm/s. For detection, a PID–ELCD (A), an ECD (solution concentration, 0.01–0.2 μg/L) (B), and an ECD (solution concentration, 0.001–1.0 μg/L) (C) were used.
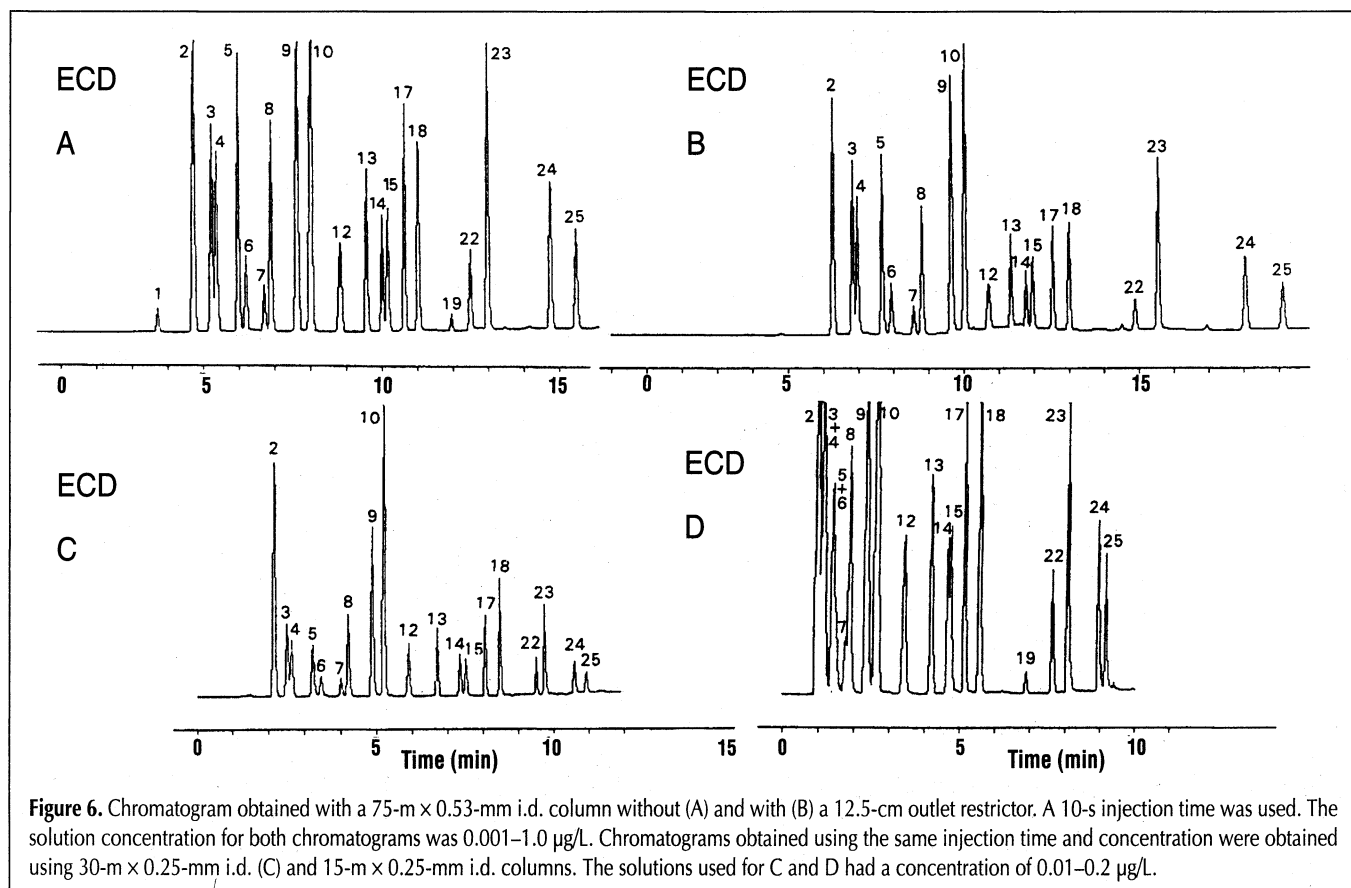
aromatics and olefins that are included in the EPA and EU methods, and the overlap of analyte detectability is such that some confirmation of detection is built in by their use.

When the chromatograms from the analyses obtained on the different columns are studied, the inverse relationship of column diameter and number of theoretical plates per meter is obvious. Rather than cutting the columns to maintain a constant number of theoretical plates, columns were used in the standard lengths in which they are normally available. As the diameters of the columns changed, the thickness of the stationary phase film changed in the same ratio; that is, the phase ratio was held constant from column to column. Hence for a given stationary phase, solute retention factors (k) would be affected only by the solute and temperature conditions. One other factor to consider is that both optimum gas velocities and optimum practical gas velocities (15) vary inversely with column diameter and length. It should be possible to significantly shorten analysis times without any adverse effect on resolution by resorting to a shorter column with a smaller diameter.

We attempted to change flow velocities to more closely reflect ideal conditions for each column and to adjust the program parameters to maintain the same degree of analyte separation from column to column. This should have translated into reduced analysis times with shorter and/or smaller diameter columns (Figures 2–5).

Duplicate sample vials were loaded with test solutions containing analyte concentrations sufficient to achieve good detection levels, as shown in Table I and Figures 2–5. When headspace injections were made from the same solution into smaller diameter columns, the detector responses decreased with column diameter. The most logical explanation for this phenomenon is that as the pressure drop through the column increases (going to smaller diameter columns), the quantity of sample-laden gas injected from the sample loop (which commences each injection at the same pressure) decreases, affecting detector response. To prove this point, a restrictor was attached to the end of the column with the lowest pressure drop (75 m × 0.53 mm), effectively raising column head pressure at the time of injection to 10.29 psi, which is equivalent to that generated by the 30-m × 0.25-mm column (10.43 psi). Figure 6 compares results obtained using the 75-m × 0.53-mm column without a restrictor (A) (the head pressure at the time of injection was 6.52 psi) and the 75-m × 0.53-mm column with a restrictor attached (B) (head pressure at the time of injection was 10.29 psi). This seems to establish that the quantity of sample-laden gas contained in the sample that is actually injected onto the column is strongly influenced by the column head pressure at the time of injection. Consequently, it was necessary to prepare test solutions containing different levels of analyte for each column diameter. These are shown in Table I. A corollary to these data would suggest that for any given diameter, shorter (i.e. lower pressure drop) columns would achieve greater detector response and component resolution would decrease as a square root function. To check this theory, the 30-m × 0.25-mm column was cut in half. Figure 6 compares the results obtained with the 30-m × 0.25-mm column (C) (head pressure at the time of injection was 10.43 psi) and

Figure 6. Chromatogram obtained with a 75-m × 0.53-mm i.d. column without (A) and with (B) a 12.5-cm outlet restrictor. A 10-s injection time was used. The solution concentration for both chromatograms was 0.001–1.0 μg/L. Chromatograms obtained using the same injection time and concentration were obtained using 30-m × 0.25-mm i.d. (C) and 15-m × 0.25-mm i.d. columns. The solutions used for C and D had a concentration of 0.01–0.2 μg/L.

15-m × 0.25-mm column (D) (head pressure at the time of injection was 6.58 psi) under the same analysis conditions.

Conclusion

Direct comparisons between purge and trap systems and static headspace systems are complicated by a number of factors. The apparatus used for purge and trap analysis is often perceived as mechanically complicated in comparison with the typical static headspace apparatus. Periodic maintenance of traps, valves, and sample gas lines is required for reliable performance. Those variables that influence the results obtained by purge and trap include the volume, concentration, and temperature of the sample, purge flow and time, nature of the trap, and desorption temperature, flow, and time. Analyses can suffer from elongation of solute bands introduced into the column during the desorption step. Higher gas flow rates increase the efficiency of the desorption step but usually preclude the use of smaller diameter columns, except when a split interface is used. Generally, much lower concentrations of pollutants can be detected by purge and trap when causation is observed for possible analyte breakthrough during purging or poor recoveries during extraction and desorption. However, the principles of operation are fairly simple, and purge and trap methods can usually be adapted and optimized for most sample matrices by changing only a few parameters.

Once equilibrated, the static headspace system produces results that can be duplicated. As with the purge and trap system, there are several parameters that require precise control to obtain this objective. The temperature must be controlled and (in the apparatus used in this study) a constant sample volume must be maintained in the vial and the headspace. Also, during the injection process, the column inlet pressure, vial pressurization, and the duration of the sample loop fill and flush times all have an influence on the resulting sample band. In particular, different column dimensions and the pressure drop can have a profound influence on the results.

The simplicity of using a single ECD is appealing, but this must be balanced against its lack of response to nonhalogenated molecules and its often nonlinear response to varying degrees of halogens. The ECD also displays anomalies due to water vapor that occur during detection of early eluting solutes. The first of these limitations is addressed by combining the ECD and PID in series, a recent development in Europe that tends to accomplish goals similar to the EPA-recommended PID–ELCD combination. Although the ELCD is more maintenance inten-

sive and is prone to the generation of tailing peaks, it is less prone to anomalies caused by water vapor. Unlike the ECD, the ELCD response is selective to halogens only. Finally, contemporary ELCDs exhibit improved peak shape, stability, and dependability, especially in tandem detector usage.

References

1. U.S. Environmental Protection Agency. Methods for the Determination of Organic Compounds in Drinking Water, Washington, D.C., 1988, EPA-600/4-88-039.
2. Deutsches Institut für Normung. Deutsche Einheitsverfahren zur Wasser Abwassser-, und Schlammuntersuchung; Geneinsam erfassbare Stoffgruppen (Gruppen F) **38:** 4,5,9 (1991).
3. M.F. Mehran, M.G. Nickelsen, N. Golkar, and W.J. Cooper. Improvement of the purge and trap technique for the rapid analysis of volatile organic pollutants in water. *J. High Resol. Chromatogr. Chromatogr. Commun.* **13:** 429–31 (1990).
4. C. Merrit, Jr. and J.T. Walsh. Programmed Cryogenic Temperature Gas Chromatography Applied to the Separation of Complex Mixtures. *Anal. Chem.* **35:** 110 (1963).
5. D.R. Rushneck and J. Rockford. Cryogenic injection and chromatographic separation of cigarette smoke. *J. Gas Chromatogr.* **3:** 318–19 (1965).
6. J.G. Moncur, T.E. Sharp, and E.R. Byrd. Focused cryogenic trapping for dynamic headspace and pyrolytic analysis of polymers on a fused silica capillary column. *J. High Resol. Chromatogr. Chromatogr. Commun.* **4:** 603–11 (1981).
7. D. Decker. New low volume injector. *J&W Separation Times* **6(3):** 5 (1992).
8. A.K. Vickers. Want to pick a GC column for volatile analysis? Here's how. *Today's Chem. Work* **4:** 37–40 (1994).
9. H. Hachenberg and A.P. Schmidt. *Gas Chromatographic Headspace Analysis.* John Wiley & Sons, Chichester, U.K., 1977.
10. B. Kolb, C. Bicher, M. Auer, and T.C. Voice. Simultaneous determination of volatile aromatic and halogenated hydrocarbons in water and soil by dual-channel ECD/PID equilibrium headspace analysis. *J. High Resol. Chromatogr. Chromatogr. Commun.* **17:** 299–302 (1994).
11. P. Wylie. Trace analysis of volatile compounds in water using the HP 19395A headspace sampler. Hewlett-Packard, Palo Alto, CA, 1985, Application Note 228-40.
12. A.K. Vickers and L.M. Wright. An automated GC/MS system for the analysis of volatile and semi-volatile organic compounds in water. *J. Automatic Chem.* **15:** 133–39 (1993).
13. A.S. Williams. The analysis of 524.2 compounds utilizing a split inlet. *Tekmar Company TekNote,* Vol. 1, No. 2, 1994.
14. D. Rood and A.K. Vickers. GC analysis of volatiles using headspace and purge and trap samplers. Presented at Chromatography '94, Sydney, Australia, July 26, 1994.
15. W. Jennings. *Analytical Gas Chromatography.* Academic Press, San Diego, CA, 1987.