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AUTOMATED QUARTZ INJECTOR/TRAP FOR FUSED-SILICA CAPILLARY COLUMNS

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SUMMARY

An automated quartz injector/trap was developed for a Perkin-Elmer 3920 gas chromatograph. The injector/trap serves to concentrate gaseous or liquid samples without introducing organic contaminants. The concentrated sample is volatilized and transferred to a second trap made by cooling a small section of a fused-silica capillary column. Reconcentration in the capillary column preserves band-shape and provides a system which delivers quantitative results on a variety of samples. Liquid samples show relative standard deviations of 1 % and 2 %, respectively, for isothermal and temperature-programmed analyses. A detection limit of less than 1 ppb is expected, with a flame ionization detector, for samples of *n*-octane in air.

INTRODUCTION

The growing interest in the monitoring of air pollution, in the diagnosis of disease states, and in the characterization of aromas and odors, demands rapid and accurate measurement of organic compounds at parts-per-billion (ppb*) levels. The measurement of concentrations at the ppb level can be performed with gas chromatographs equipped with flame ionization detectors (FIDs). However, because of limitations in FID sensitivity, the analysis requires injection of several milliliters of a gaseous sample or several microliters of a liquid sample into a column.

The introduction of these large volumes into a capillary column requires special techniques to preserve the efficiency of the column: gaseous samples are concentrated in traps[1–6], while liquid samples are concentrated via the solvent effect[7] or by means of extracolumnar devices[8].

Concentration techniques are frequently plagued by artifacts caused by the surfaces contacting the samples. Traps packed with solid materials may retain compounds strongly enough to introduce large quantitation errors, or in extreme cases, cause the total loss of some compounds. Another problem associated with concentration techniques is the introduction of significant levels of contaminants, along with

* Throughout this article, the American billion (10^9) is meant. Concentrations of gaseous samples are expressed as v/v.

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the sample, into the analytical system. This problem is particularly important when measuring compounds present at ppb levels and below.

Inert traps for gaseous samples[9,10] and injectors for liquids[11,12] have been reported; however, these devices are designed to handle only one type of sample: either gaseous or liquid. Rijks *et al.*[13] reported a capillary trap for condensing material contained in gaseous or liquid samples. The authors reported analyses on 1-ml and 0.2-μl volumes of gaseous or liquid samples directly charged into the trap by means of syringes, but long waiting times were necessary to allow the unwanted solvent to pass through the column. The authors suggested the use of an appropriate exhaust between the the trap and column to minimize this drawback.

In this report we describe an automated injector/trap for fused-silica capillary columns. The system is designed to perform rapid, artifact-free, quantitative measurements of nanogram and subnanogram amounts of materials contained in large volumes of either gaseous or liquid samples.

EXPERIMENTAL

Modified gas chromatograph

A block diagram of this unit is shown in Fig. 1. A Perkin-Elmer 3920 with dual FIDs was modifed by the installation of a quartz injector/trap, a heated four-port valve and actuator, and a second trap for the concentration of materials at the head

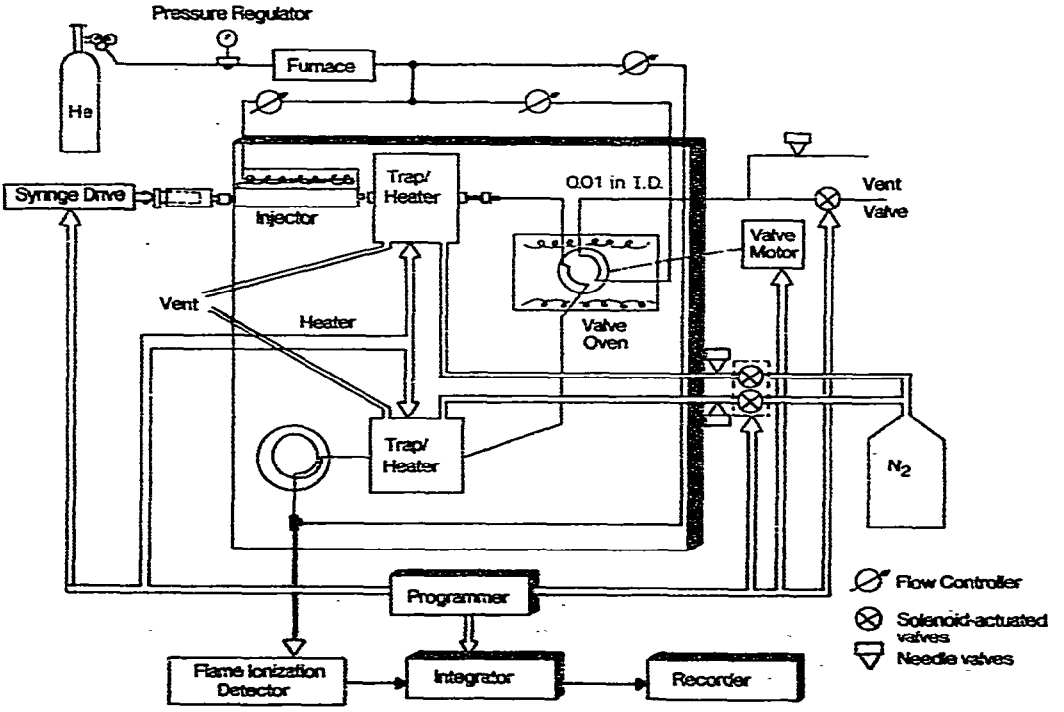

Fig. 1. Functional diagram of a gas chromatograph equipped with injector/trap system. Four-port valve is shown in the "inject" position.

of the column. The unit was also equipped with "ultra clean" grade flow controllers (Model 8744, Brooks, Hatfield, PA, U.S.A.), and a double pattern metering valve (Nupro, Willoughby, OH, U.S.A.) to match pressures when the four-port valve is switched. Organic materials present in the helium carrier gas were converted into carbon dioxide and water by flowing the gas over copper (II) oxide heated to 700°C by means of an electric furnace (Lindberg, Watertown, WI, U.S.A.).

The quartz injector/trap (first trap) is shown in Fig. 2. This unit was made by wrapping 24 loops of 2.68 Ω/ft. glass-insulated nichrome wire (Pelican Wire, Naples, FL, U.S.A.) around a 6-cm section of a quartz tube (part D) 28.5 cm long (Scientific Quartz, Fairport Harbor, OH, U.S.A.). This tube is 3 mm O.D. × 1 mm I.D. The wrapped section corresponds to the trapping section of the injector and is packed with quartz fibers. The trapping section is enclosed in a PTFE jacket (C) which serves to contain the liquid nitrogen used for cooling the trap. The trapping temperature is monitored and controlled via an iron-constantan thermocouple (Thermoelectric Co., Saddle Brook, NJ, U.S.A.) attached externally at the midpoint of the trap. The PTFE jacket is connected to the injection port (A) by means of a brass barrel (B) fitted at both ends with Swagelok nuts. The injection port was made by drilling a 1/16-in. hole on the side of a reducing union (1/8 to 1/16 in.) followed by insertion of a 1/16 in. O.D. piece of tubing. After soldering, the tube connects the injection port to the carrier gas source.

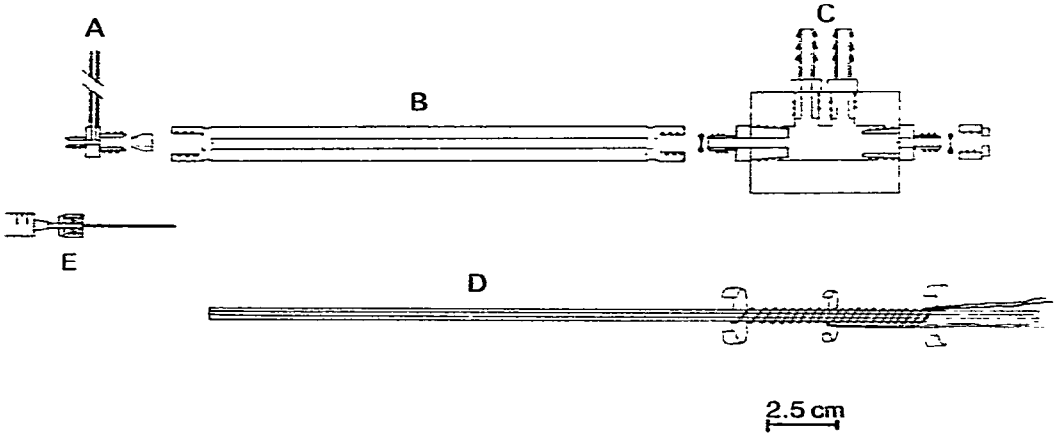

Fig. 2. Diagram of injector/trap for a Perkin-Elmer 3920 gas chromatograph. A = Modified injection port; B = brass barrel; C = PTFE jacket; D = quartz tube with thermocouple and heating wire; E = adapted syringe.

The injection port is sealed by a Vespel ferrule (Altech, Arlington Heights, IL, U.S.A.). The samples are introduced by means of gas-tight syringes equipped with a 1.5-cm section of 1/16 in. stainless-steel tubing and a Swagelok nut (E). This fitting mates with the body of the reducing union used as the injection port. Gaseous samples of less than 1 ml are injected by hand. Larger volumes are introduced by means of an infusion pump (Sage Instruments, Cambridge, MA, U.S.A.) mounted so that the syringe needle is aligned with the injection port. The infusion rate is 10 ml/min or less.

A heated four-port valve (Carle Instrument, Fullerton, CA, U.S.A.) serves to vent unwanted solvents or to transfer the contents of the trap to the column. The valve is mounted inside the column oven and is switched by a motorized actuator

mounted externally to the chromatograph (Fig. 1). An auxilliary heater is necessary for quantitative transfer of some materials. The heater was made by wrapping nichrome wire around a three-section piece of insulated aluminium sheet and mounting this unit so that it fits around the valve. The surface temperature of the valve was monitored by a thermocouple attached to the valve body.

Materials transferred through the valve are reconcentrated in the fused-silica column by making the column part of a second cold trap (Fig. 1). This trap is similar to the trap described above except for the replacement of the quartz tube by an insulated 1/16 in. O.D. × 0.02 in. I.D. stainless-steel tube *ca.* 15 cm long. The column is passed through the tube prior to connection to the valve. A 25 m × 0.2 mm I.D. SP-2100 fused-silica column (Hewlett-Packard, Palo Alto, CA, U.S.A.) was used throughout this work.

The system was operated under a constant pressure of 20 p.s.i. The column and injector pressures were adjusted to 15 p.s.i. by means of the needle valves built into the flow controllers. The controllers only served as variable restrictors because the system flow-rates (less than 1 ml/min) are below their operating range. The column back-pressure on the injector/trap was simulated by adjusting the double pattern needle valve connected at the end of a 1 m × 0.01 in. I.D. tubing.

The chromatograms were integrated by a Varian CDS 111 integrator and displayed by a Perkin-Elmer 056 recorder.

Programmer

All the necessary operations are controlled by a programmer built around an Intel 8010 single board computer. Communication between the programmer and operator is by a keyboard and an alphanumeric display, while the control of the instrumentation is done with opto-isolated relays. The relays are switched according to a time sequence determined by the operator. Four relays can be driven from analogue comparators used to sense the cooling and heating cycles of the traps. These temperatures are set by potentiometers accessible to the operator.

The software is written in PL/M and is designed to perform the interactions with the operator in the background while carrying the systems operations in the foreground. Therefore, timing and controlling functions have the highest priority and yet the computer is free, most of the time, to allow the operator to monitor the status of the experiment or to change parameters during the run.

System operation

The operations performed by the automated system are: trapping of materials of interest in the quartz injector/trap and venting of the solvent, desorption and transfer of materials from the quartz trap to the column, reconcentration in the column followed by desorption and elution. These operations are shown in Fig. 3. The analysis begins by injecting a sample while the four-port valve is in the "load" position. In this position the injector/trap is connected to the atmosphere via the 0.01-in. I.D. tubing and vent valve. The materials of interest are retained in the trap section of the injector while most of the solvent is vented, the solvent injected being either gaseous or liquid.

The trapping of liquids uses the solvent effect to concentrate materials in the trap: the temperature of the trap is controlled a few degrees below the boiling point of

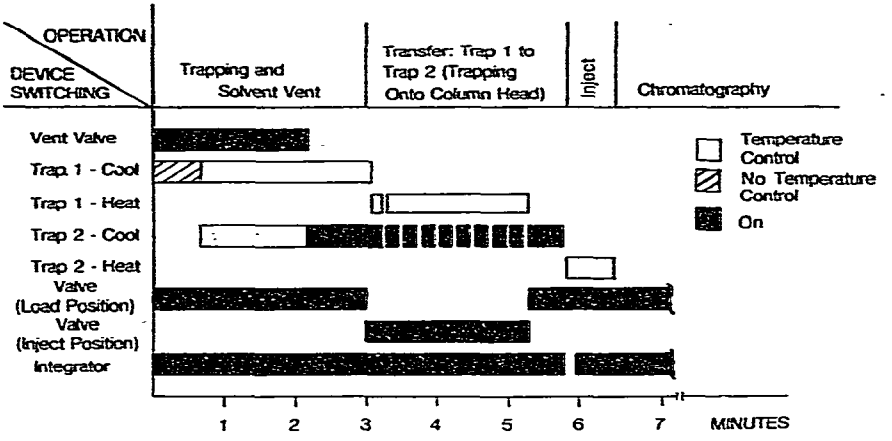

Fig. 3. Typical program for the injection of gaseous and liquid samples.

the solvent. Gases are trapped in a similar fashion except that the first trap temperature is low enough to prevent losses of any material of interest. This temperature depends on the mass of quartz fibers used to pack the first trap, the smaller masses require lower temperatures for quantitative trapping. Throughout this work the trap was packed with a 2.5-cm long bundle of fibers weighing *ca.* 5 mg. When the trapping is complete (Fig. 3), the valve is switched from the "load" to the "inject" position and the trap heated to 270°C in *ca.* 9 sec. The temperature is allowed to drop to 190°C and is controlled at this temperature for the remaining time required to transfer materials from the first trap to the column. The transfer time can be programmed by the operator to accommodate materials that may adsorb to the internal parts of the valve. The transfer was optimized for some compounds by the use of the valve heater. For example, both band-shape and recovery of *n*-hexadecane improved when the valve was heated to 210°C during transfer.

The materials transferred to the head of the column (second trap) are reconcentrated by keeping a small section of column at −150°C or below by flowing liquid nitrogen into the PTFE jacket. The materials are desorbed by heating the stainless steel tubing encasing the column to 300°C in 10 sec. This step marks the beginning of the gas chromatographic run. To insure complete desorption, the programmer keeps the temperature of the tube at 220°C for an additional 30 sec.

RESULTS AND DISCUSSION

The collection efficiency of the quartz injector/trap (first trap) depends on trap temperature, mass and type of packing material, and linear velocity of the sample as it travels through the trap. The desorption depends primarily on the first two factors mentioned.

The internal temperature of the trap was measured by a thermocouple placed inside the quartz tube. This thermocouple was positioned opposite to the external thermocouple used to monitor and control the trap temperature. The instantaneous temperature recorded by the thermocouples agree to ±10°C over the range −100 to

200°C. Therefore, the trapping and desorption temperatures measured by the external thermocouple are a good indication of the actual conditions experienced by the sample.

The conditions required to collect and desorb materials contained in the column (second trap) were established empirically because of the difficulty in measuring the actual temperature inside the column.

The temperature of the first trap and its heating profile with respect to time were measured with packings of quartz fibers ranging in mass from 23 to 5 mg. The lower mass was selected because of the favorable desorption profiles measured with highly surfacephilic materials (free carboxylic acids and alcohols). However, the low mass limits the linear velocity through the trap to 30 cm/sec for maximum collection efficiency. Consequently, the maximum infusion rate for a gaseous sample is 10 ml/min.

Although the cooling and heating of the traps are reproducible, cooling produces unavoidable changes in oven temperature. These changes, and the changes in pressure due to valve switching, combine to produce variations in the retention time: the range of standard deviations is 0.03–0.05 and 0.06–0.12 min for isothermal and temperature-programmed runs, respectively. However, the retention times are independent of the solvent used. We observed no differences in the retention times of hydrocarbon mixtures in *n*-pentane, isopentane, dichloromethane or air. An exception is the injection of gaseous samples exceeding 10 ml and having high relative humidity: the retention time of materials present in these samples decreased and the standard deviations increased compared to values obtained by injecting smaller volumes. This behavior is caused by the formation of an ice plug in the capillary column which obstructs the gas flow and increases the back-pressure when the column is cooled to −150°C. When the column is heated to start the chromatography, the ice plug is vaporized. This results in an increase in the linear velocity of the carrier gas and a reduction of retention times. An air volume of 20 ml, at 50% relative humidity, is the largest practical sample volume for the 0.2-mm I.D. column when the first trap temperature is below 0°C.

The analysis of gaseous samples was performed by keeping the first trap at −100°C. The experimentally determined composition of four dilutions of an *n*-hydrocarbon mixture (C_6, C_7 and C_8) in air agrees to ±10% relative to the nominal composition of the mixture for injections containing a total mass of hydrocarbons ranging from 210 to 1.2 ng. The results are shown in Table I. A chromatogram of the 1.2-ng sample is shown in Fig. 4, where the masses of *n*-hydrocarbons (C_6, C_7 and C_8) injected are 400 pg per compound. These masses correspond to a concentration of 5 ppb per compound when a 20-ml sample is injected. The signal-to-noise ratio of the *n*-octane peak is better than 20. Therefore, the estimated detection limit for this compound is *ca.* 40 pg or 0.5 ppb. Residual contaminants in the syringe or air are apparent in the chromatogram. These contaminants increased the detection limit of the *n*-hexane and *n*-heptane and are responsible for the results reported in Table I for the 0.7-ng sample (*ca.* 250 pg of mass per compound).

The quantitative analysis of liquid samples of hydrocarbons is shown in Table II. The relative standard deviation is 1% when the analysis is performed under isothermal conditions and increases to *ca.* 2% for temperature-programmed runs. These results were obtained while injecting liquid samples ranging in volume from less than

TABLE I

DISTRIBUTION OF *n*-HYDROCARBON (C_6, C_7 AND C_8) STANDARDS IN AIR SAMPLES

Volume taken (ml)	*Total mass injected (ng)*	*Composition (% found)*		
		C_6	C_7	C_8
0.1	210	31.7 ± 0.6	35.5 ± 0.2	32.9 ± 0.8
1.0	11.6	32.1 ± 0.4	35.2 ± 0.0	32.8 ± 0.4
10.0	0.7	37	35	29
20.0	1.2	29	37	34
Nominal composition (%)		32	34	34

1 to *ca.* 4 μl. The peak area increased linearly with volume injected as shown in Fig. 5. The relative deviation of an individual value from the "best fit" value is less than 10%. The smallest volume injected is an exception. The larger relative error is probably caused by the reading error of the syringe. A typical chromatogram is shown in Fig. 6.

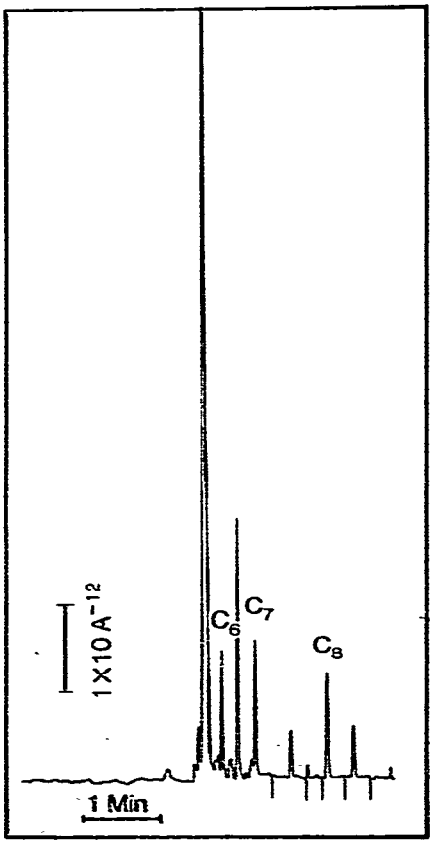

Fig. 4. Chromatogram of *n*-hydrocarbons (C_6, C_7 and C_8) in a 20-ml air sample. The amounts injected (400 pg) correspond to concentrations of *ca.* 5 ppb per compound.

TABLE II

REPRODUCIBILITY OF HYDROCARBON ANALYSES UNDER ISOTHERMAL AND TEMPERATURE-PROGRAMMED CONDITIONS

A: Isothermal analysis: 170°C, injection port 200°C. B: Temperature-programmed analysis: 140°C isothermal hold 4 min, 8°C/min to 190°C, final hold 2 min. Injection port 200°C.

Conditions	*Injected volume (μl)*	*Composition (% found)*			
		C_{10}	C_{12}	C_{14}	C_{16}
A	1.6		25.0	34.0	41.0
	0.5		24.9	34.7	40.4
	0.8		25.1	33.7	41.2
	0.3		25.1	34.5	40.4
	1.1		24.9	34.1	41.0
Mean			25.0	34.2	40.7
Relative standard deviation (%)			0.4	1.3	1.0
Nominal composition (%)			26	34	40
Sample concentration		25 ng total mass of standards per microliter of pentane			
B	3.8	14.8	22.8	29.0	33.5
	2.5	14.8	22.7	29.1	33.5
	0.5	14.8	21.9	28.9	34.4
	1.0	14.2	22.4	29.3	34.1
	1.2	14.5	22.4	29.3	33.7
	0.8	14.5	21.3	29.0	35.3
	0.7	14.7	21.9	29.0	34.4
	1.3	14.0	22.5	29.1	34.3
Mean		14.5	22.2	29.1	34.1
Relative standard deviation (%)		2.0	2.2	0.5	1.7
Composition by independent GC		14.7	21.3	29.3	34.7
Nominal composition (%)		17	22	28	33
Sample concentration		30 ng total mass of standards per microliter of pentane			

The remaining solvent, pentane, does not interfere with the *n*-decane peak since the boiling point difference between these two compounds is *ca.* 140°C. We have successfully performed analyses of *n*-C_8 in pentane solutions where the boiling point difference is 90°C. Compounds having even smaller boiling point differences with the solvent could be analyzed by improving the temperature control of the injector/trap.

All liquid samples were injected by the use of a solvent flush technique where the sample was followed by an air segment and a small amount of solvent. The volume of solvent is comparable to the needle volume, and suffices to displace the sample from the needle. Low recoveries were obtained when a hot needle injection, akin to that described by Grob and Neukom[14], was used to introduce the sample. The syringe needle was equilibrated in the injection port for over 30 sec prior to the injection of a sample. Except for the 5-mm section of needle joining the syringe barrel and the Swagelok adapter, the lowest needle temperature is 120°C. This temperature was measured at the point where the adapter and injector mate, the rest of the needle

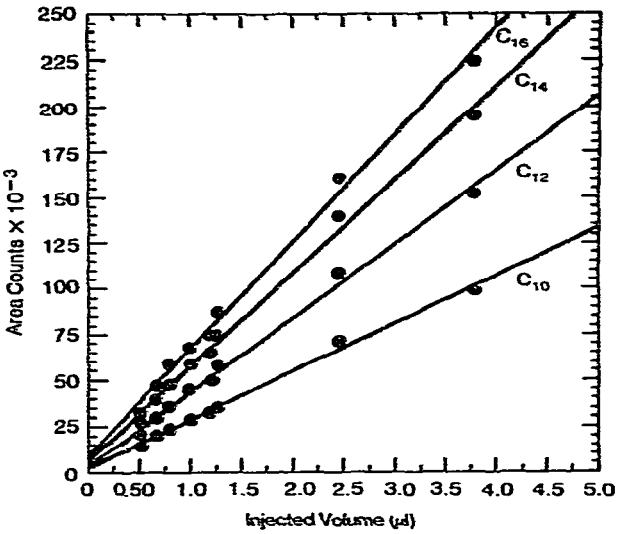

Fig. 5. Dependence of integrated area on volume of hydrocarbon standard injected.

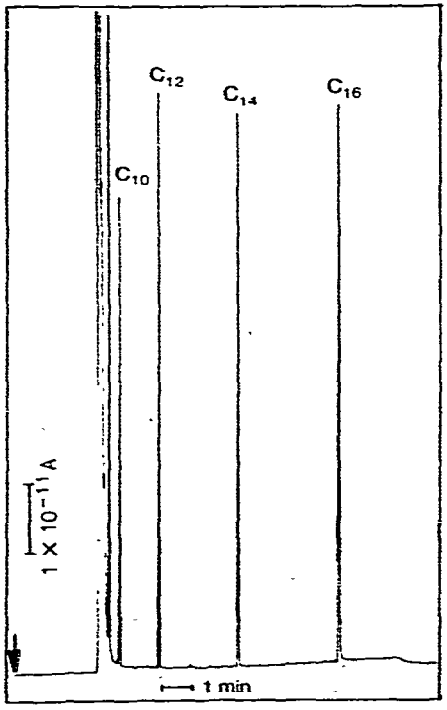

Fig. 6. Temperature-programmed analysis of *n*-hydrocarbons. Temperature program: 140°C isothermal hold 4 min, 8°C/min to 190°C, final hold 2 min. Sample volume, 3.8 µl.

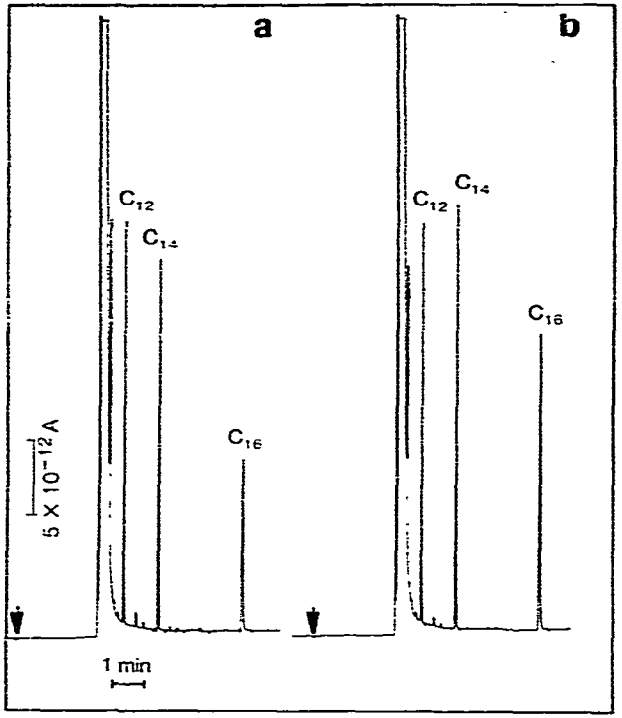

Fig. 7. Influence of injection method on quantitation. Injector temperature, 200°C. Isothermal run (170°C): a, hot needle injection; b, solvent flush injection. Injection of 1-μl sample containing a total C_{12}–C_{16} mass of 25 ng.

(*ca.* 3 cm) is at the injector temperature (200°C). Discrimination of *n*-hexadecane (b.p. 288°C) is apparent in the chromatogram shown in Fig. 7, and the chromatogram suggests a slight loss of *n*-tetradecane. The extent of the losses are shown in Table III. The area ratio of $C_{12}/(C_{12} + C_{14})$ is higher for the hot needle injection, indicating a small loss of C_{14}. However, the loss is small enough to preclude a significant change in the standard deviation of this ratio. The standard deviation for the ratio $C_{12}/(C_{12} +$

TABLE III

EFFECT OF INJECTION METHOD ON QUANTITATION OF A HYDROCARBON MIXTURE

Injector temperature, 200°C, isothermal run, 170°C.

Injection method	*Composition (% found)*			*Area ratio*	
	C_{12}	C_{14}	C_{16}	$\frac{C_{12}}{C_{12} + C_{14}}$	$\frac{C_{12}}{C_{12} + C_{16}}$
Solvent flush	25.0	34.2	40.8	0.422 ± 0.005	0.380 ± 0.005
Hot needle	30.1	37.2	32.6	0.448 ± 0.005	0.48 ± 0.03
Nominal composition	26	34	40	0.43	0.39

C_{16}) is greater for the hot needle injection compared to the solvent flush injection and the ratio is higher than expected, corresponding to losses of C_{16} averaging 35%.

The injector/trap fused-silica column system presented here has been applied to the quantitation of known materials present in headspace samples. Equipment calibration is conveniently done by the injection of standards dissolved in liquid solvents. Demonstration of inertness and applicability to the analysis of different classes of compounds will be the subject of subsequent communications.

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