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Cryogenic-focusing, ohmically heated on-column trap for capillary gas chromatography

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ABSTRACT

A new method is presented for thermally desorbing solutes which have been cryogenically trapped on a capillary column. The trap heater is a thin layer of metallic gold applied to columns near their inlet. This layer is ohmically heated to initiate the separation. The temperature within the trap is related to the resistance of the gold layer. The trap is shown to not lower column performance relative to a split injection. Other advantages are discussed. Examples showing trace analyses of alkanes in air are given.

INTRODUCTION

Samples must be introduced as a narrow concentration pulse in elution chromatography, or column performance is compromised. Simplistically, the width of the pulse entering the column must be small relative to emerging peak widths. In the case of capillary gas chromatography (GC), geometric factors place stringent demands on the concentration profile delivered by the injector. A wide variety of inlet sytems capable of meeting these demands have been developed[1,2]. The sample characteristics are an important factor in selecting the appropriate injector. If an analyte of interest is present at low concentrations, the injection volume may contain less than a minimum detectable quantity. Cryogenic trapping is one method for increasing the amount of sample introduced without lowering column efficiency. Dilute components in a more volatile matrix are effectively concentrated within a cooled section of the stream. Subsequent warming of the trap initiates the separation as the narrow plug begins to migrate through the analytical column. The sample width is thus controlled by how fast the trap is heated rather than by the initial injection volume.

A variety of cryogenic sample traps have been described for capillary GC. Hopkins and Pretorius[3] demonstrated that electrically heating the trap was faster than using a heated gas stream[4]. This and other ohmically heated traps[5,6] were used to collect samples in a conductive tube connected to the analytical column. Burger and Munro[7] describe a thermal desorption system consisting of a length of metal tubing which was ohmically heated to desorb material from a 1-m fused-silica trap inside the heater, thus eliminating sample contact with heated metal. The trap was connected to the analytical column where further trapping was performed. Kolb *et*

al.[8] used cold nitrogen to concentrate the sample directly on the analytical capillary and then allowed the carrier gas to warm the trap, obviating any dead volume between the trap and column. A 10-cm section of aluminum coated fused silica was ohmically heated by Van Es *et al.*[9] to rapidly desorb samples from a 50-μm capillary passing through the heater. Input widths as short as 1 ms were reported. As with the apparatus of Kolb *et al.* trapping directly on the analytical column eliminates the dead volume of a connection.

This paper reports a simple on-column cryogenic trap that can be adapted to existing capillaries. The heating element is an integral part of the column. Samples can be concentrated and then separated without diminishing chromatographic performance. Several other unique features are described. The trap operation is demonstrated by analyzing some dilute samples of organic compounds in ambient air.

EXPERIMENTAL

A capillary column was prepared from untreated fused silica manufactured by Polymicro Technologies (Phoenix, AZ, U.S.A.). The empty capillary was purged with helium for 2 h at 250°C before statically coating with a 0.4% (w/v) solution of SE-30 (GC grade, Alltech Associates, Deerfield, IL, U.S.A) in pentane. The final column length was roughly 14 m with an internal diameter of 250 μm. This column was tested at 100°C and exhibited a coating efficiency of 93% for dodecane. The column was then split into two sections, 11.0 and 1.92 m in length.

An ohmically heated trap about 10 cm in length was fashioned on the exterior of both capillaries, starting 15 cm from the inlet of the 11.0-m column and 10 cm from the inlet of the 1.92-m column. Metallic gold was applied by depositing Liquid Bright Gold (No. 7621, Engelhardt, Hanovia Liquid Gold Division, East Newark, NJ, U.S.A.) directly on the polyimide outer coating and heating to 310°C for 20 min. Liquid Bright Gold is a true solution of gold in an organic matrix. At elevated temperatures, the organic liquid pyrolyses leaving a thin metallic film. During the heating step, the column interior was purged with helium while the exterior remained in air. The deposition and curing process was repeated three times. The resulting conductive layer is clearly visible and resists abrasion. Electrical leads were attached to the gold layer *ca.* 5 cm apart. Connections to the gold were made through electrically conductive fibers surrounding the capillary at each end of the trap. When installed, the gold layer did not contact the oven walls or the injection port.

The cryogenic focusing trap was evaluated chromatographically using a Varian VISTA 4600 GC (Varian Instruments, Walnut Creek, CA, U.S.A.) equipped with a split/splitless capillary injector. Solutes were detected by flame ionization detection (FID) with the capillary positioned flush with the flame jet tip. Chromatograms were digitally recorded using a CHROM-1 analog-to-digital board (Metrabyte, Taunton, MA, U.S.A.) operating within a PC's 286 microcomputer (PC's Ltd., Austin, TX, U.S.A.). The software controlling the data acquisition was Labtech Notebook (Laboratory Technologies Corporation, Wilmington, MA, U.S.A.). Detector sensitivity was set at $4 \cdot 10^{-12}$ A full scale. Detector output was digitized at 20 Hz. Moment analysis of the resulting data was performed with software written in Pascal (Borland International, Scotts Valley, CA, U.S.A.).

Columns were connected to the split/splitless injector and the FID system in the

normal fashion. The conductive column section was then placed in a cryogenic vessel partially filled with liquid nitrogen such that the trap was roughly 2 to 3 cm above the liquid level. The capillary entered and exited at the lid through constricted openings with most of the vapor vented well away from the column to prevent ice forming on the capillary outside the cryogenic container. Both electrical connections remained outside the vessel and were not cooled. Electrical currents through the trap were between 50 and 150 mA for these experiments. These currents required voltages between 10 to 15 V. Except for the variable-voltage power supply and switch, the entire trap assembly was located in the column oven.

Gas-phase samples containing a mixture of four normal alkanes were prepared at four different concentrations. A stock mixture containing pentane, hexane, heptane, and octane was made by adding the individual neat liquids to a 1-l flask. The liquid volumes were adjusted to produce an equimolar mixture of 2000 parts-per-million-by-volume (ppmv) of each alkane in ambient air. Single stage dilutions of the stock mixture produced samples containing 50, 100 and 200 parts-per-billion(10^9)-by-volume (ppbv) of each component. The samples were thoroughly mixed by a magnetic stirring bar.

All chromatographic separations were performed isothermally at 35°C. The injection volume was 5 μl for the 2000-ppmv stock mixture. Split injections were always used for this concentrated sample. For the three dilute mixtures, the injection volume was 1 ml. Dilute samples were injected with the split flow off for the first 90 s. The amount of each compound introduced into the capillary column is given in Table I for both injection procedures taking into account losses due to splitting. The values for the dilute samples are only an estimate, as they assume quantitative transfer of sample from the injector to the column before the split valve is opened.

The effect of sample trapping on elution profiles was investigated using the 1.92-m column. A plug injection was approximated by injecting 5 μl of the 2000-ppmv gas mixture under split conditions. By cryogenically trapping the sample and then heating the trap to initiate the separation, any decrease in performance relative to a normal split injection should be apparent. The split flow was maintained at 1.03 ml/s throughout these separations. Vapor phase injections of 5 μl were thus split 70:1 with a linear flow-rate through the column of 30 cm/s. After collecting the sample for 120 s in the cooled trap, the sample zone was rapidly heated by passing a current of 120 mA through the trap. Heating continued until all peaks were detected. Chromatograms recorded under these conditions were compared with chromatograms taken without

TABLE I

SAMPLE MASS INTRODUCED INTO CAPILLARY COLUMN ASSUMING QUANTITATIVE MASS TRANSFER FOR THE 1-ml INJECTIONS

Sample concentration	Injection volume	Split	Solute mass (pg)			
			C_5	C_6	C_7	C_8
2000 ppmv	5 μl	100:1	290	350	410	460
200 ppbv	1 ml	None	590	700	810	930
100 ppbv	1 ml	None	290	350	410	460
50 ppbv	1 ml	None	150	180	200	230

trapping or heating. Trapping occurred at the temperature above the liquid nitrogen, about $-150°C$ in this experiment. During the heating step, the temperature was estimated to be above 150°C.

The dilute samples were separated on the 11.0-m column by concentrating virtually the entire sample in the trap. For these dilute mixtures, the gas phase injection volume of 1 ml was injected by syringe over a 10-s interval with the split flow off. After 90 s, the split flow valve was opened to purge the injector body of any remaining sample. At 120 s after the start of the injection, the trap was heated to initiate solute migration along the column. For comparison, a 5-μl split injection of the stock solution was separated without trapping.

Finally, measurements were made to establish whether the temperature of an electrically heated trap could be determined from its resistance. For this experiment, the trap was broken off from the column so that a miniature thermocouple, 0.013 mm diameter (Omega Engineering, Stamford, CT, U.S.A.), could be placed inside the capillary. The trap temperature could then be directly measured. The chromatographic oven was programmed from 35 to 240°C at 5°C/min while a constant voltage of 1.000 V was applied across the trap. By measuring the current through the trap, the resistance across the trap could be calculated from Ohm's law. After measuring the resistance as a function of temperature during external heating, the trap was heated ohmically by increasing the current in a stepwise fashion. With the oven held at 35°C, the resistance was again taken from simultaneous measurement of current and voltage while directly measuring the trap temperature.

RESULTS AND DISCUSSION

To ascertain the contribution to peak variance due to the cryogenic trap, the shortest possible column was studied to maximize the effects from all sources of extra-column band broadening. The separations were also performed isothermally to prevent the solute focusing encountered with temperature programming. Under such demanding conditions, the trap must be capable of rapid heating to vaporize the sample components in a narrow plug. Heating that is slow relative to the temporal length of a split injection would be readily apparent as an increase in peak variance, commonly measured as the second statistical moment. Any injection perturbations which asymmetrically distort the plug will also lead to asymmetric distortions in the

TABLE II

SECOND AND THIRD STATISTICAL MOMENTS FOR NORMAL AND TRAPPED SPLIT INJECTIONS ON A 1.92-m COLUMN

Mean ± 1 standard deviation ($n = 7$).

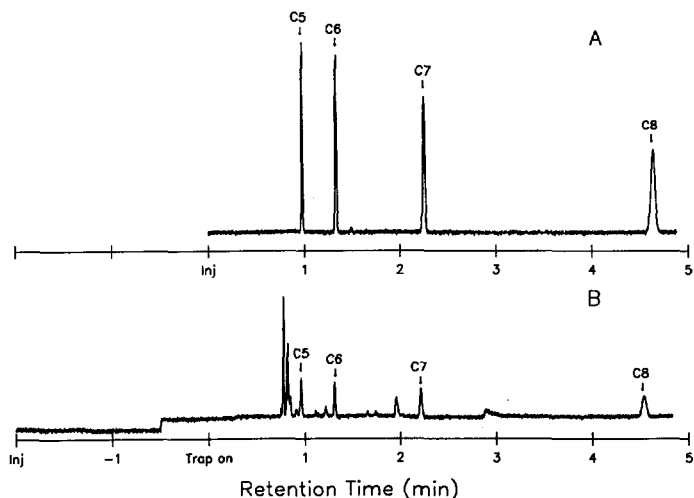| Sample	2nd Moment · 10^2 (s^2)		3rd Moment · 10^2 (s^3)	
	Normal	Trapped	Normal	Trapped
C_5	6.11 ± 0.49	5.33 ± 0.19	2.31 ± 0.48	1.78 ± 0.15
C_6	8.68 ± 0.59	7.81 ± 0.55	4.26 ± 0.64	3.58 ± 0.71
C_7	9.39 ± 1.81	9.95 ± 0.86	3.64 ± 2.96	5.30 ± 1.14
C_8	20.59 ± 0.55	17.56 ± 0.73	2.68 ± 0.34	2.40 ± 0.29

Fig. 1. Chromatograms of pentane, hexane, heptane and octane on an 11 m × 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. The additional peaks are presumably due to the air dilution.

resulting solute peaks. Such peaks will have a third statistical moment greater than zero.

Split injections performed without trapping were compared with split injections which were trapped for 120 s. Mean values for the second and third statistical moments of each peak are given in Table II for normal and trapped injections. It is clear that sample trapping does not impair the peak shape relative to a normal split injection. The larger values for heptane arose from a very small impurity eluted on the tail of the peak. The precision undoubtedly suffers from the limited digitization rates[10] imposed by this equipment for these rapid elution times ($t_0 < 6$ s), but is still better than 10% relative standard deviation (R.S.D.) for the second moment and 20% R.S.D. for the third. The demands of an injector for this short column are severe. The absence of band broadening for trapped injections relative to normal split injections demonstrates the ability of this trap to rapidly vaporize solutes.

A longer column was used for separating dilute gas samples in order to provide adequate resolution between the compounds of interest and extraneous trace components present in the sample matrix. A typical split-injection separation of the sample at a concentration of 2000 ppmv is shown in Fig. 1A. In this case, a 5-μl vapor phase injection is split at a ratio of 100:1. This chromatogram is featureless except for the 4 solutes.

Fig. 1B demonstrates the trapping and subsequent analysis of a 1-ml sample at a concentration of 50 ppbv (a dilution of 40 000 from A). The gaseous sample is injected without benefit of splitting 2 min before initiating the separation. Over a 90-s period, the sample slowly passes into the column at the carrier flow-rate of 0.0123 ml/s, moving from the injector into the oven to be trapped in the cooled section of the capillary. The injection port volume cannot be quantitatively swept at this flow-rate in 90 s, therefore, the splitter valve is opened after 90 s to completely flush the port

TABLE III

FIRST STATISTICAL MOMENTS FOR AN 11.0-m COLUMN

Mean $\pm$ 1 standard deviation ($n \geqslant 5$).

Sample	Split injection (2000 ppmv), first moment (s)	Trapped injection (50, 100, 200 ppbv), first moment (s)
C_5	58.27 $\pm$ 0.11	57.68 $\pm$ 0.20
C_6	79.52 $\pm$ 0.23	78.83 $\pm$ 0.22
C_7	134.78 $\pm$ 0.37	133.04 $\pm$ 0.24
C_8	277.46 $\pm$ 0.35	272.12 $\pm$ 0.33

before warming the trap. The action of the valve creates a slight baseline disturbance. The separation begins when current is applied to the trap, indicated as time zero in Fig. 1B. Other components of ambient air present in the sample are also concentrated and then detected by FID. Even with these background peaks, the four components of interest are eluted at this level without significant interference.

Because these samples were prepared from ambient air, the absence of methane in the chromatograms was initially puzzling. Methane is present at a concentration of roughly 1.6–1.7 ppmv[11] in the atmosphere, or about 40 times greater than the dilute alkane samples. However, the vapor above liquid nitrogen only cools the trap to $-150°C$. This is well above the boiling point of methane. Thus, methane is not concentrated within the trap and is eluted as a broad peak indistinguishable from the baseline.

The reproducibility of retention times, as given by the standard deviation of the first statistical moment, is shown in Table III for split and trapped injections. The precision is comparable for the two methods. No differences were observed between the 50-, 100- and 200-ppbv samples. The mean retention times are slightly less for the trapped injections because the separation begins at the trap, about 15 cm downstream from the inlet.

A plot of peak area *vs.* sample concentration is shown in Fig. 2 for two compounds with greatly different retention ratios. The precision is indicated by error bars
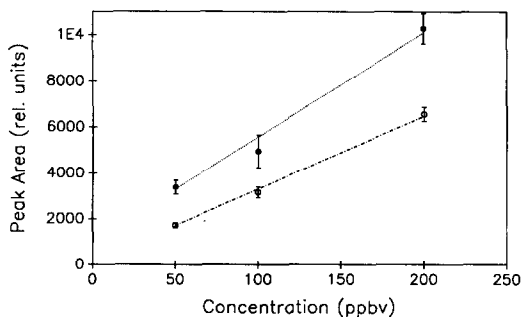

Fig. 2. Peak area *vs.* concentration for an 11 m $\times$ 250 μm I.D. capillary column coated with 0.4% (w/v) SE-30. $\bigcirc$ = Pentane, k = 0.305; $\bullet$ = octane, k = 5.16. Samples were trapped for 2 min. Mean $\pm$ 1 standard deviation (n = 3 or 4).
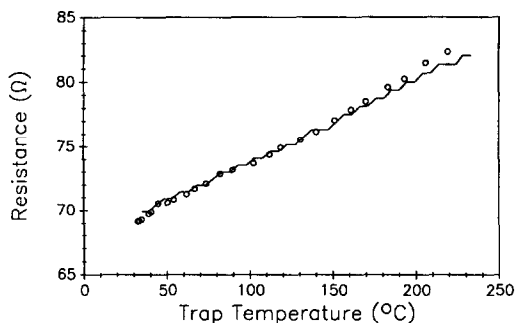
Fig. 3. Trap resistance *vs*. trap temperature. The trap temperature was measured inside the capillary. — =
Trap resistance measured as trap was heated externally. ○ = Trap resistance measured as trap was heated
ohmically.

of ± one standard deviation. If peak areas were reported relative to an internal
standard the precision would improve considerably. Digitization error for these small
signals also contributes to the scatter. Even so, the precision for all solutes at 50 ppbv
is better than 10% R.S.D. For replicate split injections with much larger signals, the
precision is 3% R.S.D.

The trap resistance varies linearly with the temperature when heated externally
as shown by the line in Fig. 3. The stepwise increase is due to the digitization limita-
tions in reading the current through the trap. The circles in Fig. 3 show how the
resistance changes with temperature when the trap was ohmically heated. As expect-
ed, the correspondence between the two sets of data is quite good. This confirms that
the relationship between the trap's resistance and temperature is independent of how
the trap is heated. The tedious operation of inserting the thermocouple into the trap
was required to establish this independence. In practice, it is not necessary to measure
the temperature within the capillary directly, even for calibration. The trap temper-
ature can be easily determined as a function of resistance by assuming the oven and
the trap to be at the same temperature during calibration. Because the thermal mass
of the trap is extremely low, this assumption is valid.

The relationship between trap resistance and temperature is an attractive fea-
ture of this cryogenic trap. The temperature can be determined from the voltage and
current used to heat the trap. No external thermal sensor, which would cause a cold
spot, is needed. With a suitable feedback system, the temperature of the trap could be
easily controlled to within 5°C. This should facilitate trace level capillary column
separations of volatile, thermally labile compounds such as peroxyacetic nitric an-
hydride (PAN)[12]. This compound can be analyzed isothermally without cryogenical-
ly cooling the column, but some means of concentrating the sample at the column
head is required. The applicability of the cryogenic trap is being explored. It is reason-
able to expect the sensitivity for PAN to be increased two or three orders of magni-
tude relative to the alkanes by substituting an electron-capture detector (ECD) for the
FID. This should make it possible to perform PAN determinations in ambient air at
the parts-per-trillian level.

Other trap heating profiles may also be desirable for certain samples. A multi-
step, or temperature-programmed trap warming would crudely prefractionate sam-

ples. The least volatile components could be retained and later removed during back-flushing while heating the trap. The negligible thermal mass of the trap allows rapid cycling between the temperature limits set by the cooling chamber and the decomposition of the polyimide layer on the capillary.

Accurately controlled trap heating should be equally applicable for supercritical fluid chromatography (SFC). In this separation technique, the partition ratio of solutes also changes with temperature, however, higher temperature causes the mobile phase density to decrease and the solute partition coefficient to favor the stationary phase. Thus, unlike GC, increased temperature causes longer retention. To trap solutes in SFC, the trap would be warmed. Solute migration would commence when the trap was allowed to cool. Here, the speed of cooling is important and the low thermal mass of this trap should prove ideal. The concept of concentrating solutes within a heated zone of a capillary SFC column was suggested several years ago[13], but a suitable trap with low thermal mass was unavailable at that time. A capillary trap could also be connected upstream from a packed SFC column to concentrate samples and sharpen the concentration profile of the injection.

Phillips et al.[14] have described a thermal desorption modulator for GC based on an electrically conductive metallic paint. The design requirements of a modulator are similar to those of a cryogenic trap[15,16]. Conversely, the trap presented herein should be useful for multiplex chromatography. The gold layer is an excellent thermal conductor and has a thickness on the order of nanometers as opposed to 40 μm for paint[14]. In addition, the gold layer is free from any binders present in paint. These non-metallic components conduct heat poorly compared with gold and could slow the cooling cycle of a modulator. They may also possibly limit the maximum allowable modulator temperature. Thus, a cryogenic trap based on a thin layer of metallic gold has inherently faster thermal slew rates and may provide certain advantages as an injection modulator.

CONCLUSIONS

The cryogenic trap described in this paper exhibits a variety of attractive characteristics. Its low thermal mass allows rapid heating and cooling. This quality permits samples to be vaporized on a short enough time scale for isothermal analysis without contributing to band broadening. Rapid cooling should also render the trap useful for thermal modulation chromatography and SFC. Unlike some other cryogenic traps, the chromatographic stream is free from connections. All trapping occurs within the column itself. This also eliminates any sample contact with heated metal surfaces. Although a heated splitter was used for this study, gentler methods could easily be substituted.

Other positive features arise from the electrical properties of the gold layer. Because the layer is so thin, its resistance is high and it can be heated with minimal currents. Thus, only thin wire leads and voltages between 10 and 15 V are required. Such currents and voltages can be easily controlled without elaborate circuitry. Because of these features, this trap could readily be used in a fully automated system. Resistance across the trap leads varies directly with the trap temperature, in effect forming a resistance thermometer. By measuring the trap current and voltage, the trap temperature can be determined. With an appropriate feedback circuit, the tem-

perature could be accurately controlled. Since the gold layer itself poses no practical thermal limits, the trap temperature may range from that of the cryogenic bath to the maximum operating temperature of the column.

Capillaries can be equipped with the cryogenic trap after they have been coated. Thus, commercially prepared columns may be retroactively fitted with a trap. If the stationary phase cannot tolerate the required curing temperature, it should be possible to locally heat only the trap section while purging with an inert gas from the detector end. The gold layer, once applied, is quite durable and can easily be installed before coating if heating would damage the phase or column deactivation. Because the gold coating does not prevent the use of any other injection technique, all capillaries could have the thermal trap applied near the inlet before coating. The gold application step is simple and inexpensive, less than US$ 1.00 of gold solution was needed to prepare the traps described above.

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