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QUANTITATIVE ASPECTS OF THE PROGRAMMED-TEMPERATURE VAPORIZATION TECHNIQUE OF SAMPLE INTRODUCTION IN PARALLEL CAPILLARY COLUMN AND MICROBORE CAPILLARY COLUMN GAS CHROMATOGRAPHY

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SUMMARY

Two new application fields of the programmed-temperature vaporization technique are described. In the first, the use of microbore capillary columns has been tested, and in the second, the installation of two different columns with the same injector but leading to two different detectors has been evaluated, mainly from the point of view of accuracy in determination. The reported results show that all introduction problems have been overcome and that both of these techniques can now be used in routine gas chromatographic analysis with accurate quantitative results.

INTRODUCTION

The development of a sample injection technique based on programmed-temperature vaporization (PTV)[1–3] has not only resolved many problems related to the introduction of sample into capillary columns, but has also created the other possibilities. Theory and practice have demonstrated that decreasing the internal diameter of the chromatographic column remarkably improves the efficiency and shortens the analysis time[4–6]. The advantages for the separation of complex mixtures are obvious, but the possibility of operating with a much shorter analysis time and at lower temperatures is also important.

As is well known, the major drawback of these columns is their extremely low capacity. Amounts of substance higher than 5–10 ng overload the column. Consequently, the sampling difficulties with the traditional hot sample injections give, in the majority of cases, only semiquantitative data. On the other hand, because of the extremely small diameter of microbore columns, the "on-column" injection technique is not suitable.

In the PTV technique, the sample is introduced by means of a syringe into a capillary precolumn, kept at low temperature, and then evaporated and transferred to the main capillary column. For this reason, capillary columns can be used with a bore even much smaller than 0.1 mm.

The peak identification in chromatograms is still a well-recognized weakness of gas chromatography (GC). It is standard practice to use relative retention and retention indices[7]. Even if the capillary column technology has greatly improved the

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situation, the possibility of two components exhibiting identical retention behaviour on a given column still exists. However, by determining retentions on two high-resolution columns of different polarities, the level of confidence in retention times or indices as criteria of identification can be greatly increased.

Following the advent of fused-silica columns, several investigators have utilized this technique, taking advantage of the small outside diameter of these columns, by mounting two columns in parallel inside the same vaporizer with a remarkable gain in analysis time and retention data reliability[8,9]. However, the quantitative evaluation is in many cases dubious if the sample is injected according to the traditional techniques. Also, "on-column" injection is not suitable because of the typical lack of reproducibility of retention values and for understandable practical reasons.

The PTV technique has been evaluated for injections into microbore capillary columns according to different sampling modes and also for the simultaneous introduction of sample vapours into two different columns.

EXPERIMENTAL

Gas chromatography was carried out with a DANI 3800 HR-PTV gas chromatograph, equipped with flame ionization or nitrogen–phosphorus detectors. The detector signals were processed by a dual-channel Shimadzu CR2A-X computing integrator. The microbore capillary column (5 m × 80 μm I.D.) was persilanized and coated in our laboratory with a 0.15-μm layer of OV-1, while the fused-silica columns used for the parallel capillary technique were supplied by J&W.

RESULTS AND DISCUSSION

PTV operation with microbore capillary column

A hydrocarbon mixture from C_{10} to C_{32} was used to test the microbore column in the total injection mode. Fig. 1 shows the chromatogram obtained by programming the oven temperature from 30°C to 270°C at 20°C/min. To avoid the problem of overlaoding, 0.5 μl of a solution containing 5 ng/μl of each hydrocarbon was injected. To compensate for the low carrier gas flow-rate through the vaporizer dur-

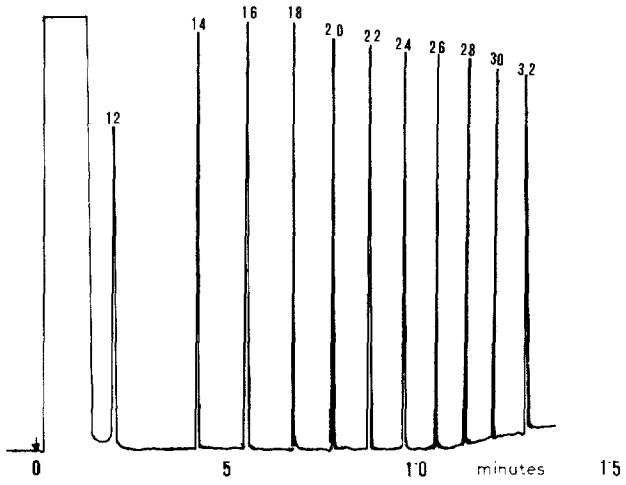

Fig. 1. Hydrocarbon analysis in a microbore glass capillary column (5 m × 0.08 mm I.D.) packed with 0.15-μm OV-1. Carrier: hydrogen, 2 bar. Temperature programs: column, 30°C for 2 min then raised at 20°C/min to 270°C; PTV, 50°C to 280°C, splitter closed for 80 sec. Sample: 0.5 μm hydrocarbon mixture, C_{12}–C_{32}, 5 ng/μl of each in hexane. Total injection mode.

TABLE I

HYDROCARBON ANALYSIS IN A MICROBORE CAPILLARY COLUMN

Quantitative results from an average of five injections.

Hydrocarbon	*Area (%)*	*Standard deviation (%)*
C_{12}	9.6	1.3
C_{14}	9.8	0.4
C_{16}	9.7	0.2
C_{18}	9.3	1.4
C_{20}	9.0	1.0
C_{22}	9.0	1.3
C_{24}	8.7	1.5
C_{26}	8.8	0.8
C_{28}	9.1	1.2
C_{30}	8.5	1.0
C_{32}	8.4	0.9

ing the transfer step, the pressure of the carrier gas was 2 bar and the splitter was kept closed for 80 sec, giving as a consequence, a large solvent peak. This assures the complete transfer of the hydrocarbons to the column which, during this step, was kept cold.

The first point to note is the short analysis time and the low retention temperature. The most interesting aspect is however the accuracy and reproducibility of the quantitative data, as reported in Table I.

Having overcome, the sampling problem, we were very interested in using the microbore capillary columns and PTV injection technique for ultra trace analysis and for the determination of substances which are subject to degradation at high operating temperatures or adsorption on an imperfectly deactivated column. It is clear that by drastically decreasing the residence time in the column as well as the effective surface area of the column, processing of these substances will be much easier and the quantitative data more accurate.

Examples of applications are shown in Fig. 2, for the determination of benzodiazepines and of three aromatic amines, widely used as rubber antioxidants. The sample was introduced by the solvent split technique, eliminating the solvent before the transfer of the substances to the column. The nitrogen–phosphorus detector used for this test proved to be very reproducible in response, because it was not loaded by solvent, as is usually the case. It is also important to note the retention temperature of all the substances, which is 60–70°C lower than with conventional columns.

PTV operation with parallel capillary columns

Two columns were mounted in the same PTV by using a soft graphite ferrule and assembled so as to have the inlet at the same level and protruding about 5 mm inside the PTV liner. The column outlets were connected to two different flame ionization detectors, as shown in Fig. 3. A dual-channel computing integrator was used for recording and calculations (relative % concentrations and retention index). The two columns supplied with hydrogen at a pressure of 0.6 bar showed a very similar flow-rate (± 5%). The sample (0.5 μl of a hexane solution containing 100 ppm of each hydrocarbon) was introduced according to the total injection mode. The sample vapours entered the two columns split uniformly, with a small difference in total area, and produced quantitative practically identical results, (calculated from the average of five injections).

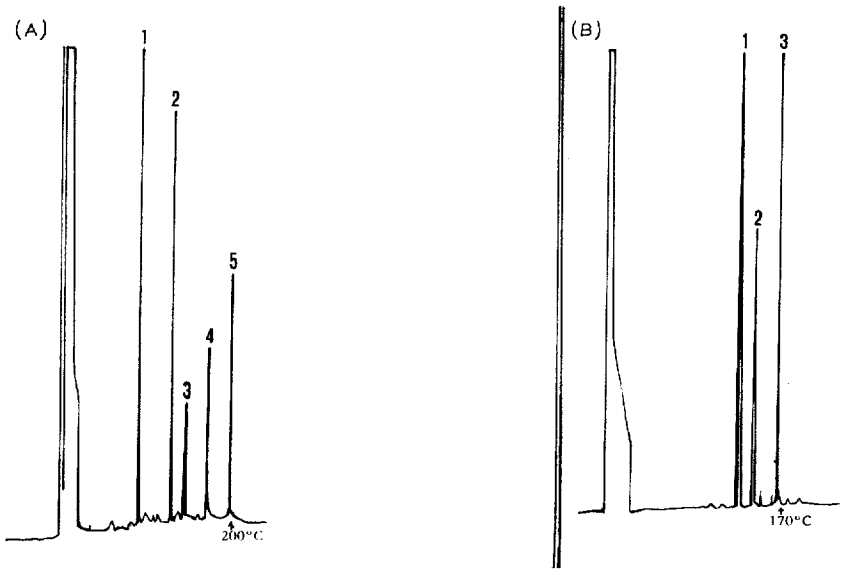

Fig. 2. Sampling in a microbore capillary column (details as in Fig. 1). Temperature programs: column, 80°C to 210°C at 8°C/min; PTV, 50°C to 280°C. Detector: nitrogen–phosphorus. Sampling mode: solvent split, split 50 ml/min, 7 sec on 80 sec off. Sample: A, 1 μl benzodiazepines (each 100 pg) in methanol; B, 1 μl rubber antioxidants (each 500 pg) in ethyl acetate. Peaks: A, 1 = medazepam; 2 = diazepam; 3 = desmethyl diazepam; 4 = temazepam; 5 = flurazepam; B, 1 = N-isopropyl-N-phenyl-*p*-phenyldiamine (IPPD); 2 = phenyl-β-naphtylamine (PBNA); 3 = N-(1,3-dimethylbutyl)-N-phenyl-*p*-phenyldiamine (DBPPD).

A summary of quantitative and qualitative data, together with the dual chromatogram, is reported in Fig. 4.

The validity of the technique was also tested with parallel columns of different lengths and I.D.s. Column A was a 25 m × 0.33 mm I.D., SILAR-5A; Column B was 15 m × 0.25 mm I.D., SE-54. In this case, a sample of butter fatty acid methyl esters was introduced undiluted into the cold vaporizer as usual and the vaporizer temperature was increased after the injection. The splitting valve was open all the

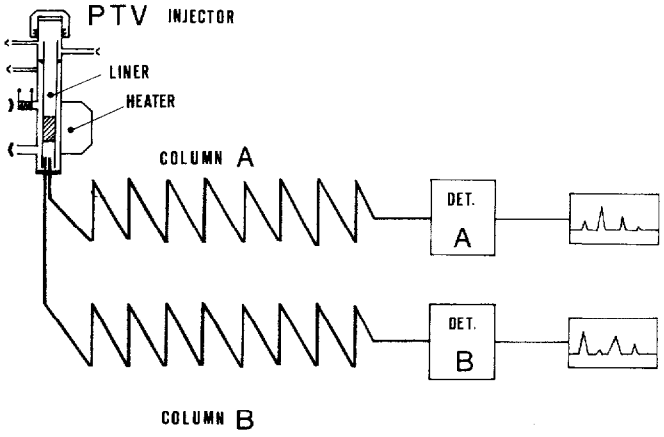

Fig. 3. DANI 3800-HR parallel column mounting in PTV injector.

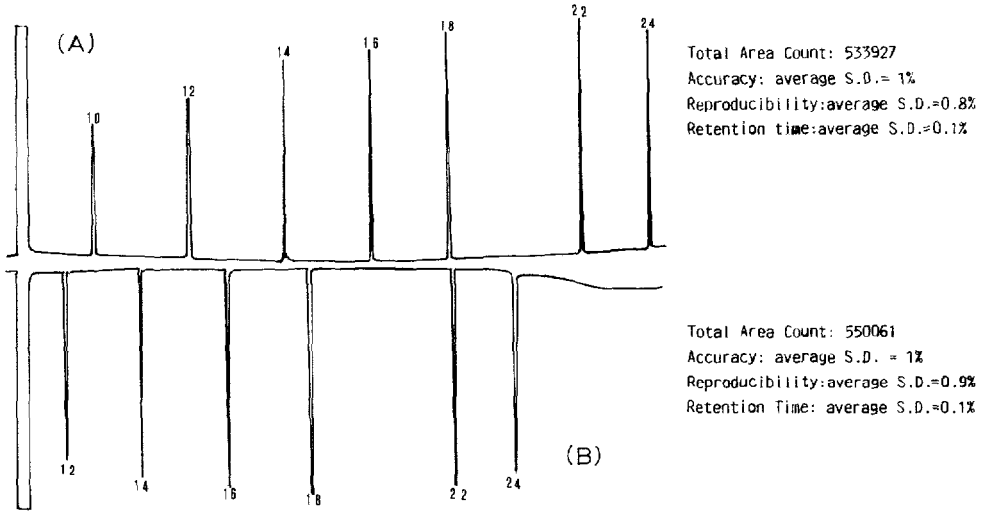

Fig. 4. Total injection in parallel capillary columns. Capillary columns: A, fused silica 15 m × 0.25 mm I.D., SE-54; B, 15 m × 0.25 mm I.D., Carbowax. Carrier: hydrogen, 0.6 bar. Temperature programs: column, 60°C for 1 min then raised at 10°C/min to 220°C, held for 5 min; PTV, 50°C to 250°C, splitter closed for 30 sec. Sample: 0.5 μl hydrocarbon mixture C_{10}–C_{24}, 10 ng of each in hexane. Sampling mode: total injection. Detectors: flame ionization, attenuation ×10 ×32.

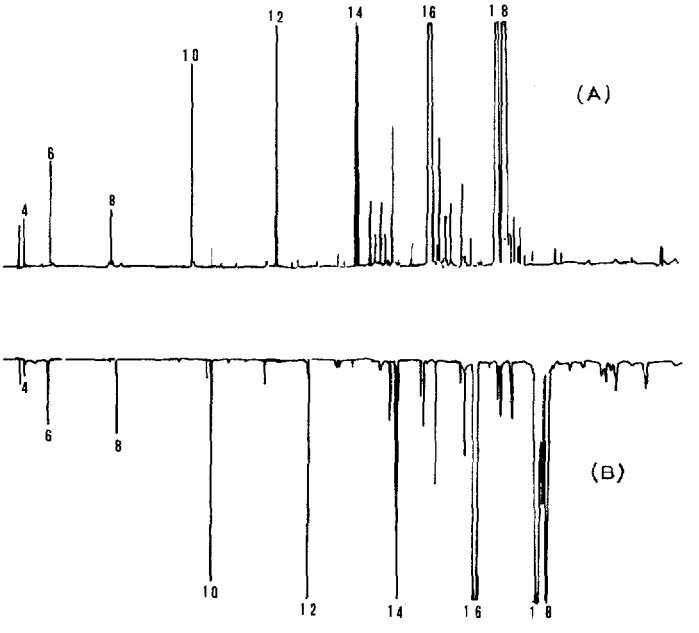

Fig. 5. Split injection in parallel capillary columns. Capillary columns: A, fused silica, 25 m × 0.33 mm I.D., SILAR 5A, B, 15 m × 0.25 mm I.D., SE-54. Carrier: hydrogen 0.6 bar. Temperature programs: column, 50°C for 1 min then raised at 5°C/min to 195°C; PTV, 50°C to 250°C, split 200 ml/min. Sample: 0.1 μl undiluted butter fatty acid methyl esters. Split injection mode.

TABLE II

FATTY ACID METHYL ESTER ANALYSIS IN PARALLEL CAPILLARY COLUMNS

Quantitative and qualitative results from an average of five injections.

Carbon No.	*SILAR capillary column*			*SE-54 capillary column*		
	R.I.	*Area*	*% of main peaks*	*R.I.*	*Area*	*% of main peaks*
C_4		10,200	2.5		4850	2.5
C_6		5136	1.2		2447	1.3
C_8	1387	3679	0.9	1136	1710	0.9
C_{10}	1594	8592	2.0	1326	4073	2.1
C_{12}	1799	11,383	2.7	1531	6526	3.1
C_{14}	2010	44,343	10.1	1730	21,085	10.9
$C_{16}+$	2236	127,911	30.5	1937	56,536	29.5
$C_{16}-$	2262	6541	1.6	1907	2440	1.3
$C_{18}+$	2480	56,402	13.2	2135	24,619	12.9
$C_{18}-$	2514	106,230	25.3	2117	48,872	25.4
Total	S.D. = 0.1%	410,250		S.D. = 0.1%	191,850	

time, as in the split injection mode, and the split flow-rate was adjusted to 200 ml/min. Fig. 5 shows the typical dual chromatogram response of the dual computing integrator. Cold injection and PTV produced identical quantitative values to those obtained with the split technique[10].

Similar quantitative results are obtained with the parallel column system, as shown in Table II, where the retention indices of the most important fatty acid methyl esters are reported.

CONCLUSIONS

The PTV injection technique is now a well-established sample introduction system in capillary column GC. We have demonstrated the extension of the application of this injector to a special column arrangement and special column sizes and solved the sampling problems. The parallel column arrangement provides a powerful means of peak identification. Microbore capillary columns can now be used for routine analyses. Both techniques are easily duplicated to obtain high levels of accuracy. The injection into a parallel capillary column system and into microbore capillary columns may be performed with ordinary syringes and thus allows the use of an automatic liquid sampler, providing full automation capability.

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