Application Note No. 002

Selecting the Injection Mode in Capillary Gas Chromatography

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Introduction

The introduction of liquid samples in gas chromatography has been a problem ever since the introduction of this technique into routine laboratories. Especially in capillary gas chromatography extraordinary demands are placed on the sample introduction device. An extremely small sample amount has to be introduced accurately and rapidly in a reproducible manner into the smallest possible gas volume. this gas plug must be transferred into the column without any losses by degradation, adsorption or discrimination. It is evident that this can only be achieved by employing very sophisticated inlet devices. For routine analysis of liquid samples four injection techniques are available: split, splitless, on-column and programmed temperature vaporising injection. In this short contribution the principles, and the advantages and disadvantages of these four injection techniques will be discussed. Keywords in the comparison of these techniques are discrimination, thermal degradation and applicability of the individual techniques for trace analysis. Special attention is paid to the selection of the most appropriate injection technique for a given application. The discussion is generally limited to liquid samples.

Split injection

In the split injection mode the liquid sample is introduced into a heated injection chamber. Due to the high injection temperature instantaneous evaporation of the (liquid) sample occurs. A relatively high carrier gas flow is continuously introduced into the injector and rapidly mixes with the samples vapours. The major portion of the resulting gas plug is vented via the split exit leaving only a small fraction of the gas to be actually introduced into the column. The splitting serves two purposes. Firstly, it reduces the size of the sample to an amount compatible with the extremely low sample capacity of capillary columns. Secondly, it effectively flushes the liner so that narrow bands are introduced on to the column. As only part of the sample (typically between 1 and 5%) enters the column, split injection is not suited for trace analysis. When using flame ionisation detection, the detection limits are approximately 50 ppm (w/w). A second disadvantage of split injection is the discrimination of higher boiling components. In the heated liner additional evaporation of the more volatile sample constituents from the needle cannot be avoided. Hence, the actual composition of the sample that enters the column is no longer a correct representation of the real sample. Transfer of low-boiling components is favoured over that of high boiling species. Quantitative transfer is only obtained for components with a boiling point below that of approximately n-C_{20}. Finally, split injection is not suitable for the analysis of thermally unstable components. Degradation of these components in the heated injection chamber is likely to occur, especially when using liners packed with glass wool or containing glassfrits. Despite the disadvantages of split injection summarised above, this technique is still one of the most widely used injection nowadays, mainly due to its ruggedness and its ease of use.

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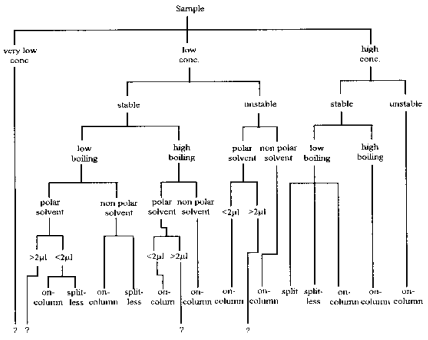

Figure 1. Decision diagram for the section of the most suitable injection technique.
Guidelines:
Conc. ranges: very low: < 0.5 ppm, low: 0.5 - 50 ppm, (FID). Boiling points: high: above approx. n-C_{20}, low: below approx. n-C_{20}

Splitless Injection

The hardware required for splitless injection is very similar to that used in split injection. Again, the sample is introduced into a heated liner where it evaporates rapidly. During transfer of the plug of vapour into the column by means of the column flow, the split exit remains closed. After approximately 20-60 seconds the split vent is opened to remove the remaining traces of vapour from the liner. Refocusing of the sample components can be obtained by selecting a low initial oven temperature. This gives rise to the so-called solvent effect and to cold trapping. These refocusing mechanisms sharpen the input bands of the early eluting and the later eluting components, respectively. Optimum refocusing of the solute peaks by the solvent effect is only obtained if the condensed solvent forms an homogeneous film in the inlet of the column. This in turn is only obtained if the polarity of the solvent is not too high. For highly polar solvents like for example methanol, only very small volumes (<approx 2 µl) can be introduced. For larger volumes, a significant peak distortion is generally observed. Analogous to the situation in split injection fractionation of the sample caused by expulsion of more volatile components from the syringe needle and the retention of the less volatile species in the needle can occur. Thermal degradation is generally more pronounced than in split injection because of the much longer residence time of the components in the heated liner. In contrast to split injection, splitless injection is suited for trace analysis because with this technique the entire sample is introduced on to the column.

On-column Injection

In the on-column injection mode the liquid sample is introduced directly into the unheated inlet of the capillary column without an intermediate evaporation step. During the course of the temperature program the vapour pressure of the solutes increases and the chromatographic process begins. By using an initial temperature below the boiling point of the solvent selective evaporation and, hence, discrimination is avoided. For more volatile components, the situation is similar to that found in splitless injection, being refocused by the solvent effect. By using a retention gap, band broadening due to flooding of the column by the liquid sample can be avoided. As again the entire sample is introduced into the column this technique is suitable for trace analysis, and thermal degradation is absent due to not employing a heated injection system. From these characteristics it is clear the on-column injection is superior to both split and splitless injection. Despite its significant advantages, on-column injection has not gained widespread acceptance in routine analysis. This is mainly due to the less rugged nature of the technique and the practical difficulties in automation.

Comparison of conventional split, splitless and on-column injection

In selecting the proper injection technique for a particular application a number of factors must be considered. Apart from the concentration levels of the components in the sample, account must be made of their boiling points and thermal stabilities. Also the nature and properties of the solvent can affect the ultimate choice of the injection technique. Moreover it appears that the ultimate choice of the injection system is often, at least in part, determined by the mere availability of the various injection systems.

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Figure 1 shows a Decision Diagram which can be used for selecting the proper injection technique for a given application. In constructing this diagram only conventional split, splitless and on-column injection have been considered. A question mark in the diagram indicates that a particular type of sample cannot be analysed using one of the conventional injection techniques.
The first important parameter in the process of selecting the proper injection technique for a particular application is related to the concentration of the components in the sample. High concentrations (> 50 ppm, FI detection) can be analysed directly with hot split injection or, after dilution, with hot splitless or cold on-column injection.
Concentrations below between approximately 0.5 and 50 ppm require the use of hot splitless or on-column injection. Split injection of these samples is only possible after a suitable preconcentration step.
A second important parameter to consider is the boiling point of the solutes. For example, if the sample contains high boiling components, hot injection techniques cannot be used and, for this type of sample, only cold on-column injection can be used.
Apart from the concentrations and the boiling point of the components, the thermal stability should be considered when selecting an injection technique. For components liable to thermal degradation, cold on-column injection should always be the method of choose.
Finally, the polarity of the solvent can effect the ultimate choice. Large volumes of polar solvents introduced on to non-polar or intermediate polarity columns will give rise to distorted peaks as severe flooding of the column inlet occurs.
From Figure 1 it is evident that the analysis of highly diluted samples using one of the conventional injection modes is impossible. As there is a continuous need for lower detection limits, this is a serious shortcoming of the conventional injection techniques. Apart from problems in the low concentration range, a few other question marks appear in the figure. These question marks are mainly related to the analysis of relatively large volumes of polar solvents. An alternative to solve these two problems in an elegant and easy way is programmed temperature vaporiser injection.

Programmed Temperature Vaporising Injection

The programmed temperature vaporiser injector (PTV) closely resembles the classical split/splitless injector, with the primary difference being the temperature control. In the PTV injector different independent temperature plateaux, iso-times and programming rates can be used which makes this injector a very flexible inlet device. Hot split and splitless, cold split or splitless injection and, after the introduction of a special insert, cold on-column injection can all be performed using only one injector. Combining a cool injection step with a controlled vaporisation eliminates a number of important disadvantages associated with the use of conventional hot sample inlets. In the cold injection modes, discrimination is absent as transfer of the sample into the chromatographic system is performed in the liquid state. Additionally, thermal degradation is less likely to occur. Apart from the five possible injection modes described above, PTV injectors can also be used for the introduction of very large solvent volumes. This type of injection is called the solvent vent injection. In this injection mode a large volume of sample is introduced into the liner at a controlled speed. The initial inlet conditions are arranged so that the solvent is vented via the split line while the components are trapped and preconcentrated. At the end of the sample introduction process the split vent is closed and the liner is heated. In this way very large sample columns up to 250 ml have been introduced on to 320 mm capillary columns. The solvent vent injection can also be used for the introduction of polar solvents. As the solvent is vented prior to introduction in to the GC column, no band distortion occurs.

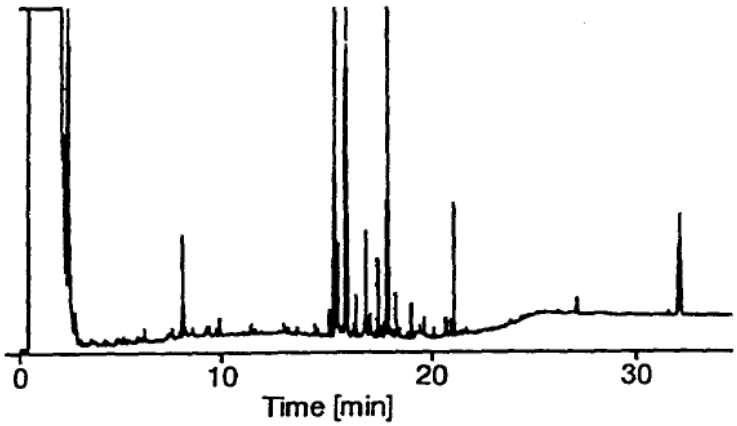

Figure 2. Large volume sampling: Analysis of 250 µl of a hexane extract (1:50) of Baikal lake water.

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An example of a large volume injection using a PTV injector in the solvent vent mode is given in figure 2. This figure shows the analysis of a hexane extract of water from the Baikal Lake. 100 ml of Baikal Lake water was extracted with 2 ml of hexane. Of this hexane sample 250 µl was injected at an injection rate of 80 µl/minute to obtain detection limits in the low ppt range.
From this example, it is clear that the PTV injector is an excellent system for the introduction of large sample volumes in capillary GC. Due to the introduction of large sample volume detection limits can be improved more than 100 times.

Conclusion

PTV type injection systems are very flexible inlet systems for capillary gas chromatography. Up to six different injection modes can all be performed using just one injector. Several types of samples, for example highly diluted samples or samples containing polar solvents, that cannot be analysed using one of the conventional techniques, can conveniently be handled using PTV injectors.

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