CRYOGENIC FOCUSSING, OHMICALLY HEATED ON-COLUMN TRAP

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ABSTRACT

A procedure is described for depositing a conductive layer of gold on the exterior of a fused-silica capillary used in gas chromatography. By subjecting a section of the column near the inlet to a thermal cycle of cryogenic cooling and ohmic heating, volatile samples are concentrated and subsequently injected. The performance of this trap as a chromatographic injector is demonstrated. Several additional applications are suggested and the unique properties of this device are discussed.

INTRODUCTION

The importance of temperature and its effects on physico-chemical processes cannot be overemphasized. With few exceptions, process rates increase with the temperature. In gas chromatography (GC), a linear increase in temperature exponentially raises the vapor pressure of solutes partitioned between the stationary and mobile phases. The sequential elution of progressively less volatile, and generally larger, solutes by steadily increasing the column temperature has long been practiced in GC. Thus, samples with a broad range of individual solute volatilities can be analyzed in a single separation. Conversely, dilute vapor samples may be concentrated as a narrow band by passing the sample stream through a cooled region. This trapping region is quickly warmed to release the material in a sharply defined pulse where the solute concentration has been greatly enhanced over the original dilute stream. A novel solute trap for capillary chromatography has been recently developed in this laboratory which controls the temperature in a short section of the analytical column. By carrying out the concentration within the column itself, many problems associated with precolumn concentration schemes are avoided. The design, construction, evaluation, and use of a chromatographic trap based on an ohmically-heated column section illustrates the unique characteristics of this technology. Many of these same features also suggest other novel applications, including some outside the field of chromatography.

In elution chromatography, sample mixtures must be introduced into the analytical column as a zone which is spatially narrow relative to the separated zones of individual components which later emerge. A second requirement dictates that the sample quantity introduced must be detectable. Numerous injection devices have been developed which meet these criteria (1). An appropriate technique should be selected based on the sample and its accompanying matrix. Cryogenic trapping is one strategy particularly well suited for samples which must be concentrated prior to separation by GC.

The principle of cryogenic trapping is straightforward. Chilling a region of the flow stream lowers the sample vapor pressure and causes solutes to be concentrated in a stationary zone. Following the concentration step, the trapped material is then heated to quantitatively transfer the sample into the separating column. It is important to heat the trap quickly so that all material leaves as a narrow band. Under proper conditions, sample concentrations in this discrete plug may be increased four or more orders of magnitude above their original level. Two points are crucial in the design of a cryogenic trap. First, the trap volume must be small, approximately the same size as the ultimate injection volume. Second, the trap must be capable of rapid heating to quickly vaporize the trapped material and avoid drawing out the narrow injection zone.
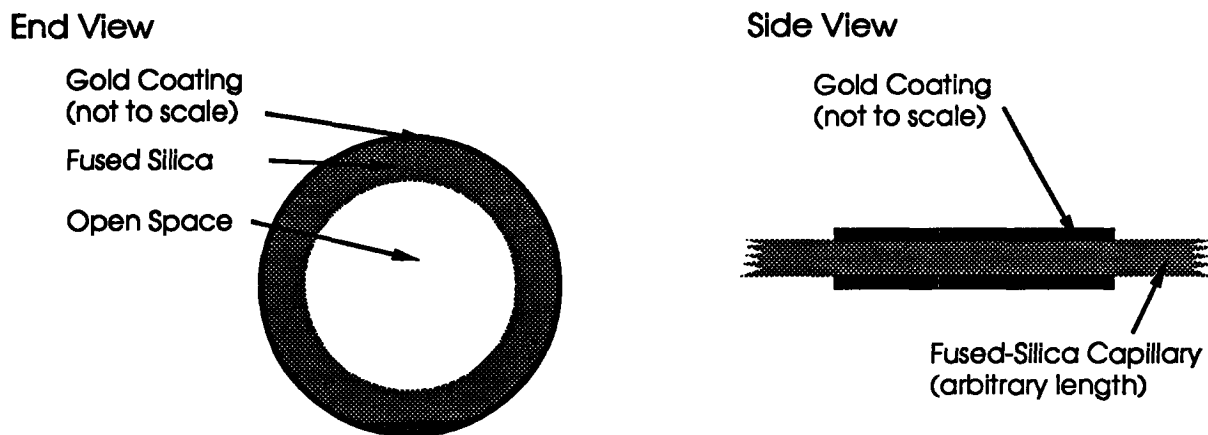
End View

Gold Coating
(not to scale)

Fused Silica

Open Space

Side View

Gold Coating
(not to scale)

Fused-Silica Capillary
(arbitrary length)

Figure 1.   Schematic of a gold layer on a capillary column. For clarity, the polyimide layer and stationary phase are not shown.

PROCEDURE

Fabrication of the on-column trap entails depositing a thin layer of gold on the outside of a fused-silica capillary column about 10 cm from the inlet and extending for a length of 10 cm. Any commercial capillary column is suitable for operation with this trap. This evaluation was done with 0.25-mm i.d. columns which were statically coated (on the inside) with a 0.25-μm thick coating of SE-30 (dimethyl silicone) and showed a coating efficiency of 93% for dodecane at 100°C. Two lengths, 11.0 and 1.92 m, were used to isolate any diminishment of column efficiency due to trapping. The gold layer is applied as a gold complex dissolved in volatile oils (Liquid Bright Gold, No. 7621, Engelhard, Hanovia Liquid Gold Division, East Newark, NJ). The solution is applied with a brush and dries to an even coating in air. Once dry, the entire column is placed in an oven and heated to 310°C for 20 min. Heating drives off the residual solvent and decomposes the organic portion of the gold complex leaving a specular layer of metallic gold on the outer capillary wall. The application and firing process is repeated three times to yield a gold layer about 0.3 μm thick. During heating, the column interior is purged with helium to remove any trace decomposition products which may evolve from the stationary phase. The outer polyimide coating of the capillary column is unaffected by the gold layer. Because this gold layer is so thin, the remarkable flexibility of fused-silica columns is retained.

Figure 1 shows a schematic representation of the trap on a capillary column. A polyimide layer is applied to the outside of fused-silica tubing during the manufacturing process to protect against damage. The trap is easily visible over the polyimide layer and resists abrasion. When not in use, the trap does not alter the performance of the column in any way. Ferrules seal equally well to gold and polyimide, however, ferrules are easier to remove from the gold layer because they stick less.

Capillary columns outfitted with a gold trap were installed in a gas chromatograph (Varian VISTA 4600, Varian Instruments, Walnut Creek, CA) configured as shown in Figure 2 for purposes of evaluation. A split/splitless injector allowed the trap performance to be characterized and compared with conventional injection techniques. For routine analyses with the cryogenic trap, a sample loop is substituted for the split/splitless injector. Electrical connections to the gold layer are made by wrapping conductive fibers around both ends of the trap. A variable voltage source regulates the potential across the trap. The voltage and current are monitored simultaneously. The trap is bent such that the region between the electrical leads is held above liquid nitrogen contained in a Dewar. The trap and its lead connections remain electrically isolated from the Dewar and gas chromatograph. The trapping mode is actuated by turning off the voltage source and allowing the trap to cool to -150°C. When a voltage is applied, the trap temperature quickly rises and samples are driven off the trap. For the traps described here, voltages between 10 and 15 V were used. Due to the thinness of the gold layer, the trap resistance is relatively high and the current is on the order of 100 mA.
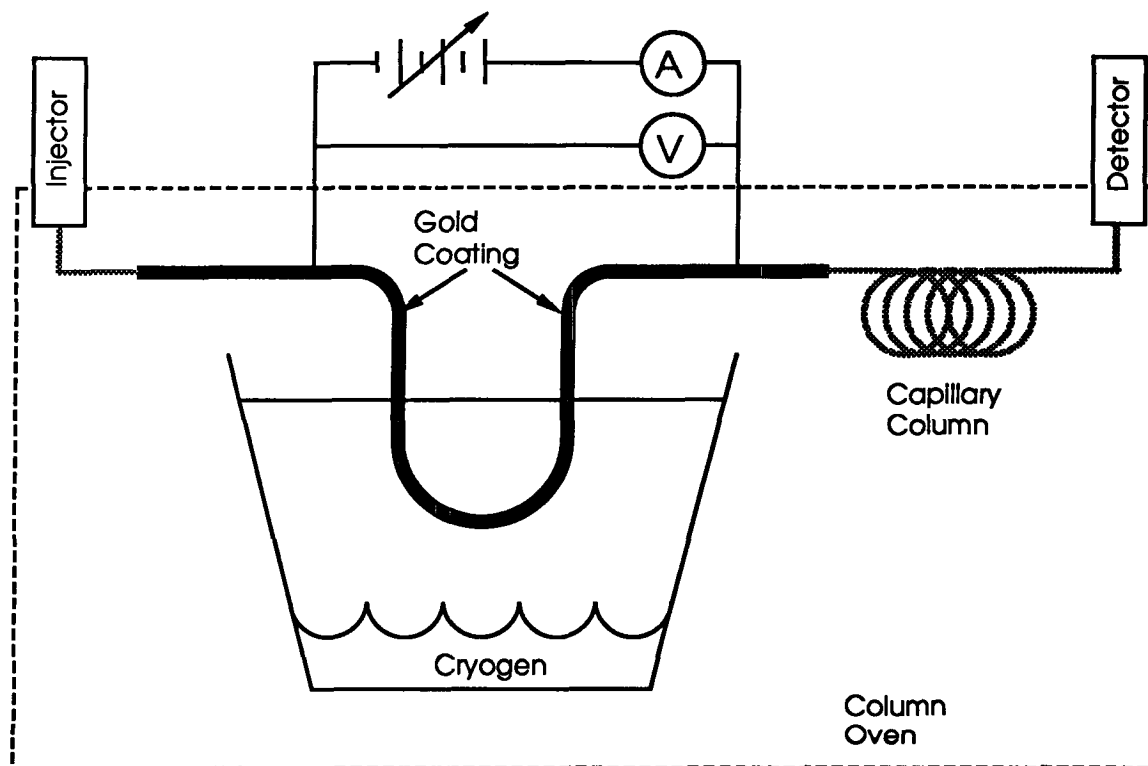
Figure 2.   Schematic diagram of capillary trap installed in gas chromatograph.

Separated solutes were detected by a flame ionization detector (FID) as they elute from the column. For the purposes of this study, moment analysis (2) was used to accurately characterize the shape of solute peaks. The detector output was stored digitally at 20 Hz.

EVALUATION

Operation of the gold-coated capillary section as a trap for capillary chromatography is illustrated by three demonstrations. First, the temperature of the trap can be accurately monitored during operation by simply measuring the electrical resistance. Most materials exhibit increased electrical resistance as the temperature rises. The resistivity of pure gold has a temperature coefficient of 0.0034 per °C (3). This relationship was confirmed experimentally for these traps by directly measuring the internal temperature using a miniature iron-constantan thermocouple (Omega Engineering, Stamford, CT) carefully inserted into a capillary. While the GC oven temperature was raised, the trap resistance was measured. Next, with the oven off, the trap was ohmically heated by increasing the current in a step-wise fashion. By also measuring the voltage across the trap during ohmic heating, the trap resistance was calculated using Ohm's law and recorded as a function of the directly measured temperature.

The line in Figure 3 shows the resistance across the trap as a function of temperature while the chromatograph oven was used to heat the capillary. The step-wise nature of the line is due to digitization error in measuring the resistance. The open circles correspond to the trap resistance calculated from Ohm's law as the trap is ohmically heated. In both cases, the trap resistance increases linearly with temperature. The apparent temperature coefficient of resistance is 0.001 per °C and is independent of whether the trap is heated externally or ohmically. Resistance in the leads and connections accounts for the difference between the experimental and reference values. Note the tedious operation of inserting the thermocouple is performed here
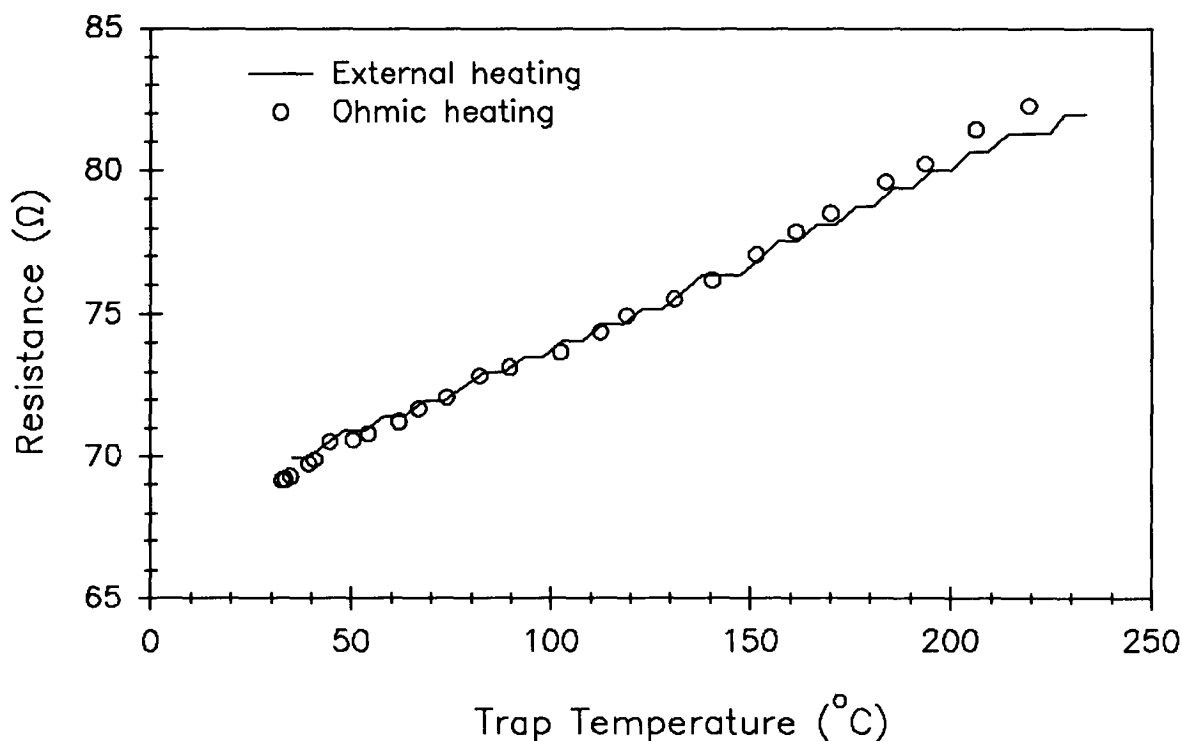
Figure 3.   Trap resistance vs. trap temperature. The trap temperature was measured inside the capillary.

only to establish that the effective coefficient of resistance can be measured by external heating. In actual use, a new trap is calibrated merely by programming the oven temperature while measuring the resistance.

Second, the ability of the trap to quantitatively capture and release volatile samples is demonstrated using the 11-m capillary. This length was chosen to provide complete separation of the C5 - C8 normal alkanes. A stock solution of 2000 parts-per-million-volume (ppmv) in room air was sequentially diluted to 50-, 100-, and 200-parts-per-billion-volume (ppbv) in air. Figure 4A shows a separation of the stock solution using a conventional split injector. The small injection volume and the 99% of sample dumped to the vent define the amount of sample actually reaching the column and detector to be 300 pg/component. These losses are necessary in split injections to provide a narrow injection band. Figure 4B shows a separation of the stock solution diluted by a factor of 40,000 (50 ppbv) injected with a trap. The sample volume has been increased to 1 mL. In this case, there is roughly 150 pg/component on column. The additional peaks in Figure 4B are due to various compounds in the air used to dilute the stock solution. Methane, though present in ambient air at 20 times the level of the other alkanes is not concentrated at the trap temperature and, therefore, is not detected.

The trapping period was two minutes in this case, but longer periods (and larger sample volumes) can be accommodated easily. The chromatogram in Figure 4B indicates where heating commenced, thus beginning the separation. This corresponds to the injection time for a split injection. The uniformity of retention times is evident from Figure 4. Statistical evaluation of repeated injections has shown retention times for trapped samples are reproducible to <0.3 s and indistinguishable from split injections (4).
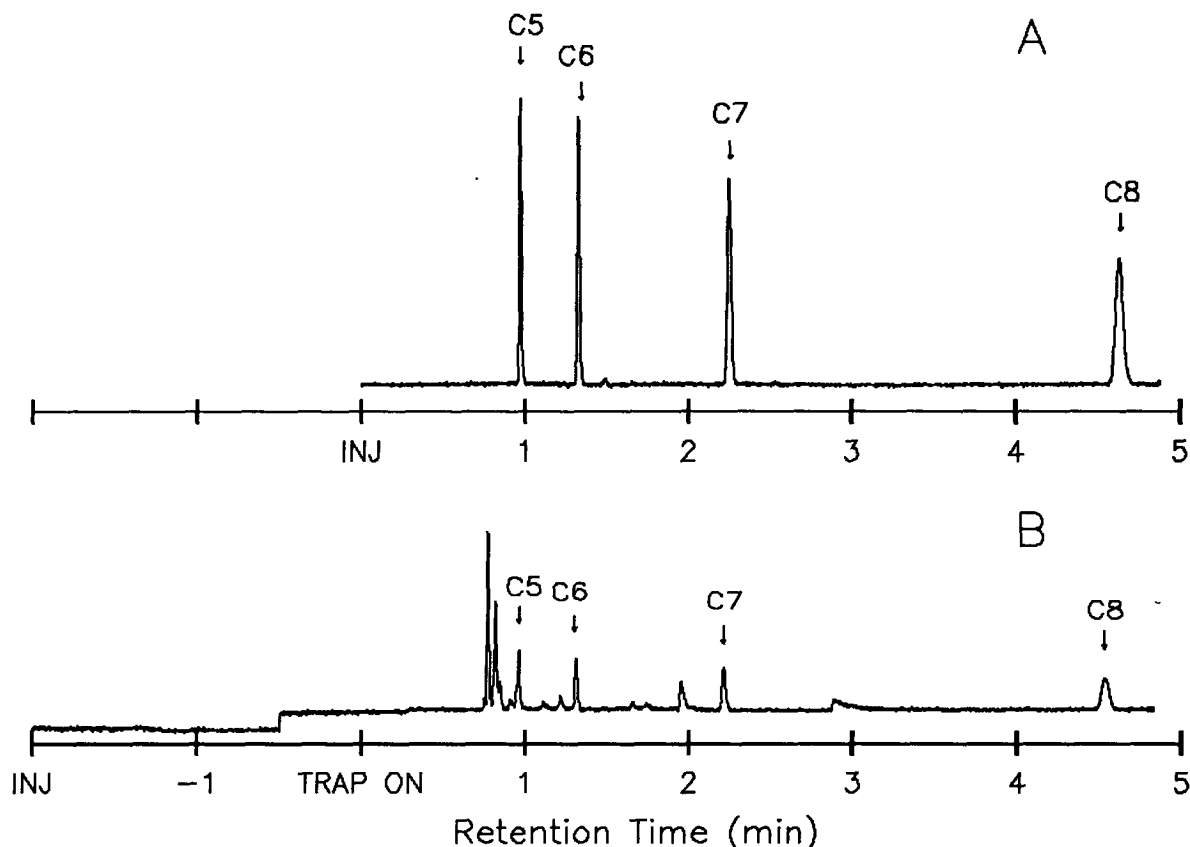
Figure 4.   Chromatograms of pentane, hexane, heptane, and octane on an 11 m x 250-μm i.d. capillary column coated with 0.4 w/v% SE-30. (A) 5-μL vapor-phase injection of 2000 ppmv, split 100:1. (B) 1-mL vapor phase injection of 50 ppbv, no split, trapped for 2 min.

Quantitative trapping is demonstrated in Figure 5 as a plot of peak area vs. concentration for two solutes of different retention ratios. Error bars indicate ± 1 standard deviation. Digitization error for these small signals contributes to the scatter. The precision for all solutes at 50 ppbv is better than 10% RSD. Replicate split injections with larger signals show a precision of 3% RSD. As with any injection technique, referencing peak areas to an internal standard would greatly enhance the precision of quantitation.

Third, the effects of trapping on peak shapes are illustrated. As stated earlier, samples must be delivered to the analytical column in a narrow concentration pulse. To measure the ability of the trap to release samples as a well-defined pulse, a 1.92-m column was used. This short column length maximizes any contributions to peak variance from the injection technique. A slow release during the heating step would be readily apparent as broad peaks in the resulting chromatogram. For comparison, a 100:1 split injection provides an "ideal" sample inlet system.

The parameters used to characterize the peak shapes were the second and third statistical moments calculated from the digitized chromatograms. The second moment (or variance) is related to the peak width and increases with retention time for isothermal separations. Significant departure from an ideal injection profile
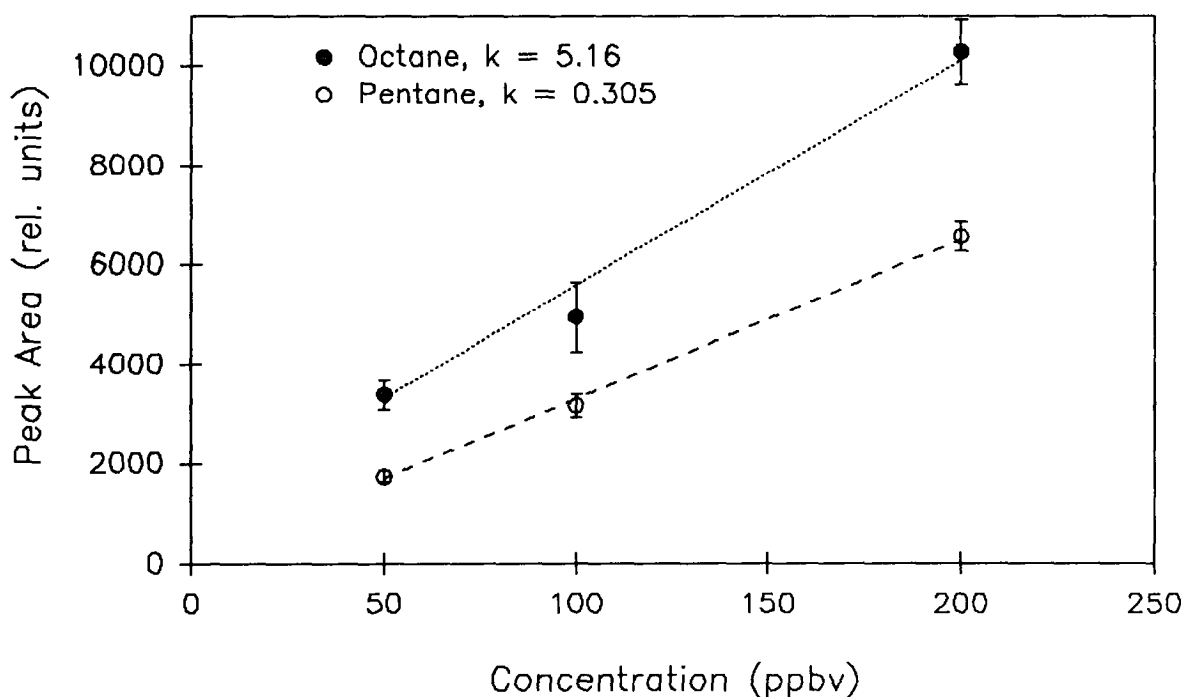
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Figure 5.   Peak area vs. concentration for solutes on the column of Fig. 4. Samples were trapped for 2 min. Mean ± 1 standard deviation.

causes the second moment to increase relative to an ideal injection. The third moment is a measure of peak asymmetry and is zero for an ideal peak.

The behavior of the column trap relative to a split injection is shown in Table I. The second and third moments for peaks from a trapped injection compare favorably with the "ideally" shaped peaks from a split injection. (Heptane exhibited a very minor impurity which degraded its peak shape.) Because longer columns are less demanding of the injection profile, these results, obtained under artificially demanding conditions, confirm the suitability of this trap for chromatographic purposes.

TABLE I

Second and third statistical moments for split and trapped injections on a 1.92-m column.

Sample	2nd Moment x 10^2 (sec^2)		3rd Moment x 10^2 (sec^3)	
	Split	Trapped	Split	Trapped
C5	6.11 ± 0.49	5.33 ± 0.19	2.31 ± 0.48	1.78 ± 0.15
C6	8.68 ± 0.59	7.81 ± 0.55	4.26 ± 0.64	3.58 ± 0.71
C7	9.39 ± 1.81	9.95 ± 0.86	3.64 ± 2.96	5.30 ± 1.14
C8	20.59 ± 0.55	17.56 ± 0.73	2.68 ± 0.34	2.40 ± 0.29

Mean ± 1 standard deviation (n = 7).

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POTENTIAL APPLICATIONS

In the future, the temperature in the trap may be accurately controlled using a simple feedback circuit. Such a circuit would allow trapped compounds to be sequentially removed by programmed heating. Provided sufficient differences in volatility exist, unwanted compounds could be back-flushed from the trap and prevented from entering the column and detector. For example, water present in atmospheric samples could be eliminated from the chromatographic analysis. This would greatly speed the analytical throughput.

The device described in this report shows potential far beyond its use as an injection device for gas-phase elution chromatography. Due to its low thermal mass and high thermal slew rates, the trap is ideal for multiplex chromatography (5), an approach where samples are repeatedly injected at intervals less than the analysis time of an individual injection. The resultant detector output is then mathematically deconvoluted to provide continuous (rather than batch) concentration information.

In supercritical fluid chromatography (SFC) (6), the mobile-phase density controls solute retention. A capillary trap could be used to increase the temperature in a localized column section, thus trapping non-volatile solutes on the walls. To inject the sample, the current would then be turned off and the trap allowed to cool. This reverses the protocol for injecting trapped samples in capillary GC as described above. Using a thermal trap for SFC was suggested several years ago (7), and preliminary results using other heaters have been reported (8). Use of the ohmically-heated trap described here is being evaluated.

Another potential application related to SFC is the construction of a controllable flow restrictor. Drawn out capillary tips are used to maintain back pressure in columns upstream of atmospheric pressure detectors (9). These tips generally offer a fixed restriction which differs from that required for optimal flow. Furthermore, density programming is often used to enhance separations, causing the flow rate to change during an analysis and making it impossible to maintain the ideal mobile-phase velocity. Adjusting the tip temperature would alter the location where the supercritical-fluid mobile phase converts to a gas. Because gases have about the same viscosity as fluids, but are two orders of magnitude less dense, warming the tip increases the back pressure generated in a trap. Regulation of the restrictor temperature has been advocated as a method to control column flow by Berger and Toney (10). From theoretical considerations, Berger concludes that high temperatures and short heated zones are required for SFC (11). This author goes on to declare that poor thermal contact in ordinary heaters make heat transfer into a fluid difficult. The possibilities of using an ohmically-heated, gold-coated restrictor are intriguing in view of the excellent heat transfer between the gold layer and the internal passage. The integral thermometric feature of the gold layer should permit accurate control of the flow through the analytical capillary, even during pressure programming.

A section of gold-coated capillary could function as an inert, fast response, flow controller for gases. As the temperature increases from 0° to 300°C, most gases vary in viscosity by a factor of two. A short section of capillary inserted in an otherwise unrestricted flow stream acts as a limiting restriction. Changing the temperature in this restriction by ohmic heating would then change the flow for the entire system. This technique would be practical only for controlling flows over a modest range, but the fast response, lack of moving parts, and the inert chemical nature of the wetted surfaces are attributes which would distinguish such a controller from its mechanical counterparts.

SUMMARY OF ADVANTAGES

The performance of the ohmically-heated trap as an injector for capillary GC has been demonstrated in a preliminary fashion. This trap exhibits a unique combination of features which should prove useful for other applications, some of which have been proposed in this paper. A review of these features may suggest additional applications.

Minimal Thermal Mass - The amount of gold applied is very small and contributes little to the thermal mass over the length of the trap. Because the total combined thermal mass of capillary and gold is low, rapid

thermal slew rates are possible with low power input as shown in the experiments above. Rapid cooling is also facilitated. Consumption of cryogen is minimal in cycling between heating and cooling.

No Moving Parts - In the configuration used for this study, the trap remained exposed to cryogen, even during ohmic heating. No valves were needed to switch flow streams. The current was remotely turned on and off with a relay.

No Compromise with Other Injection Methods - The gold layer does not preclude the use of any other injection technique if on-column trapping is not desired. In this case, the column containing the trap is merely connected to the injector as an ordinary capillary column.

Connection Free - The trap is formed as an integral part of the analytical column. Unlike other purge and trap systems, there are no mechanical junctions to broaden the injection pulse as it moves from the trap into the separation portion of the column. No on-column focussing, such as temperature programming, is necessary. Isothermal separations are particularly useful for highly volatile samples. In high-pressure systems, reducing the number of connections diminishes the possibility of leaks.

Inert Wetted Surface - Because the trap is deposited on the column exterior, samples only contact the inert, interior surface of the capillary. The elimination of fittings encountered by the concentrated sample also minimizes the opportunity for catalytic decomposition of injected components. This feature is crucial for labile compounds.

Applicable to Existing Columns - Virtually any capillary column may be fitted with a capillary trap. The application of the gold layer is relatively simple and may be done with readily available equipment. In cases where the stationary phase would not withstand the temperature needed to fire the gold layer, the column should be purged with an inert gas from the detector end while heating only the trap section.

Efficient Heating - Unlike metal tubes or coils of resistance wire, the gold layer is so thin that the electrical resistance is on the order of 100 Ω. Due to the low thermal mass and intimate contact between the gold and capillary, only 1 - 2 W of power is needed to heat a trap to 300°C, even when the surrounding gas is at -150°C. The currents required (50 - 150 mA) are quite modest and can be carried by fine connecting wire (which maintains the low thermal mass).

Homogeneous Temperature - The liquid gold solution is designed to cover surfaces uniformly. Properly applied, the gold layer is also highly uniform. Within the precision of the thermocouple used (± 1°C), no variation in temperature was observed over a 10-cm length during heating.

Integral Thermistor - As shown above, the resistance across the trap is linearly related to the trap temperature over a wide range. An external temperature sensor, which would add to the thermal mass, is not required.

Wide Temperature Range - The gold layer does not, by itself, impose any temperature limits on the trap. The minimum trapping temperature for this trap is determined by the cryogen. Liquid nitrogen is satisfactory for virtually all organic compounds. Above 350°C, the polyimide on fused silica begins to oxidize and the column becomes extremely brittle.

Controllable Temperature - Any temperature over the available range can be maintained with a constant voltage source. Temperature control would be greatly enhanced by using a feedback system to adjust the voltage and achieve a constant resistance. The low power requirements of this trap are easily supplied without elaborate circuitry.

Low Cost - The material needed to prepare a trap costs less than $1.00. (Most of this is wasted by inefficient application.) Coating the entire capillary length would not significantly increase the cost of an

analytical column and could provide a high-temperature alternative to the polyimide layer currently protecting most fused-silica capillaries.

ACKNOWLEDGEMENT

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