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# SOLVENT EFFECTS IN CAPILLARY GAS CHROMATOGRAPHY

## DETERMINATION OF TRACE AMOUNTS OF CHLOROFORM AS AN EXAMPLE

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SUMMARY

The trace analysis of solvents in dilute solutions by capillary gas chromatography (GC) is often difficult because of partial solvent trapping effects. The problems of solvent effects with such samples are shown by the example of chloroform. Two solvent effects, solvent trapping and phase soaking, are discussed in relation to the determination of chloroform. It is shown that there are only a few possibilities of creating practically perfect chloroform peaks: (a) water as a solvent and on-column injection; (b) diethyl ether as solvent with Pluronic L61, OV-1701 or similar stationary phases, on-column injection and splitless sampling at column temperatures below 15°C; (c) acetone as solvent on OV-1701 or similar stationary phases with a free choice of sampling technique. All other solvents and conditions tested produced distorted peaks owing to partial solvent trapping which was not corrected by phase soaking. Peak distortion could be reduced by the choice of a volatile solvent and by increased retention power of the column (long and/or thick-film columns).

## INTRODUCTION

Trace amounts of chloroform must be determined in a wide range of samples, *e.g.* in drinking water, where chloroform may be present as a result of chlorination of the raw water.

Trace amounts of chloroform may be determined by two gas chromatographic (GC) methods, via either the gas or the liquid phase. It can be determined by the direct headspace method, *i.e.*, by injection of gas taken from above the thermostated sample. Enrichment on adsorbents and thermal desorption resemble the direct headspace method as far as no solvent is involved. The alternative method deals with dilute solutions of chloroform as may be obtained from liquid samples and from liquid extractions and solutions resulting from clean-up or fractionation procedures. This paper deals exclusively with chloroform in diluted solution. It reports on the problems that arise due to solvent effects in capillary columns and explores the possibilities of avoiding peak distortions.

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Chloroform is not adsorptive and at first sight it would appear to be a very easy compound to determine. However, as soon as chloroform is injected together with large amounts of solvent (splitless or cold on-column injection), the peak often becomes broad and distorted. In complex mixtures it "disappears" from the chromatogram. No chloroform is detected because its "peak", a poor hump, is regarded as a baseline instability.

In early analyses of drinking water[1] we (and many others) seldom detected any chloroform. Fig. 1 may illustrate why. It shows a chromatogram of a mixture resembling an extract of drinking water. The lower chromatogram was obtained by a split injection of a relatively concentrated solution. In its early part massive peaks of benzene, chloroform and toluene are observed. In the analysis of the dilute solution injected in the splitless mode (Fig. 1a), the early part of the chromatogram is dis-

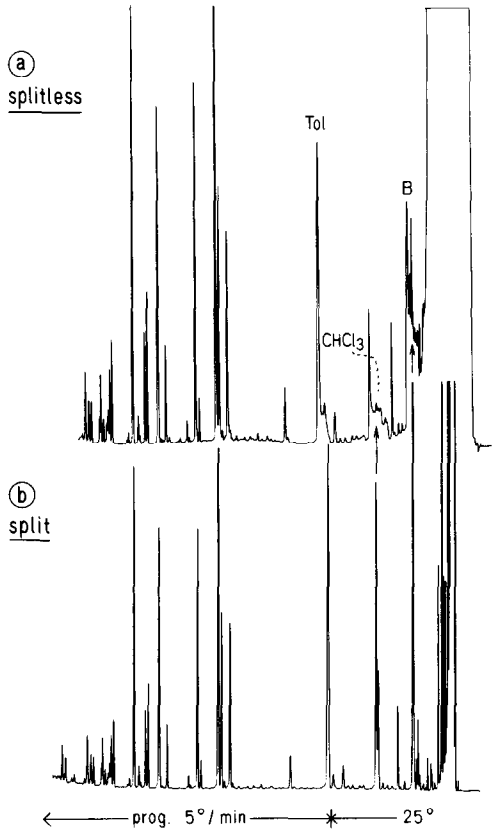


Fig. 1. Illustration of the problems that may arise by partial solvent trapping during the determination of volatile trace components. Sample, mixture of gasoline, benzene and chloroform, dissolved in hexane; 20 m × 0.32 mm I.D. glass capillary coated with Pluronic L61; 0.3 atm of hydrogen as carrier gas; temperature programme as indicated. Chromatogram b resulted from a split injection (1 $\mu$l sample volume, 40:1 splitting ratio) of a relatively concentrated solution. These conditions practically excluded solvent effects. In chromatogram a, obtained by splitless injection (2.5 $\mu$l sample volume) of a dilute solution, the peaks of benzene and chloroform are strongly distorted and the toluene peak still considerably distorted by partial solvent trapping.

turbed. Without some understanding of the background of the technique, the chromatogram is likely to be misinterpreted. The toluene peak in Fig. 1a appears to be fused with a minor component. A mass spectrum of this smaller peak would give a confusing result because the ions of toluene dominate the small alkane completely. In fact, the toluene peak has the shape of a chair with a shoulder eluted in front of the large maximum[2]. The minor component sits on this chair (compare peak sizes with the split injection). The integrator would find insufficient amounts of toluene. The situation with benzene is even worse. The hump following the solvent peak in Fig. 1a carries some sharp peaks, but none of them is benzene. The hump is not an overloaded, very polar or otherwise undesirable component, but the benzene. The peak shape approaches a rectangle or stool, as shown previously[2]. Unless present in large amounts, benzene is likely to be overlooked, especially in mixtures more complex than that in Fig. 1.

For toluene and benzene the solution is relatively simple. The distortion of their peaks is due to the use of hexane as the solvent, which gives rise to partial solvent trapping and (at least on Pluronic L61, the stationary phase used) no important reconcentration by phase soaking. As soon as a more polar solvent is selected, *e.g.*, dichloromethane, diethyl ether or carbon disulphide, the two peaks elute with a perfect shape. The case of chloroform is more complex. Again, the peak in Fig. 1a with the approximate retention time of chloroform is not related to chloroform; it is the alkane eluted shortly before chloroform in the lower chromatogram. Chloroform is represented by the hump eluted slightly earlier.

Chloroform is a difficult sample component with regard to solvent effects because there are only a few possibilities of producing acceptable peaks of it with splitless or on-column injection. A number of other volatile components behave similarly. We have concentrated on chloroform because the principles discussed for this solute are also valid for most of the others.

Dilute samples must be injected by the splitless or the cold on-column technique. Both methods introduce large amounts of solvent (0.5–5 $\mu$l and more) into the column. The usual column temperature is around 25°C. In splitless sampling most solvents recondense under these conditions and on-column sampling introduces the condensed solvent directly into the head of the column. The amount of solvent injected is comparable to the amount of stationary phase present in the whole capillary column, and it must be expected that the solvent acts as an additional, although only temporary, stationary phase. This is of particular importance because in the first moments of a run nearly all of the solvent is concentrated in the first few tens of centimetres of the column inlet, forming a layer with a thickness that renders the regular stationary phase negligible. The sample components are, at least at first, dissolved in this temporary stationary phase. It is hardly surprising that this situation influences the chromatography of the sample. It alters retention times, but as most sample components elute as perfect peaks, it may still be neglected in many analyses. Solvent effects are useful for a majority of samples, but they are disturbing in instances such as chloroform[2].

The solvent effects were described in previous papers[2–5] and the principles are repeated here only as far as they are relevant to the determination of chloroform.

## SOLVENT TRAPPING

Two solvent effects should be considered separately in order to understand the shapes of the chloroform peaks when injected with different solvents and on to different columns. The first, solvent trapping, is created by the condensed solvent in a 10–100 cm long inlet section of the column. In splitless sampling, recondensation of the solvent is required if a solvent effect is needed to reconcentrate the solute bands which became broad as a result of the slow sample transfer from the injector to the column (splitless period of 40–60 sec with appropriate carrier gas flow-rates[6]). As cold trapping[7] is excluded for samples that contain chloroform, a successful splitless injection relies on the solvent effect.

Cold on-column sampling requires a column temperature that is below (under certain conditions up to a few degrees above) the boiling point of the solvent, in order to prevent back-flow of sample vapour from the column inlet into the injector[8,9]. Back-flow is prevented by control of the evaporation speed, and thus by creation of a volume of sample vapour per unit time that remains below the carrier gas flow-rate. This forces us to accept an increased presence of liquid sample in the column inlet. Hence, both sampling techniques create the conditions for solvent trapping effects.

Solvent trapping is useful as long as it is "full trapping", *i.e.*, the solvent is able to retain all of the material of a sample component until it has completely evaporated itself. Full solvent trapping reconcentrates bands that have become broad owing to slow transfer (splitless injection), gives the bands an extra retention time corresponding to the evaporation time of the solvent in the column inlet and releases them afterwards within a short time, providing narrow initial bands. Full solvent trapping may be regarded as the normal case. Most alkanes and the aromatics eluted beyond toluene (the major peaks beyond the toluene peak) in Fig. 1 are fully trapped.

For chloroform, however, we were not able to find a solvent that was able to retain it fully. Chloroform evaporated prematurely from the solvent layer — the solvent trap leaked. Chloroform was "partially trapped". Partial solvent trapping produces broad and distorted solute bands. The typical band shape of a partially trapped component ranges between the two extremes shown for chloroform in Fig. 2 according to the retention power of the solvent with respect to the solute.

Chloroform injected as a solution in hexane gave a broad stool-type peak. It evaporated from the hexane layer at a fairly constant rate during 75 sec. Its evaporation was completed before the solvent had evaporated itself (which took 105 sec). Thus hexane only had a weak trapping effect on chloroform.

Diethyl ether retained (trapped) chloroform more efficiently than hexane. The chair-type peak shown in Fig. 2b indicates strong but not complete trapping. The shoulder eluted first represents the partially trapped (prematurely evaporated) material. Most of the material, however, eluted as a sharp peak. It was retained until the ether had evaporated, *i.e.*, was fully trapped and released during a short time. Thus the solvent trapping effect of diethyl ether was close to full trapping. The interpretation of Fig. 2b is complicated by the fact that diethyl ether produced a second solvent effect (phase soaking) on the Carbowax 400 column, which nearly halved the width of the chloroform band originating from the partial solvent trapping.

The shape of the chloroform band as it left the solvent trapping step (thus before modification by phase soaking) was found to be between those in Fig. 2a and b for all organic solvents tested.

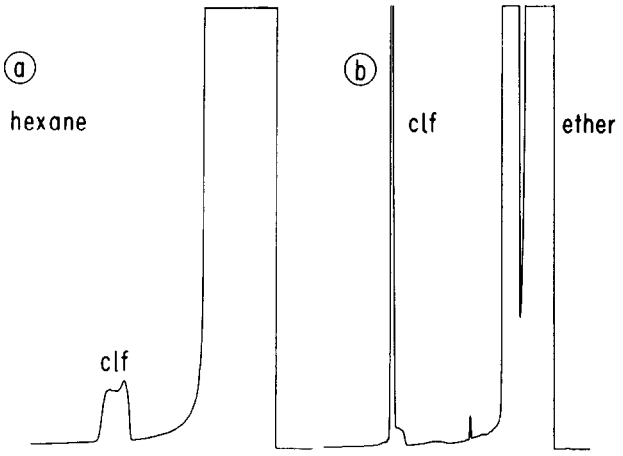


Fig. 2. The two extremes of peak deformation by partial solvent trapping, ranging between a weak trapping by hexane (a) and nearly full trapping by diethyl ether (b). Column, 30 m × 0.30 mm I.D. glass capillary, Carbowax 400; 0.3 atm of hydrogen as carrier gas; sample volume, 4 $\mu$l; on-column injections at 27°C. clf = chloroform.

Water showed no significant broadening of the chloroform band. The retention of chloroform in an aqueous layer was sufficiently low to release the solute virtually immediately on injection, a "non-trapping effect". Thus, as far as solvent trapping was concerned, water was the only solvent that produced an acceptable initial band shape for chloroform.

## PHASE SOAKING

The other solvent effect of importance takes place beyond the flooded inlet section in the coated column. The solvent located in the inlet section saturates the carrier gas during its evaporation, which may last between a few seconds and several minutes. The solvent vapour may be retained by the stationary phase, increasing the film thickness and decreasing the viscosity of the stationary liquid. Both of these factors, and in many instances an additional change in the polarity of the stationary phase by the solvent, increase the retention power of the "soaked" in comparison with the solvent-free stationary phase. Some combinations of soaking solvents and stationary phases were found to retard the migration of certain solutes by factors exceeding ten[5]. As the solvent in the column inlet is evaporated, it starts to withdraw from the coated column. During this process the rear of a solute band leaves the soaked zone earlier than the front; it is no longer retarded and moves more rapidly than the front of the band, giving rise to a reconcentration effect. The strength of the reconcentration effect depends primarily on the retardation of the solute in the soaked stationary phase. Retardation depends on the amount of solvent retained by the stationary phase and the increase in the retention power by the soaking due to adjustment of the polarity of the stationary phase to the solute. A retardation of the solute by a factor of about three is sufficient to give complete reconcentration of partially trapped solutes[5].

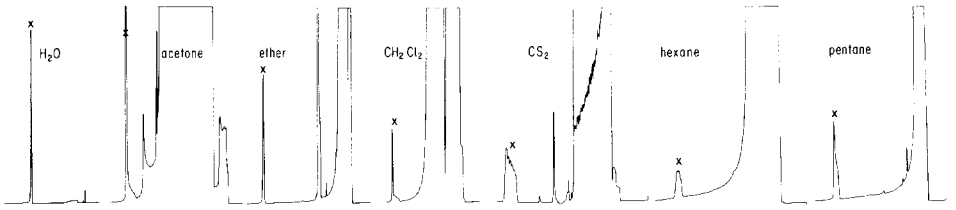


Fig. 3. Chloroform peaks obtained by on-column injections with various solvents on to a 17 m × 0.32 mm I.D. Pluronic L61 column with a non-coated pre-column of length 1.5 m. Sample volume, 5 μl, except for water (3 μl); 0.2 atm of hydrogen as carrier gas; column temperature 27°C. All solvents produced partial solvent trapping effects except for water, which hardly trapped chloroform at all. Diethyl ether reconcentrated the broadened band by phase soaking.

The solvents pentane and hexane were neither significantly retained by polyglycol stationary phases (Carbowax 400 and Pluronic L61) nor did they specifically increase the retention power of the soaked phases for chloroform. Accordingly no significant reconcentration of the chloroform band was detected. The chloroform peaks as they eluted from the Pluronic L61 column (90% polypropylene and 10% polyethylene glycol) are shown in Fig. 3. Carbon disulphide reconcentrated the strongly distorted chloroform band by a factor of nearly two. Phase soaking with dichloromethane reconcentrated by a factor of 2.2. Diethyl ether produced a perfectly shaped peak (Fig. 3). As diethyl ether did not fully solvent trap the chloroform, the perfect shape of the final peak is due to complete reconcentration by phase soaking. The same strong phase soaking effect was observed on a thick-film OV-1701 column (Fig. 4), but not on the Carbowax 400 column (Fig. 2). Thus, of the organic solvents tested, diethyl ether was the only solvent giving a perfect chloroform peak on Pluronic L61.

Chloroform injected with water produced a perfect peak. This may be explained by nearly perfect non-trapping and an unusual phase soaking effect. On the one hand, chloroform eluted before the solvent which produces a "reverse solvent effect"[10]. Reverse solvent effects normally broaden solute bands because the rear of the solute band is retarded in the soaked zone for a longer time than the front. On the

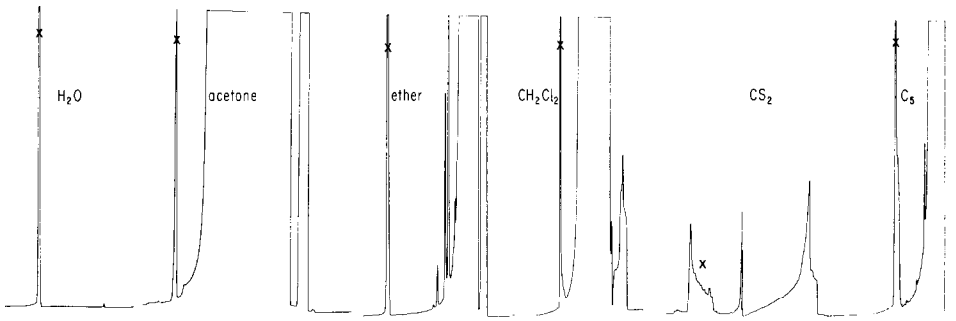


Fig. 4. The peaks of chloroform eluted from a 13 m × 0.31 mm I.D. glass capillary coated with 1.12 μm of OV-1701, including an uncoated inlet of length 2 m. On-column injections of 5 μl sample volumes except for water and acetone (3 μl); 0.2 atm of hydrogen as carrier gas. Reconcentration due to phase soaking was stronger than on Pluronic L61; acetone even gave full reconcentration.

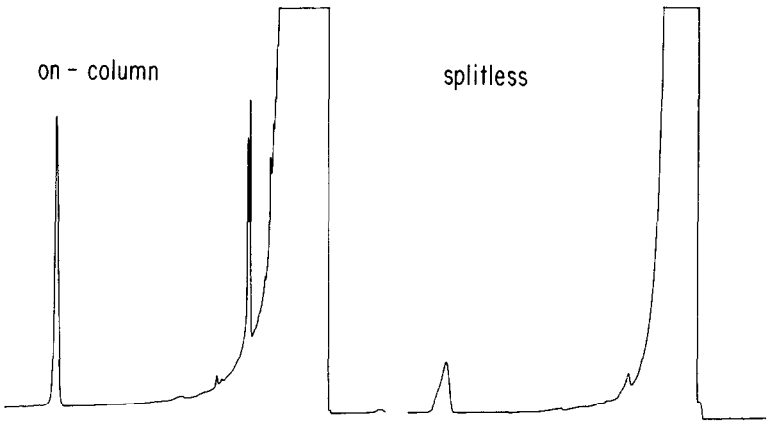


Fig. 5. Chloroform in diethyl ether, injected on-column and splitless on to a 20 m × 0.32 mm I.D. Pluronic L61 column with a 1-m uncoated inlet section. Sample volume, 2 $\mu$l (including the syringe needle for the splitless injection). Column temperature, 25°C; 0.25 atm hydrogen as carrier gas. In splitless injection, the solvent did not recondense; hence there was no solvent trapping. The dilution of the solvent vapour in the injector also caused the phase soaking effect to be weak. The peak still represents the shape of the chloroform band broadened by the slow sample transfer from the injector to the column (splitless period 30 sec). Solutions in diethyl ether must be injected on-column or, if splitless, into a column cooled below 15°C.

other hand, the phase soaking by water has reversed-phase characteristics, resulting in reconcentration rather than broadening of the band.

Non-polar stationary phases are in general inconvenient for the determination of chloroform because of the difficulty of resolving the solute from the solvent. However, a thick-filmed (1.1 $\mu$m) OV-1701 column (Fig. 4) gave some interesting results and might be an alternative to the medium polarity polyglycol columns. Only hexane could not be resolved from chloroform. OV-1701 columns are characterized by improved stability of the retention characteristics, reduced bleeding and better thermal stability than columns coated with low-viscosity polyglycols. In addition, phase soaking effects of several solvents were found to be stronger than on Carbowax 400 and Pluronic L61. Pentane reconcentrated by more than a factor of two, dichloromethane by a factor close to five and acetone was the second solvent (beside diethyl ether) providing complete reconcentration of the chloroform band. Unfortunately, carbon disulphide, the solvent we used to extract charcoal filters, *e.g.*, with the closed-loop stripping procedure[11], still gave very poor chloroform peaks.

To summarize, phase soaking allows the production of perfect chloroform peaks with diethyl ether on Pluronic L61, OV-1701 and similar stationary phases and with acetone on OV-1701-type stationary phases. Water, giving a non-trapping effect, is still acceptable because the reverse solvent effect involved has reversed-phase characteristics, and hence phase soaking does not broaden the chloroform band.

## SPLITLESS OR ON-COLUMN INJECTION?

So far, solvent effects have been discussed as if it does not matter whether the

solution is introduced by the splitless or the on-column injection technique. In fact, Figs. 2–4 were obtained by cold on-column sampling.

In splitless sampling two points must be considered that are not important in on-column injection: recondensation of the solvent in the column and reconcentration of the band broadened by the slow sample transfer from the injector to the column.

Diethyl ether was shown to produce perfect chloroform peaks by on-column injection. As shown in Fig. 5, this is not the case for splitless sampling at a column temperature of 25–30°C. At this temperature, only about 10°C below the boiling point of diethyl ether, the solvent does not recondense in the column inlet. Because of the dilution with carrier gas, its partial vapour pressure does not reach saturation and therefore there is no solvent trapping effect. The ether vapour was even too dilute to produce a strong phase soaking effect. Fig. 5 indicates that the initial band width of chloroform after the transformation by phase soaking (base width of the peak minus the base width of the chloroform peak obtained by on-column injection) was 15 sec. As the transfer time (splitless period) was 30 sec, phase soaking reconcentrated by a factor of two.

It may be concluded that diethyl ether solutions should either be analysed by on-column injection (at column temperatures up to 40°C) or by splitless sampling into a column cooled below 15°C.

Fig. 6 shows that the peak of chloroform injected splitless in an aqueous solution is deformed in a similar manner to that in Fig. 5 in the diethyl ether solution. Again, the chloroform band, broadened by the slow sample transfer, was not reconcentrated, although in this instance the solvent (water) was almost completely

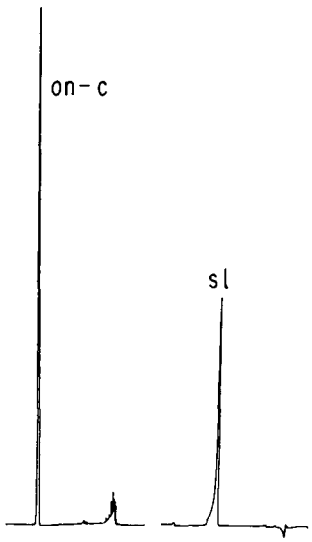


Fig. 6. Splitless (sl) and on-column (on-c) injections of aqueous chloroform solutions on to the Pluronic L61 column in Fig. 3. Sample volumes, 2 $\mu$l. Splitless sampling gave a broadened peak as in Fig. 5 (diethyl ether solution). In this instance the reconcentration did not fail because of missing recondensation of the solvent but because water neither trapped the solute in the column inlet nor reconcentrated it efficiently by phase soaking. Aqueous samples must be injected by the on-column method.

recondensed (its evaporation in the column inlet took about 10 min). The reconcentration nevertheless failed, because water did not trap the chloroform. Thus chloroform started to be chromatographed as if there had been no condensed water. The width of the chloroform band was slightly reduced by the phase soaking effect described above, from 30 sec (splitless period) to about 20 sec. For the aqueous solution we do not know of a method of eliminating the band broadening by the splitless injection. Thus on-column sampling must be applied.

It was recently shown that the determination of chloroform in aqueous solutions by on-column injection and electron-capture detection (ECD) is a promising method[12]. In this instance very thick-film non-polar columns were applied. Other types of columns may be used if the water does not destroy the preparation of the support surface of the column.

If splitless sampling causes solvent trapping, the results are similar to those obtained by on-column injection, because the partial solvent trapping usually predominates over the deformation of the peak. This is shown in Fig. 7 by a comparison of the peak shapes of chloroform injected as a hexane solution by the splitless and the on-column method. Thus the results shown in Figs. 3 and 4 are valid also for splitless sampling with the exceptions discussed earlier (water, diethyl ether and pentane).

On-column injection for the determination of trace amounts of volatile compounds such as chloroform has a number of advantages. It is more accurate and more precise than splitless sampling; there is no band broadening due to the introduction of the sample into the column, which excludes splitless injection in some instances or renders it more troublesome. Finally, splitless injection restricts the sample size to 1–2.5 $\mu$l, whereas on-column injection allows a choice between 0.2 and 5 $\mu$l (with some precautions even much more).

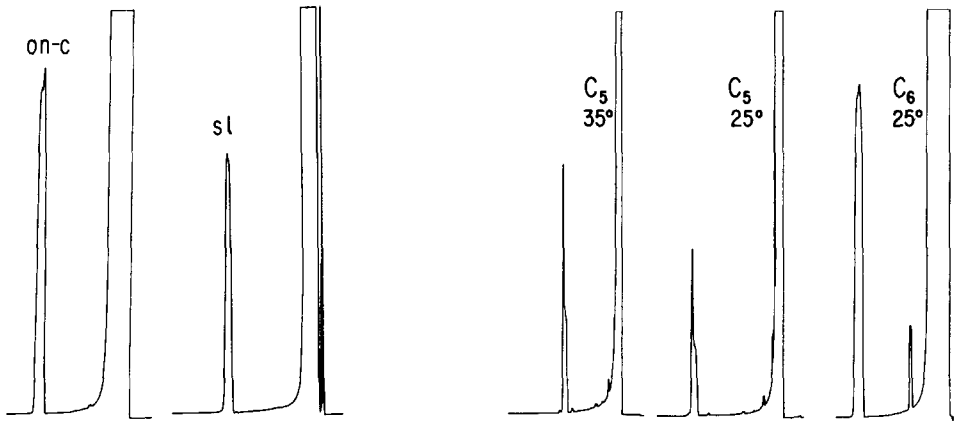


Fig. 7. Splitless (sl) and on-column (on-c) injections of chloroform in hexane on to the Carbowax 400 column as in Fig. 2. Sample volume, 2.5 $\mu$l; splitless period, 30 sec. Partial solvent trapping predominated the peak deformation.

Fig. 8. On-column injections of chloroform in pentane and hexane on to the Carbowax 400 column as in Fig. 2. Sample volume, 2 $\mu$l. Hexane produced a broader chloroform peak than pentane because of the prolonged evaporation time of the solvent in the column inlet. An increase in the column temperature from 25 to 35°C reduced the peak broadening owing to a shortened evaporation time, but the retention time of the chloroform was reduced accordingly.

COMPROMISES

The above discussions concentrated on the principles of the solvent effects involved in the determination of a sample component such as chloroform. Only a few solution could be offered in order to overcome the problems fundamentally, and these solutions are not realistic for many applications. Hence there remain applications that call for compromises, where solvents other than the recommended ones must be used, and conditions need an optimization to allow the peak distortion to be reduced to a level that no longer hinders the analysis. For this optimization the factors are listed that determine the degree of peak distortion.

Peak distortion is usually directly related to the evaporation time of the solvent in the column inlet. Thus, for a given column, there is an interest in minimizing this evaporation time. The time required for the evaporation of a solvent in the column inlet depends primarily on its boiling point and its polarity (evaporation energy?) If 5 $\mu$l of pentane evaporated within 50 sec, the same amount of hexane under the same conditions required 230, dichloromethane 160, acetone 320 and carbon disulphide 260 sec for their evaporation. A conclusion, however, is impeded by the fact that the increased evaporation time of the more polar solvents is in most instances balanced by a reinforced phase soaking effect.

Pentane as a solvent gives rise to less peak distortion than hexane, but even in this instance the results were more complex than expected. The strong increase in evaporation time from pentane to hexane (factor of five) did not go along with a corresponding increase in the peak broadening (a factor of two, as shown in Fig. 8) because these alkanes trap the chloroform only weakly. The chloroform band is not broadened according to the evaporation time of pentane and hexane.

Fig. 8 also compares the chloroform peak obtained by on-column injection of the pentane solutions at 25 and 35°C. Evaporation of the solvent and the solute from the solvent layer is accelerated at increased column temperatures and peak broadening is therefore reduced. The evaporation time is also reduced if the carrier gas flow-rate is increased. However, neither parameter (column temperature or carrier gas flow-rate) improves the final result because they also reduce the retention time of the solute.

The evaporation time of the solvent and of the partially trapped solute is approximately proportional to the sample volume. A reduction in the sample size improves the chloroform peak. This is shown in Fig. 9 for on-column injections of pentane solutions on to the Pluronic L61 column. A sample size of 0.25 $\mu$l gave no significant loss of the column efficiency, obviously at the cost of the sensitivity of the method.

On a given column the room for improvement is limited and the selection of the column is more important. Two factors should be considered: the strength of the phase soaking effect by the type of the stationary phase and the chromatographic retention of the column with respect to chloroform. OV-1701 showed more efficient reconcentration by phase soaking than the polyglycol-type phases. On the other hand, its retention with respect to chloroform is low. Chromatographic retention improves the results because the proportion of the peak broadening by partial solvent trapping on the total peak width decreases with increasing retention time, *i.e.*, increasing peak broadening due to the chromatographic process. This is true in both

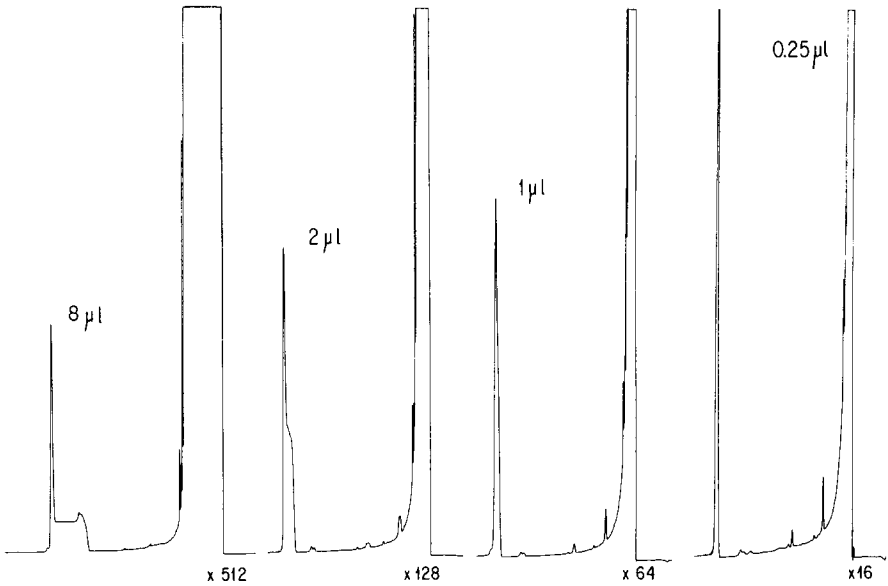


Fig. 9. Dependence of the peak broadening by partial solvent trapping on the sample volume. On-column injections of chloroform in pentane on to the Carbowax 400 column as in Fig. 2. For the sample volume of 0.25 µl no loss of the column efficiency was observed.

isothermal and temperature-programmed runs where the cold trapping effect reduces the band width.

The chromatographic retention time is proportional to the column length and also to the film thickness of the stationary phase[13]. The latter is the more important parameter because in practice it is more conveniant to increase the film thickness of the stationary phase than the column length. Films of low-viscosity polyglycols such as Carbowax 400, Pluronic L61 or Ucon LB 550 are limited to thicknesses below 0.4–0.6 µm (depending on the pre-treatment of the support surface). Immobilized phases, however, form stable films up to a thickness of several micrometres[14]. If at present the polyglycols of moderate polarity (Pluronic L61 and similar types) and thick-film OV-1701 columns are of similar suitability for the determination of chloroform under non-ideal conditions, a thick-film silicone stationary phase of higher polarity would be preferable.

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