A Syringe and Cartridge Method for Down-Hole Sampling for Trace Organics in Ground Water

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ABSTRACT

A newly developed technique which allows the down-hole sampling and subsequent analysis of ground water for trace organic contaminants was tested during an investigation of contaminant migration at an inactive landfill site in Burlington, Ontario, Canada. The sampling device, which is lowered down piezometers with a tube, consists of a small cylindrical cartridge of sorbent material attached to a syringe. Vacuum or pressure applied at the surface controls the movement of the plunger in the syringe. The volume of the syringe determines the volume of sample water that passes through the cartridge. The cartridge is removed from the syringe at the surface. One cartridge is used for each sampling; the syringe is reusable. The residual water in the cartridge is removed in the laboratory, and the cartridge is desorbed to a fused silica capillary column for analysis by gas chromatography (GC). The analyses discussed here were performed on a GC/mass spectrometer/data system (GC/MS/DS). Of the many organic compounds that were identified in the samples, three compounds were clearly landfill-related: 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene. The three compounds were found at levels substantially above blank levels in 9, 5, and 5 piezometers, respectively. The average concentrations were 14., 5.3, and 0.88 μg/l (ppb), respectively. The pooled coefficients of variation for the analyses for the three compounds were 27., 6.9, and 6.4%, respectively. The volatility of 1,1,1-trichloroethane was probably the cause of the greater variability in its analytical data. The main advantages of the technique over most conventional sampling methods include: (1) down-hole sampling in a manner which minimizes the potential for volatilization losses; (2) avoidance of passage of the sample through long sections of tubing that may contaminate the sample or cause adsorptive losses; (3) convenience of sample handling, storage, and shipping; and (4) high sensitivity.

INTRODUCTION

The number of ground-water systems which are recognized as having become contaminated with trace organic compounds are steadily increasing. In many cases, the compounds of interest are relatively volatile, often being members of the list of "purgeable" U.S. Environmental Protection Agency (EPA) priority pollutants (Keith and Telliard, 1979). Such compounds are usually present in ground water at low levels [ng/l (ppt) to mg/l (ppm)]. These typically low concentrations as well as high volatilities place stringent requirements upon the sampling and analytical method(s) selected for ground-water monitoring programs.

When attempting to obtain a sample for analysis by a method such as purge and trap (Bellar and Lichtenberg, 1975), many of the procedures used to bring samples of ground water to the

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...for the exposure of the sample to the ... volatilization losses which may then occur can ...use artifacts. Landfill leachates high in methane ...d carbon dioxide are particularly troublesome in ...is regard. A possible means of circumventing this ...latilization loss problem is provided by the ...sorption/thermal desorption (ATD) method ...veloped for water samples by Pankow *et al.* ...982a, 1982b, 1982c, 1983), and for air samples ... Zlatkis *et al.* (1973) and Pellizzari *et al.* ...975a, 1975b).

Aqueous ATD involves the: (1) passage of a ...ater sample through a prepared cartridge of ...rbent material (e.g., Tenax-GC); (2) drying of the ...rtridge; (3) thermal desorption of the cartridge ... a fused silica capillary gas chromatography (GC) ...lumn at approximately −80°C; and (4) a temper-...ure program GC run with some type of detector. ...enax-GC is an attractive sorbent for this type of ...ork since it is very thermally stable. Its possible ...se for water sampling was first considered by ...rtsch *et al.* (1975). This sorbent has been shown ... be effective in trapping aqueous chlorinated ...nzenes and other similar nonpolar compounds ...ankow *et al.*, 1982a, 1982b, 1982c). Its ability ... sorb the very volatile purgeable compounds is as ...t unknown. Recovery studies are now underway ... Pankow's laboratory to determine these ...ficiencies.

Regardless of whether or not Tenax-GC ...oves to be the aqueous ATD sorbent of choice ... all compounds of interest, the ATD method in ...neral is attractive for certain ground-water ...mpling situations. This is the case because it is ...ch sensitive and easily adaptable to down-hole ...mpling procedures. The sensitivity of the method ...ses from the fact that 100% of the sorbed ...ganics are transferred to the GC column. Within ... limits posed by breakthrough losses (Pankow, ...sen, and Wojcik, 1983), the mass amount of ...alyte sorbed can be increased by increasing the ...lume sampled. The adaptability of ATD to ...wn-hole sampling is due to the fact that the ...rtridge alone and not the actual water sample is ...turned to the laboratory. Therefore, it is not ...cessary to bring a sample to the surface and risk ...latilization losses; passage of the sample through ... cartridge can occur down-hole.

The ATD-based down-hole sampling tech-...que discussed here was developed in response to ...need to obtain reliable measurements of trace ...ganic contaminant levels in ground water down-...adient of the Bayview Park Landfill in Burlington,

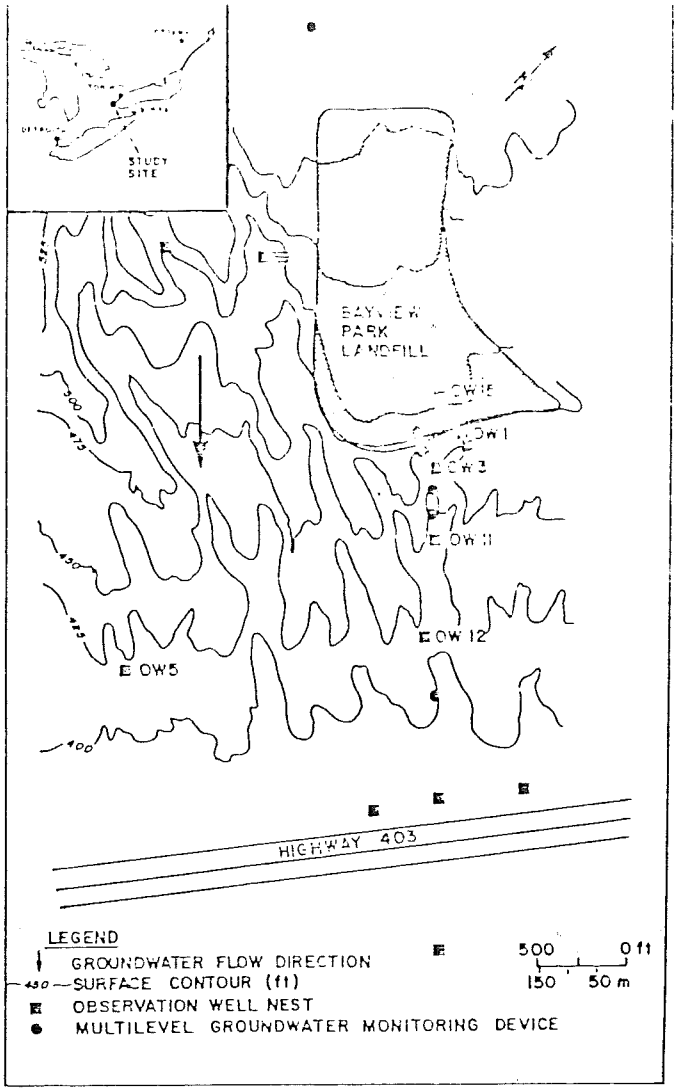

Fig. 1. Map showing surface drainage features and locations of multilevel sampling devices at the Burlington site.

Ontario. This 18 hectare landfill (Figure 1) began to receive waste from the City of Burlington in 1961. It was closed and covered over with earth in 1972. It is situated on the edge of the Niagara Escarpment where bedrock is either exposed at the surface, or covered by a thin veneer of clay till. The bedrock is fractured red Paleozoic shale of the Queenston Formation which extends to depths of over 100 m.

Ground-water movement is to the southeast and towards Lake Ontario (3.5 km away). It flows in the fractured shale along the slope of the escarpment which corresponds to the regional slope in the water table. Downgradient of the landfill there is a 3 km long expanse of land that is partly forested and is unoccupied. The land surface further downgradient is characterized by industrial

and urban areas of the City of Burlington which extend to the shore of Lake Ontario.

The fact that the Bayview Park Landfill is situated on fractured shale makes it particularly interesting. This is the case because many groundwater systems that are receiving waste materials or have received them in previous years are fractured in a manner which makes them quite permeable to ground water and solute transport. For example, fractured shale of the Queenston formation also exists within the stratigraphic sequence at landfill and hazardous waste disposal sites in the Niagara Falls area where leakage of contaminants through the shale and other formations is of concern. Furthermore, compared to porous media where much information exists on the theory of contaminant migration (Bear, 1972; Fried, 1975; Freeze and Cherry, 1979), and on such behavior at field sites (MacFarlane *et al.*, 1983; Cherry *et al.*, 1983a; Egboka *et al.*, 1983; Sudicky *et al.*, 1983; Dance and Reardon, 1983; Nicholson *et al.*, 1983; and Greenhouse and Harris, 1983), contaminant migration in fractured systems is poorly understood.

Initial attempts at the Bayview Park Landfill by Cherry *et al.* (1983b) and Hewetson and Cherry (1983) to delineate a zone of contamination on the basis of inorganic parameters (major ions, transition metals and heavy metals) and organic indicator parameters [dissolved organic carbon (DOC), chemical oxygen demand (COD), phenols, and organic nitrogen] were unsuccessful because of the naturally high levels of these parameters; typical chloride and DOC concentrations in the area of the site are 3,000 and 500 mg/l, respectively. It was hoped that: (1) the ATD method with detection by mass spectrometry would provide the sensitivity necessary to allow the determination of landfill-derived organic contaminants in the zone of contamination; and that (2) the study would provide a perspective on the applicability of ATD to ground-water sampling and analysis. Once a suite of landfill-derived compounds are identified at representative sampling locations, it should be possible, with more extensive sampling, to delineate the full extent of the zone of contamination as well as the rates of contaminant migration.

EXPERIMENTAL

ATD Cartridge Preparation

The cartridge bodies were of Pyrex glass (Figure 2). The bed length, I.D., and O.D. were 5.4, 0.40, and 0.64 cm, respectively (bed volume = 0.68 ml). A 2.5 cm piece of 2.0 mm I.D., 0.64 cm O.D. glass tubing was fused to the inlet end of the cartridge main body, and a 1.5 cm piece was fused to the outlet end. The cartridges were packed with 0.11 g of resieved 35/60 mesh Tenax-GC (Alltech Assoc., Inc., Los Altos, California). The Tenax-GC was held in place with silanized glass wool (Supelco, Inc., Bellefonte, Pennsylvania). Cartridge conditioning was carried out by passing 0.5 l of glass distilled acetone through each cartridge, vacuum drying for 20 min, then thermally desorbing for 3 h at 300°C with 30 ml/min of helium gas which had been pre-cleaned by passage through a Supelco oxygen trap and then through a molecular sieve trap in liquid nitrogen.

The cartridges were then capped on their inlet ends with clean brass Swagelok (Crawford Fitting Co., Solon, Ohio) endcaps with Teflon ferrules. Following Krost *et al.* (1982), prior to use, all Teflon parts were degassed under a vacuum at 110°C for 2 h. The outlet ends of the cartridges were each fitted with a brass Swagelok 0.25 in. to 0.125 in. reducing union which was silver soldered to a 3.0 cm long, 25 gauge needle with a Luer hub

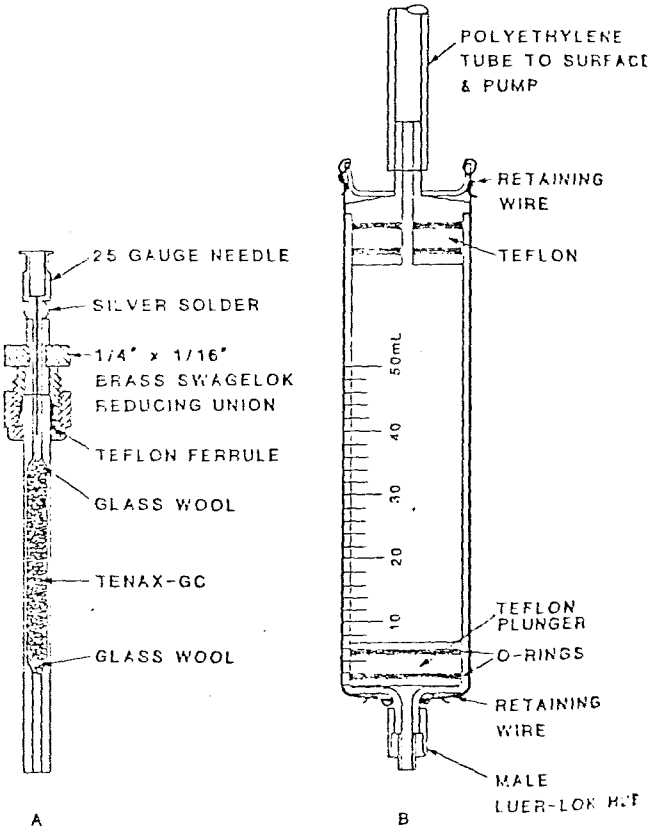

Fig. 2. Down-hole cartridge sampling device including: (A) ATD cartridge with needle restriction; and (B) glass syringe with Teflon and rubber O-ring plunger.

Figure 2). The latter served as a flow restrictor. The dimensions of the needle were selected so that the flow rate through the cartridge would not exceed 0.1 ml/s with a total pressure differential of one atmosphere (10.3 m of water column) across the cartridge/needle system. The flow rate of 0.1 ml/s was selected, based on the dimensions of the cartridge and the recommendations of Pankow *et al.* (1982b). For piezometers which had more than 10 m of water column above the desired sampling interval, additional flow restriction was achieved by placing a 3.25 cm long pre-cleaned section of 0.15 mm O.D. piano wire inside of the needles of the cartridges.

Prior to shipment to the field, each entire cartridge system was evacuated, then forcibly wetted by releasing the vacuum with water which had been pre-cleaned by: (1) passage through an activated carbon bed, and (2) boiling with simultaneous sparging with nitrogen which had been pre-cleaned by passage through a molecular sieve trap in liquid nitrogen. The Luer hub was then sealed with a Teflon plug, and the entire cartridge system stored in a muffle-furnaced Pyrex culture tube with a Teflon cap liner. The cartridges were prepared in groups so that each group contained one blank cartridge. After preparation, all of the cartridges were shipped (together with several copies of the down-hole syringe sampling device to be described below) via overnight air courier from the Oregon Graduate Center to the University of Waterloo.

Syringe Sampling Device

The syringe sampler (Figure 2) was a glass and Teflon version modeled after a similar polyethylene and rubber device developed by Gillham (1982) for sampling for inorganic constituents in ground water. Concerns about contamination and losses associated with polyethylene and rubber led to their replacement. Glass syringes with a 50 ml capacity and Luer-lock fittings were obtained from Popper and Sons (New Hyde Park, New York). The top rim was removed from each syringe with a glass cutting wheel. In this manner, the O.D. of the device was reduced to that of the syringe body (2.3 cm). The device could then pass down sample piezometers constructed from schedule 40, 3.8 cm I.D. PVC tubing. The sharp edges were ground smooth with the wheel, but could not be fire-polished since this type of glass cracks easily when heated because of its high coefficient of thermal expansion. A movable plunger and an upper tube coupling were machined from Teflon. O-ring grooves were included on both parts. Since the O-rings would not contact the sample, conventional Buna-N O-rings were used. Prior to assembly, each syringe was washed with warm laboratory detergent, rinsed with deionized water, sonicated in acetone, then hexane, then acetone again, rinsed with deionized water, then baked at 110°C for one h. The O-rings were washed with warm detergent, rinsed with deionized water, rinsed with acetone, then vacuum-outgassed at 110°C for one h.

Sample Piezometers and Sampling Procedures

The sampling points used were the OW ("observation well") sample piezometer nests installed between 1979 and 1981 by Morrison Beatty, Ltd. (1981) (Figure 1). These piezometers are conventional PVC standpipe piezometers with 0.7 m long slotted screens. They were installed and sealed in holes drilled by the hollow-stem auger method. While most of these piezometer tubes are 3.8 cm I.D., some are 3.2 cm I.D. The piezometers were bailed dry a few days prior to sampling (February and March 1983) to remove nearly all of the standing water. For the 3.8 cm I.D. casings, sampling was carried out by: (1) connecting a polyethylene tube to the Teflon coupling on the upper end of the syringe; (2) pressurizing the tube with a hand vacuum/pressure pump (Model 7090, Cole-Parmer, Chicago, Illinois) so that the movable plunger was forced to the zero volume position; (3) locking a cartridge onto the Luer fitting; (4) lowering the cartridge/syringe down the piezometer tube to near the slotted interval; (5) releasing the pressure and/or pulling a vacuum on the tubing to allow the sample to pass through the cartridge and into the syringe; (6) bringing the device to the surface; and (7) removing the cartridge, resealing it with the Swagelok endcap and Teflon Luer plug, and replacing it in the culture tube for air courier shipment back to the Oregon Graduate Center. It should be noted that the low pressure portion of the sampler occurred in the exit end of the needle. In this manner, the needle served to control the flow rate as well as eliminate degassing prior to or in the cartridge. At the point in time during which cartridges from a given set were used in sampling, the endcaps on the blank cartridge from that set were removed and the cartridge was thereby opened to the atmosphere. The blank cartridge was then immediately closed again, and returned to its culture tube for shipment.

For the 3.2 cm I.D. PVC casings, it was not

possible to sample down-hole. Approximately one l of ground water was brought to the surface with a stainless steel bailer previously rinsed with methanol and sample water. The sample was then transferred to a glass erlenmeyer flask. The syringe and cartridge were prepared and assembled as described above. The cartridge was then partially submerged. A vacuum was then applied with the pump to allow the sample to be pulled through the cartridge. Further handling of the cartridge proceeded as described above for down-hole sampling.

Cartridge Desiccation, Desorption, and Analysis

Upon arrival at the Oregon Graduate Center, each cartridge was dried according to a two-step centrifugation/vacuum desiccation method. This desiccation does not cause losses for the analytes of interest. The cartridges were then resealed and refrigerated for a maximum of two weeks before desorption and analysis occurred. The desorption procedure began with the addition of 2.0 μl of a standard solution in methanol (containing 10 ng/μl each of toluene-d8 and 2-bromo-meta-xylene) directly to the sorbent at the sampling inlet end. The cartridge was then placed in a thermal desorption block described in detail in Pankow (1984). Briefly, the oxygen and the majority of the methanol were purged from the cartridge for 10 min with 10 ml/min of helium carrier flowing into the cartridge inlet. The flow was reversed, and the cartridge desorbed for 20 min at 250°C with 30 psi helium directly to a 30 m 0.35 mm I.D. SE-54 fused silica capillary column (J&W Scientific, Rancho Cordova, California) mounted in a Finnigan 4000 GC/MS/DS (by passing it through a transfer line to within 5 mm of the MS source), and held at −80°C during the desorption. The high efficiency of the drying procedure served to prevent the plugging of the column with ice during the desorption step. The analyses were carried out using a carrier gas linear velocity of 45 cm/s, MS scanning from 35 to 450 in 0.5 s, and a GC temperature program of −80° to 250° at 10° C/min. The transfer line, source, and MS manifold temperatures were maintained at 225°, 225°, and 100°C, respectively. The electron multiplier was maintained at 1600 V during the chromatographic runs.

GC/MS/DS Identification Procedures

The procedures utilized in the analysis of the data were designed so that all identifications reported would be of a "confirmed" nature (Christman, 1982). Following the analysis of a standard containing known amounts of each of the target and internal standard compounds, relative retention times (RRT) and relative response factors (RRF) were calculated using the GC/MS/DS software. The internal standard compounds toluene-d8 and 2-bromo-m-xylene eluted in the early and late portions of the chromatogram, respectively, and each was used in the RRT and RRF calculations in its respective chromatographic region. The mass spectral ions used for peak area quantitation of toluene-d8 and 2-bromo-m-xylene were 98 and 184, respectively. The 26 target analytes that were specifically sought in the samples (and the ions used for peak area quantitation) included: 1,1-dichloroethene (61), dichloromethane (84), trans-1,2-dichloroethene (61), 1,1-dichloroethane (63), chloroform (83), 1,1,1-trichloroethane (97), 1,2-dichloroethane (98), tetrachloromethane (carbon tetrachloride) (117), benzene (78), 1,2-dichloropropane (63), trichloroethene (trichloroethylene) (130), bromodichloromethane (83), trans-1,3-dichloropropene (75), toluene (91), cis-1,3-dichloropropene (75), 1,1,2-trichloroethane (83), dibromochloromethane (129), tetrachloroethene (129), chlorobenzene (112), ethylbenzene (91), bromoform (171), 1,1,2,2-tetrachloroethane (83), 1,3-dichlorobenzene (meta-dichlorobenzene) (146), 1,4-dichlorobenzene (paradichlorobenzene) (146), 1,2-dichlorobenzene (ortho-dichlorobenzene) (146), and hexachloroethane (117).

The identification of the compounds in a sample data file was carried out by manual means to avoid misassignments. To this end, the system software was first used to plot the extracted ion current profiles (EICPs "ion chromatograms," or "mass chromatograms") for up to seven characteristic ions of each target compound in a narrow (±25 s) window. The center of the window was predicted on the basis of the predetermined RRT of the compound and the observed internal standard RT. An identification was considered to be confirmed if: (1) the EICPs all maximized within ±1 s of each other, and very near to the predicted RT; and (2) the intensities of all of the plots relative to the most intense EICP were within ±20% of those observed in a standard run which had been carried out within 6 h of the sample run under consideration. Computer matching of the background-subtracted spectrum at the peak maximum with the data system's mass spectral library was used to further confirm the assignment.

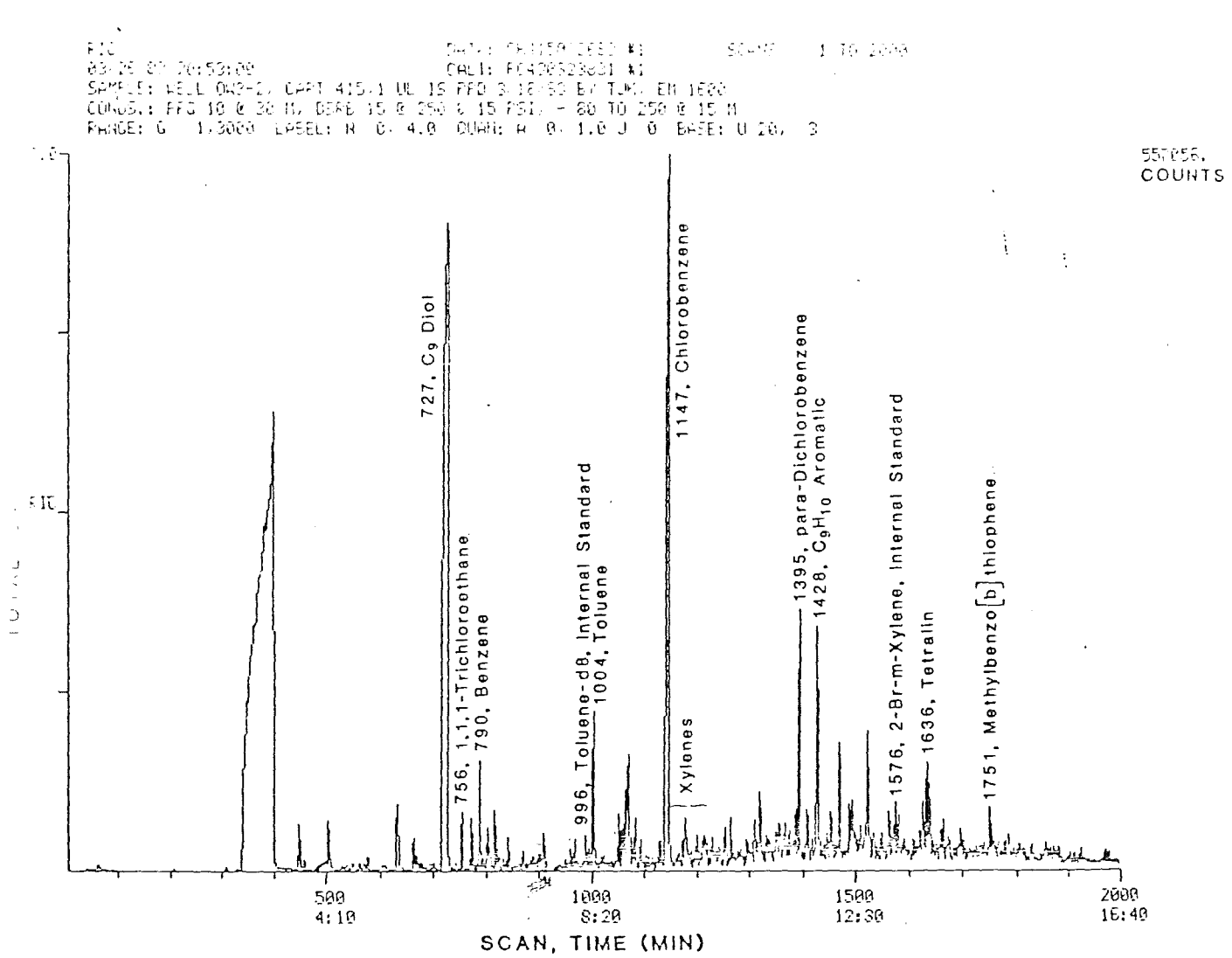

Fig. 3. Fused silica capillary column GC/MS/DS chromatogram obtained with 54 ml of water from OW 3-2.

RESULTS

Of the over 26 compounds that were specifically sought in the samples, three clearly landfill-related compounds were 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene. A variety of naturally-present compounds were also identified in the samples. Some of these identifications are given in Figure 3 which is the chromatogram obtained for piezometer OW 3-2 with Cartridge 415. The concentrations of 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene together with the associated blank levels are presented in Table 1. The volumes sampled are also given. Volumes substantially greater than 50 ml (the nominal capacity of the syringes) occurred when the O-ring on the movable plunger leaked somewhat, allowing water to pass up into the tube which led to the surface. This problem may be overcome through the adjustment of the O-ring groove tolerances. Although breakthrough is of general concern, it is encouraging to note that there is no dependence on the sample volume for the data (above blank levels) obtained for piezometers OW 11-1 and OW 11-3.

The gas chromatographic mean retention times for the compounds 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene were 402, 585, and 720 s, respectively. The means of the absolute values of the deviations between the predicted and observed retentions times were 7.7, 3.1, and 1.5 s, respectively. The fact that 1,1,1-trichloroethane and chlorobenzene displayed greater variability is because they were more influenced by a certain amount of unavoidable variability in the low temperature portion of the GC temperature program.

Although it is known that the value of the

relative standard deviation (coefficient of variation, or CV) for the concentration of an analyte as given by an analytical method is a function of the concentration of the analyte (Glaser *et al.*, 1981), the assumption will be made that to a first approximation it is independent of concentration for these analyses. This allows one to pool replicate data and obtain estimates of the CV (Davies and Goldsmith, 1972). The data sets which were included in this pooling process, marked with an asterisk in Table 1, were limited to those piezometers for which the concentrations were substantially above blank levels. The blank values (calculated by dividing the μg amounts of each compound found on a blank cartridge by the smallest sample volume employed, or 0.050 l) were not subtracted from the data prior to the calculation of individual standard deviations. The pooled CV were therefore

Table 1. Concentrations of Selected Organic Compounds in $\mu g/l$ (ppb) in Bayview Park Landfill Samples from OW Sample Well Series (Volume Sampled Data Are Given in ml)

Well	*Midpt. slotted depth (m)*		*Cartridge number*	*Volume sampled*	*1,1,1-trichloroethane*	*Chloro-benzene*	*Para-dichlorobenzene*
OW 15-3	27.7		419	50	35.*	3.4*	0.37*
surface			421	50	38.	2.9	0.35
		Blank	409	-0-	0.17	0.89	0.041
OW 1-2	8.2		402	56	0.30*	11.*	1.8*
down-hole			404	58	0.41	12.	2.0
		Blank	409	-0-	0.17	0.89	0.041
OW 1-4	20.8		570	65	25.*	0.080	0.003
down-hole			580	60	13.	0.051	ND
		Blank	640	-0-	0.18	0.042	0.001
OW 3-2	7.3		415	54	0.94*	8.0*	1.5*
surface			416	50	1.6	8.3	1.6
		Blank	418	-0-	0.40	0.91	0.011
OW 3-3	14.3		411	54	7.6*	0.90	0.013
down-hole			412	56	11.	0.74	0.011
			413	57	8.4	0.72	0.008
		Blank	418	-0-	0.40	0.91	0.011
OW 3-4	21.0		559	54	48.*	0.19	ND
surface			560	50	30.	0.16	ND
		Blank	640	-0-	0.18	0.042	0.001
OW 11-1	3.0		554	60	0.24	2.8*	0.52*
down-hole			555	105	0.12	2.9	0.57
		Blank	505	-0-	0.25	0.029	ND
OW 11-2	14.8		552	62	1.4*	0.025	0.001
down-hole			553	68	2.0	0.026	ND
		Blank	505	-0-	0.25	0.029	ND
OW 11-3	22.4		591	61	5.7*	0.044	0.005
down-hole			593	188	6.1	0.027	0.009
			596	58	7.7	0.050	0.007
		Blank	505	-0-	0.25	0.029	ND
OW 12-3	19.4		558	56	11.*	0.84*	0.051*
down-hole			600	46	9.3	0.75	0.057
		Blank	505	-0-	0.25	0.029	ND
OW 5	7.6		650	50	0.50	0.053	ND
surface			680	50	0.53	0.051	0.002
		Blank	780	-0-	0.50	0.045	0.001
Average concentration on * data sets:					14.	5.3	0.88
Average blank level ($\mu g/l$):					0.30	0.38	0.011
CV based on pooling of * data sets:					27.%	6.9%	6.4%

erved to be 27., 6.9, and 6.8 % for 1,1,1-tri-
chloroethane, chlorobenzene, and para-dichloro-
benzene, respectively.

In view of its substantially higher volatility, it
not surprising that the 1,1,1-trichloroethane data
uld exhibit the highest CV. There are too few
ta points to allow a statistical distinction to be
de between those samples which could be
tained down-hole and those which had to be
tained at the surface. Some of the variability
y reside in errors associated with the cartridge
ndling and analysis which occurred after the
mpling.

The average blank values for 1,1,1-trichloro-
thane, chlorobenzene, and para-dichlorobenzene
re 0.30, 0.38, and 0.011 μg/l, respectively. A
ank cartridge prepared by exposing it to a section
f the type of O-ring used in the syringe device
owed no contamination from these compounds.
t is probably significant that the two compounds
ith the highest blank levels are also the two
mpounds with the highest vapor pressures (96.0
d 11.7 torr, respectively, vs. 1.2 torr for para-
chlorobenzene) (Callahan *et al.*, 1979). These
1,1-trichloroethane and chlorobenzene blank
vels in conjunction with other, generally lower-
vel trace analyses by aqueous ATD underway in
ur laboratories (Pankow *et al.*, 1983), indicate
hat a portion of the contamination is cross-
ontamination from samples to blanks. It will
herefore be possible to lower this contamination
vel by increasing the isolation which each
artridge receives subsequent to sampling.

The down-hole syringe and cartridge tech-
ique provides some unique advantages over con-
entional methods for obtaining ground-water
amples for analysis for trace organic compounds.
n effect, each cartridge is a dedicated sampler. The
echnique is convenient for acquiring samples from
epths near the piezometer tip or well screen.
ince the cartridge itself is quite small in diameter
0.64 cm), the possibility exists for modifying the
ethod for very narrow piezometers such as those
eveloped by Cherry *et al.* (1983a, 1983b) and
lewetson and Cherry (1983) for multilevel
ampling. If the piezometer is pumped or bailed
rior to sampling, the sample will represent ground
ater which recently flowed into the piezometer
nd also traveled only a short distance upward in
he piezometer. This water will contact only a
mall percentage of the total, potentially adsorp-
ive casing surface. If the sample is taken at the
iezometer tip after a freshly pumped well has
een allowed to recharge, the sample will not be
expected to provide [illegible] pressure, and volatilization will be minimized.

Sampling down-hole also allows the possibility of not pumping or bailing many water columns prior to sampling. This is of particular interest in view of the controversy that currently exists regarding the number of water column volumes that should be removed from a well or piezometer before sampling can occur. Since most pumping methods cause the mixing of fresh formation water with water which previously existed in the water column, it is generally desirable to pump considerably more than one column volume when sampling permeable formations. Down-hole sampling techniques such as those described in this paper have the advantage of allowing the sampler to be placed near the bottom of the piezometer when the pump is operating near the top of the water column. While the low permeability of the shale at the Bayview Park Landfill prevented the use of this configuration in this study, its application in higher permeability formations would allow the sample to represent new formation water even when only a small total volume is removed from the water column.

While the same water could be sampled conventionally by placing a pump at the piezometer tip, losses by adsorption and volatilization may be problematic as the sample rises in the tube leading to the surface. The use of a conventional bailer equipped with a one-way valve may eliminate the sorption loss problem, but volatilization at the surface remains a source of uncertainty. If a pump/tube assembly or a bailer is not dedicated to each piezometer, a process which involves additional expense, cross-contamination may also occur.

A disadvantage associated with the syringe and cartridge down-hole sampling technique as developed here is the cost in labor time in preparing the cartridges as compared to cleaning glass sample vessels as, for example, for purge and trap analyses. However, for many sampling applications, the many advantages of this sensitive technique outweigh the cost of preparation. Furthermore, it is likely that such costs will be reduced in the future as the method develops. Uncertainties with regard to breakthrough losses are currently under field investigation by the authors through the use of several cartridges in series. Studies are also currently underway in Pankow's laboratory concerning how the magnitude of breakthrough may be reduced through the variation of sorbent type and sampling conditions.

CONCLUSIONS

A down-hole syringe and cartridge sampling technique based on the analytical method ATD and analysis by GC/MS/DS has been developed for the determination of μg/l levels of organic contaminants in ground water. The convenience of the technique for field use and the reproducibility of the results were encouraging during an application of the technique to the study of the zone of contamination downgradient of a landfill located on fractured shale in Burlington, Ontario. The technique enables samples to be obtained from any depth in piezometers or wells in a manner that minimizes losses due to volatilization and sorption on sampling equipment. In essence, each cartridge is a dedicated sampler in that it is not used in more than one piezometer or well. Because the sample exists as a small, lightweight, porous cartridge regardless of the water volume that is sampled, the sample is in a form that is very convenient for packaging and shipping by mail or by air courier between field sites and distant analytical laboratories. Further work is underway in our laboratories to improve the technique.

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