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SAMPLING TECHNIQUES IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

Four different sampling methods for capillary gas chromatography, including split and splitless sampling, have been investigated with respect to precise and accurate qualitative and quantitative analysis. A new method of direct sampling for capillary columns is presented and compared with the known techniques with respect to resolution, reproducibility of retention, decomposition of sensitive sample components and discrimination of high-boiling components in quantitative analysis. Multi-dimensional arrangements using capillary columns for the "main" separation as the most flexible and efficient sampling devices are discussed. If by selective sampling in such set-ups only a partial analysis of those components is achieved, which are of real interest in a particular analytical problem, analysis time can be saved and the performance of the separation can be improved.

INTRODUCTION

In high-resolution capillary gas chromatography (GC), special sampling techniques have to be applied because of the very low sample capacities (nanograms per component) and, moreover, these columns are operated at low carrier gas flow-rates (0.5–4 ml/min) and generate steep peak profiles.

The sampling techniques and conditions have to be carefully adapted to the analytical problems concerned, especially when dealing with complex mixtures characterized by wide ranges of component concentrations, volatilities and polarities. They may also contain components with low thermal and/or catalytic stability, and often complex mixtures consist simply of numerous constituents, sometimes isomeric, that cannot be separated in a single chromatographic run even with optimal separation efficiency and selectivity.

In qualitative GC analysis, preferably "response" information from selective detection by GC–mass spectrometry (MS), a nitrogen flame-ionization detector or an electron capture detector is used, whereas retention data merely serve the purpose of comparison with known chemical compounds. The potentialities of precisely measured standardized retention data in the form of data collections and retention rules for identification have not been fully recognized up to now. In our opinion, the precision of retention index measurements nevertheless cannot be decreased by using unreliable sampling techniques.

The technical difficulties involved in sampling are increased when quantitative analyses of trace components in complex mixtures of the above-mentioned types are carried out. The identification and quantitation of known or expected chemical compounds is, of course, less elaborate than the analysis of completely unknown or unexpected species.

The major requirements for optimal quantitative and qualitative analyses of complex mixtures can be summarized as follows:

(i) adequate separation efficiency, *i.e.*, sharp and symmetrical peak profiles;

(ii) high repeatability and reproducibility of retention measurements;

(iii) high precision and accuracy in quantitation by peak area measurements (*i.e.* no discrimination of components by volatility, polarity or concentration);

(iv) minimal thermal and catalytic decomposition of sensitive sample components.

In this paper, we report our investigations on various known and new sampling techniques with regard to the above requirements. We shall deal with four principal sampling methods and their optimal parameters of operation, namely split, splitless, direct and selective sampling.

The devices for "direct" sampling using capillary columns have been developed by ourselves[1]. "Selective" sampling involves the use of double column systems, as described previously[2–5]. These systems include an isothermal or temperature-programmed pre-separation, and intermediate trapping in the first part of the main column, which preferably is a capillary column. As in direct sampling, the significant separation with high resolution (the "main" separation) is initiated from the short inlet section of the column itself, which acts as a trap for the species selected from the pre-separation.

We have carried out various qualitative and quantitative test experiments on the performance of the four methods described, in order to make a critical comparison and to characterize the different methods in terms of their efficiency in particular applications.

SPLIT SAMPLING

Since the early days of capillary GC, only split injection was applied for many years because the direct introduction of the very small amounts of sample that could be used without overloading the columns could not be effected with the classical septum–syringe technique used with packed columns. The smallest sample volumes (*ca.* 0.1 μl) which can be injected with just sufficient precision using a 1–10-μl syringe are still much too high for capillary columns, especially with undiluted mixtures that contain only a limited number of components.

In the past, however, the split sampling technique was considered to be unreliable with regard to precision and accuracy because of discrimination effects according to molecular size, polarity and concentration of the components. Meanwhile, it was shown by several workers that split sampling of complex mixtures can also be performed with excellent qualitative and quantitative precision without being restricted to a limited range of important parameters such as sample volume, splitting ratio and component concentration, by choosing a vaporization tube of suitable geometry and material (surface properties) and by proper heating of the vaporization

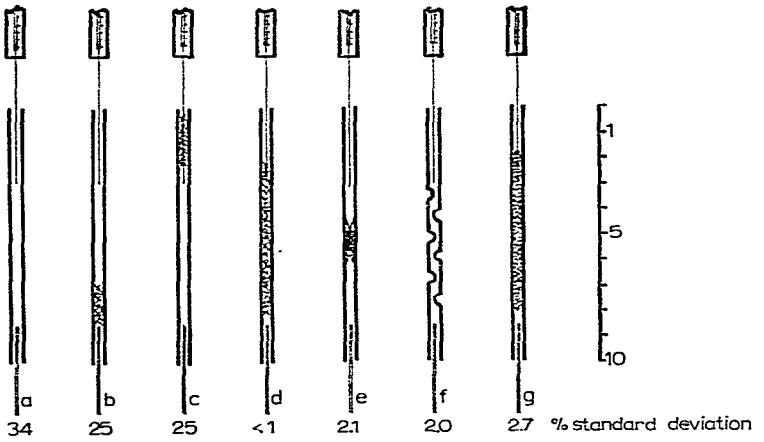

Fig. 1. Vaporisation tubes for homogenization of sample vapour–carrier gas mixture with split sampling. Relative standard deviation of repeatability of peak area ratios of methanol to 2-ethyl-1-hexanol. (a) Empty tube; (b) short glass-wool plug in the splitting region; (c) short glass-wool plug in the injection region; (d) long and tight glass-wool plug; (e) Jennings tube; (f) deformation of cross-section; (g) chromatographic support packing.

chamber, including the splitting region, the transfer lines and the carrier gas before entering the injector.

At sample volumes not exceeding 1–2 μl and at carrier gas flow-rates not higher than 300 ml/min in the glass insert, vaporization tubes with the following geometry have been used successfully: length, 60–100 mm; I.D., 2–3 mm; O.D., 4 mm; material, glass. Complete vaporization of the injected sample without aerosol formation and perfect mixing (homogenization) with the carrier gas, which has to be pre-heated before entering the injector, should be attained in such tubes. The vaporization tube should be easily replaceable in practical work for cleaning purposes, *i.e.*, removal of involatile residues. Several types of vaporization tubes have been tested and have proved to be more or less effective (see Fig. 1): (1) loose or tight packings of deactivated glass- or quartz-wool; (2) packings of glass beads or chromatographic support[6]; (3) deformation of cross-section[7]; and (4) a special construction as described by Jennings[8].

Packings with deactivated glass-wool that were not too loose proved to be superior to other means of homogenization with regard to the standard deviation of the repeatability and accuracy of relative peak area measurements (molecular weight discrimination). Chromatographic support material can also be used successfully. Both types of packings exhibit large and not completely inactive surfaces, which may give rise to decomposition of sensitive sample components. The surface areas of typical chromatographic support materials are even higher, and are probably much higher than necessary. In this respect, the two constructions (e) and (d) are to be preferred, although the "mixing" of sample vapour with the carrier gas and the avoidance of aerosols is not as perfect as with the packed versions. In Fig. 1 the standard deviation of the repeatability of the relative peak areas of methanol (b.p. 69°) and 2-ethyl-1-hexanol (b.p. 185°) are given for the various vaporization tubes and for different types of glass-wool packings. The length, tightness and position of the glass-wool plug were also varied in relation to the position of syringe needle at injection

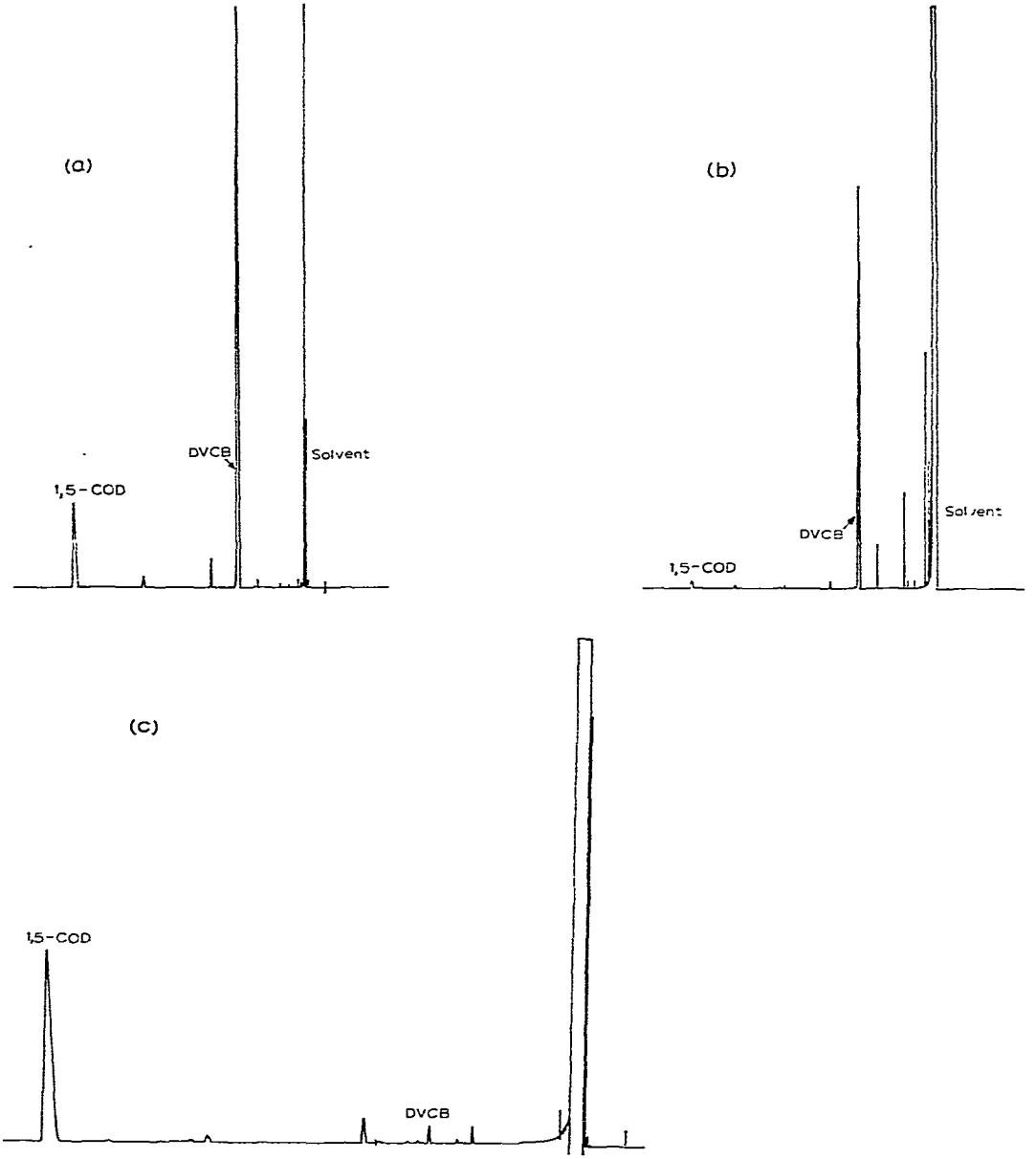

Fig. 2. Decomposition of sensitive sample components: comparison of direct, split and splitless sampling. Thermal conversion of divinylcyclobutane (DVCB) into 1,5-cyclooctadiene (1,5-COD). (a) Split sampling: 1 μl of DVCB, 1:10 in *n*-pentane, splitting ratio 1:50. Column: 50 m SP-400. Temperatures: column, 40°; injector, 270°. Carrier gas: hydrogen (1 bar). (b) Direct sampling (macroversion): 2 μl of DVCB, 1:1000 in *n*-pentane. Column: 50 m SP-400. Column temperature: 40°. Carrier gas: hydrogen (1 bar). (c) Splitless sampling: 1 μl of DVCB, 1:1000 in *n*-pentane. Column: 60 m SP-400. Temperatures: column, 40°; injector, 260°. Carrier gas: hydrogen (2 bar).

and the splitting region (a–d). The best results were obtained with version (d). In the split mode of sampling, very short residence times of the sample vapour in the splitter result provided that the flow-rates of the split streams, *i.e.*, the splitting ratios, are not to low. Short residence times are optimal for a short inlet plug and minimize the thermal and catalytic decomposition of sensitive sample components, but require optimal homogenization of the sample–carrier gas mixture. This can be seen from the chromatograms in Fig. 2 and the data in Table I for the thermal conversion of divinylcyclobutane into 1,5-cyclooctadiene (Cope rearrangement). Fig. 2 shows the chromatograms of divinylcyclobutane obtained with three different sampling techniques. Even with the short residence time of the sample in the over-heated injector in split sampling, conversion of divinylcyclobutane into cyclooctane cannot be completely avoided. The dependence of the conversion on residence time, *i.e.*, on the split flow-rate, can be seen from the data in Table I.

TABLE I

DECOMPOSITION IN SAMPLE VAPORIZATION

Thermal rearrangement of divinylcyclobutane (DVCB) into 1,5-cyclooctadiene (COD) and 4-vinylcyclohexene-1 (VCH) as a function of carrier gas flow-rate (residence time) in the injector block. Temperatures: column, 62° (no conversion in the column takes place); injector, 290°.

Flow-rate (ml/min)	*Relative peak areas (%)*		
	DVCB	*VCH*	*COD*
200	53.8	2.5	38.8
100	38.9	3.1	52.2
5	2.6	7.0	81.4

Split sampling can be used with both isothermal and temperature-programmed modes of column operation. Under optimal vaporization and homogenization conditions in the vaporization tube, the adjusted injector temperature for mixtures with a wide range of volatilities is much higher than that of the column, the temperature of which has been optimized for resolution (a difference of 100° and more is common). When the column is temperature programmed, the initial temperature may be so low that, at least for the high-boiling components of the vaporized mixture, condensation or trapping in the first section of the column occurs. If the complete transfer of the sample is guaranteed, this trapping effect is desirable because the profile of the initial sample plug is sharpened and the influence of the sampling procedure on the final bandwidth of the separated species is minimized.

With split sampling, the influence of the time of sample introduction and the transfer into the column on the final bandwidth is negligible because of the high carrier gas flow-rates between the carrier gas inlet and splitting region.

In Fig. 3, quantitative data for the temperature-programmed GC analysis of even-numbered C_{18}–C_{34} *n*-alkanes, a typical mixture with a very wide range of boiling points (196–492°) using various sampling techniques are given.

Excellent results for split sampling are obtained if the heating of the injector (considering also heat transfer resulting from the high split flow-rate) and the homogenization are carried out properly. The given data were obtained with a tight glass-wool packing as shown in Fig. 1 [version (d)].

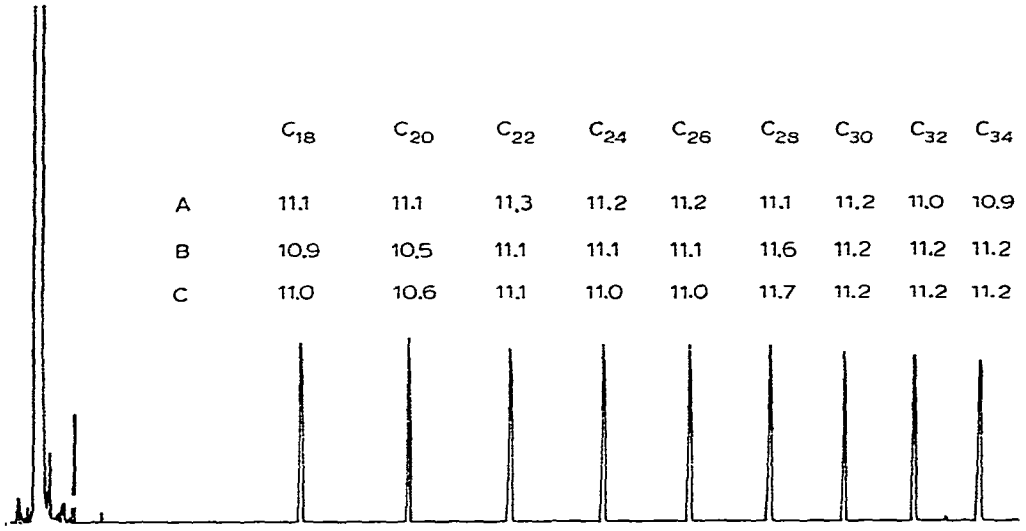

Fig. 3. Sampling techniques in temperature-programmed capillary GC. Discrimination of high-boiling components with A, direct, B, split and C, splitless sampling. Relative peak areas of C_{18}–C_{34} *n*-alkane mixture containing 11.1% by weight of each homologue diluted in *n*-undecane. Column: 25 m OV-101, 0.25 mm I.D. Temperature: 120° to 280° at 3°/min. The given values are averages from 10 measurements for split and splitless sampling and from 6 measurements for direct sampling. The standard deviation of the repeatability was not higher than 1% at all three methods.

SPLITLESS SAMPLING —SPLIT SAMPLING WITH LOW SPLITTING RATIOS

In trace analysis, the application of split sampling with high splitting ratios cannot be used. The sample load on the column for the trace components can be increased only by decreasing the splitting ratio, whereas the volume of sample injected can be increased only in a restricted manner, *i.e.*, with respect to the volume of the vaporization tube. If the split flow-rate is decreased to zero, *i.e.*, if the splitting valve is completely closed, all of the vaporized sample is led into the column (provided that there are no leaks in the system). In this instance the column flow-rate determines the rate of transfer of sample vapour to the column inlet.

By increasing the column load with respect to signals of sufficient intensity only from the components present at low concentrations, overloading of the column by the major components which are present in the mixture occurs. Peak broadening, distortion of symmetry and overlapping of the solvent or main component peaks with peaks of trace components may arise. In many practical environmental and biochemical analyses, trace amounts of low-volatility components in large amounts of solvents have to be sampled, separated and detected. These types of samples are met especially after previous extraction, enrichment and derivatization procedures. Primarily the solvents used should have very high purity, in view of the subsequent GC analysis, and have to be selected according to the sample preparation procedure (extraction, derivatization) used. It was shown by Grob and Grob[9], however, that the volatility and polarity of the solvent have a strong influence on the performance of the sampling procedure. The common Grob procedure of splitless sampling[10] is

mostly applied, together with temperature programming of the column. During injection and the subsequent transfer of the vaporized sample into the column, the splitting valve remains closed. In our experience, closing times of the splitting valve of 1–2 min are necessary, possibly depending on the volatility range of the sample. The inlet plug width is determined by the carrier gas flow-rate (*i.e.*, also the column diameter), the volatilization time of the sample and therefore sometimes also the closing time of the splitting valve.

With temperature programming, the cold inlet of the column (the temperature difference between the injector and the column may be up to 200°) acts as a cold trap with additional solvent effects of the stationary liquid on the sample vapour pressure.

If the boiling point of the solvent of the sample is higher than the column temperature (minimum 20°), large amounts of the solvent can also be condensed in the first section of the column and dilute the stationary liquid. The less volatile trace components are transferred into the column with retardation, *i.e.*, after the solvent. In the column inlet they are stopped by trapping in the stationary liquid (cold solvent) plug. The condensed solvents act, for a certain period, like the stationary liquid and increase the amount of the latter. By this type of trapping, a sharpening of the inlet profile is achieved, as was shown by Grob and Grob[9] and other workers. Improved detection and resolution of these components is achieved by this "concentration" effect. The procedure can be applied in isothermal and temperature-programmed separations if the boiling point of the solvent is adapted to the column temperature at the time of sample introduction. If the column temperature has to be adjusted in isothermal work according to the volatility range of the sample and the necessary resolution (selectivity), the solvent cannot be selected without considering its boiling point [see chromatograms (c) and (d) in Fig. 6]. With *n*-octane as the solvent, a much higher resolution in the early section of the chromatogram is obtained than with the much more volatile *n*-pentane. The initial temperature of the temperature programme was 100°. The boiling points of *n*-octane and *n*-pentane are 125° and 36°, respectively.

Advantages and limitations of splitless sampling

On the basis of various test measurements and experience derived from practical applications, we came to the following conclusions:

(1) The transfer of the vaporized sample is slow (determined by the carrier gas flow-rate through the column) and causes peak broadening. This can be seen especially with isothermal column operation when no additional "trapping" or "concentration" effect[10] by solvent condensation, etc., affects the sharpness of the peaks. The so-called "concentration" effect sharpens only the profiles of those peaks which are eluted later than the solvent, whereas the early peaks exhibit broader profiles [compare chromatograms (c) and (d) in Fig. 6].

(2) Large amounts of solvents condensed in the column inlet for attaining the "concentration" effect change the polarity of the stationary liquid. The retention times, especially for components with volatilities similar to that of the solvent, are changed considerably, depending on the polarity of the solvent and stationary liquid and on the amount of sample injected (see Table II).

(3) The transfer of high-boiling sample components may not be completed when the splitting valve is re-opened, and discrimination of these components may

TABLE II

SPLITLESS SAMPLING: INFLUENCE OF POLARITY AND VOLATILITY OF SOLVENTS ON THE RETENTION BEHAVIOUR OF LOW-BOILING SPECIES (*n*-BUTANOL)

Column: polypropylene glycol, I.D. 0.25 mm, glass capillary. Carrier gas: nitrogen. Column temperature: 100°.

Solvent	*Kováts retention index of n-butanol*	
	Split sampling (splitting ratio 1:100)	*Splitless sampling*
n-Pentane	891.5	890.8
n-Heptane	891.0	889.2
Diethyl ether	891.6	899.2
Methanol	890.9	910.5

result. Test experiments with C_{18}–C_{34} *n*-alkane mixture for quantitative reliability revealed that discrimination of the high-boiling components can be avoided only by proper heating of the injection section, considering also heat transport by the carrier gas. If the vaporization tube temperature is too high in relation to the boiling point of the solvent, losses of high-boiling components may also be caused. The same effect occurs, of course, with split sampling. The explosive vaporization of the sample in both techniques probably gives rise to a repulsion effect whereby sample residues pass into cold parts of the inlet system, where they may be adsorbed. The optimization of injector temperature, carrier gas flow-rate and boiling point of the solvent therefore has to be carried out with great care.

(4) Long residence times in the vaporization chamber, which is heated with regard to the sample components of lower volatility, give rise to conversion or decomposition of sensitive sample components. Comparison of the chromatograms in Fig. 2a and Fig. 2c and the data in Table I indicate the dependence of divinylcyclobutane conversion on the split or sample transfer flow-rate. By adjusting the split flow-rate to a low value (for example, a splitting ratio of 1:5) and by adequate increase of the sample volume, if necessary, faster sample transfer without losing too much of the intensity of the trace peaks by the splitting can be achieved. At low split flow-rates, back-diffusion of high-boiling components which have been retarded in the split-flow lines by adsorption or condensation may also cause discrimination by molecular size.

DIRECT SAMPLING

Direct sampling involves introduction of the sample into capillary columns without previous vaporization outside the column[1]. Regarding the above-mentioned restrictions and difficulties of split and splitless sampling with previous vaporization, we came to the conclusion that by introducing liquid samples directly into capillary columns improvements in the quantitative and qualitative analyses of complex mixtures could be attained. The problems of homogenization in split sampling and of sample vapour transfer in splitless sampling can be avoided easily as much as the negative effects of adsorptive surfaces of mostly over-heated vaporization tubes. Furthermore, both sampling techniques suffer from the septum problem. At high

vaporizer temperatures, which are necessary at least with mixtures that contain high-boiling components, decomposition products of the septum enter the carrier gas continuously as impurities. With temperature programming, chromatographic peaks (ghost peaks) of these decomposition products are obtained because they are previously trapped in the column inlet before starting the programme. Methods of avoiding these ghost peaks, such as septum flushing, cannot be discussed here.

We therefore developed two versions of a direct sampling system for capillary columns, both involving the same sluice system (see Fig. 4). There is no need to heat any parts of the sampling device, including the column inlet, to temperatures beyond the column temperature. As pointed out before, it is difficult or even impossible in some instances to introduce sample volumes large enough to yield the optimal load of the column for each component in order to achieve a sufficient signal-to-noise ratio to be able to examine interesting trace components. Sample volumes of 1–2 μl generally have to be used in the case of mixtures that contain large amounts of solvents or undiluted mixtures that.contain numerous components.

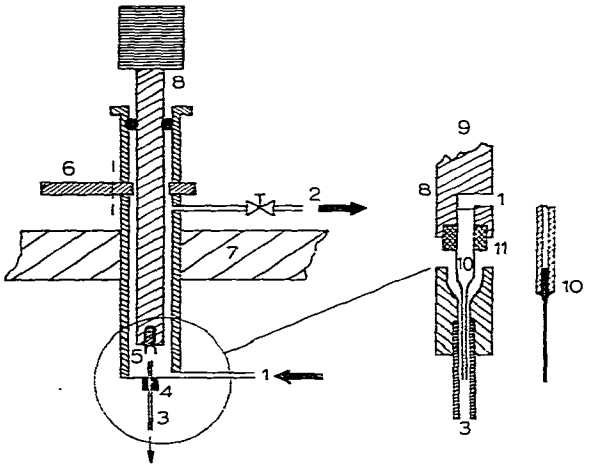

Fig. 4. Direct sampling of liquids into capillary columns. Macro- and micro-versions. 1 = Carrier gas inlet; 2 = carrier gas outlet; 3 = capillary column; 4 = graphite gasket; 5 = crucible for sample; 6 = sluice valve; 7 = insulation of column oven; 8 = rod for sample introduction; 9 = micro-version of direct sampling; 10 = micro-pipette for sampling of nanolitre volumes; 11 = silicone rubber gasket.

In the "macro-version" of the new system, a glass, aluminium or gold crucible of volume 5 or 10 μl is attached to a rod which is introduced into the chromatographic flow system via a sluice. The liquid sample is contained in the crucible and the end of the column dips into the sample in the loading position. As long as the column inlet is closed by the liquid sample, the pressure of the carrier gas at the column inlet increases whereas the pressure inside the column decreases. The sample is displaced into the column, where the chromatographic elution is initiated after volatilization in the first coils of the column. The resolution of the isomeric hydrocarbons in a mixture of Fischer–Tropsch alkanes is the same as with split sampling (see Fig. 5). For "direct" sampling the mixture was diluted with *n*-octane (1:100),

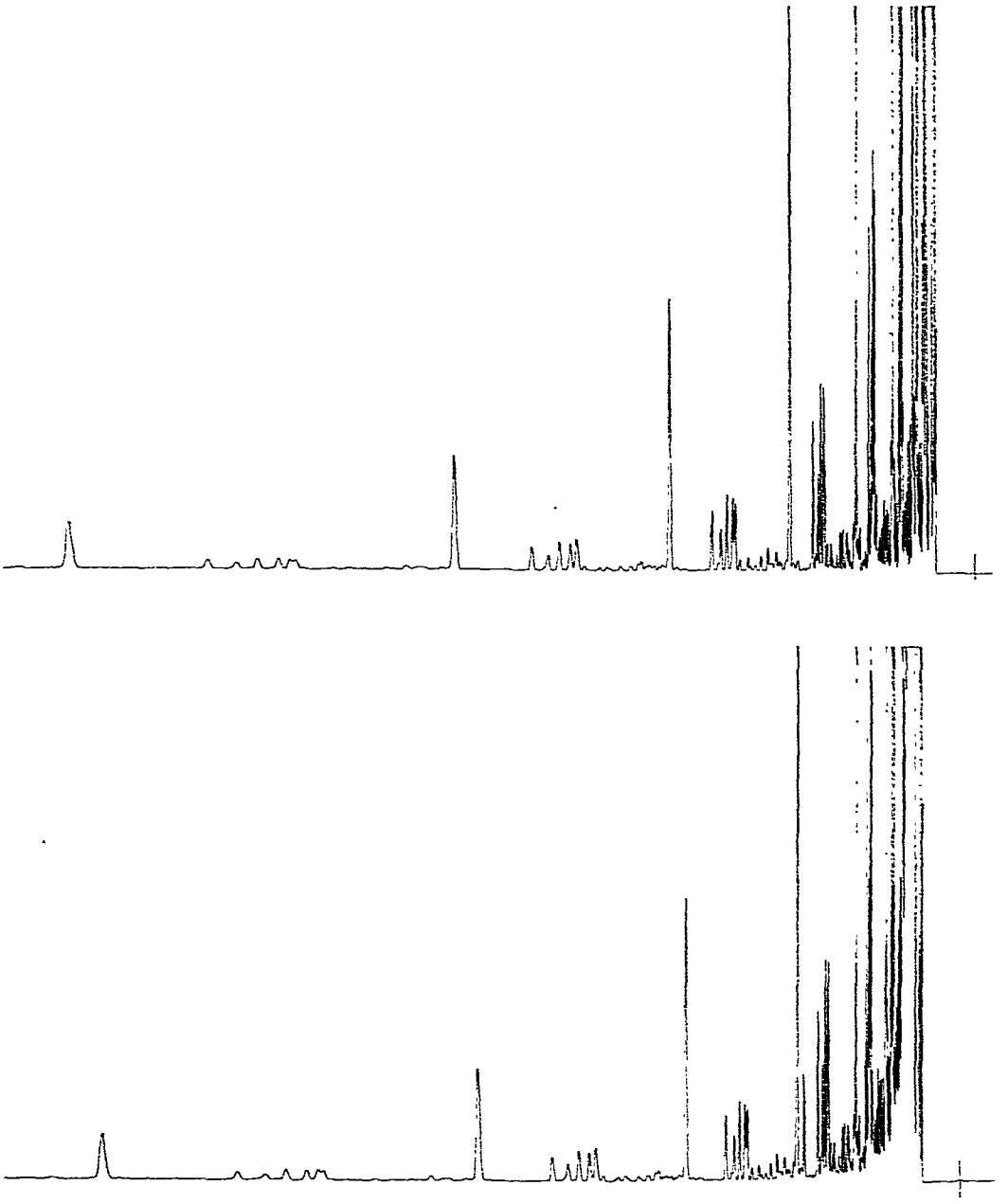

Fig. 5. Resolution and relative peak areas of Fischer–Tropsch alkanes with direct and split sampling. Direct sampling (bottom) (macro-version): 1 μl (diluted with *n*-octane, 1:100). Split sampling (top): 1 μl (splitting ratio 1:100). Column temperature: 120°. Column: 50 m SP-400 silicone oil, 0.25 mm I.D. Carrier gas: hydrogen.

whereas for split sampling the mixture was introduced without dilution but with a splitting ratio of 1:100. The quantitative data given for comparison in Fig. 3 for the C_{18}–C_{34} *n*-alkane mixture were obtained without any difficulties by direct sampling, whereas with split sampling complete but not too "explosive" vaporization and perfect homogenization had to be guaranteed by selecting an adequate (not too low) injector temperature. With splitless injection, even more important parameters such as the boiling point of the solvent, injector and column temperature and carrier gas flow-rate before, during and after introduction of the sample have to be optimized carefully. Nevertheless, precise and accurate quantitative results were obtained finally with all three sampling methods. The chromatograms of the thermally unstable divinylcyclobutane (see Fig. 2) indicate that direct injection without using any vaporization step in extra-heated devices is the most suitable technique for preventing the formation of artefacts.

In the macro-version of the direct sampling technique, large amounts of solvent which dilute the significant sample species are fed into the column as in splitless sampling. However, no peak broadening is observed [see chromatograms (a) and (b) in Fig. 6] and/or retention deviations of the early peaks in the chromatogram, even with a low-boiling solvent, and therefore no "concentration" effect is required. The resolution in direct sampling is independent of the solvent volatility and is of the same order as when using the "concentration" effect of *n*-octane as a solvent in splitless sampling.

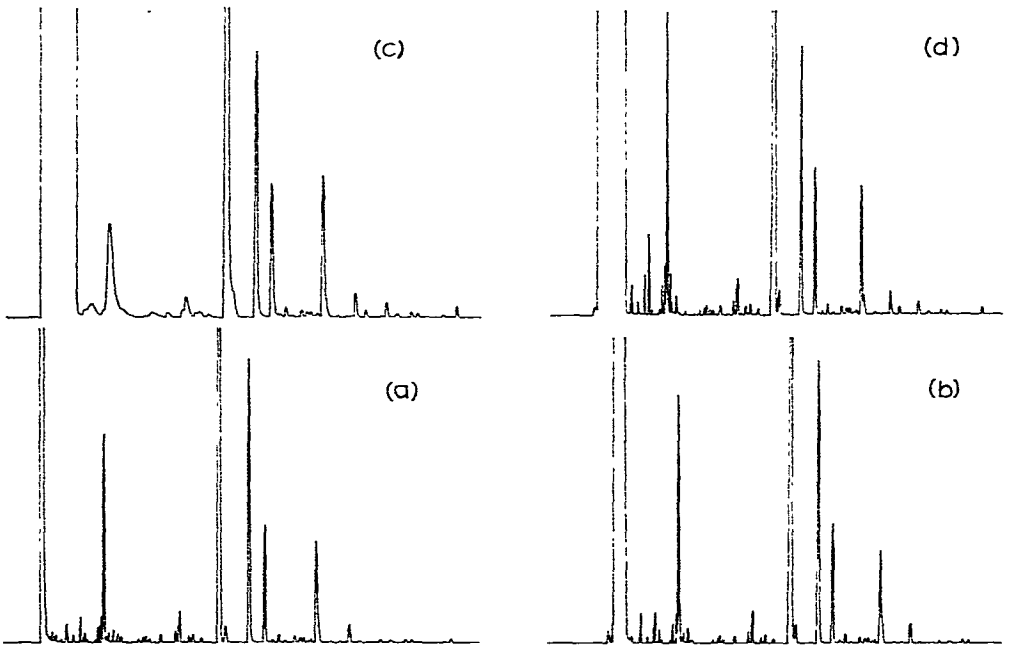

Fig. 6. Influence of solvent effects on resolution and retention: comparison of splitless and direct sampling. (a) Direct sampling, solvent *n*-pentane (b.p. 36°); (b) direct sampling, solvent *n*-octane (b.p. 125°); (c) splitless sampling, solvent *n*-pentane; (d) splitless sampling, solvent *n*-octane. Sample: lavender oil. Column: 30 m × 0.25 mm I.D. Marlophen 814. Temperature: programmed from 100 to 210° at 4°/min.

The broad solvent peak profiles in splitless sampling correspond to the closing period of the splitting valve, *i.e.*, the sample transfer time, which was 60 sec in both instances. In the case of *n*-pentane as the solvent (c), the sample peaks are much broader in comparison with those of chromatogram (d) obtained with *n*-octane as the solvent ("concentration" effect). The much sharper solvent peak profiles with direct sampling can be explained by the rapid vaporization of the sample inside the column itself. No retarded sample transfer which may also cause broadening of the sample peaks in chromatogram (c) with splitless sampling is observed with direct sampling. A comparison of chromatograms (b) and (d) reveals slight but not significant differences in peak resolution. These differences may also be caused by the injection technique in both sampling methods, which is not repeatable enough with respect to the resolution of the small peaks.

In order to minimize the sample volume to be introduced directly into the column and to achieve a finer and more reproducible adjustment of sample volume, the "micro-version" shown in Fig. 4 was developed. Small amounts (nanolitre range) of undiluted sample which are optimal for typical capillary columns can be sampled without adding solvents of dubious purity, in order to overcome the difficulties of sampling of small volumes.

Fig. 4 shows the construction of the rod into which movable capillary pipettes of adequate and defined volumes are placed. The displacement of the sample from the pipette into the column is effected by the carrier gas, which flows through a hole into the inner volume of the rod. The rod is introduced into the chromatographic system via the same sluice system as in the macro-version. The most critical feature of the construction is the centring of the capillary pipette tip when introducing it from the rod into the capillary column inlet. The variation of sample volume is achieved by using different pipettes of defined length and internal diameter. In Fig. 7 chromatograms obtained with three different sampling volumes are given.

The advantages and disadvantages of this technique can be summarized as follows.

Advantages

Direct sampling avoids the need for specially heated vaporization chambers of critical volume, flow conditions and surface properties.

No septum and no syringe are necessary for the introduction of the sample into the chromatographic system.

No splitting and previous homogenization have to be carried out.

Diluting solvents do not influence the peak width and retention, especially of early peaks (as in splitless injection).

In the micro-version, large amounts of diluting solvents do not have to be used.

Disadvantages

Non-volatile sample constituents are accumulated in the column inlet.

The variation of sampling volume cannot be effected with the same flexibility as with a syringe.

The stationary liquid may be washed away from the surface of first column coils. Deterioration of the coating in the first few centimetres of the column also occurs, however, in splitless and split sampling. In direct sampling, a solution of the

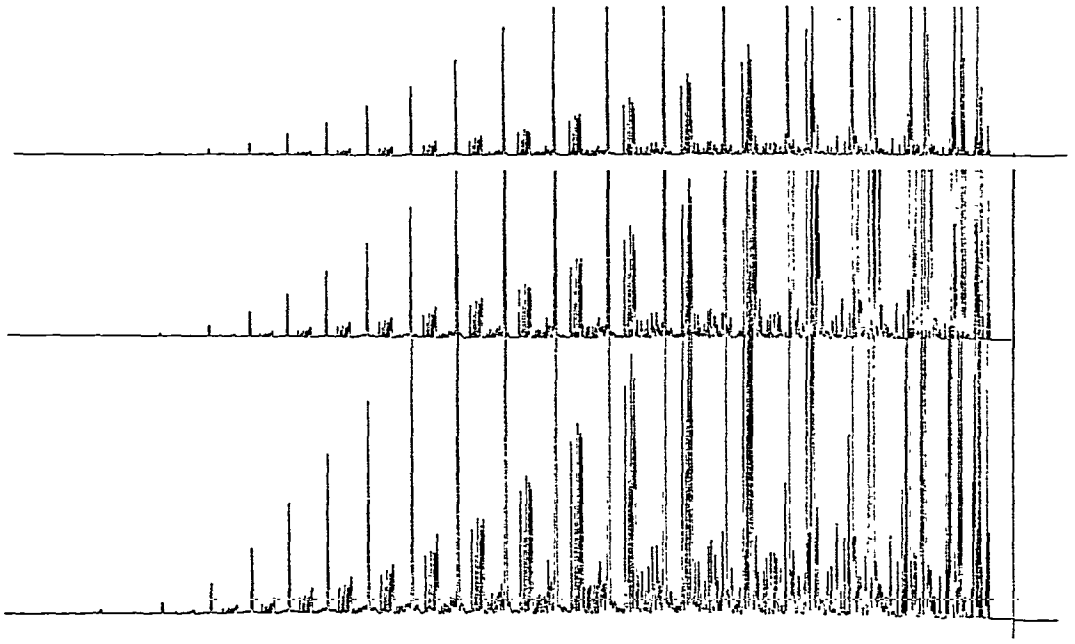

Fig. 7. Variation of sampling volume in direct sampling (micro-version). Sample: Fischer–Tropsch hydrocarbons. Column: 50 m × 0.25 mm I.D. SP-400. Temperature: ambient to 250° at 4°/min. Carrier gas: hydrogen (0.8 bar).

stationary liquid can easily be injected for re-coating, unlike the sampling methods with external vaporization.

SELECTIVE SAMPLING, INCLUDING INTERMEDIATE TRAPPING

In previous papers[3–5] we have described double-column systems[11] by means of which only those constituents from the eluate from the pre-separation are selected the optimal separation and quantitation of which are significant for the analytical problem concerned. In the system described by us, the main column is always a high-resolution capillary column. In relatively simple valveless chromatographic systems (Fig. 8), the removal of large amounts of solvents and of uninteresting components with very high retentions can be executed (by cutting and back-flushing) using isothermal or temperature-programmed pre-separation. The transfer of eluate cuts from the pre-column to the main column is carried out by automated valveless flow switching. Broad and distorted peak profiles, for example arising from pre-separations in packed columns, are improved and sharpened by trapping in the inlet of the pre-column. The main separation is started from the column itself, a short section of which acts as a trap by cooling–heating procedures, cold or hot nitrogen being blown on to the column. In most isothermal separations we observed that extra heating of the trap above the column temperature is not necessary, and heating of the trap by the column oven up to the required temperature before trapping is sufficient. The resolution and precision of retention are not further improved by overheating the trap. By

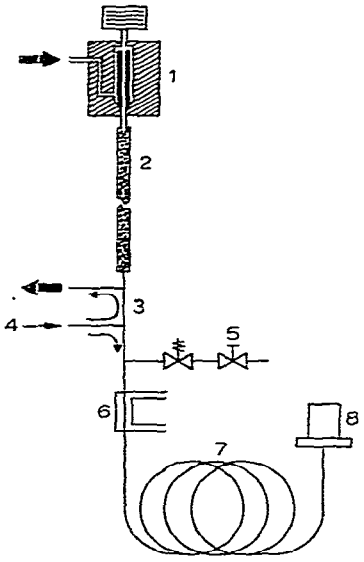

Fig. 8. Selective sampling into capillary columns in double-column systems. State of removal of solvents or volatile components or removal of heavy ends after transfer of the selected portion of the eluate from the pre-column into the main column. 1 = injector (split/splitless/direct); 2 = packed (or capillary) column; 3 = coupling piece; 4 = carrier gas inlet for main column; 5 = splitting valve; 6 = cold trap with stationary liquid (section of column); 7 = main column (capillary); 8 = detector.

using this sampling mode, no excessive amounts of solvents, no adsorption phenomena at the injector surfaces and no unsuitable flow conditions disturb the performance of sampling. The trapping procedure generates an inlet plug profile of optimal sharpness and symmetry without using additional solvents of special volatility.

According to our practical experience, there are several reasons for incorporating the removal of large amounts of solvents or derivatization reagents and the back-flushing of components with high retentions from a pre-separation. Solvents, major sample constituents and derivatization reagents considerably disturb the performance of detectors such as electron capture, nitrogen flame-ionization and MS detectors; by back-flushing, sample residues are removed from the chromatographic system without spending too much time on the elution of components with very high retentions in the normal flow direction. The required flow-switching operations should be valveless and carried out in all-glass systems, of course. Several examples of the use of a double-column system for selective sampling on to capillary columns have been described previously [3–5].

Fig. 9 shows the analysis of trace amounts of 2-nitronaphthalene (26 ppm) in 1-nitronaphthalene. "Heart cutting"[4,10] was applied in order to remove the large amount of the major component (the determination of which was not of interest) by re-injecting the relevant part of the eluate from the pre-separation. Venting of the eluate between the two columns was stopped at the point which is marked by a vertical dotted line in the chromatogram. The eluate flow was then directed into the main column and the sample species contained in it was trapped in the column inlet by blowing cold nitrogen into the column. After the significant parts of the eluate

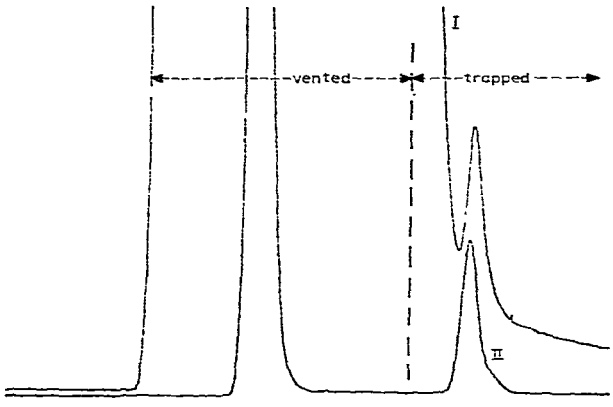

Fig. 9. Separation of trace amounts of 2-nitronaphthalene (26 ppm) from large amounts of 1-nitronaphthalene by selective sampling in a double-column system (heart cutting + trapping). I, Pre-separation, 17 m OV-225, 0.25 mm I.D. column; II, main separation after trapping and re-injection, 17 m OV-225, 0.25 mm I.D. column. Temperatures: column, 160°; injector, 240°; detector, 300°; Carrier gas: helium (0.7 bar).

from the pre-separation had reached the main column, the "trap" was heated (not much beyond the oven temperature). The chromatogram of the trapped material is also shown in Fig. 9. No overlapping of the two isomers can be seen because of the dramatic change in their relative proportions. Quantitation of the trace components has to be effected, of course, by means of an internal standard which has to be contained in the trapped part of the pre-separation eluate. When the change in selectivity does not further improve the separation of two species present in extreme relative proportions, heart cutting is the only method for discovering trace components that have been overlapped. If the pre-column and main column are coated with the same liquid stationary phase and all-glass connections between the two columns with a zero dead volume are used, intermediate trapping may not be necessary in all instances[3–5]. By trapping of the transferred eluate components, retention time measurements in the main column are made without the contribution of the polarity of the pre-column because an independent starting point for retention measurements in the main separation is achieved. When using a packed pre-column and when heart cutting on tails of large solvent peaks[4] is carried out, intermediate trapping is necessary in order to re-sharpen the peak profiles which are too broad after leaving the pre-column (see analysis of aqueous solutions of phenols[3]). As pointed out in previous papers, enrichment of trace components after repeated pre-separations can also be achieved by intermediate trapping[2].

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