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VERSATILE ALL-GLASS SPLITLESS SAMPLE-INTRODUCTION SYSTEM FOR TRACE ANALYSIS BY CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A simple, versatile all-glass sample introduction system is proposed which can be easily coupled to the sample inlet part of commercially available gas chromatographic instruments without substantial modifications. The system allows the analysis of trace amounts of organic substances in large gaseous samples with narrow-bore open-tubular columns. The components are concentrated in a cooled capillary trap coated with OV-101 stationary phase and thermally vaporized in the presence of a negative temperature gradient across the trap in the direction of the carrier gas flow. A simple modification of the system is described for the introduction of concentrates released thermally from adsorbent-packed traps. The influence of various factors on trapping and separation efficiency, qualitative and quantitative reliability, possible applications and limitations are discussed.

INTRODUCTION

Splitless introduction of samples is a particularly attractive technique for trace analysis with capillary columns. This technique renders it possible to utilize fully the high sensitivity of capillary gas chromatographic (GC) analysis and the results of quantitative analysis are more reliable owing to well defined sample charges. On the other hand, special steps must be taken with splitless sample introduction techniques to arrange that the initial sample-charge band in the column is sufficiently narrow, in order to avoid severe losses in separation efficiency and, consequently, a decrease in the sensitivity of analysis.

There are essentially three ways to obtain a sharp initial band in the capillary column, each having certain advantages and limitations:

(i) Cryogenic condensation. The sample-charge vapours being swept from the injection chamber by the carrier gas are trapped in a cold zone at the column inlet, whereupon the deposit is thermally vaporized and chromatographed. The cold zone can be created simply by immersion of a section of the column[1,2] at its inlet and/or

a pre-column[3] attached to the column inlet in a liquid nitrogen bath. Several more sophisticated designs of injection port based on the principle of cryogenic condensation have been described. Cramers and Van Kessel[4] employed a stream of expanding carbon dioxide to create a cold section at the inlet of the column and demonstrated the performance of the arrangement by an analysis of compounds boiling at temperatures above the boiling point of *n*-undecane. Groenendijk and Van Kemenade[5] cooled the inlet of a steel capillary column by pulling an appropriate part of the column out of the thermostat and blowing a stream of air on it. The system was used for the analysis of derivatives of steroids. The automatic Pye sample introduction system for capillary columns is based on a similar principle[6]. Murray[7] described a rather complicated arrangement for transferring concentrates of headspace volatiles from adsorbent-packed traps into wide-bore (0.5–0.75 mm) capillary columns. The cold zone was created in a pre-column packed with Chromosorb W (40–60 mesh) coated with 10% OV-101, cooled by a "cold finger" filled with liquid nitrogen. Arrangements involving the use of various exchangeable capillary pre-columns[8] and/or microtraps[9] as well as the "selective injection" described by Schomburg *et al.*[10] also can be classified in this category of sample introduction technique.

The application of all of these methods usually requires rather extensive modifications of the sample inlet port of the gas chromatograph. The applicability of a given instrumental arrangement is limited in most instances just to the range of problems for which the arrangement has been developed.

(ii) Utilization of the "solvent effect". Grob and Grob[11,12] were the first to show that the solute components can be efficiently focused by virtue of the temporarily enhanced sorption capacity due to a large solvent zone at the capillary column inlet. This effect was also studied and utilized by others[13]. Considering the very delicate transitory physical situation in which the formation of the initial band of solutes in the column takes place with this mode of sample introduction, it is easy to conceive that the initial width of the band will depend on a number of experimental factors, such as the chemical nature and physical properties of the solvent, sample size, time for which the given amount of sample is being charged into the inlet port, design and temperature of the inlet port, carrier gas flow-rate, regime of purging the inlet port with the carrier gas and column temperature. Although the utilization of the solvent effect can certainly be considered as an attractive complementary splitless sampling technique, the necessity to optimize various experimental parameters for a particular analytical problem and the irreproducibility of retention times are the main limitations to the wider use of this technique.

(iii) Direct on-column injection. By employing special adapters to the inlet port and special sample chargers it is possible to introduce small amounts of sample directly into the capillary column[14,15]. The instrumentation is rather sophisticated and requires very fine manipulation. Recently, the Grob arrangement[15] for direct introduction of sample into the capillary column was made available commercially[16]. Low-volatility substances can be introduced into the capillary column by the falling needle technique[17] and/or by the similar technique of instant sample vaporization[18]. In addition to being limited merely to work with low-volatility solutes, the latter two techniques are difficult to automate.

The sample introduction system described in this paper relates to the tech-

niques of category (*i*). It can be used for charging large-volume gaseous samples, gaseous concentrates liberated from concentration traps and for liquid samples. The system can easily be coupled with any gas chromatograph and/or a GC–MS combination and is amenable to automation. The system was mentioned briefly in a recent paper[19]. In this paper we discuss the performance characteristics, possible applications and limitations of the system.

EXPERIMENTAL

Analysis of directly charged samples

A schematic representation of the overall arrangement of the splitless sample introduction system is shown in Fig. 1. The all-glass trap proper (3), already described previously[19], is inserted in the injection port (4) of the gas chromatograph. The capillary inside the jacket is cooled or heated by an auxiliary stream of gas (nitrogen) directed by two metal three-way valves either via a cooling (6) or a heating (5) line. The arrangement of the cooling system provides for any suitable coolant to be used with regard to a given problem.

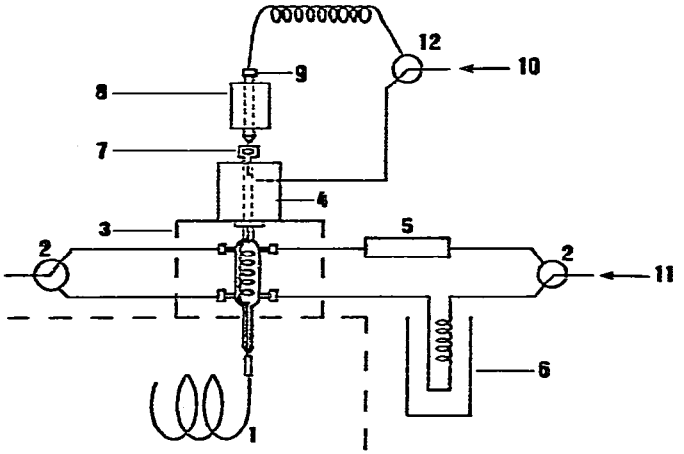

Fig. 1. Schematic representation of the splitless sample injection system. 1 = Capillary column (connected to the system by shrinkable PTFE tubing); 2 = three-way metal valves; 3 = trapping capillary (in a thermally insulated jacket); 4 = injection port; 5 = heater; 6 = coolant; 7 = septum; 8 = auxiliary oven; 9 = Tenax trap (connected to carrier gas supply); 10 = carrier gas inlet; 11 = auxiliary gas inlet; 12 = three-way valve.

By employing a dry-ice–ethanol mixture as the coolant, a temperature as low as −60° was attained in the centre of the jacket at a nitrogen flow-rate of 6–10 l/min through the cooling line. The power capacity of the heater (5) was chosen so as to attain inside the jacket a temperature of above 150° within 20 sec after switching the stream of nitrogen over to the heating line. The septum (7) is placed on the upper face of a short piece of thick-walled glass capillary (length 2 cm, O.D. 6.2 mm, I.D. 0.4 mm) which protrudes into the inlet of the injection port, thus preventing the former from excessive heating and minimizing its bleeding. Fig. 1 shows the injection mode.

After having cooled capillary 3 to the desired temperature, the sample is introduced by injection through the septum or via a sampling loop, and a volume of carrier gas corresponding to at least five times the volume of the inner space of the inlet port is allowed to purge the charge into the trapping capillary. The purging period takes about 10 min at the usual carrier gas flow-rates. Then the auxiliary stream of gas is switched over to pass through the heating line, upon which the deposit is flash-vaporized and swept by the carrier gas into the column.

Analysis of concentrates from enrichment traps

The system can easily be modified for the introduction of concentrates released thermally from adsorbent-packed traps while still preserving the possibility of introducing samples directly. A three-way valve (12) is connected into the carrier gas line (10), by means of which the stream is led either directly into the inlet port proper (the configuration shown in Fig. 1) or via a concentration trap (9). In our experiments the adsorbent-packed trap was a stainless-steel tube (6 cm × 4 mm I.D.) packed with Tenax GC (60–80 mesh) (Alltech Ass., Arlington Heights, Ill., U.S.A.). The trap is connected by one end to the carrier gas supply line and to the other end is attached a gas-tight hypodermic needle.

During the desorption period the trap is placed in a pre-heated oven (8) adjacent to the injection port, the needle being stuck through the septum. The carrier gas stream is directed by stopcock 12 to pass via the trap (9), thus transporting the gradually desorbed components into the cooled capillary trap (3). A desorption time of 7 min was chosen, the oven (8) being kept at 250°. After the desorption period has been completed, stopcock 12 is switched to its initial position. The trap is pulled out of the oven, and, after having allowed an additional 5–10-min period to purge the injection port with the carrier gas, capillary 3 is warmed by switching valves 2 to the configuration in which the auxiliary gas stream passes through the heating line.

Coating of the capillary trap

The capillary is washed with 5–10 ml of methylene chloride (GC-spectral quality, J. T. Baker, Philipsburg, N.J., U.S.A.) and then filled with a 1% solution of benzyltriphenylphosphonium chloride (Aldrich-Europe, Janssen Pharmaceutica, Beerse, Belgium) in methylene chloride. After 10 min, the capillary is gently emptied and dried by a slow stream of nitrogen. Then the capillary is filled with a 10% solution of OV-101 (Applied Science Labs., State College, Pa., U.S.A.) in *n*-hexane (Merck, Darmstadt, G.F.R.), emptied slowly (at a linear liquid plug velocity of below 1 cm/sec), and dried for 30 min by a stream of nitrogen at ambient temperature. The last three steps, starting with filling the capillary with the OV-101 solution, are repeated three times. Finally, the capillary is conditioned overnight at 150° under a stream of nitrogen.

A flame-ionization detector and an electrometer with a sensitivity of $1 \cdot 10^{-12}$ A per full-scale deflection (f.s.d.), were employed.

RESULTS AND DISCUSSION

Basic features of the system

The enrichment of trace amounts of compounds in gaseous mixtures in the

presence of a temperature gradient in a cooled capillary trap provided with a thin film of stationary phase must be conceived as a chromatographic process. Hence, the gaseous mixture is subject to a kind of temperature-gradient frontal chromatography upon entering the cooled trapping capillary, a process similar to that discussed by Kaiser[20] in his work on concentrating trace volatiles in the so-called temperature gradient tube[20]. Depending on their volatility, the components will move at different speeds through the cooled capillary and will be collected at different positions. The bands of the more volatile compounds will advance more quickly than less volatiles compounds.

The elution of the enriched compounds from the trap being heated as described above is a chromatographic process under temperature-programmed conditions. It is of crucial importance that there is a negative longitudinal temperature gradient across the trapping capillary in the direction of the carrier gas flow during both the cooling and the heating period. In this way a minimal band width will be obtained at the column inlet. Expectedly, the band width at the end of the trap will depend upon a number of factors such as volatility of the compounds, cooling temperature, length and film thickness of the trapping capillary, trapping time, the magnitude of the temperature gradient, the flow velocity of auxiliary nitrogen in the heating period and the final temperature.

The influence of some of these factors on the efficiency of trapping and the apparent plate number under the experimental conditions described above is discussed below for some aliphatic and aromatic hydrocarbons. The degree of trapping solutes and, consequently, the size of their peaks in the chromatogram, obviously depend on the duration of the trapping period and on the length of the capillary. Initially we worked with a 60-cm long trapping capillary. Later we tried capillaries of length 20 and 6 cm and found that while the performance of the 20-cm capillary was the same as that of the 60-cm capillary, a length of 6 cm was insufficient.

The coating of the trapping capillary with a liquid phase was found to be necessary for the system to function properly. Fig. 2 shows to chromatograms of identical 1-ml headspace gas samples (concentration = 10 ppb) obtained by the same procedure. The upper chromatogram refers to the case in which the trapping capillary was coated with liquid phase in the above-described way, whereas the lower chromatogram was obtained with a capillary that had been filled just once with a 10% solution of OV-101 in *n*-hexane and quickly emptied. A comparison of the two chromatograms indicates that in the second case the amount of the stationary liquid in the capillary was substantially smaller than that in the first case. Actually, a temperature of −50° was not low enough to attain quantitative trapping of *n*-hexane (2) and benzene (3); even with the capillary with the highest film thickness, only *n*-heptane (4) and the higher hydrocarbons were captured completely in this case. With the lightly coated capillary, benzene, *n*-heptane and toluene passed through.

The effect of the cooling temperature is demonstrated in Fig. 3. Two 1-ml headspace gas samples were analysed in the same way at different cooling temperatures. Chromatograms A and B refer to cases in which the trapping capillary was cooled to −55 and −10°, respectively. As would be expected, the effect of cooling the capillary is very similar to that of coating it with different film thickness of liquid phase. In order to prevent more volatile solutes from breaking through the

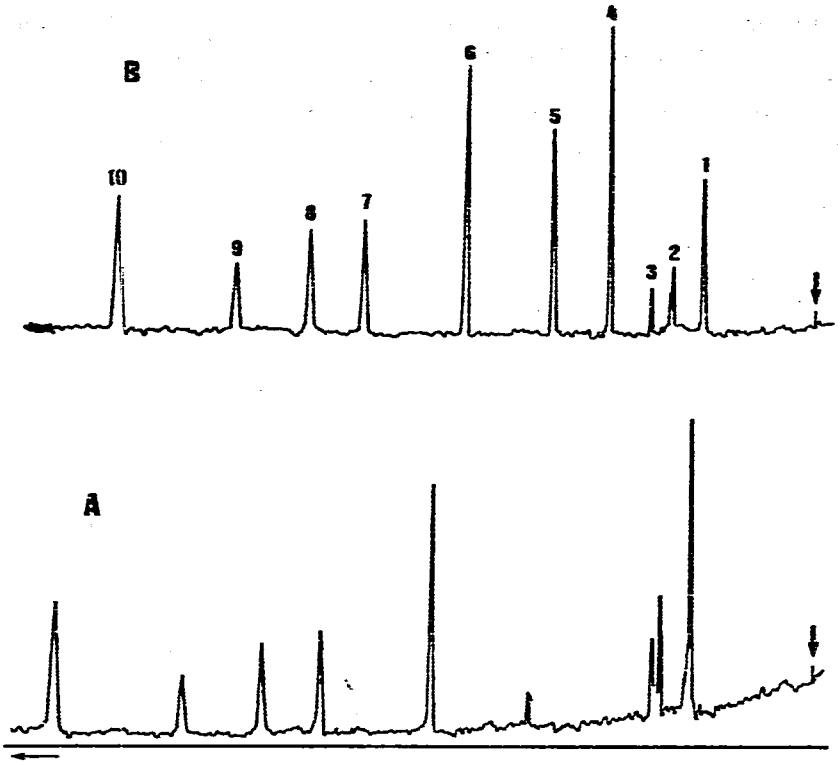

Fig. 2. Illustration of the performance of the system with the trapping capillary with (A) a thin film and (B) a thicker film. 1 = Acetone; 2 = *n*-hexane; 3 = benzene; 4 = *n*-heptane; 5 = toluene; 6 = *n*-octane; 7 = ethylbenzene; 8 = *m*-xylene; 9 = *o*-xylene; 10 = *n*-nonane. Conditions: see Table I.

cooled trapping capillary, the temperature of the latter can be further decreased by employing a more efficient coolant (*e.g.*, liquid nitrogen) and/or by increasing the flow-rate of nitrogen in the cooling/heating line (*cf.*, item 11 in Fig. 1).

The overall effect of all of the experimental factors mentioned above is demonstrated in Fig. 4. The plate number per unit column length is plotted as a function of capacity ratio for splitless sample injection with the cooled capillary trap and injection with the use of a splitter. Preliminary experiments showed that when the heating power is kept constant a further decrease in the cooling temperature will result in a decrease in the separation efficiency, particularly for more volatile compounds. Because the bands of volatile compounds advance more quickly than less volatile compounds in the cooled capillary their actual width in the cooled capillary trap is relatively larger. This results in a decreased separation efficiency after vaporizing the deposit.

The temperature of auxiliary nitrogen in the heating period is also an important factor with respect to the separation efficiency. Too low a heating power will result in slow vaporization of the deposit and, consequently, in excessively broad initial solute bands and a reduced separation efficiency. This effect may be

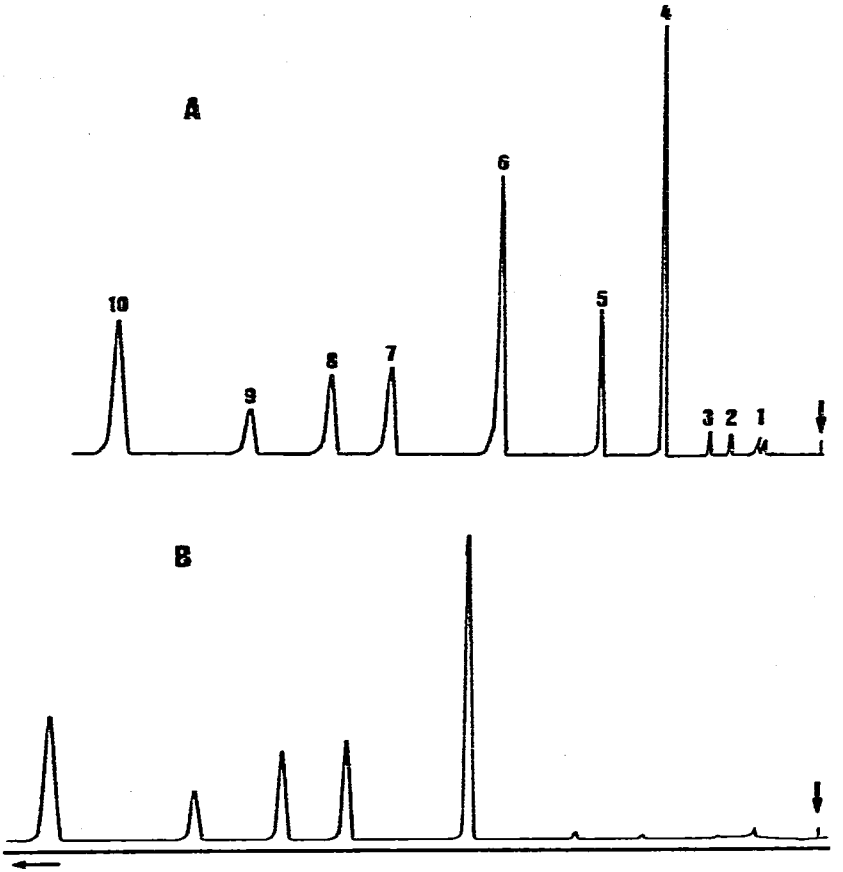

Fig. 3. Illustration of the performance of the system with the trapping capillary cooled to (A) −55° and (B) −10°. Peaks as in Fig. 2. GC conditions: 10 m × 0.25 mm I.D. stainless-steel column coated with squalane, 70°, nitrogen carrier gas, column inlet excess pressure $1 \cdot 10^4$ Pa (0.1 atm).

expected to manifest itself up to a temperature at which the vaporization of the deposit is virtually instantaneous. Further increases in the heating temperature will have no significant effect on the separation efficiency.

The upper temperature limit is governed by the thermal stability of the liquid film in the trapping capillary and/or the thermal stability of the solutes. A preliminary experiment, applying nitrogen at ambient temperature (with the heater off) instead of hot nitrogen to warm the capillary cooled to −55°, showed that the separation efficiency was reduced by about 30%. The temperature just sufficient for flash vaporization of the deposit obviously depends on the temperature to which the trapping capillary has been cooled. The influence of the cooling temperature and the speed of heating the trap on the band width at the column inlet, retention time and column efficiency for compounds of different volatility appears to be complicated and will be published elsewhere after a more detailed analysis.

Qualitative aspects

In a previous paper[19] we indicated the possibility of employing the splitless

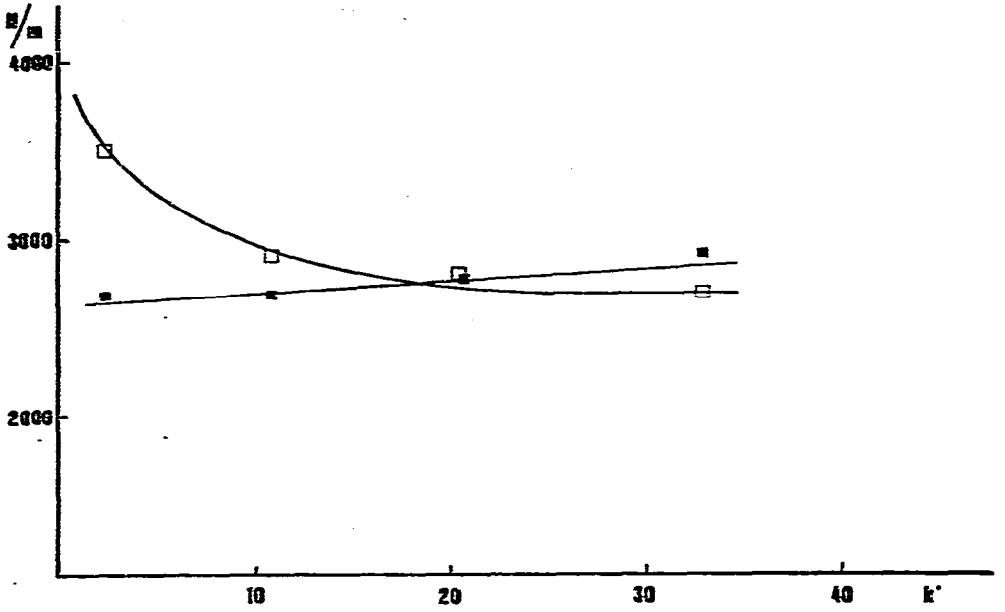

Fig. 4. Dependence of the plate number per unit column length (plates per metre) on the solute capacity ratio (k) with sample injection using a splitter (□) and with splitless sample injection (■). GC conditions as in Fig. 2.

injection system in high-precision measurements of retention indices. Table I contains some additional data to demonstrate this feature of the system. The retention indices obtained by injecting the sample with the use of a splitter and with the use of the splitless injection system are indeed virtually identical. The conditions used for the measurements were as follows: column No. 3 as described previously[19] (squalane, 70°), nitrogen carrier gas and column-inlet excess pressure $3 \cdot 10^4$ Pa (0.3 atm). The dead retention time was calculated from the linear relationship between the logarithm of the adjusted retention time and the carbon number of *n*-alkanes in both instances.

TABLE I

RETENTION INDICES OF SOME AROMATIC HYDROCARBONS ON SQUALANE AT 70° (I_{sq}^{70})

(a) Injection with splitter; (b) splitless injection.

Compound	$I_{sq}^{70°}$	
	a	*b*
n-Propylbenzene	926.7	927.1
1-Methyl-2-ethylbenzene	955.3	955.5
sec.-Butylbenzene	980.0	980.3
n-Butylbenzene	1026.3	1026.7
1,3-Dimethyl-5-ethylbenzene	1041.0	1041.4
2,3-Dimethyl-4-ethylbenzene	1057.3	1057.7
1,2-Dimethyl-3-ethylbenzene	1077.3	1077.6

Quantitative aspects

The reliability of the results of quantitative analysis carried out by using the splitless injection system was checked earlier[19] by replicate headspace gas determinations of hydrocarbons in water. The results of the assay were satisfactory. In this work, a comparison was made of the results of quantitative analyses of 1-ml headspace gas samples injected directly into the system with a gas-tight syringe and the results of analyses of concentrates obtained from the same samples by means of a Tenax GC trap. The two situations are represented by chromatograms a and b, respectively, in Fig. 5. Chromatograms c and d represent blanks of the Tenax trap before and after analysis. Chromatogram e is a blank of the carrier gas. Chromatograms c, d and e were run at a ten-fold higher sensitivity ($5 \cdot 10^{-12}$ per f.s.d.)

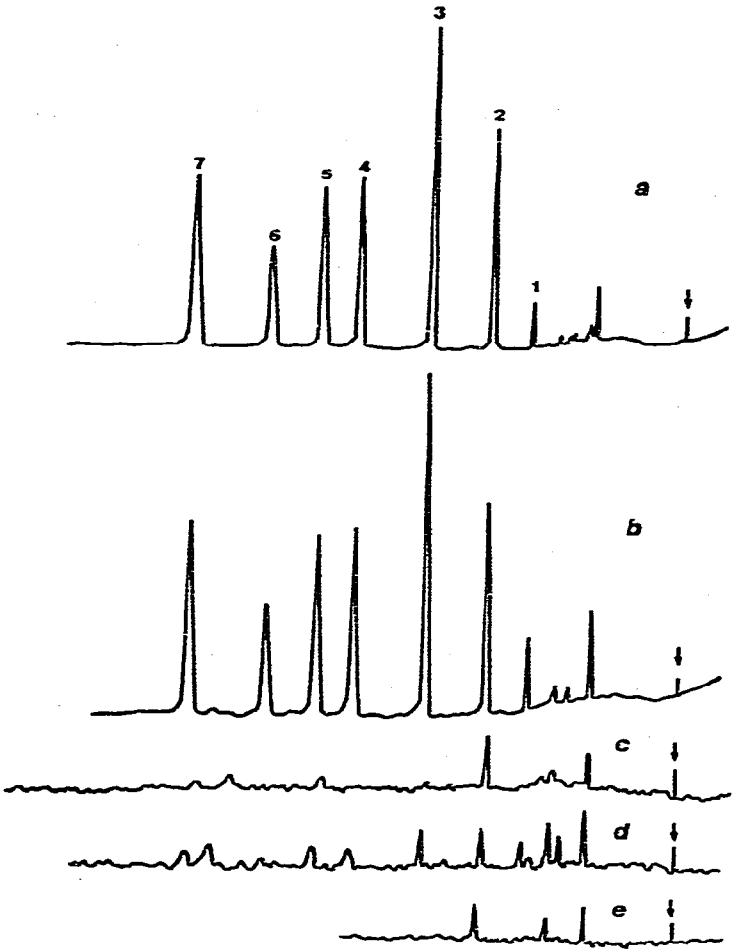

Fig. 5. Chromatograms obtained by the splitless introduction of 1-ml headspace gas samples (tens of ppb) directly by a syringe (a) and by means of a Tenax GC trap (b), (c) and (d), blanks of the Tenax GC trap before and after analysis, respectively; (e) blank of the carrier gas. 1 = *n*-Heptane; 2 = toluene; 3 = *n*-octane; 4 = ethylbenzene; 5 = *m*-xylene; 6 = *o*-xylene; 7 = *n*-nonane. GC conditions as in Fig. 3.

TABLE II

REPRODUCIBILITY OF INJECTION OF GASEOUS SAMPLES

6–8 measurements.

Approx. concentration (ppm)	*Sample volume (ml)*	*Relative standard deviation (%)*					
		n-Heptane		*Toluene*		*n-Octane*	
		h	*A*	*h*	*A*	*h*	*A*
30	1	2.6	3.7	3.7	2.9	5.4	2.3
1	1	6.6	5.3	6.1	5.5	5.3	5.0
0.1	20*	3.9	3.9	2.3	4.6	3.9	3.4

* Tenax GC trap.

than that for chromatograms a and b. It follows from the evaluation of the chromatograms in Fig. 5 that errors due to the Tenax GC memory effects do not exceed 1% of the value determined. The blank of the carrier gas indicates the presence of impurities in the latter. The peaks in chromatogram a were consistently slightly smaller than those in chromatogram b. This was probably due to a slight excess pressure of the headspace gas, causing part of the sample to escape from the syringe while carrying it over from the sample container to the gas chromatograph. In the version with the Tenax GC trap, one end of the latter (the end provided with a hypodermic needle) was inserted into the headspace of the container, whereupon a sample of the gas was sucked up by a syringe connected to the other end. As the solute components are largely sorbed by the Tenax GC packing, the losses during the carryover of the trap are negligibly small in this instance.

The reproducibility of introducing gaseous samples by mean of the splitless injection system was tested in the following way. A stock model mixture containing about 30 ppm of *n*-heptane, toluene and *n*-octane in nitrogen was prepared by injecting an appropriate amount of a solution of the hydrocarbons in acetone into a a 1-l bottle closed with a septum and pressurizing the bottle with nitrogen up to about $4 \cdot 10^{-4}$ Pa (0.4 atm). Eight replicate analyses of 1-ml samples of the mixture were carried out by the procedure described under *Analsyis of directly charged samples*. Both the peak heights and peak areas (peak height × peak width at half-height) were evaluated manually. In the same way a mixture containing about 1 ppm of the hydrocarbons, prepared in another 1-l bottle from an aliquot of the initial stock mixture, was analysed. Finally, a mixture containing about 0.1 ppm of the hydrocarbons was prepared from an aliquot of the 1 ppm mixture and analysed by using

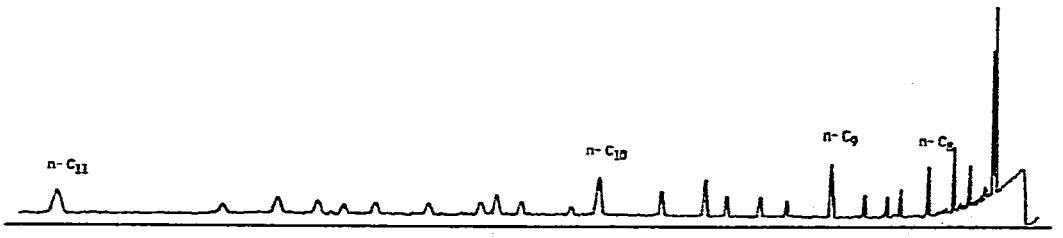

Fig. 6. Chromatogram obtained by the splitless introduction of a 1-ml sample of the headspace gas over water polluted with hydrocarbons in concentrations of 1–10 ppb. For GC conditions see Table I.

the Tenax GC trap according to the procedure described under *Analysis of concentrates from enrichment traps*. In this instance, six 20-ml samples, again sucked up into the trap by a syringe, were analysed. The results of the statistical processing of all of the above measurements are summarized in Table II. The data show very good reproducibility for all three series of measurements. Direct injections of 1-ml samples of the most dilute mixture (0.1 ppm) resulted in peaks that were merely less than three times as large as the noise at the full detector sensitivity ($1 \cdot 10^{-12}$ A). Relating the peak heights to those obtained in the analyses of 20-ml samples at the same sensitivity level gave a factor of 19.3.

Examples of applications of the system

The system described was developed for the splitless injection of large-volume gaseous samples into narrow-bore capillary columns and was recently applied to the headspace gas analysis of hydrocarbons in water[19].

Another example of the headspace determination of a complex mixture of hydrocarbons in water is shown in Fig. 6. The sudden rise of the baseline at the beginning of the chromatogram, which occurs upon switching the auxiliary gas stream over the heating line, is probably due to temporary partial choking of the trapping capillary by the large amount of water in the sample (the analysed gas–liquid system was kept at 70°). The chromatogram in Fig. 7 was obtained by injecting directly a 1-ml sample of Fischer–Tropsch reaction products.

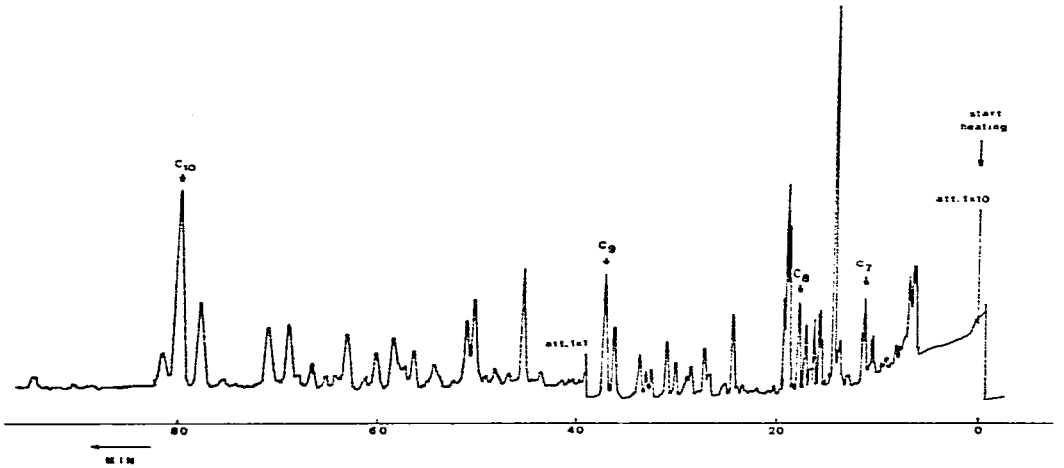

Fig. 7. Chromatogram of directly charged 1-ml sample of Fischer–Tropsch reaction products. For GC conditions, see Table I.

Examples of the use of the system to process concentrates from enrichment traps are shown in Figs. 8 and 9, respectively, by chromatograms of a car-exhaust gas and Dutch natural gas concentrated in a short column packed with Tenax GC. Both chromatograms were obtained by the procedure described under *Analysis of concentrates from traps*. As the cooling temperature was again about −55°, it is necessary to take account of some losses of the components with boiling points below 80°.

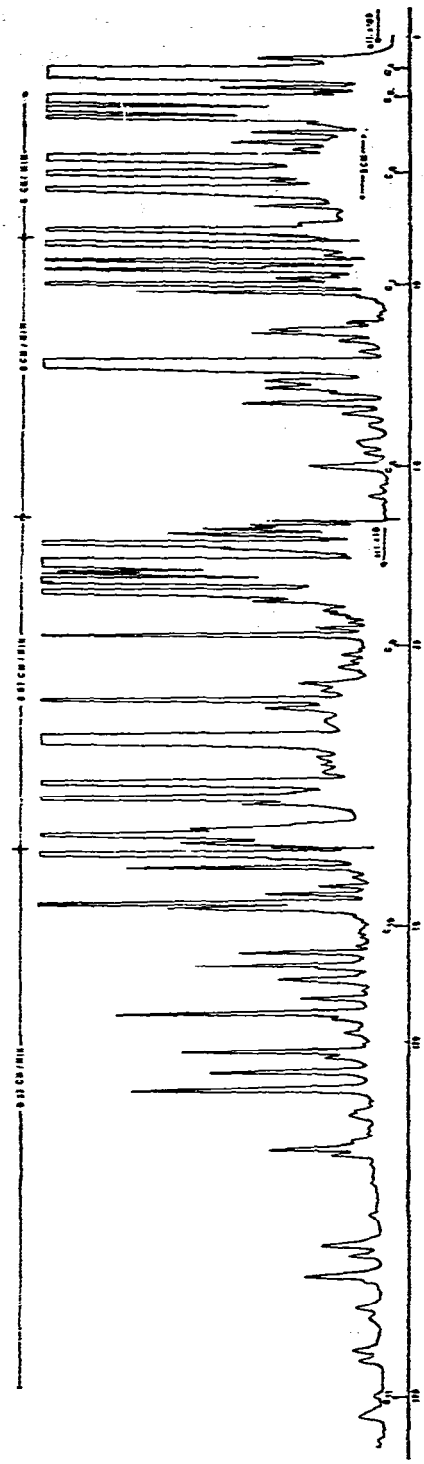

Fig. 8. Chromatogram of the concentrate of components of 50 ml of car-exhaust gas, captured in a Tenax GC trap. Conditions: stainless-steel capillary column (30 m × 0.25 mm I.D.) stationary phase squalane, cooling temperature of capillary trap −150°, desorption time of the Tenax GC trap 60 min.

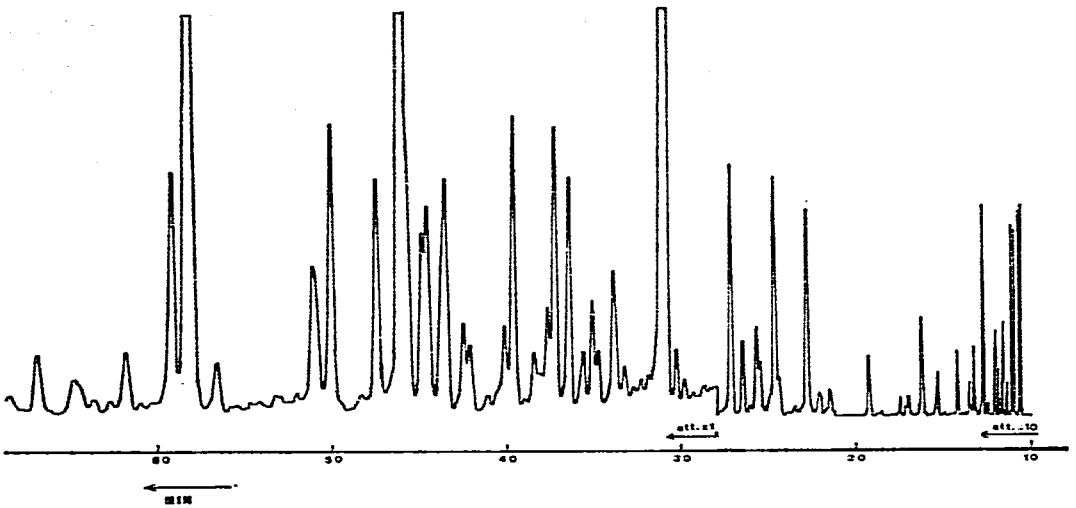

Fig. 9. Chromatogram of the concentrate of components of 5 ml of Dutch natural gas, captured in a Tenax GC trap. Conditions as in Fig. 8.

In addition to gaseous samples, the system can also be used for the splitless introduction of liquid samples into capillary columns. The cooling temperature can be chosen so as to let the solvent zone pass through the cooled trapping capillary while retaining in the latter the zones of the solute components. The chromatograms in Fig. 10 were obtained by injecting 0.2 μl of a solution of the same hydrocarbons in acetone as in the experiments referred to in Fig. 2. The concentration of the solutes was about 0.01%. Chromatogram A was obtained by injecting the sample while keeping the trapping capillary at room temperature. Chromatogram B refers to an experiment in which the capillary was cooled to −50°. In the latter instance, about 45 min were allowed to let most of the acetone pass through the GC column before starting the heating period. It should be stressed that the above experiment has unfavourable conditions, namely, the rather small differences in the boiling points of acetone and the solutes and the severe tailing of acetone peaks on the squalane column.

The long waiting time and the exposure of the GC column to excessive amounts of solvent can be substantially reduced by using a more suitable solvent (*e.g.*, pentane in the above instance) and discharging the large solvent band via an appropriate exhaust installed between the outlet of the trapping capillary and the GC column inlet. The cooling temperature can be varied over a wide range by the choice of a suitable coolant and/or by varying the flow-rate of the auxiliary gas stream. When using a twin three-way or six-way stopcock to control the auxiliary gas pathways, the whole procedure can easily be automated.

A major advantage of the system is its versatility and relative simplicity. It can easily be coupled with diverse GC instruments without any substantial modifications of their sample-inlet ports. The heat exchanger of the splitless injection system can either be placed in the column oven of the gas chromatograph, the upper part of the system being accommodated within the sample inlet port of the GC instru-

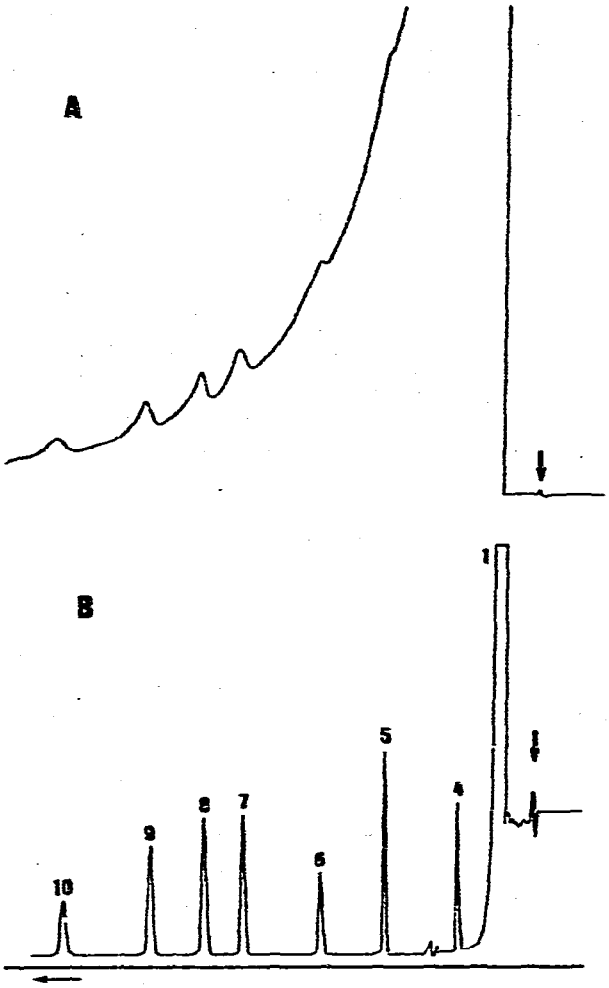

Fig. 10 Chromatograms obtained by the splitless introduction of 0.2-μl samples of a solution of hydrocarbons in acetone: (A) without cooling the trapping capillary; (B) trapping capillary kept at −50° for 45 min after injecting the sample. The start of chromatogram B corresponds to switching to the heating period. Peaks as in Fig. 2. For GC conditions, see Fig. 3.

ment, or the whole system can be situated completely outside the gas chromatograph, the outlet of the system being elongated, passed through the sample inlet port into the column oven and connected to the GC column.

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