INSTRUMENTATION AND STRATEGIES FOR HIGH-SPEED GC ANALYSIS OF ORGANOCHLORIDE COMPOUNDS

Richard Sacks and Heather Smith, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109. Phone: (313) 764-7373, FAX: (313) 647-4865, e-Mail: rdsacks@umich.edu

ABSTRACT

Cryofocusing inlet systems and tunable tandem ensembles of a polar and a nonpolar column are used to obtain high-speed separations of organochloride compounds. Injection band widths of about 10 ms are obtained using a cryofocusing inlet system containing a bare metal capillary trap tube which is cooled to a temperature of -50 to -100^{0}C. After collection of the sample vapor, rapid heating of the focused, condensed-phase sample results in a narrow vapor plug for injection onto the tandem column ensemble. Electronic adjustment of the pressure at the junction point between the columns is used to tune the selectivity of the separation for the specified set of target compounds. Separation times typically are 10-100 fold shorter than with conventional GC.

INTRODUCTION

Gas chromatography (GC) is the most widely used method for the speciation and quantitation of volatile and semi-volatile organic chloride compounds. A favorable combination of high selectivity, high sensitivity, a wide dynamic concentration range and good accuracy account for its popularity. A serious limitation of GC is protracted analysis time, typically a few minutes to over an hour depending on the complexity of the mixture and the number of target compounds. Several new technologies hold promise for obtaining dramatic reductions in analysis times. High-speed GC (HSGC) uses relatively short lengths of capillary separation column operated at unusually high carrier gas flow rates to reduce analysis times by one-to-two orders of magnitude. However, special instruments and strategies are required to reduce instrumental dead time and to cope with reduced peak capacity. These instruments and strategies are discussed in this report.

Two very significant problems are associated with the use of short columns at higher than usual flow rates for obtaining very short analysis times. These are the need for very narrow injection band widths and the reduced peak capacity associated with short columns. Equation 1 gives the separation time, which is the retention time t_{Rl} of the last eluting compound of interest.

$$t_{Rl} = (L/u)(1 + k_l) \qquad (1)$$

Here, L is the column length, u is the average linear velocity of the carrier gas in the column and k_l is the retention factor for the last component of interest. Thus, for short analyses, short columns, high gas velocities and relatively small retention factors are required.

Equation 2 expresses the height equivalent to a theoretical plate H_{ec} from extra-column sources only. Note that small plate height means more efficient instrument operation and greater resolving power for a given column length.

$$H_{ec} = \Delta t^2 u^2 / [(L(k + 1)] \qquad (2)$$

Here, Δt is the total instrumental dead time. In general, it is straightforward to reduce to insignificant

values all dead time sources except the injection band width from the inlet system. Note that as the values of the parameters in equation 1 become more favorable for shorter separation time, they become less favorable for minimizing the adverse effects of H_{ec}. For typical HSGC conditions, a conventional inlet system with a splitter will result in about a 100-fold increase in the value of H_{ec} relative to conventional GC. This seriously degrades the resolving power obtainable from the column. In order to render insignificant extra-column band broadening, the injection band width (Δt in equation 2) must be reduced to about 10 ms or less.

For simple mixtures containing only a few components, the use of special inlet systems and adequately fast detector electronics and data sampling rates, complete separations in a few seconds to a few tens of seconds are often possible. However, peak overlap probability is high, and complete separation of more complex mixtures may be very difficult with the reduced peak capacity of relatively short capillary separation columns. Peak capacity is defined as the number of peaks, if perfectly spaced at a specified resolution, that will fit in the chromatogram. The important point here is that peak capacity is proportional to the square root of column length. Thus the short columns needed to achieve short separation times (equation 1) also result in significantly smaller peak capacities. A solution to this problem is to utilize the available peak capacity more efficiently by better control of column selectivity.

EXPERIMENTAL METHODS

The inlet system used for this work is shown in Figure 1. It has been described previously [1]. Carrier gas is supplied at point CG. A 0.3-mm i.d. metal trap tube T is cooled to a temperature of -50 to -100°C by a continuous flow of cold nitrogen gas through an insulated sheath surrounding the tube. In order to collect a sample, valve V_1 is opened, and the vacuum pump VP pulls a vapor sample from sample source S through capillary restrictors R_1 and R_2 and into the trap tube. All organochloride compounds are quantitatively trapped and focused as a narrow plug near the right end of the trap tube. Permanent gases and very low molecular weight hydrocarbon compounds are not collected.

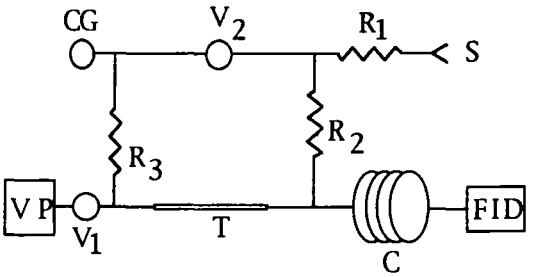

Figure 1. High-speed cryofocusing inlet system.

During sample collection, valve V_2 is closed. After sample collection is complete, V_2 is opened, and a purge flow of pure carrier gas cleans R_1 and R_2. This value is left open until the next sample is collected. After the purge is complete (about 1 s), V_1 is closed, and the trap tube is pressurized with carrier gas. This results in a reversal of flow direction through the trap tube. Next, a capacitive discharge power supply is used to resistively heat the metal trap tube to reinjection temperature typically in the range 100 to 300°C. Heating requires only a few ms, and a sample vapor plug about 10 ms in width is injected into the separation column C.

Most common detectors can be used. For this work, a flame ionization detector FID is used. An electrometer/amplifier with a time constant of about 5 ms was used to interface the FID to a 12-bit A/D board. A sampling rate of 100 Hz was used for most studies. The inlet system is mounted on a Varian 3700 GC. Capillary restrictor R_1 is connected to the Varian heated injection port, thus permitting syringe injection of liquid samples. Some samples were introduced at atmospheric pressure

from gas sampling bags. In this case, R_1 was placed directly into the gas sampling bag through a septum.

The tandem column ensemble used to achieve adjustable selectivity is shown in Figure 2. An electronic pressure controller PC with carrier gas supply CG is connected at the junction point between the non-polar first column C_1 and the polar second column C_2. The column head pressure is fixed and is the highest pressure in the system. The outlet pressure is fixed at one atmosphere. The tuning pressure P_t can be adjusted by a computer in 0.1 psi steps. As the tuning pressure is increased, the pressure drop along the first (non-polar) column decreases, and the pressure drop along the second column increases. This results in a decrease in the carrier gas flow rate in the first column and an increase in the second column.. The result is that all sample components show increased residence times on the first column and decreased values on the second column. This increases the influence of the first column on the overall selectivity of the column ensemble. If the first column is non-polar, then an increase in the tuning pressure decreases the overall polarity.

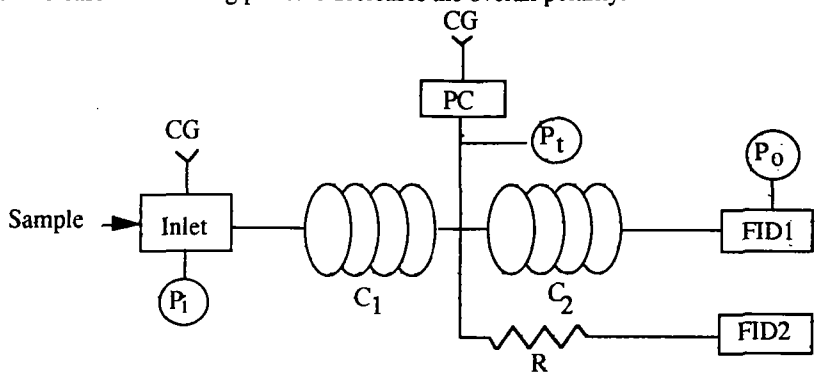

Figure 2. Pressure tunable column ensemble.

The junction point between the columns is connected via a short length of capillary restrictor R to a second detector which is used to get an independent measurement of the holdup time for the first column. Both columns are 0.25-mm i.d. fused silica capillaries about 5 meters in length with 0.25-μm thick bonded stationary phases. The polar column used polyethylene glycol as the stationary phase, and the non-polar column used 5% phenyl poly (dimethyl siloxane) as the stationary phase.

RESULTS AND DISCUSSION

Inlet System Performance. This inlet system design has been studied in detail[2], and only the salient features will be described here. The inlet system can accommodate any sample gas pressure so long as the pressure is greater than the subambient pressure in the trap tube during sample collection. For liquid samples, conventional syringe injection is used, and the restrictor R_1 (see Figure 1) replaces the column in the splitter of the conventional, heated injection port. The resulting sample vapor then is cryofocused in the metal trap tube. For vapor samples including ambient air, restrictor R_1 can be used as the sample sniffer. For direct vapor analysis, sample size and thus detection limits can be controlled by software simply by adjusting the timing of the two valves in the inlet system.

The inlet system produces injection band widths of about 10 ms and a shot-to-shot injection time jitter of only a few ms. Since the system operates as a sample vapor integrator, very dilute vapor samples can be efficiently preconcentrated in the trap tube. Detection limits less than one part-per-billion are readily achieved. Because of the gas flow direction reversal after sample collection, the sample is injected into the separation column from the same end of the trap in which it was collected. Thus, during injection, the sample plug travels through only a very short segment of the heated trap tube. This virtually eliminates sample alteration.

An important feature of the inlet system is the ability to use a flow reversal in the first column to backflush and retrap components which have not eluted from this column. To accomplish this, valve V_1 (see Figure 1) is opened at a preset time just after the elution from the first column of the more weakly retained components of the sample mixture. Valve V_2 is left open during this operation so that no new sample is collected in the cold trap. The vacuum pump then pulls carrier gas from the pressure controller through the first column in the reverse direction. The relative short column is rapidly backflushed, and all remaining mixture components are refocussed in the cold trap tube. After the backflush, the column temperature is increased to reduce retention factors for the remainder of the mixture components. The tuning pressure also is reset for the fastest possible separation of the remaining components. After the backflush is completed, V_1 is again closed, and the trap tube heated to reinject the sample residue. Since trapping is quantitative for all organic chloride compounds, this backflush-recycle operation can be repeated several times for complex mixtures which cover a wide boiling point range.

Pressure Tunable Column Ensembles. When two columns of different polarity are connected in tandem, the retention pattern is the weighted average of the retention patterns obtained from the separate column[3]. The weighting factors f_{np} and f_p for the non-polar and polar columns, respectively, are just the fraction of the total holdup time that can be ascribed to each of the separate columns. This is given in Equations 3 and 4.

$$f_{np} = tm_{np}/(tm_{np} + tm_p) \quad (3)$$

$$f_p = tm_p/(tm_{np} + tm_p) \quad (4)$$

Here, tm_{np} and tm_p are the carrier gas holdup times for the two columns, respectively. The values of the weighting factors are adjusted by adjusting the pressure at the junction point between the columns. Retention factors for the target compounds on the two individual columns are used with a window-diagram optimization technique to determine the best column weighting factors for the target compounds. The best weighting factors give the greatest resolution of the worst case pair of mixture components (critical pair). For this purpose, relative resolution R has been defined as in Equation 5[4].

$$R = \Delta k/(k_a + 1) \quad (5)$$

Here, Δk and k_a are the difference in retention factors for a component pair, and k_a is their average value. The value of relative resolution is independent of column length, and once the best weighting factors are determined, the total column length is adjusted to give the number of theoretical plates required to achieve an adequate separation. Finally, the pressure at the column junction is adjusted to give the desired weighting factors.

Figure 3 shows data for a mixture of ten relatively low boiling point organochloride compounds. A number of common solvents is included. The upper portion of the figure shows plots of overall retention factors k for the tandem combination of a polar (polyethylene glycol) column and a non-polar column. The horizontal axis plots the weighting factor F for the polar column. The retention factor values along the left vertical axis (F = 0) corresponds to values from the non-polar column only. Values along the right vertical axis (F = 1.0) corresponds to values from the polar column only. The straight lines connecting the end points for each of the compounds give the overall retention factors for the tandem column ensemble using the indicated polar column weighting factor.

For ever F value where a pairs of the lines cross in the upper plots of Figure 3, the corresponding compounds are the critical pair and will coelute. Thus, the relative resolution is zero. These crossings correspond to the zero points in the window diagram shown in the lower portion of Figure 3. As the weighting factor changes from one of the coelution values, the relative resolution increases until a different component pair becomes the critical pair, and the relative resolution decreases

again. This generates a collection of windows of finite resolution. The window giving the largest resolution (best separation of the worst case component pair) identifies the weighting factor giving the corresponding elution pattern from the tandem column ensemble.

For this mixture, the optimal polar-column weighting factor is 0.43. The corresponding relative resolution value of 0.042 suggests that this mixture can be completely separated in less than 30 s. Note that separation time decreases as the square of the relative resolution. Thus, using only the polar column or only the non-polar column, the separation would take more than ten times longer.

CONCLUSIONS

The combination of a high-speed, cryofocusing inlet system and a pressure tunable tandem column ensemble can be used to achieve high-speed GC separation of low-molecular weight organochloride compounds. For isothermal separations, tuning is straightforward, and temperature optimization usually results in further reductions in separation time. For wide boiling point range mixtures such as PCBs, the high-precision backflush and recycle capabilities of the inlet system should allow for the sequential analysis of a series of cuts from a single sample. Each cut is separated isothermally but at progressively higher temperatures. With electronic pressure control, the column ensemble can be separately tuned for each sample fraction. These studies are in progress.

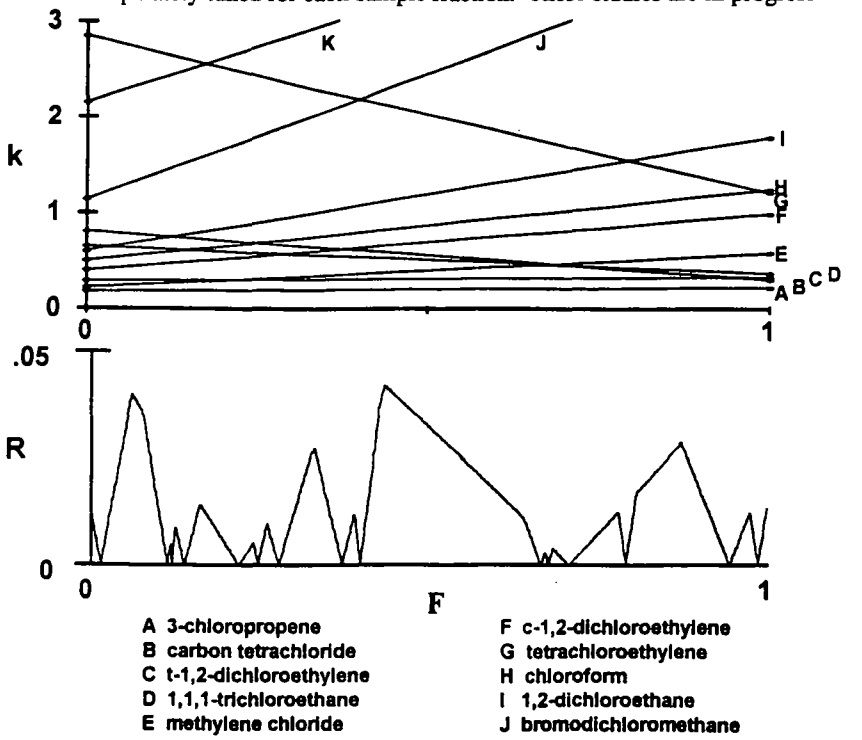

Figure 3. Overall retention factor plots (top) and the corresponding resolution window diagram (bottom) for a ten-component mixture of organochlorides

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