Journal of Chromatographic Science, Vol. 28, December 1990

Evaluation of a Nitrogen-Cooled, Electrically Heated Cold Trap Inlet for High-Speed Gas Chromatography

Robert F. Mouradian* and **Steven P. Levine†**
Department of Environmental and Industrial Health, University of Michigan, Ann Arbor, Michigan 48109

Richard D. Sacks
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Abstract

Gas chromatography has the potential to be a much faster method of separation than is usually realized. If column operating conditions are optimized for speed and injection band width is minimized, some simple separations can be completed in a few seconds. A prototype cryofocusing system for producing narrow injection bands with 0.25-mm i.d. columns is described here. The gas-cooled and electrically heated inlet produces injection bands with widths of about 10–20 ms. In the present study the system is evaluated using mixtures of common organics, including alkanes, aromatics, alcohols, ketones, and chlorinated hydrocarbons. Quantitative trapping and reinjection is achieved for all tested compounds. Coefficients of variation are less than 3% for peak area and less than 0.2% for retention time. Base-line separation of simple mixture is achieved with retention times of less than 10 s. By using the cold trap inlet with a low-dead-volume detector and a high-speed electrometer, the efficiency available from commercial capillary columns can be better utilized, and retention times for some routine separations may be reduced to a few seconds.

Introduction

Gas chromatography (GC) is often used for routine, repetitive analysis of simple mixtures. For some of these applications, the use of 2–5-m capillary columns operated at linear velocities of 100–200 cm/s offers the possibility of greatly decreased analysis times. This potential for high-speed analysis was first demonstrated by Desty in 1965, when he reported the separation of as many as 15 components in less than 2 s (1). Since then, a number of studies have appeared which discuss both the theoretical and practical aspects of high-speed GC (2–7).

Many of these studies have emphasized the importance of minimizing extracolumn band broadening and have stressed the use of extremely narrow, 50–100-μm i.d. columns. Although these extremely small diameter columns do provide the highest separation speed, it is often possible to achieve adequate high-speed separation using columns with diameters up to 0.25 mm. Because these larger diameter columns have greater sample capacity, they may be useful in a wider range of routine analytical applications.

An extended form of the Golay equation, first presented by Gaspar (4) and more recently discussed by Villalobos (8), indicates that under optimal conditions a 0.25-mm i.d. column with a 0.1-μm stationary phase should be capable of achieving 5000–7000 effective plates with retention times of 5–10 s. Although this number is low compared to most capillary systems, it is comparable to the number of plates achieved by many packed-column systems with retention times of several minutes or more. It follows, therefore, that some routine GC separations that are currently performed on packed columns or nonoptimized open tubular columns could be performed much more quickly with a capillary system that is optimized for speed.

While the theoretical potential of capillary columns for high-speed analysis is well known, limitations in commercially available equipment, especially inlet systems, have prevented general application of high-speed techniques. With most commercial instruments, the major factors that limit analysis speed are the width of the initial band produced by the inlet system and the response time of the electrometer. Efficient separation with retention times of 5–10 s and a column diameter of 0.25 mm requires an initial band width of about 20 ms or less and an electrometer response time of about 5 ms. For purposes of comparison, most capillary GC systems produce injection band widths of 50–500 ms and feature electrometer response times of 150 ms or longer. Smaller injection bands can be obtained with a conventional inlet splitter operated at high flow rates. However, under these conditions sample size is significantly reduced and it is often difficult to obtain acceptable reproducibility and avoid discrimination effects.

In response to the requirement for narrow injection bands, a number of experimental inlets have been described. Among designs that have been successfully demonstrated are systems based on fluid logic gates (5,9–11) and mechanical inlets, including a modified six port rotary valve (12) and a piston-driven sliding valve which acts as a high-speed splitter (13).

Other reports (14–16) described a prototype cold trap that was used as a vapor collection device and may also serve as a focusing system for rapid analysis of simple mixtures. The design, which expanded on the innovative work of Hopkins and Pretorius (17), featured a stainless steel cold trap that was cooled

* Current address: National Institute for Occupational Safety and Health, 4676 Columbia Parkway, R-11, Cincinnati, Ohio 45226.
† Author to whom correspondence should be addressed.

by a continuous flow of cold nitrogen and was resistively heated by a current pulse from a capacitor discharge power supply.

More recently, van Es et al. described a fast GC system that utilized a similar inlet (18). In their design, a 50-μm capillary column was used for the separation. The upstream end of the column was threaded through a larger diameter, aluminum clad capillary, which served as the heating element. Their trap was also cooled by a flow of nitrogen gas and was heated by running a current from a transformer through the aluminum coating on the outer capillary. Using this system, the authors observed initial band widths as small as 1 ms.

Although each of the previous designs was shown to produce narrow injection bands, most were not evaluated for use in routine analytical procedures, and in some cases they do not appear to be practical for a wide range of applications. In this report, we present the results from a systematic, quantitative evaluation of an improved cold trap inlet that may be useful for reducing analysis times in many routine applications. Data concerning trapping efficiency for a variety of organics, trap heating characteristics, and chromatographic performances are presented. The system described could be added to most capillary GC systems, and in many cases it would allow the analyst to shorten retention times without loss of resolution or reproducibility.

Experimental

Description of the cold trap

The cold trap system is shown schematically in Figure 1. The trap chamber was placed inside the oven of a Varian 3700 GC. A conventional splitter system, operated at split ratios ranging from 50:1 to 500:1, was used as the primary inlet. All injections were made with a Hewlett-Packard 7673A autosampler. As indicated in the diagram, the splitter outlet was connected to a 50-cm × 0.20-mm i.d. untreated fused-silica capillary, which served as a transfer line between the primary inlet and the cold trap.

The downstream end of the transfer line was connected to a 9-cm × 0.25-mm i.d. Monel 400 capillary, which served as the actual cold trap. A slight coil in the trap tubing allowed for length changes associated with cooling and heating during the trapping and reinjection cycle. The trap tubing was enclosed in the lower half of a small, two-chambered Teflon box. A flow of cold nitrogen entered the upper chamber and then moved through a baffle into the lower chamber to cool the interior of the box. This baffled two-chamber design was developed to minimize problems with nonuniform cooling.

The nitrogen was cooled by running it through a coil of copper tubing immersed in liquid nitrogen. Downstream from the liquid nitrogen bath, the internal diameter of the cooling line was reduced from ¼ in. to 1/16 in. This allowed pressure to develop in the cooling coil and resulted in the formation of a small amount of liquid nitrogen inside the cooling line. This mixture of liquid and gaseous nitrogen sprayed into the upper chamber of the Teflon box and provided more efficient cooling than could have been achieved with a similar system operated at atomospheric pressure. The trap temperature was controlled by adjusting the nitrogen pressure and was monitored with a thermocouple. This design allowed the trap temperature to be easily controlled to within ±5°C at temperatures as low as −150°C.

At the end of the Teflon chamber, the trap tubing was connected to a short length of multistrand copper wire, which served as an electrical contact to allow resistance heating of the trap. The copper wire was wrapped tightly around the trap tubing, soldered in place, and then covered with electrical tape. The power supply used to heat the trap for reinjection was similar to that described in an earlier publication (15). The design includes two circuits, a variable-voltage capacitor discharge system for rapid heating and a transformer-based sustainer circuit that was used to prevent the trap from cooling too quickly. The capacitor discharge system supplied a 10–20 msec pulse of up to 75 A at 35–75 V.

Operating conditions and chromatographic equipment

All chromatograms were collected isothermally at column temperatures of 35–60°C from a 5-m × 0.25-mm i.d. fused-silica column with a 0.1-μm bonded methylsilicone stationary phase (Quadrex). The carrier gas was hydrogen, which was supplied at a flow rate of 2.5–3 mL/min to produce linear velocities of 140–175 cm/s. The injector and detector were heated to 225°C. A Varian flame ionization detector was used in all experiments. To minimize the effective dead volume, the column was moved close to the base of the flame.

Test mixtures were prepared either without solvent or in high-purity CS_2 provided by the Dow Chemical Company. The injection volume was 2.5 μL in all cases, and the split ratio ranged from about 50:1 to 500:1 depending on the sample concentration.

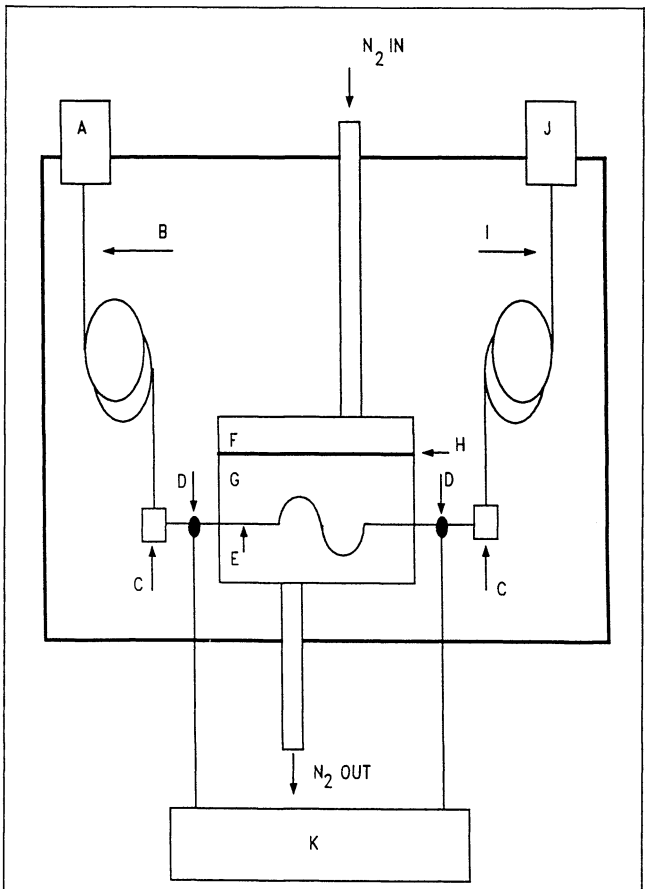


Figure 1. Diagram of the cold trap inlet system. (A) Syringe injection port, (B) fused silica transfer line, (C) low-dead-volume unions, (D) electrical contacts, (E) trap tube, (F) upper chamber of the cold trap, (G) lower chamber of the cold trap, (H) baffle, (I) capillary column, (J) flame ionization detector, (K) capacitor discharge power supply.

Chromatographic data were collected at frequencies ranging from 200 to 400 Hz, depending on the peak width. A custom-built electrometer-amplifier with a response time of 5 ms was provided by HNU Systems. Computer hardware included an 80286/287-based personal computer and a Data Translation DT2801 analog-to-digital converter. Data acquisition was controlled by using Labtech Notebook (Laboratory Technologies), and the data was analyzed with software developed in our laboratory.

Trap temperatures were measured with 36 gauge type J thermocouples (Omega) spot welded to the approximate center of the trap tubing. The thermocouple output was amplified with a high-speed differential amplifier built in-house and was then directed to the analog-to-digital converter and sampled at 500 Hz.

Results and Discussion

Design considerations

A number of design considerations were found to be important in determining the durability and performance of the system. The quality of the electrical contacts is especially important in determining trap life. In order to provide a low-resistance electrical pathway, the contacts should cover as large a surface area as possible. It is also important that the trap tubing not be held too rigidly, or mechanical stresses caused by temperature-related length changes will tend to shorten the trap life. A standard injector septum with a small hole through the center was found to provide a good seal at the end of the cold trap without holding the tube too tightly.

The choice of trap material and dimensions also affects durability and reinjection performance. An ideal material would have high electrical resistivity, low chemical activity, and a low coefficient of thermal expansion; would be highly malleable; and would not work-harden. A number of materials, including stainless steel, nickel, platinum, Monel 400, and an alloy of 30% copper–70% nickel, were evaluated for use as trap tubes. Although platinum appeared to have the most desirable characteristics, the cost was considered prohibitive, and the work reported here was done with a trap made of Monel 400. Stainless steel, which was used in some early studies (14,15), is the least expensive and most readily available material. However, it is the least desirable choice because of its tendency to work-harden and become brittle.

Another factor affecting trap durability and performance is the wall thickness of the trap tubing. Increasing wall thickness will obviously increase the strength and durability, but the decreased electrical resistivity and increased thermal mass make rapid heating and cooling more difficult. For a trap made of hard-tempered Monel 400 with an internal diameter of 0.25 mm, a wall thickness of 0.18 mm provided a good combination of strength and performance.

Trapping and reinjection efficiency

Cold traps have been used in GC for many years (19–21). Even under optimal conditions, the efficiency of open tubular capillary trap designs has been questioned (22). Since the short, open tubular trap used in these experiments may be less efficient than some other designs, a careful evaluation of trapping efficiency was necessary.

In order to test trapping and reinjection efficiency, samples were injected without using the cold trap, and average peak areas were calculated for each compound. Identical injections were then made with trapping and reinjection at various trap temperatures, and the peak areas were compared to those obtained without use of the cold trap. In addition to comparing peak areas obtained with and without trapping, the FID response was monitored during the entire process to allow any breakthrough of the sample to be detected. Because the sample concentrations were very high, even a small amount of breakthrough could be noticed.

Figure 2 presents an example of the results obtained during a trapping experiment performed with a mixture of seven aromatics. The initial syringe injection was made at the time marked zero, and the trap heater was triggered at 40 s. Tracing D was obtained without cooling the trap and shows the chromatogram that would be obtained with zero trapping efficiency. Tracing C shows the chromatogram obtained when the trap temperature was dropped to 0°C. The sample was not efficiently trapped, but there was a noticeable deterioration of the initial chromatogram. Tracing B shows the chromatogram obtained with a trapping temperature of −50°C. Under these conditions the sample was partially retained, producing a general elevation of the base line. When the heater was triggered, the trapped portion of the sample was reinjected to produce the chromatogram that starts at about 45 s. Tracing A shows the chromatogram obtained when the trap was cooled to −100°C. At temperatures this cold or colder, trapping was quantitative with recoveries of 100% and no detectable breakthrough. The chromatogram produced by reinjection under these conditions is therefore comparable to that shown in Tracing D.

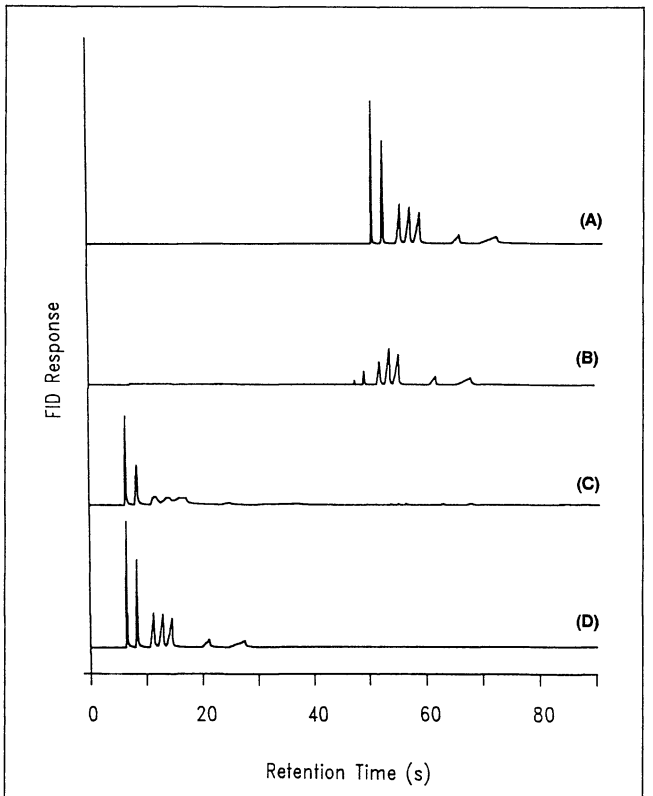


Figure 2. Chromatograms showing breakthrough and reinjection at various trap temperatures. All reinjections were made with a 55-V pulse approximately 40 s after the initial injection; (A) trapped at −100°C, (B) trapped at −50°C, (C) trapped at 0°C, (D) without trapping. Peaks: (1) benzene, (2) toluene, (3) chlorobenzene, (4) *o*-xylene, (5) *m*-xylene, (6) 4-ethyltoluene, and (7) 1,2-dichlorobenzene.

Trapping efficiencies for a number of compounds that are important in environmental monitoring or in industry are presented in Table I. At temperatures of −100°C or colder, each of the tested compounds was effectively trapped and reinjected. Apparent trapping efficiencies of greater than 100% are attributed to a transient decrease in the split ratio caused by condensation of the sample in the cold trap. These variations in trapping efficiency for different compounds may introduce some error during quantitative analysis of liquid mixtures with split injection. This effect has been described by other authors (23) and can be eliminated by using a similar system with a gas sampling loop and no splitter. As discussed in the following section, peak area reproducibility for replicate injections was very good, with coefficients of variation ranging from 1 to 5% or less in all cases.

In addition to the results presented in Table I, trapping efficiency was also measured for 1% solutions of aromatics prepared in CS_2. The trapping efficiencies obtained in those experiments were not significantly different than those measured without solvent.

As indicated by the data presented in Table I, many materials can be effectively trapped and reinjected at −100°C. However, trapping behavior is not easily predicted on the basis of boiling point or freezing point, and in most cases an effective temperature must be experimentally determined for each type of sample. Highly volatile materials, which may be gases at room temperature, and low-volatility materials, which may be difficult to revaporize, have not yet been tested and may be difficult to trap and reinject with this system.

In a similar test, Graydon (22), using open tubular traps operated at liquid nitrogen temperatures, reported trapping efficiencies as low as 14% for some highly volatile compounds. However, for materials with boiling points similar to those used here, trapping efficiencies were greater than 90%.

Along with the choice of test materials, the duration of the trapping cycle may also be an important consideration. In the application described here, the trapping cycle normally lasts only 5–10 s so any slow loss of the trapped material will be negligible.

The overall efficiency of the cold trap as a high-speed injection system is also dependent on how fast the sample can be revaporized and on the stability of the sample during the trapping and reinjection process. Figure 3 shows the trap temperature during heating cycles that were initiated at various reinjection voltages. Each data point on the graph represents the average reading from five heating cycles and has a relative standard deviation of less than ±10°C. Some of the early data points are missing because of interference from the initial discharge of the capacitors. This problem became more severe at higher voltages.

At an initial capacitor charge of 40 V (D), the trap temperature increased from −170°C to a peak of −50°C in about 12 ms. Charging the capacitors to a higher initial voltage resulted in both faster heating and higher maximum temperatures. At an initial charge level of 55 V (A), the trap reached a peak temperature of nearly 200°C in about 20 ms.

The effect of capacitor charge on reinjection efficiency was also investigated for those compounds listed in Table I. The results indicate that, for the materials used in these tests, maximum efficiency was achieved at voltages of 50–55 V, which corresponds to peak temperatures of about 150–200°C. As expected, reinjection at lower voltages results in wider peaks and may not vaporize the less volatile components of the mixture being analyzed. This selective vaporization of less volatile components may present a problem for some separations. However, it could also be useful in cases where the operator wishes to analyze trace levels of a highly volatile component with minimal interference from a less volatile solvent or from other components of the sample.

Table I. Trapping and Reinjection Efficiency for 23 Compounds Tested at Three Different Trapping Temperatures*

Compound	Boiling point (°C)	Melting point (°C)	Efficiency (%) Trapping temperature (°C) −50	−100	−150
Isoprene	34	−146	2	88	134
Pentane	36	−130	1	48	108
Dichloromethane	40	−95	3	123	129
Acrolein	53	−87	12	119	123
Chloroform	62	−64	4	143	132
Methanol	65	−94	7	98	99
Hexane	69	−95	3	101	105
Tetrachloromethane	77	−23	7	124	86
Acrylonitrile	77	−83	13	124	127
2-Butanone	80	−86	9	111	102
Benzene	80	5	4	98	†
Propanol	97	−127	104	113	113
Heptane	98	−91	16	107	113
Isooctane	99	−107	17	116	119
Toluene	110	−95	27	112	†
Butanol	117	−90	110	110	95
Tetrachloroethylene	121	−19	27	122	115
Octane	126	−57	67	104	100
Chlorobenzene	132	−46	89	113	†
m-Xylene	139	−48	105	112	†
o-Xylene	144	−26	106	110	†
Nonane	151	−51	103	103	100
4-Ethyltoluene	162	−62	107	112	†

* n = 5 for each compound.
† Not tested.

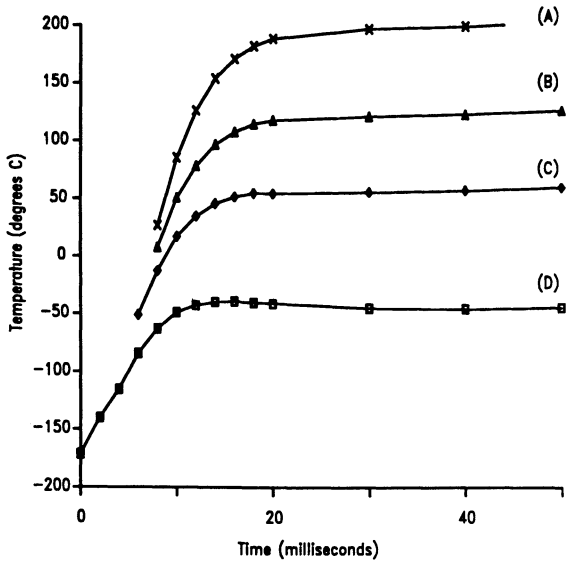


Figure 3. Trap temperature profiles during reinjection at various voltages. Each data point represents the average of five readings with the relative standard deviation of less than ±10°C in all cases. At higher voltages the early data points are lost due to interference form the capacitor discharge power supply. (A) 55 V, (B) 50 V, (C) 45 V, (D) 40 V.

If reinjection voltage is increased above 60 V, recovery efficiency tends to decrease. At these higher reinjection voltages, trap temperatures can rise to 350°C or hotter. Under these conditions, late-eluting peaks often become smaller as new, early-eluting peaks appear. This is apparently caused by pyrolysis of the larger molecules. Even for more stable compounds, recovery efficiency may decrease at higher voltages. This is believed to occur because rapid expansion of gases during the heating cycle increases pressure in the trap tubing and forces some of the sample to flow backwards into the splitter. This effect was more dramatic in earlier designs that used a shorter transfer line between the splitter and cold trap.

Because the thermocouple response may involve a signficant lag, the true heating rate may actually be faster than that indicated. The cooling rate, however, was slow relative to thermocouple response times, so peak temperature measurements are thought to be accurate. Despite the response lag inherent in thermocouple-based temperature measurements, the data presented here indicate that the trap does heat quickly enough to produce injection bands with widths of 20 ms or less, which is adequate for rapid analysis on a 0.25-mm column.

Chromatographic performance

The effect of cold trapping on the separation of a test mixture containing benzene, toluene, chlorobenzene, and *m*-xylene is illustrated in Figure 4. Tracing A shows a chromatogram obtained when the injected sample was trapped at −100°C and reinjected with a 55-V pulse. Tracing B represents the chromatogram obtained with syringe injection and no cooling of the trap. Although the sample moves through the trap system under these conditions, the use of low-dead-volume unions and trap tubing that matches the internal diameter of the column minimizes peak broadening in that area. Removal of the trap tubing was found to produce no improvement in performance for the nontrapped samples.

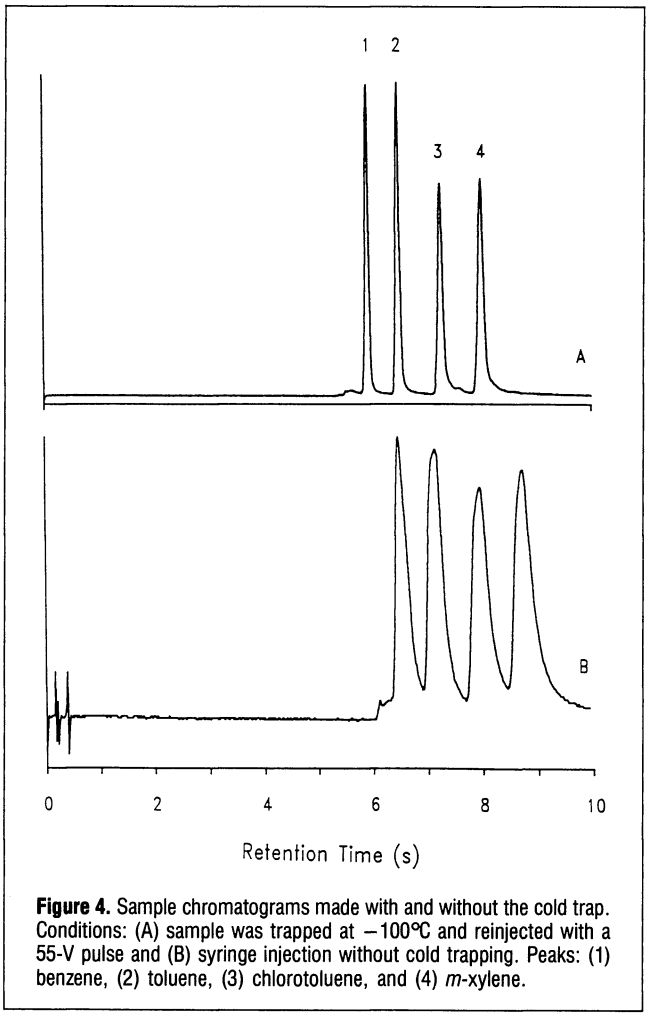


Figure 4. Sample chromatograms made with and without the cold trap. Conditions: (A) sample was trapped at −100°C and reinjected with a 55-V pulse and (B) syringe injection without cold trapping. Peaks: (1) benzene, (2) toluene, (3) chlorotoluene, and (4) *m*-xylene.

As Figure 4 illustrates, trapping and reinjection produces noticeably sharper peaks and an improvement in resolution. The retention times for the four major peaks shown in tracing A are 5.98 s, benzene; 6.54 s, toluene; 7.33 s, chlorobenzene; and 8.07 s, *m*-xylene. For benzene, cold trapping reduced the peak width at half height from about 230 ms to 75 ms. The number of effective theoretical plates for *m*-xylene was increased from about 50 for the untrapped sample to 2500 for the trapped sample. Although the improvement is clearly demonstrated in this example, the effect is even more dramatic when retention times are shorter and when conditions are optimized for speed.

To test the system repeatability, a series of 24 replicate chromatograms was run over a 90-min time period using the same mixture of benzene, toluene, chlorobenzene, and *m*-xylene. The coefficients of variation for peak areas measured with and without use of the cold trap are presented in Table II. These data indicate that the cold trap introduces no significant increase in variability for peak area. In fact, for some separations, the improved peak shape and resolution may result in less integration error and improved repeatability.

While retention time is not considered a reliable identification tool in the analysis of unknown mixtures, it is often useful in applications involving routine or repetitive analysis of samples from a known source. Using the computer-controlled high-speed inlet, standard deviations of less than 0.01 s were recorded for retention times ranging from 5 to 10 s.

Although the system described here should be considered a prototype, this study indicates that it can significantly improve the injection band widths produced by a conventional capillary inlet system. The smaller injection band produced by the cold trap inlet improves chromatographic performance and increases the number of available plates for retention times of less than 10–15 s. By using a cold trap inlet similar to the one described here with a GC system optimized for speed, it may be possible to signficantly reduce retention times without loss of chromatographic quality. For some routine, repetitive applications this could result in a reduced sample turnaround time and in significant cost savings.

Acknowledgments

The authors acknowledge Lauri Mendenhall and George Capps of Prototype Design Inc. for engineering and technical

Table II. Coefficients of Variation for Peak Areas Measured from Chromatograms Made With and Without the Cold Trap

	Benzene	Toluene	Chloro-benzene	*o*-Xylene
With trapping (n = 24)	2.4%	1.8%	1.9%	1.5%
Without trapping (n = 8)	1.6%	1.5%	1.9%	7.3%

assistance in the development of the capacitor discharge power supply and temperature measurement devices. Dr. Sam Norwood is also acknowledged for his support at the inception of this project. Dr. Colin Poole is acknowledged for his assistance in reviewing and commenting on the manuscript.

This research was supported by The Centers For Disease Control, National Institute for Occupational Safety and Health Grant R-01-0H02303, U.S. Environmental Protection Agency Grant R814389-01, and the Dow Chemical Company Health and Environmental Studies Laboratory.

References

1. D.H. Desty. Capillary columns: Trials tribulations and triumphs. In *Advances in Chromatography,* Vol 1, J.C. Giddings and R.A. Keller, Eds. Marcel Dekker, New York, 1965, pp. 199–228.
2. D.H. Desty, A. Goldup, and W.T. Swanton. Performance of coated capillary columns. In *Gas Chromatography,* N. Brenner, J.E. Callen, and M.D. Weiss, Eds. Academic Press, New York, 1962, pp. 105–135.
3. J.C. Sternberg. Extra column contributions to chromatographic band broadening. *Advances in Chromatography,* Vol 2, J.C. Giddings and R.A. Keller, Eds. Marcel Dekker, New York, 1966, pp. 203–270.
4. G. Gaspar, R. Annino, C. Vidal–Madjar, and G. Guiochon. Influence of instrumental contributions on the apparent column efficiency in high speed gas chromatography. *Anal. Chem.* **50:** 1512–18 (1978).
5. G. Gaspar, P. Arpino, and G. Guiochon. Study in high speed gas chromatography. *J. Chromatogr. Sci.* **15:** 256–61 (1977).
6. A. van Es, J. Janssen, R. Bally, C. Cramers, and J. Rijks. Sample introduction in high speed capillary gas chromatography; Input band width and detection limits. *HRC&CC* **10:** 273–79 (1987).
7. C.P.M. Schutjes, E.A. Vermeer, J.A. Rijks, and C.A. Cramers. Increased speed of analysis in isothermal and temperature-programmed capillary gas chromatography by reduction of the column inner diameter. *J. Chromatogr.* **253:** 1–16 (1982).
8. R. Villalobos and R. Annino. The computer aided optimization of capillary columns for minimum time analysis and minimum detectability. *HRC&CC* **12:** 149–60 (1989).
9. R.L. Wade and S.P. Cram. Fluidic logic sampling and injection system for gas chromatography. *Anal. Chem.* **44:** 131–39 (1972).
10. R. Annino and J. Leone. The use of coanda wall attachment fluidic switches as gas chromatographic valves. *J. Chromatogr. Sci.* **20:** 19–26 (1982).
11. C.P.M. Schutjes, C.A. Cramers, C. Vidal–Madjar, and G.J. Guiochon. Fast fluidic logic injection at pressures up to 25 bar in high-speed capillary gas chromatography. *J. Chromatogr.* **279:** 269–77 (1983).
12. R.J. Jonker, H. Poppe, and J.F.K. Huber. Improvement of speed of separation in packed column gas chromatography. *Anal. Chem.* **54:** 2447–56 (1982).
13. R. Tijssen, N. van den Hoed, and M.E. van Kreveld. Theoretical aspects and practical potentials of rapid gas analysis in capillary gas chromatography. *Anal. Chem.* **59:** 1007–1015 (1987).
14. B.A. Ewels and R.D. Sacks. Electrically heated cold trap inlet system for high-speed gas chromatography. *Anal. Chem.* **57:** 2774–79 (1985).
15. L.A. Lanning, R.D. Sacks, R.F. Mouradian, S.P. Levine, and J.A. Foulke. Electrically heated cold trap inlet system for computer-controlled high-speed gas chromatography. *Anal. Chen.* **60:** 1994–96 (1988).
16. R.F. Mouradian, S.P. Levine, R.D. Sacks, and M. Spense. Measurement of organic vapors at sub-TLV concentrations using fast gas chromatography. *Amer. Indus. Hyg. Assoc. J.* **51:** 90–95 (1990).
17. B.J. Hopkins and V.J. Pretorius. Rapid evaporation of condensed gas chromatographic fractions. *J. Chromatogr.* **158:** 465–69 (1978).
18. A. van Es, J. Janssen, C. Cramers, and J. Rijks. Sample enrichment in high speed narrow bore capillary gas chromatography. *HRC&CC* **11:** 852–57 (1988).
19. G. Schomburg, H. Husmann, and F.J. Weeke. Aspects of double-column gas chromatography with glass capillaries involving intermediate trapping. *J. Chromatogr.* **112:** 205–217 (1975).
20. J.A. Rijks, J. Drozd, and J. Novak. J. Versatile all-glass splitless sample-introduction system for trace analysis by capillary gas chromatography. *J. Chromatogr.* **186:** 167–81 (1979).
21. D. Kalman, R. Dills, C. Perera, and F. DeWalle. On-column cryogenic trapping of sorbed organics for determination by capillary gas chromatography. *Anal. Chem.* **52:** 1993–94 (1980).
22. J.W. Graydon and K. Grob. How efficient are capillary cold traps? *J. Chromatogr.* **254:** 265–67 (1983).
23. K. Grob, Jr. and H.P. Neukom. Dependence of the split ratio on column temperature in split injection capillary gas chromatography. *J. Chromatogr.* **236:** 297–306 (1982).

Manuscript received January 22, 1990;
revision received May 10, 1990.

Organotin Compounds and Tungsten Tin Complexes

Liquid Chromatographic Separations

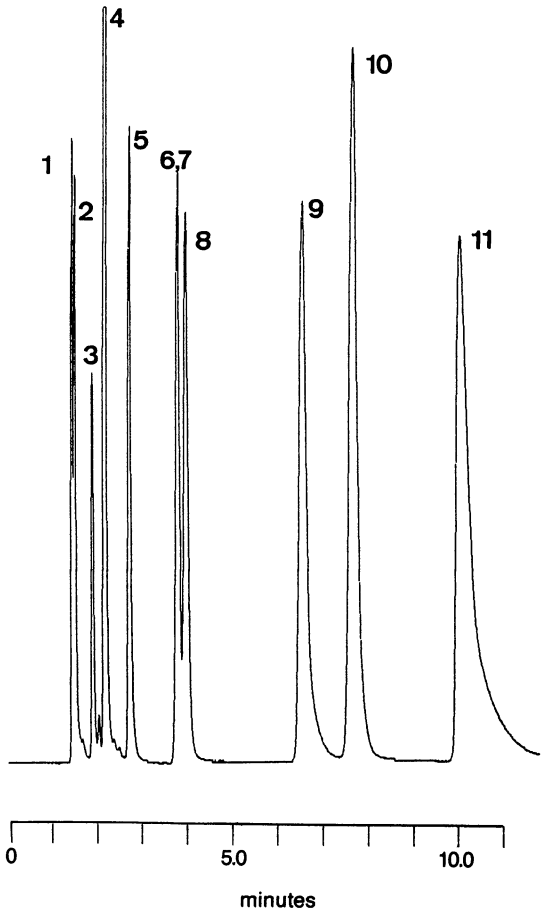
LC126 Organotin Compounds

Conditions:

Column:	3-μm RoSil CN (Bio-Rad RSL N.V.), pretreated with ICl
Column dimensions:	0.46 × 15 cm
Mobile phase:	90:6:4 hexane–tetrahydrofuran–acetonitrile
Flow rate:	1 mL/min
Detection:	220 nm UV, time constant 50 ms

Peaks:

1 $(C_2H_5)_4Sn$
2 $(CH_3)_4Sn$
3 $(iC_3H_7)_4Sn$
4 $(C_6H_5)_4Sn$
5 $(C_2H_5)_3SnCl$
6 $(C_6H_5)_3SnCl$
7 $(CH_3)_3SnCl$
8 $(iC_3H_7)_2SnCl_2$
9 $(C_6H_5)_2SnCl_2$
10 $(C_2H_5)_2SnCl_2$
11 $(CH_3)_2SnCl_2$



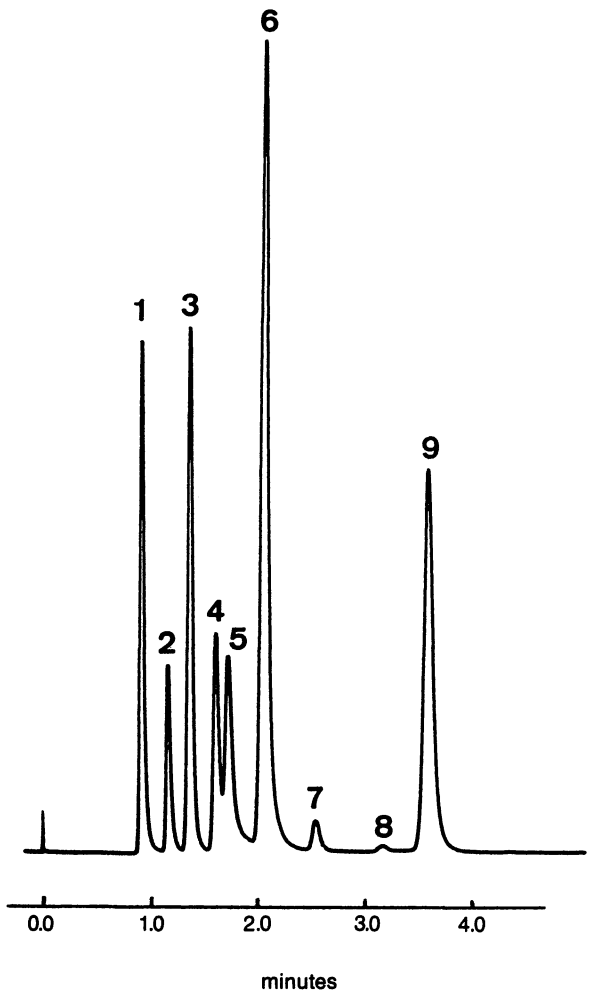
LC127 Tungsten Tin Complexes

Conditions:

Column:	3-μm RoSil CN (Bio-Rad RSL N.V.)
Column dimensions:	0.46 × 15 cm
Mobile phase:	10:90 tetrahydrofuran–hexane
Flow rate:	2 mL/min
Detection:	220 nm UV

Peaks:

1 $W(CO)_6$
2 $(i\text{-}C_4H_9)_3SnW(CO)_3(\pi\text{-}C_5H_5)$
3 $(CH_3)_3SnW(CO)_3(\pi\text{-}C_5H_5)$
4 $(i\text{-}C_4H_9)_2SnClW(CO)_3(\pi\text{-}C_5H_5)$
5 $W_2(CO)_6(\pi\text{-}C_5H_5)_2$
6 $(CH_3)_2SnClW(CO)_3(\pi\text{-}C_5H_5)$ + $(i\text{-}C_4H_9)_2Sn(WICO)_3(\pi C_5H_5)_2$
7 $(CH_3)_2Sn(W(CO)_3\pi\text{-}C_5H_5)_2$
8 unidentified
9 $ClW(CO)_3(\pi\text{-}C_5H_5)$



LC126 and LC127 are reproduced by permission of Dr. Chris Dewaele of Bio-Rad RSL N.V. (Begoniastraat 5, B-9731 Eke, Belgium).
Atlas Consultant: Leslie S. Ettre.

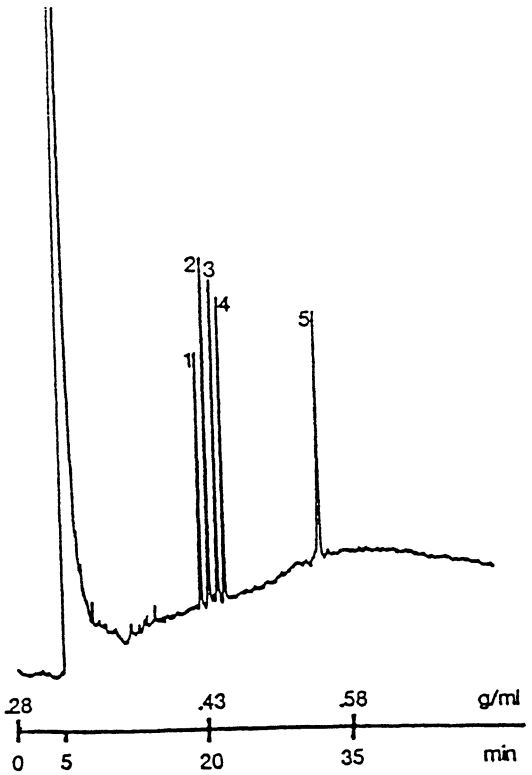
Barbiturates, Free Fatty Acids

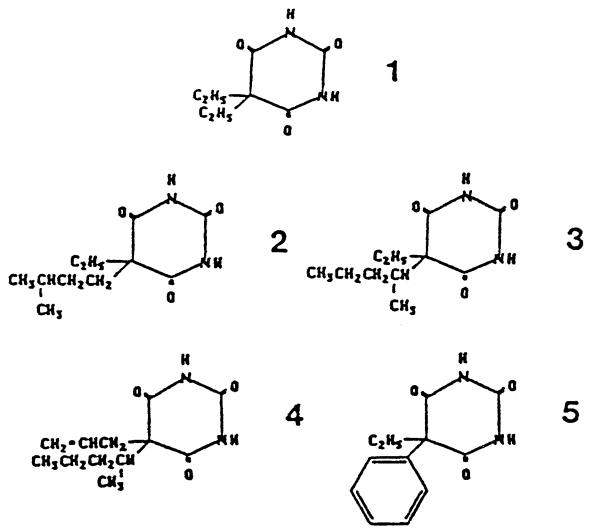
Supercritical Fluid Separations

SFC96 **Barbiturates**

Conditions:

Column phase:	Glyme 1A
Column dimensions:	0.15-μm film thickness, frit restrictor 10 m × 0.05 mm i.d.
Mobile phase:	CO_2
Density:	as shown
Column temperature:	120°C
Detector:	flame ionization (350°C)
Sample introduction:	200-nL loop (timed split), 0.25 mg/mL

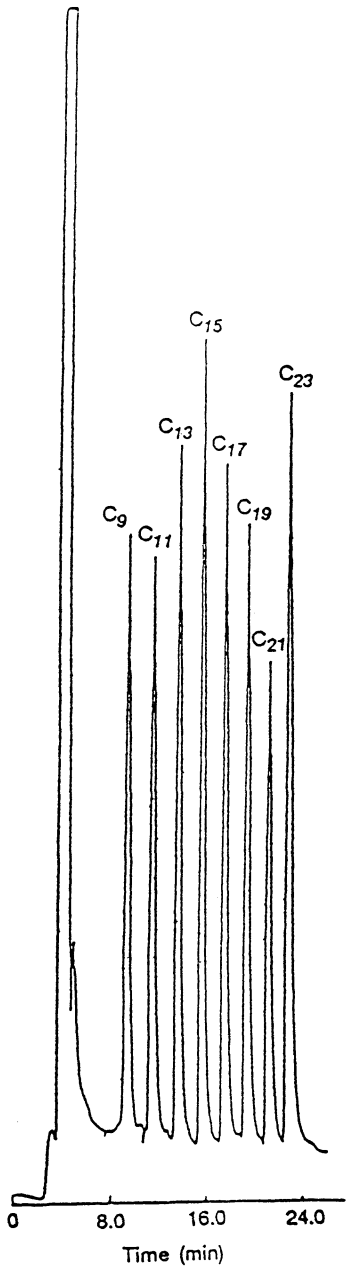




SFC97 **Linear Saturated Free Fatty Acids**

Conditions:

Column phase:	Omni-PAC™ - μmPRN-300 (Dionex) polystyrene
Column dimensions:	150 × 0.75 mm i.d., 5-μm particle
Pressure:	200 atm to 415 atm at 8 atm/min (frit restrictor)
Mobile phase:	CO_2
Column temperature:	170°C
Detector:	flame ionization (375°C)
Sample introduction:	timed split



SFC96 is reproduced by permission of Christine Rouse and M.L. Lee, Brigham Young University (Department of Chemistry, Provo, UT 84602) and SFC97 is reproduced by permission of Frank Yang, Dionex Corporation (1228 Titan Way, Sunnyvale, CA 94086).