Optimization and Application of the Large Volume On-Column Introduction (LOCI) Technique for Capillary GC with Preliminary On-Line Capillary Solvent Distillation/Concentration

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Summary

This report describes an on-line capillary GC injection system which enables on-column injection of a hundred or more microliters, and yields separations comparable with those obtained from on-column injection of 1–2 microliters of solutions a hundred times more concentrated. Precision, carry-over, linearity, and discrimination are comparable with those of classical sample-introduction techniques. A selection of polar and high boiling compounds has been examined, and excellent peak shapes obtained for hundreds of injections. Initial results indicate that maintenance and long-term reproducibility will also be comparable with those of classical techniques.

The instrument utilizes a version of the large volume on-column injector with solvent diversion described in an earlier communication, with the addition of a method for independent heating of the retention gap. This modification reduces the effects of activity in the retention gap and improves the capability of the technology to handle complex mixtures. It also increases reliability and system lifetime, fits readily into most GC ovens, is easily automated, and should be compatible with all capillary GC detectors.

1 Introduction

Techniques involving retention gaps for performing on-column injection of comparatively large volumes, *i.e.* 50–500 µL, on to capillary GC columns have been in use for several years. Many modifications of this technique have been developed, but most continue to suffer from many of the original shortcomings while exploiting the strengths of on-column and large volume injections [1, 2]. Allowing large sample volumes to enter and flow through the analytical column can reduce column efficiency for volatile compounds and may significantly reduce column lifetime, increase analysis time, interfere with the performance of many detectors, and significantly increase maintenance. Severe limits are, furthermore, placed on many routine chromatographic analyses utilizing this technology owing to difficulties in resolving materials which are band-broadened in space, *i.e.* spread initially over the length of the retention gap and not fully focused when entering the analytical column.

For large volume capillary GC injections to become a routine part of trace organic analysis, it is important that a simple, reliable, and automated system be developed to overcome these weaknesses. Although a controllable splitter between the end of the separation column and the detector has been used to divert the solvent [1], the dead volume introduced to the system at that point can cause significant peak tailing, thus limiting its utility. *Grob* has suggested reducing the effect of band broadening in space by introducing a plateau in the temperature program to enable elution from a retention gap and focusing on the analytical column. Although useful for a limited number of analytes, the method quickly complicates the GC temperature program, and may cause other chromatographic problems when multi-component mixtures (such as the list in EPA Appendix 9) are analyzed.

A diversion valve has been placed between the retention gap and the analytical column [3, 4] in an effort both to reduce the amount of solvent reaching the analytical column and to increase reliability while reducing difficulties involved with interfacing the large volume system with various detectors. If *Grob's* [1] description of the physical processes is correct, the lighter compounds accumulate primarily on the trailing edge of the solvent and the heavier compounds are deposited evenly along the length of the deactivated retention gap and so the divert valve can remain open for a length of time sufficient to eliminate most of the solvent from the chromatographic system. Though this approach solves the diffi-

culties associated with the introduction of large solvent volumes to the analytical column and detector, difficulties with peaks broadened in space owing to polarity, boiling point, dead volume in the splitter, retention gap polarity, *etc.*, remain.

Schomburg et al. [5] introduced an on-column technique with a retention gap and a "T" between the retention gap and the column. The method was used as an injector operated in the split mode. This instrument essentially operates as do the traditional fixed-split injection gas chromatographic techniques, except that it achieves on-column injection. Split ratios between 1:10 and 1:200 were achieved by varying the restriction.

Noy et al. [6] investigated an on-line liquid chromatography–gas chromatography (LC-GC) vaporizer – cold trap – column system with a splitter between the cold trap and the column. The splitter is designed to sweep both the split line and the valve continuously. *Despite the several* apparent similarities with the instrument described in this report, this sample introduction system makes use of a injection port vaporizer with subsequent trapping of the gaseous analytes. This approach is similar to conventional splitless GC methods and is basically a physical variation of the splitless injection technique. In essence, the separation of the analytes and the solvent is conducted when all the components are in the vapor phase and the technique therefore features many of the same strengths and weaknesses of splitless injection. These are discussed in detail in many introductory GC texts. Because the analytes are in a gaseous state, the subsequent trapping must be quite selective for this technique to trap volatile materials while allowing the evaporated solvent to pass through. Indeed, in the optimum configuration of the system, *Noy et al.* observed considerable difficulties trapping, from hexane, hydrocarbons as close in boiling point as n-C_{14}. Components more volatile than n-C_{15} were partially lost during trapping and exhibited poor peak shape.

Buskhe, Berg, Gyllenhaal, and *Greibrokk* [7] introduced a splitless injection system for capillary supercritical fluid chromatography which is similar in construction to that of *Morabito, Hiller,* and *McCabe* [3]. It included a venting valve through which the mobile phase could be excluded from the analytical column. The authors observed that, "the mechanisms for solvent/solute separation are quite different in GC and SFC." *Buskhe et al.* were unable to accomplish solvent re-focusing by this technique.

Nitz, Drawert, and *Julich* [8] utilized a cryogenic trap packed with Tenax to capture materials from large volumes of gases for later thermal desorption on to capillary columns. The capillary column was bypassed while the concentration step occurred. During the rapid thermal desorption, with the column temperature kept low, a thermal re-focusing effect was observed which enabled good peak shapes to be obtained for compounds with boiling points about 70 °C higher than the initial oven temperature. Solvent focusing of the low molecular weight species could not be achieved when there was no solvent present. The physical mechanism for the separation may be much like that observed by *Morabito, Hiller,* and *McCabe* [3], but without the solvent re-focusing to provide additional separation of solvent and analyte.

Morabito, Hiller, and *McCabe* [3] described a system for solvent diversion which was a modification of the large volume system originally introduced by *Grob* [1]. With it, samples of several hundred microliters could be injected, yet by diverting the majority of the solvent, resolution of the most volatile compounds was maintained and the chromatograms resembled those obtained from injection of 1–3 microliters of solutions several orders of magnitude more concentrated. Although shown to give very satisfactory results with non-polar materials such as toluene and a selection of chlorinated aromatic compounds, the application of the technique to routine analyses of high boiling compounds, polar compounds, and solvents was not evident. Difficulties with such compounds have been reported by *Grob* [1] and by *McCabe, Hiller,* and *Morabito* [2] for similar techniques without the solvent diversion.

Biedermann, Grob, and *Meier* [9] published an application of solvent diversion to LC-GC. Although the diversion vent was closed manually, the method appeared satisfactory. They, also, observed the excellent utility of solvent diversion for obtaining a considerable reduction in the amount of solvent passing on to the analytical column and through the detector. The application was, however, also limited to relatively non-polar analytes such as alkanes, alkenes, and aldehydes.

Barcarolo [14] applied the diversion technique of *Morabito et al.* [3] to a fully concurrent eluent evaporation LC-GC instrument with electron capture detection (ECD). This had the advantages of solvent removal from the analytical column and the detector, while the ECD gave sufficient selectivity with large signal-to-noise ratios for chlorinated pesticides. When isooctane was used as solvent, the earliest eluting chlorinated material observed was hexachlorobenzene [14].

Very recently, *Bicchi et al.* [12] used the method of *Morabito et al.* [3] but added a "retaining precolumn" to help retain compounds with boiling points near to that of the solvent. They showed good recoveries of nonane in hexane using this method. Earlier work by *Bicchi et al.* [10–11] had used a splitting technique similar in principle to that of *Schomburg et al.* [5].

This report describes the introduction of several solutions to the difficulties described above which have proven successful in this laboratory. For complete removal of the effects of dead volume in the solvent split device described earlier [2], a very small (0.01–0.05 mL/min) controlled leak was added to the valve. Although this split causes some sample also to be diverted, the amount was both very small and reproducible.

Additional difficulties have been found in the utilization of retention gaps in this laboratory [2]. Perhaps the most annoying of these to the routine user has been the need to prepare special gaps which can be used to examine polar compounds, and the limited lifetimes of these gaps in such analyses. These compounds are band-broadened in space on newly prepared retention gaps; although, when the gaps are new, the compounds are refocused when reasonable temperature programming rates are used, when the gap begins to acquire a history of use, often after only one "real" sample, the analytes begin to become so strongly adsorbed that they cannot be refocused (Figure 5).

In an effort to address this shortcoming in the routine use of large volume injections, the utility of heating the retention gap independently of the analytical column has been investigated. By raising the temperature of the surface of the retention gap after the analytes have been deposited by the evaporating solvent, the migration rate of the analytes is considerably increased. Polar analytes are not retained on a hot surface, even if some surface polarity is present. Because the analytical column is kept near the initial run temperature throughout the heating process, however, the heavier and more polar analytes are thermally focused in a very narrow band at the head of the analytical column.

Several advantages were expected from this modification: (a) the broadening of the late eluting compounds and tailing of polar peaks should be severely reduced as the effect of activity and boiling point differences on retention are sharply diminished; (b) the effective lifetime of the retention gap should be extended; and (c) the use of "coated" retention gaps (commercial columns used as retention gaps) can be contemplated, owing to the relative mobility of the analytes at higher temperature compared with the lower temperature of the analytical column. The use of commercially prepared columns as retention gaps is particularly appealing because of the wide availability of a variety of stationary phases from commercial sources. The preparation of a wide variety of retention gaps to address widely different solvent polarities has been a particular problem when polar solvents, such as dichloromethane, methanol, and water are used.

2 Experimental

Figure 1 presents a diagram of the system used in this work. The conditions used for each analysis are given in **Table 1**. All materials were purchased from commercial sources. A 6-port Valco (Houston, TX, USA) valve with a Teflon® (DuPont) loop was used for injection. The "retention gaps" are detailed in Table 1; columns and retention gaps were purchased from Restek (Bellefonte, PA, USA). The arms of the "press-fit T" (Hewlett-Packard, Palo Alto, CA, USA) were all of 0.32 mm i.d. The "T" was coupled to the retention gap with a 0.53 to 0.32 mm press-fit union, from Hewlett-Packard, and a short piece of 0.32 mm i.d. deactivated fused silica. The divert valve was a high temperature Valco 4-port valve. Both valves were controlled with Valco digital valve interfaces, *via* a PE Nelson (Cupertino, CA, USA) Access Chrom Model 940 A/D box.

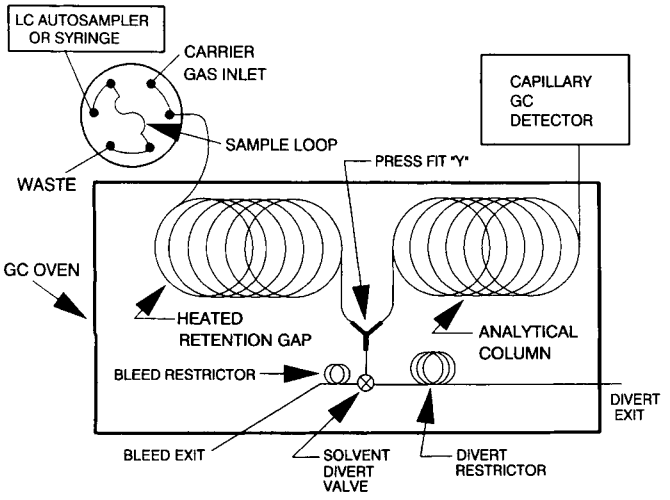

Figure 1

Large volume on-column GC instrument.

The bleed restrictor was a 1.4 m × 0.05 mm i.d. piece of fused silica capillary tubing; the vent restrictor was a piece of 0.35 mm i.d. fused silica capillary tubing *ca* 0.7 m long and served primarily to remove the solvent vapors from the oven to a hood, while regulating the vent flow to a reasonable velocity. Care had to be taken to keep the length of the vent restrictor quite short, or to add insulation and an additional heater, to keep the flow unrestricted when solvents which might condense at room temperature were used.

The heated retention gaps and columns were assembled starting with a neatly coiled, four to six inch circle of the silica tubing tied with small lengths of narrow-gauge wire to prevent unwinding. The exact diameter of the coil was dependent upon the GC oven size. The coil was then wrapped tightly with eight to ten feet of 29-gauge double glass-insulated Nichrome 60 wire (approx. 5.7 Ω/ft.) from Pelican Wire (Naples, FL, USA). Wrapped with the silica tubing was a 28-gauge wire, glass insulated, type-J thermocouple. Several feet of the thermocouple leads as well as *ca* one foot of silica tubing from each end were left outside the wire wrap. A layer of 25 mm wide fiberglass cloth tape (Fisher Scientific, Pittsburgh, PA, USA), was double-wrapped over the Nichrome wire, leaving the ends of the silica tube, Nichrome wire, and thermocouple outside. The glass tape was tied on with narrow-gauge wire to prevent unraveling.

The Nichrome wire was attached, by means of two connectors formed from 1/8" stainless steel tubing tapped for two 0–80 screws, to copper leads of 20-gauge wire. A short piece of Nextel® (3M Company, St Paul, MN, USA) ceramic insulation, 14-gauge, was placed over the connectors to prevent shorting. The remainder of the copper leads out of the oven were insulated with 20-gauge fiberglass tubing. The thermocouples, Nextel insula-

Table 1

Chromatographic conditions.

	Figure 3	Figure 4	Figure 5	Figure 6	Figure 7
Retention Gap	10 m × 0.53 mm i.d. IP deactivated fused silica, Restek #10032 for all chromatograms				
Column[a)]	1	1	2	1	1
Injection volume	100 µL for all chromatograms				
Temperature program[b)]	1	1	1	2	1
Retention gap temp [°C]	220	260	220	220	220
Detector temp [°C]	250	265	250	250	250
Divert on time	0.0 min for all chromatograms				
Divert off time [min]	2.12	varying	1.15	2.12	2.12
Carrier gas (helium) pressure [psi]	12	12	13	12	12
Detection	FID for all chromatograms				
Bleed restrictor i.d. [mm]	0.05	0.05	0.025	0.05	0.05
Bleed restrictor length [cm]	Varying	144	9	144	144
Divert restrictor	70 cm × 0.32 mm i.d. for all chromatograms				

[a)] 1: 30 m × 0.32 mm i.d., 0.25 µm film DB-5; 2: 30 m × 0.32 mm i.d., 1.0 µm film, RTx-5

[b)] 1: 65 °C, 7 min, 10°/min to 250 °C, 5 min hold; 2: 65 °C, 7 min, 8°/min to 300 °C

tion, and fiberglass tubing were purchased from Omega Engineering (Stamford, CT, USA).

A variable transformer was used to supply the heater power. Typical settings of 35–60 V AC, produced temperatures of 200 to 300 °C inside the wrapping. Cooling times to 65 °C between chromatographic runs varied, but were about 3–5 min longer than for the column alone. Additional cooling could have been supplied to the heated gap had it been required. Only on/off control was needed for the retention gap heater. On/off control was provided by switching the input of the variable transformer with a commercial, 3–30 V DC input, 220 V AC output, solid state relay (Crydom D1210; Newark Electronics, Chicago, IL, USA) controlled *via* contact closures provided by the PE Nelson A/D box and a 12 V DC power supply (Radio Shack, Cat. #22-127D, Fort Worth, TX, USA).

The column, vent, and bleed restrictor flow rates were measured with a digital bubble meter from J&W Scientific (Folsom, CA, USA) and adjusted by varying the head pressure of the retention gap and the length of the restrictor coils. The vent restrictor coil was placed in the oven of the gas chromatograph with an externally mounted vent to atmosphere. The bleed restrictor flow was also vented outside the oven.

All target compounds were purchased from Alltech Associates (Deerfield, IL, USA) or Chem Service (West Chester, PA, USA) and were >97 % purity. Test mixtures were prepared in Burdick & Jackson (Muskegon, MI, USA) high purity LC or GC-MS grade hexane. Teflon sample loops were used for experimental convenience only. They provided an easy visual confirmation that the sample had entered the retention gap smoothly, which helped ensure that an even film was formed inside the retention gap. When the oven temperature was too high, this motion was seen to proceed in sudden bursts, occasionally even reversing direction. There may be compatibility problems with other analytes and solvents with this style of sample loop, but no difficulties were observed in this work.

3 Results and Discussion

The timing of the various valves and relays during the course of a typical chromatogram is illustrated in **Figure 2**. In short, the divert valve was opened at the same time as the rotation of the injection valve. After the solvent and volatile compounds had been concentrated to a small volume of liquid on the retention gap, the divert valve was closed and the solvent and other components which were volatile at the injection temperature eluted on to the analytical column. The retention gap heater was then turned on and the less volatile and/or more polar components which had been deposited along the retention gap with the evaporation of the solvent were refocused on to the analytical column.

In addition to the advantages to the analytical column and detector of reducing the volume of solvent, the injection of sample on to the column and the subsequent solvent evaporation are facilitated by the rapid flow of carrier gas through the injection loop. Temperature programmed GC can begin at any time once the divert valve has been closed, and depends primarily upon the analyte of interest.

Variations in the chromatogram which resulted from reducing the length of the bleed restrictor are displayed in **Figure 3**. As the length was reduced, the flow through the bleed restrictor increased. It is clearly apparent that at very low flows the dead

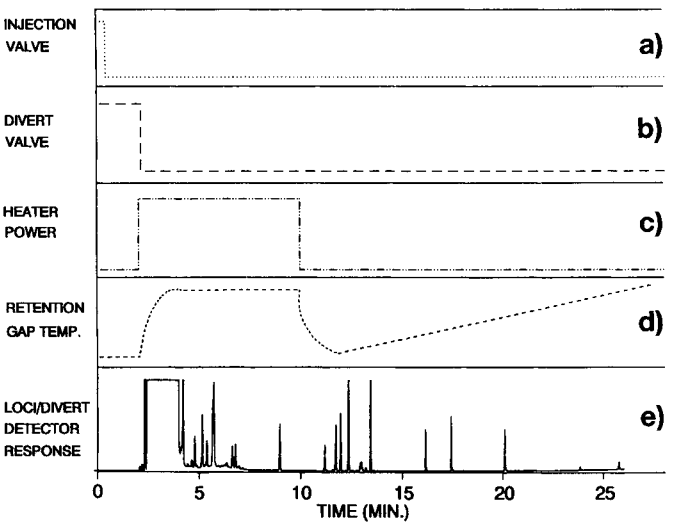

Figure 2

Timing diagram used for controlling valves and understanding the use of the large volume heated on-column injection system: (a) injection valve opens at t = 0 and closes at t = 0.2 min; (b) divert valve opens at t = 0 and closes at t = 2 min; (c) heater power on at t = 2 and off at t = 10 min; (d) variation of retention gap temperature with time (estimated); (e) variation of FID response with time.

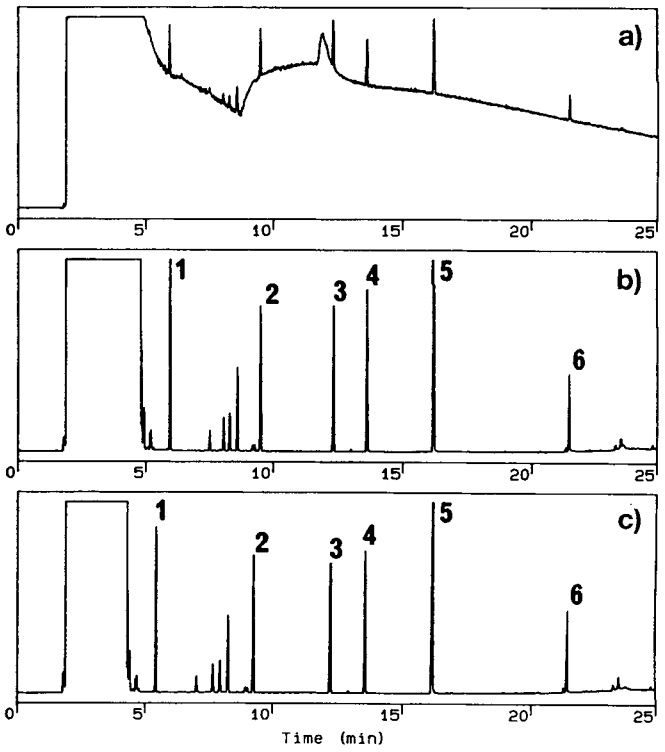

Figure 3

Effect of varying the bleed restrictor flow on the gas chromatograms obtained from chlorinated benzenes and chlorinated phenols: bleed restrictor flow (a) ≈0.017 mL/min, (b) 0.023 mL/min, (c) 0.035 mL/min; 1, chlorobenzene (790 µg/L); 2, 1,3-dichlorobenzene (780 µg/L); 3, 1,3,5-trichlorobenzene (910 µg/L); 4, 2,6-dichlorophenol (930 µg/L); 5, 2,4,5-trichlorophenol (2700 µg/L); 6, pentachlorophenol (870 µg/L).

volume has a considerable effect on the chromatogram. This was evident primarily in the persistently high baseline in Figure 3a caused by slow leakage of the solvent back into the analytical column as the oven temperature was increased. As the length of the bleed restrictor was reduced, the baseline of the chromatogram in Figure 3b returned to normal. At this point, some splitting of the analytes has taken place. Estimates of the split for the chromatogram in Figure 3c placed the loss at 2–4 %. The loss was nearly two orders of magnitude smaller than the gain in the amount of sample injected by use of the diversion. A slight reduction of the peak heights of the analytes is apparent in Figure 3c, although the chromatographic resolution and peak shape remain satisfactory. Earlier work in this laboratory was evidently successful because of the presence, initially undetected, of a very small continuous leak in the solvent splitting valve [3].

A series of chromatograms obtained with increasing divert times are presented in **Figure 4**. As expected, the relative peak heights of the analytes remained constant as long as solvent diversion was stopped before the hexane in the retention gap had fully evaporated. When the solvent diversion was continued until the solvent had completely evaporated, a sharp reduction was observed in the peak heights of those components which move on the retention gap at the oven temperature in use (65 °C) (Figure 4d). The transition was quite rapid, and required accurate timing of the divert valve under routine conditions.

The chromatogram in Figure 4a shows conditions approaching those recommended by *Grob* [1] for large volume on-column injection without divert; under the conditions used here, however, the flow rates with no divert were too low to enable adequate evaporation and transfer of the solvent in the time allotted. Figure 4a, therefore, shows "chair" effects arising as a result of the solvent film entering the separation column. At these low flow rates, the retention gap was not long enough to contain the solvent film. As the flow rate increases, the solvent film is expected to thicken, enabling the retention gap to accommodate a greater volume of solvent per meter [1].

Except for the zero divert time chromatogram of Figure 4a, Figure 4 shows the same behavior as that in the first solvent diversion technique introduced by *Morabito*, *Hiller*, and *McCabe* [3].

Figure 4c illustrates a near optimum divert time. Here, most of the solvent has been removed from the system, but the analytes remain both solvent and thermally focused and the peaks are not observably diminished or distorted. Because the amount of solvent entering the analytical column has been so drastically reduced, the resolution in the early portion of the chromatogram has been significantly enhanced in comparison with that observed by *Grob* [1]. This result is clearly apparent in the recovery data listed in **Table 2**, which shows 60–70 % recoveries for heptane and isooctane in hexane, and 90+% recoveries for higher boiling analytes. With the divert, heptane and isooctane are clearly resolved from each other and from the solvent, despite a difference of only 1° between the boiling points of the analytes.

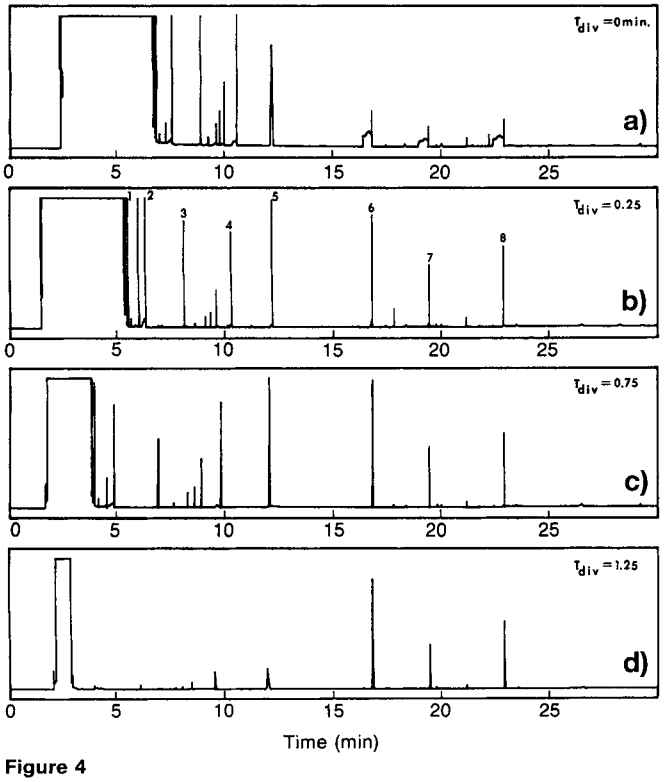

Figure 4

Effect of varying the solvent diversion time on chromatograms obtained from hydrocarbons in hexane: diversion time [min] (a) 0.00, (b) 0.25, (c) 0.75, (d) 1.25; 1, *n*-heptane (630 µg/L); 2, *n*-octane (600 µg/L); 3, *n*-nonane (570 µg/L); 4, *n*-decane (610 µg/L); 5, *n*-undecane (720 µg/L); 6, *n*-tetradecane (660 µg/L); 7, *n*-hexadecane (370 µg/L); 8, *n*-nonadecane (540 µg/L).

Table 2

Recovery and precision data for hydrocarbons in hexane.[a]

Compound	% Recovery Solvent Diverted	No Divert	*RSD*[b]
n-Heptane	65	NA[c]	0.8
Isooctane	62	NA	0.8
n-Nonane	94	91	0.4
n-Decane	98	96	0.6
n-Undecane	100	98	0.4
n-Tetradecane	100	99	1.2
n-Hexadecane	100	100	1.2
n-Nonadecane	102	101	1.4
n-Docosane	97	96	1.0
n-Tetracosane	97	ND[d]	1.1
n-Octacosane	100	ND	2.1

[a] analyte concentrations ranged from 1.84 to 2.12 µg/mL
[b] $n = 4$
[c] analyte not separated from solvent under these conditions
[d] not determined

In fact, even the best grades of hexane obtained commercially showed the presence of contaminant peaks, which suggests the utility of this method for the evaluation of extremely pure solvents. This method might also be very useful for environmental applications: conventional methods routinely require several hundred-fold concentration prior to analysis. In the more common practice of large volume injection on to capillary columns, the first peak resolved from the solvent would normally be nonane [2].

The concentration mechanism occurring here is partially described in the literature [1], and is similar to fractional distillation. As long as hexane remains in the retention gap, the composition of the vapor exiting the retention gap is dominated

by it. Unlike the description given by *Grob*, some of the more volatile analytes are probably partially lost from the vented end of the retention gap as the analytes are initially evenly distributed along its length. As the evaporation proceeds, the bulk of the compounds able to move on the retention gap at these temperatures concentrate on the evaporating edge of the solvent (the end closest to the injection port). Two effects help to recondense these volatile compounds on the solvent evaporation front: firstly, the retention gap is much cooler near to where the solvent is evaporating and, secondly, the solvent provides a film in which the analyte can dissolve. This results in a drastic reduction of the amount of volatile analytes escaping from the solvent vent, but does not eliminate it. This effect is visible here because of the increased resolution in the early portion of the chromatogram which results from use of the solvent diversion system.

A comparison of results obtained from independently heated retention gap and the older solvent diversion system without heating have been presented in **Figure 5**. Figure 5a was obtained after installation of a new retention gap. When the gap was not heated, peak number 6, pentachlorophenol, disappeared into the baseline after approximately fifty injections of the standard (Figure 5b). When the retention gap was heated after closing the divert valve (Figure 1), however, the peak in Figure 5c was identical with that acquired earlier, within the limits shown in Table 2. During the entire study of over four hundred injections the reproducibility did not vary, remaining approximately equal to that listed in Table 2 for the linear hydrocarbons.

Linearity and carry-over for a selected group of chlorobenzenes and chlorophenols are given in **Table 3**. Data for linearity ranges are also listed. Limits of detection are not calculated for these data but are estimated to be between 1 and 5 ppb under these conditions. Carry-over for injections of very high concentrations is less than 0.2 % and generally less than 0.01 %. It might be possible to reduce the carry-over further by the rinsing the injector and retention gap prior to each run; but that has been considered unnecessary for applications to date.

It is important to understand that these results were obtained without any attempt having been made to optimize the timing of the divert or the heated gap for any particular analyte. Optimization of the timing was performed by visual observation of the severe loss of the chlorobenzene peak, and optimization of the heated gap temperature and time was achieved solely from estimates of boiling points and velocities in the gap.

Although the effects of varying the duration and rate of heating, and the final temperature of the heating cycle were not explicitly studied, it is apparent that the heating cycle chosen must effect

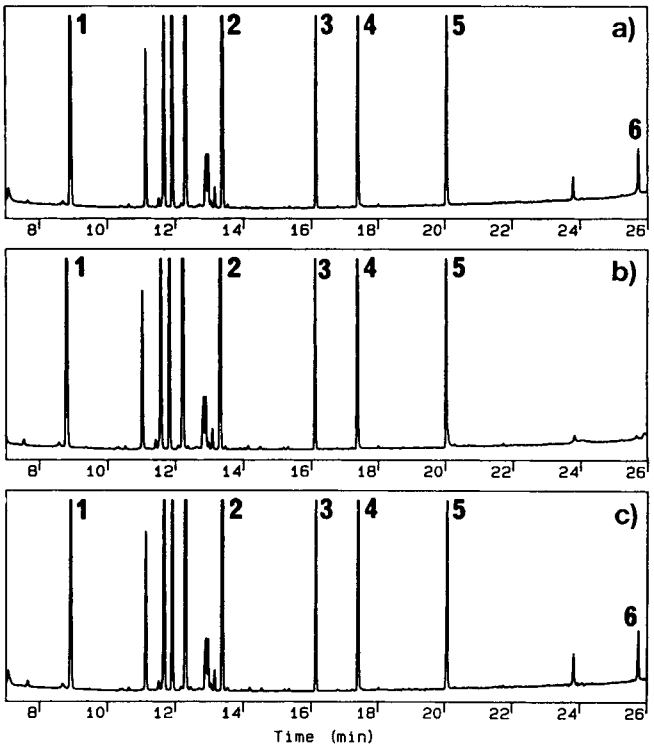

Figure 5

Chromatograms obtained from chlorinated benzenes and chlorinated phenols on large volume injection system with (a) a newly installed retention gap, (b) the same system after >50 injections of a standard solution, (c) the same system as (b) but after >130 injections with the retention gap heated independently; peak identification as for Figure 3.

elution of the retained components from the retention gap. Re-focusing must also be taking place during the entire time the components of interest are eluting from the retention gap. Longer times and higher temperatures should not significantly affect the efficiency of the process or alter peak shapes, although some changes (probably small) in retention time could occur if the length of the heated cycle was varied significantly from injection to injection. The time taken for the retention gap to reach its upper limit was approximately ten to forty seconds. A heating cycle time of ten minutes was chosen by dividing the approximate retention gap volume by the flow rate when not diverting, and then adding the time taken to heat the retention gap plus a modest safety factor. The rate of heating is not expected to be a variable affecting the chromatography.

Table 3

Linearity and carry-over data for several analytes with solvent diversion and independently heated retention gap.

Compound	Equation slope[a]	intercept[a]	R^2	Concentration range [ppb]	Estimated carry-over[b] [%]
Chlorobenzene	1.24	−10.1	0.9998	145–1230	0.06
1,2-Dichlorobenzene	1.38	−14.2	0.9991	142–1210	0.02
1,3,5-Trichlorobenzene	1.53	−3.08	0.9997	6–1420	0.02
2,6-Dichlorophenol	1.51	−1.15	0.9994	6–1445	0.05
2,4,5-Trichlorophenol	1.87	2.96	0.9998	19–4150	0.18
Pentachlorophenol	2.53	13.5	0.9991	6–1350	0.17

[a] $\times 10^{-3}$

[b] Concentrations were between 7 and 25 ppm with detector signal saturated. Estimates of carry-over are upper limits.

A comparison of chromatograms obtained from a standard of EPA 625 base – neutral analytes on the same retention gap (that used for the chlorophenols in Figure 5) with and without heating, is presented in **Figure 6**. When the gap was not heated, the peaks of the higher boiling compounds and the polar nitrosamines show considerable distortion owing to their inability to move on the retention gap when aging or contamination has increased the surface polarity. This complex mixture is easily resolved when the

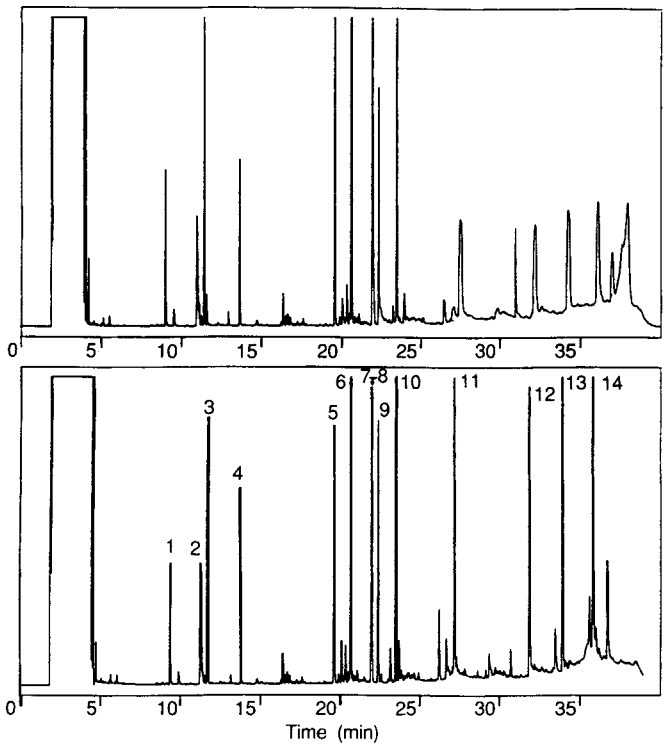

Figure 6

Chromatograms obtained from a standard of EPA 625 base – neutral analytes with (upper) retention gap heated by GC oven and (lower) retention gap heated independently of the column: 1, *N*-nitrosodimethylamine; 2, bis(2-chloroethyl) ether; 3, bis(2-chloroisopropyl) ether; 4, *N*-nitrosodi-*n*-propylamine; 5, bis(2-chloroethoxy)methane; 6, dimethyl phthalate; 7, diethyl phthalate; 8, 4-chlorophenyl phenyl ether; 9, *N*-nitrosodiphenylamine; 10 4-bromophenyl phenyl ether; 11, di-*n*-butyl phthalate; 12, butyl benzyl phthalate; 13, bis(2-ethylhexyl) phthalate; 14, di-*n*-octyl phthalate.

same retention gap is heated prior to the start of temperature programming. The higher boiling compounds, which are poorly resolved without heating, also show greatly improved peak shapes. With such complex mixtures, other proposed means of re-focusing the analytes would have been unwieldy and complicated.

The concentrations of the compounds in Figures 5 and 6 are quite similar to those commonly obtained from the extraction of EPA method 625 prior to *Kuderna-Danish* concentration. Since the method is on-column, the losses of analytes which arise from external volume reduction are eliminated. After several months of use with a large number and wide variety of samples, both real and synthetic, the retention gap was found to cause considerable tailing, even when it was heated (**Figure 7a**). When the gap was cleaned with a series of injections of methanol, dichloromethane, and hexane, while keeping the divert valve open and the analytical column disconnected from the detector the retention

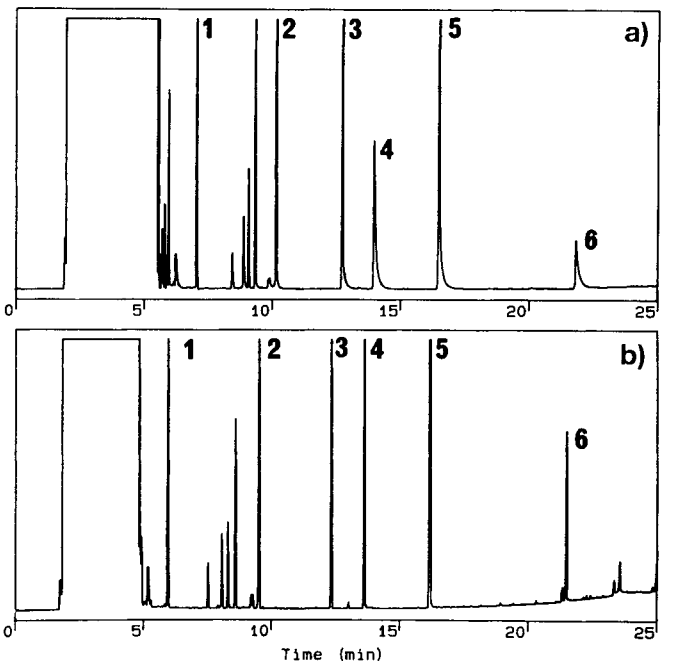

Figure 7

Chromatograms obtained from chlorinated benzenes and chlorinated phenols on large volume injection system with (a) a "dirty" retention gap, (b) the same system after "*in-situ*" cleaning of the retention gap: identification as for Figure 3.

gap regained its performance (**Figure 7b**). Although it may not be possible to use one gap indefinitely, this combination of heating and cleaning has been found to give retention gap lifetimes comparable with those of the analytical columns used under the more common splitless conditions.

Table 2 contains the results of a comparison of recoveries obtained from a single injection of the diversion technique with a heated gap used here, and from a single injection of the same compounds using the technique described by *Grob* (1). The recovery and separation of the more volatile components have been described above, and the data are normalized to *n*-hexadecane. The standard deviations for four injections are comparable with those obtained from on-column injection of a few microliters. The concentrations here are, however, much lower than could be detected by on-column injection of one or two microliters using GC-FID.

Table 4 lists a set of measured, estimated, and calculated values of many of the parameters used in the operation of this system. They have proven useful in understanding the operation of the system and are presented here as an aid in construction of similar systems. Of particular interest is the observation that without the solvent diversion system operating, the volume of the solvent (after evaporation) injected on to the column is nearly three times larger than the total volume of the system. With diversion operating, the volume of the gaseous solvent is only about 10 % of that volume.

One of the intentions of this work was to reduce the effort involved in the preparation of samples for environmental analysis. Although it has been shown how samples of environmentally interesting compounds can be handled in hexane or other similar solvents, application with dichloromethane as the extraction solvent has not yet been successful in routine application. The

Table 4

Estimates and calculated values of volumes and velocities in the LOCI system.

Estimated velocity of carrier gas in retention gap	
open divert valve	150 cm/s
closed divert valve	14 cm/s
Estimated velocity through analytical column	
open divert valve	14 cm/s
closed divert valve	36 cm/s
Ratio of flow through solvent divert restrictor to flow through column (open divert)	29
Volume of retention gap (0.53 mm i.d.)	≈6.5 mL
Volume of column (0.32 mm i.d.	≈2.5 mL
Total volume of chromatographic system (no divert)	≈9.0 mL
Estimated volume of 100 μL hexane (ideal gas, 65 °C, 1 atm.)	23 mL
Ratio of total volume to total solvent volume	0.39
Estimated amount of 100 μL solvent on to column (open divert, 2.5 min)	3.5 μL
Estimated volume of 3.5 μL hexane (ideal gas, 65 °C, 1 atm.)	0.75 mL
Ratio of total column plus retention gap volume to solvent volume entering column with divert	12.0

largest difficulties remaining in this application appear to be the ability to wet the retention gap and the control of the subsequent rate of evaporation of the dichloromethane. This may be accomplished by several methods and may be the subject of a future publication.

4 Conclusion

The method presented here enables injection of several hundred microliters of dissolved analytes on-column, yet prevents the large volume of solvent from interfering either with the separation on the analytical column or with the operation of the detector. The addition of a separate on/off heater to the retention gap forces concurrent focusing of all analytes which have not previously undergone solvent focusing effects. The method is quantitative when concentrations of very low parts per billion are used with flame ionization detection or mass spectrometric detection. Because injection is on-column, analytes are not affected by contamination of the injection port. The method is durable, reproducible, and dependable for large numbers of samples. Experience shows that retention gaps now appear to last about as long as analytical columns did earlier, and the analytical columns may last much longer.

It should be clear to chromatographers that many other modes of operation of the heated and diverted retention gap remain to be exploited. By operating under the conditions described above, for instance, but making repeated injections prior to closing the divert valve and heating, it might be possible to inject volumes of several milliliters on a capillary column with little or no effect on peak shape. Or, by operating the retention gap at temperatures above the boiling point of the solvent, yet at temperatures below the mobility of the analyte, and introducing a continuous flow of analyte, the system could be made to operate as an LC-GC interface similar to that reported by *Cortes et al.* [13]. The latter mode should prove especially interesting to environmental analytical chemists interested in automated "clean-up" of extracts containing contaminants.

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Statement of Patent Rights

The instruments and techniques described in this work are the property of Dow Chemical Company and are protected by US Patents 5,048,322 and 5,001,071.

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