HIGH SPEED GAS CHROMATOGRAPHY FOR AIR MONITORING

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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. In the work described here the system was evaluated using common organics including alkanes, aromatics, alcohols, ketones and chlorinated hydrocarbons. Quantitative trapping and reinjection was achieved for all tested compounds. Limits of detection (LOD) for many compounds, based on a 1 cm^3 gas sample, were less than 1 ppb, but for one carbon-chlorocarbons the LOD when using a flame ionization detector was inadequate. 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 to 5 m capillary columns operated at linear velocities of 100 to 200 cm/s offers the possibility of greatly decreased analysis times. This potential for high speed analysis has been documented in the literature (1-7). Under optimal conditions, a 0.25 mm i.d. column should be capable of achieving 5000 to 7000 effective plates with retention times of 5 to 10 seconds (4,8). Although this number of plates 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. Therefore, some routine GC separations that are currently performed using packed columns or non-optimized open tubular columns could be performed much faster 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 to 10 seconds 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 to 500 ms and feature electrometer response times of 150 ms or longer.

In response to the requirement for narrow injection bands, a number of experimental inlets have been described (5, 9-13). Our group has described a prototype cold trap that was used as a vapor collection device and which may also serve as a focusing system for rapid analysis of simple mixtures (14-15). The design reported by our group, which expanded on the innovative work of Hopkins and Pretorius (16), featured a cold trap that was cooled by a continuous flow of cold nitrogen, and was resistively heated using a current pulse. This design was a marked improvement over that reported earlier, which had a number of unrecognized serious flaws that prevented reliable and/or quantitative operation (17-18). More recently, van Es et al described a fast GC system that utilized a similar inlet (19). In their design, a 50 micron capillary column was used for the separation.

Experimental Section

The design and operation of the cold trap is given in detail elsewhere (14,15), and is shown schematically in Figure 1.

Operating conditions and chromatographic equipment. All chromatograms were collected isothermally at column temperatures of 35 to 60 °C using a 5 m long, 0.25 mm i.d. fused silica column with a 0.1 micron bonded methyl silicone stationary phase (Quadrex). The carrier gas was hydrogen, which was supplied at a flow rate of 2.5 to 3 ml/min to produce linear velocities of 85 to 102 cm/s. The injector and detector were heated to 225 °C. A flame ionization detector (FID) was used in all experiments. To minimize the effective dead volume, the column was moved close to the base of the flame. Both a Varian 3700 or an HNU 301 GC were used.

For trap recovery studies, test mixtures were prepared either without solvent or in high purity carbon disulfide provided by The Dow Chemical Company. The injection volume was 2.5 uL in all cases and the split ratio ranged from about 50:1 to 500:1 depending on the sample concentration. For vapor studies, samples were injected in humidified or laboratory air in volumes of 0.025-1.0 cm^3.

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 choice of trap material and dimensions affects durability and reinjection performance. An ideal material would have high electrical resistivity, low chemical activity, 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 thirty per cent copper - seventy per cent nickel were evaluated for use as trap tubes. The work reported here was done using a trap made of Monel 400. Stainless steel, which was used in some early studies (17, 18), is the least desirable choice because of its tendency to work harden and become brittle. 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 (19-23). Since the short, open tubular trap used in these experiments may be less efficient than some other designs (23), 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. 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. At temperatures of -100 °C or colder, each of the tested compounds was quantitatively trapped and reinjected. Peak area reproducibility for all compounds was very good with coefficients of variation ranging from 1 to 5 per cent, or less in all cases in which trapping was used.

Compounds tested were (given in order of increasing boiling point): isoprene, pentane, dichloromethane, acrolein,chloroform,methanol, hexane, carbon tetrachloride, acrylonitrile, 2-butanone,benzene,propanol, heptane, i-octane, toluene, n-butanol, tetrachloroethylene, octane, m- & o-xylene, nonane, 4-ethyltoluene, and 1,3-dichlorobenzene. Detailed results are given elsewhere (15). Trapping efficiency was also measured for 1% solutions of aromatics prepared in carbon disulfide. The trapping efficiencies obtained in those experiments were not significantly different than those measured without solvent. These materials can be effectively trapped and reinjected at temperatures of -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.

Limit of Detection (LOD). For monitoring volatile organics in ambient or workplace air, the LOD of the method must be very low. As of early November, 1990, the LOD's for pentane, hexane, heptane, octane, benzene, toluene, xylene, ethylbenzene, 4-ethyltoluene, 1,3,5-/1,2,4-trimethylbenzenes, and chlorobenzene have been measured and been shown to be in the range of 0.2 - 5 ppb, with the most recent results all being <1.0 ppb. (The drop in LOD has occurred as a result of improved methodology as work has proceeded over the past few months. There has not been time to re-do some of the earlier work.)

All of these values were determined based on an injection of a maximum of 1 cm^3 of air, and the use of an FID. The LOD was calculated based on a definition of three times the standard deviation of the noise.

One of the major factors contributing to the reduced LOD was the optimization of the custom-designed, high speed electrometer supplied for this project by HNU Co. A filter setting of 12 Hz was found to be optimal for GC peaks in the retention time range of 5-10 seconds.

Note that these LOD's are not achievable for one carbon-halocarbons. LOD's in the sub-20 ppb range for certain halocarbons will only be achievable with the use of an electron capture detector (ECD). Unfortunately, an ECD has, of necessity, a certain internal volume that may significantly spread peaks, and reduce the advantage of the Fast-GC method. This may require assays to be performed on a 30-60 second basis, rather than on a 5-10 second basis.

In addition, it is important to remember that the Fast-GC technique trades chromatographic resolution for speed. Although the cost of this trade is reduced by tuning the column for high speed, low retention time use (8,14), the separation of components of complex mixtures may not always be possible.

Further, the limitations imposed by the use of an isothermal GC method (necessitated by the short analysis times) limit the ability to monitor compounds of widely differing boiling point simultaneously. While this might be overcome by flow-programming methods, the extent to which such strategies will allow effective ambient air monitoring is unknown at this time.

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References

1. D. H. Desty. Capillary columns: Trials tribulations and triumphs. Advances in Chromatography, Vol 1., J. C. Giddings and R. A. Keller eds., Marcel Dekker, NY, 1965, pp. 199-228.
2. D. H. Desty, A. Goldup and W. T. Swanton. Performance of coated capillary columns. 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: N.Y. 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: 1512-1518 (1978).
5. G. Gaspar, P. Arpino and G. Guiochon. Study in high speed gas chromatography. J. Chromatogr. Sci. 15: 256-261 (1977)..
6. A. van Es, J. Janssen, R. Bally, C. Cramers and J. Rijks. Sample introduction in high speed capillary GC ; Input band width and detection limits. HRC&CC. 10: 273-279 (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 GC 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: 149-160 (1989).
9. R. L. Wade and S. P. Cram. Fluidic logic sampling and injection system for gas chromatography. Anal. Chem. 44: 131-139 (1972).
10. R. Annino and J. Leone. The use of coanda wall attachment fluidic switches as GC 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 GC J. Chromatogr. 279: 269-277 (1983).
12. R. J. Jonker, H. Poppe and J. F. K. Huber. Improvement of speed of separation in packed column GC. Anal. Chem. 54: 2447-2456 (1982).
13. R. Tijssen, N. van den Hoed and M. E. van Kreveld. Theoretical aspects and practical potentials of rapid gas analysis in capillary GC. Anal. Chem. 59: 1007-1015 (1987).

14. Mouradian, R.F., Levine, S.P., Sacks, R.D. and Spence, M.W. Measurement of Organic Vapors at Sub-TLV Concentrations Using Fast Gas Chromatography. Amer Ind Hyg Assoc J. 51:90-95 (1990).

15. Mouradian, R.M., S.P. Levine and R.D. Sacks. Limits of Detection and Recoveries for Fast-GC. J. Chromatogr., 28: 643-648 (1990)

16. B. J. Hopkins and V. J. Pretorius. Rapid evaporation of condensed GC fractions. J. Chromatogr. 158: 465-469 (1978).

17. B. A. Ewels and R. D. Sacks. Electrically heated cold trap Inlet system for high-speed GC. Anal. Chem. 57: 2774-2779 (1985).

18. 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. Chem. 60: 1994-1996 (1988).

19. A. van Es, J. Janssen, C. Cramers and J. Rijks. Sample enrichment in high speed narrow bore capillary gas chromatography. HRC&CC. 11: 852-857 (1988).

20. G. Schomburg, H. Husmann and F. J. Weeke. Aspects of double-column GC with glass capillaries involving intermediate trapping. J. Chromatogr. 112: 205-217 (1975).

21. J. A. Rijks, J. Drozd and J. Novak. J. Versatile all-glass splitless sample-introduction system for trace analysis by capillary GC. J. Chromatogr. 186: 167-181 (1979).

22. D. Kalman, R. Dills, C. Perera and F. DeWalle. On-column cryogenic trapping of sorbed organics for determination by capillary GC. Anal. Chem. 52: 1993-1994 (1980).

23. J. W. Graydon and K. Grob. How efficient are capillary cold traps? J. Chromatogr. 254: 265-267 (1983).

24. Mouradian, R.F., S.P. Levine, H.Q. Ke and H.H. Alvord. Measurement of Volatile Organics at Parts Per Billion Concentrations Using a Cold Trap Inlet and High Speed Gas Chromatography. submitted to J. Air Waste Manag. Assoc.

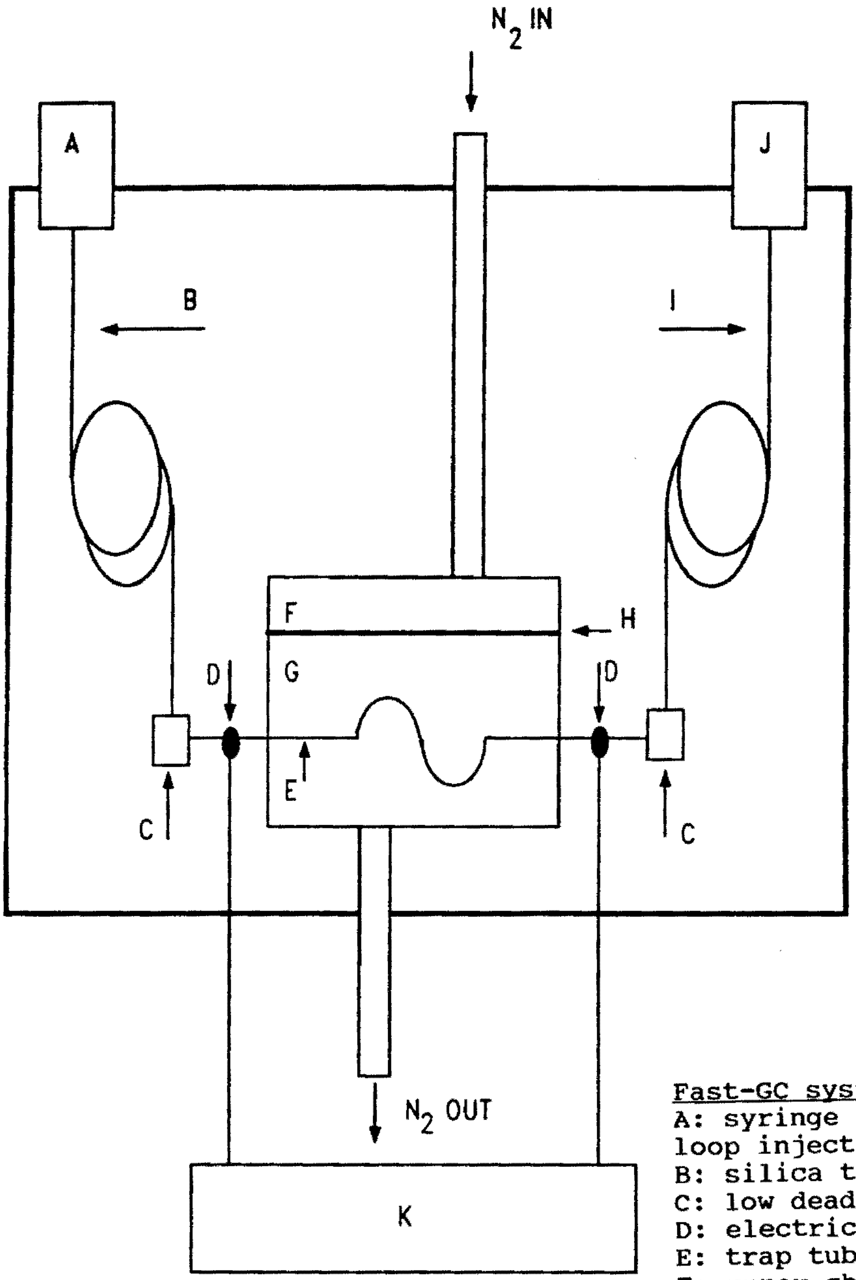

Figure 1

Fast-GC system:
A: syringe or gas sampling loop injection port;
B: silica transfer line;
C: low dead volume unions;
D: electrical contacts;
E: trap tube;
F: upper chamber cold trap;
G: lower chamber cold trap;
H: baffle;
I: capillary column
J: flame ion. detector;
K: capacitor power supply

DISCUSSION

HANK WOHLTJEN: How much energy did your capacitive discharge heater use?

STEVEN LEVINE: It's running about 30 to 70 volts discharge with a few tens of amps.

HANK WOHLTJEN: How big are the capacitors? Are they a tenth of a farad or something like that?

STEVEN LEVINE: All the details of the design is in that paper in Analytical Chemistry.

HANK WOHLTJEN: You mentioned electric cooling of the trap. What do you think you'd use for that, a refrigerator or a thermal electric?

STEVEN LEVINE: It would have to be a thermoelectric cooler. We are investigating that at this moment.

JOHN SNYDER: I was curious as to the diameter of the columns you're using.

STEVEN LEVINE: They're just 0.25 mm columns. They're very traditional columns. They're not megabore. They're not ultra small.

JOHN SNYDER: You also spoke about the dead volume in the detectors. Are you modifying traditional detectors or are you making your own detectors?

STEVEN LEVINE: We have a 90 μl dead volume ECD from HNU Systems at this point that we're working with. We feel that size is probably too big.

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