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USE OF HEART CUTTING IN GAS CHROMATOGRAPHY A REVIEW

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SUMMARY

The techniques used for heart cutting between both packed and capillary columns are reviewed Two packed columns in series with different stationary phases and heart cutting between them are shown to have a much greater separating power than a single capillary column The source of this separating power is identified and problems where the use of a single capillary column is appropriate are contrasted with problems where the use of heart cutting is appropriate The use of the technique to remove a solvent or major component so that trace components are not eluted on tails is also described

INTRODUCTION

In the petrochemical industry one of the main raw materials is naphtha, a cut from crude oil containing hydrocarbons in the carbon number range C_4 to about C_{11}. The quantitative analysis of naphtha for some individual compounds and for selected compound types is economically important If we bear in mind that there are over 600 known C_9 hydrocarbons alone, the magnitude of the problem of separation becomes apparent Fig 1 shows a chromatogram of naphtha from a non-polar capillary column One marked peak has been transferred to a packed polar column, stationary phase cyanoethylformamide (CEF) It can be seen that there are at least nine separate components to the one peak Even if we considerably increase the efficiency of the chromatography from the 150,000 plates illustrated, the chances that any one peak on the chromatogram will represent only one compound are very small

Analysis of hydrocarbons will be considered by many to be relatively easy in comparison with the analysis of the complex mixtures that occur in the life sciences Here the number of organic compounds that could be encountered is so large as to be virtually infinite The size of the problem is then limited by the minimum concentration that is of interest In most practical cases the concentration of compounds varies from several percentages downwards. A typical case might be where the selected compounds are only of interest when they are above 10 ppm in concentration Some one to two thousand compounds may be in the mixture at this level and above Although many excellent single capillary separations have been produced in this field, most attempts at quantitative analysis must be regarded with some suspicion where non-specific detectors are used

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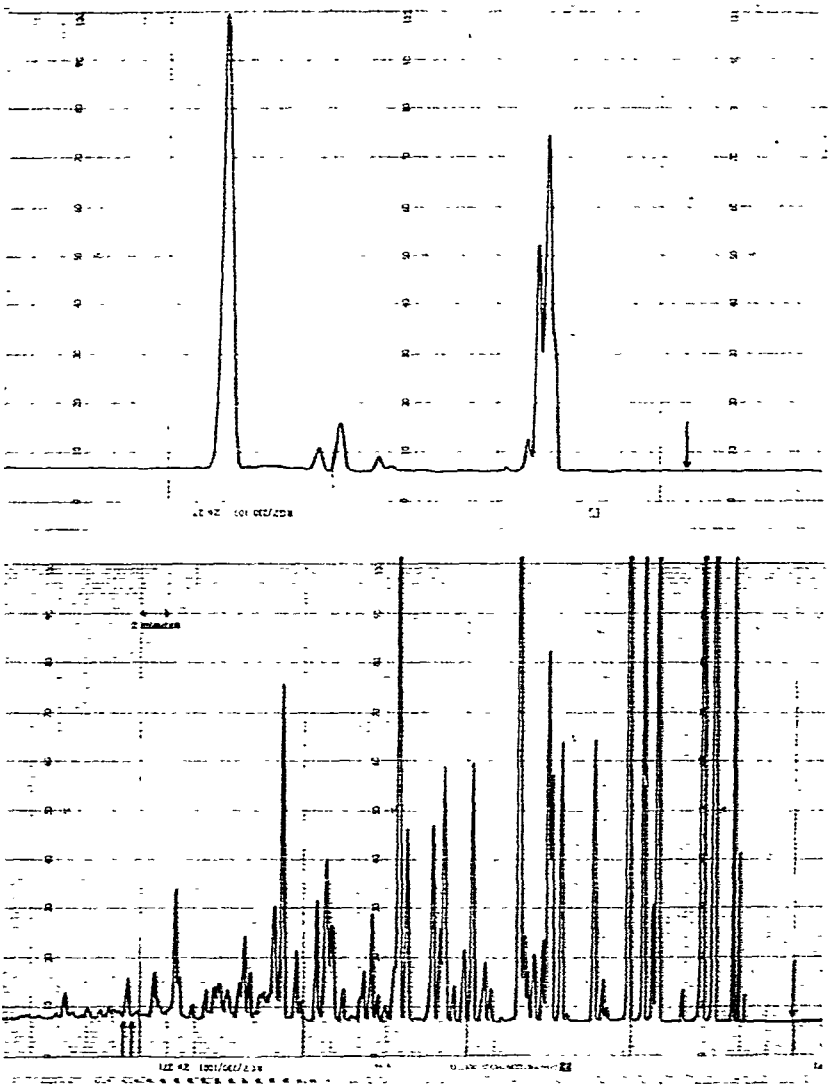

Fig. 1. Sample naptha; capillary column 15 m × 0.5 mm I.D. Apiezon L; temperature range, 50°C to 175°C at 3°C/min. Packed column 2 m × 2.4 mm I.D. 2.5% CEF; temperature, 90°C. Sample, arrowed peak, cut from capillary.

However, by the use of two-dimensional gas chromatography (GC) the problem can be reduced to a more manageable size. If we can achieve an average peak width of 30 sec for a chromatogram lasting 1 h we can transfer the desired peak with its attendant interfering compounds on to a second column. As in Fig. 1, the second column, which will have a totally different stationary phase, has only to separate the desired compound from the ten to twenty interfering compounds.

In practice the problem of obtaining the desired separation is somewhat easier than might be expected, because it is only necessary to select stationary phases and

conditions to separate the compounds of interest and unwanted cpmpounds can be sacrificed. Also several selected groups of peaks can be transferred to the second column from one injection on to the first column.

The process of transferring selected groups of peaks from the effluent of a first column to the inlet of a second column is called "heart cutting".

APPARATUS FOR HEART CUTTING

Heart cutting has been practised since the mid-1950's particularly in process GC. The early systems all used either rotary or slide valves between the two columns. These systems are reasonably successful but suffer from some disadvantages. The disadvantages include, dead and unswept volumes which reduce the efficiency of the system: the use of metal and lubricants or low friction plastics which may have undesirable adsorbtion or surface properties; temperature limitations due to the materials of construction. Also valves are often difficult to mount and operate inside a GC oven. More recent systems use a technique first described by the author in 1968 (ref. 1).

A flow-diagram of the system is shown in Fig. 2. PR1 and PR2 are pressure regulators, PR1 is set to control the inlet pressure to the system in the normal way. PR2 is set to control the pressure at the junction between the two columns at very slightly above the naturally occurring pressure. The pressures are indicated on gauges

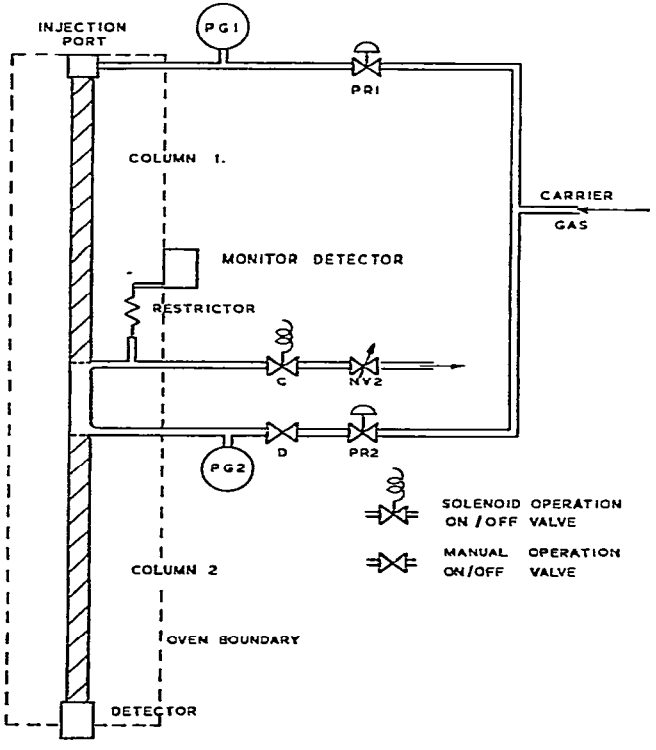

Fig. 2. Flow diagram of a heart cutting system for two packed columns.

PG1 and PG2; a manually operated on/off valve D is used in setting up only, to isolate PR2 so that the naturally occurring pressure can be read on PG2. Needle valve NV2 is set to allow somewhat more carrier gas to flow to atmosphere than flows through the first column, when on/off valve C is open. In operation, when valve C is closed carrier gas flows through column 1 and on through column 2 to the detector and the two columns act just as one single column with a mixture of the two different stationary phases. A small amount of carrier gas enters the system through PR2 to the junction of the columns. When valve C is open gas flows out through it and NV2 to the atmosphere. This gas is made up of all the effluent from column 1 plus a small amount of gas coming from PR2 to join it. PR2 supplies carrier gas to maintain the set pressure at the junction between the two columns. Thus when valve C is opened and closed the pressure at the junction of the two columns does not change, nor does the flow-rate through the columns change. The advantage of this system is that there are no valves or moving parts in the oven and in the path of the sample. Consequently none of the problems of leaks, temperature limitations or inefficiency associated with slide valves apply to this system.

The flame-ionisation detector shown in the diagram is not necessary for routine operation where valve C is operated automatically on a time basic after injection. But for method development and investigatory work it is very useful. It takes only a very small fraction of the effluent from column 1 controlled by the restrictor. The Tee piece system between the two columns should be the same internal diameter as the columns with no dead volumes. Where metal columns are used standard commercial unions can be used satisfactorily.

CHARACTERISTICS OF SEPARATIONS BY TWO-DIMENSIONAL GAS CHROMATOGRAPHY

The system described so far is primarily suited for use with two packed columns. Two packed columns have so much more separating power than a single capillary column that for most analytical purposes this is all that is needed. Fig. 3 illustrates this. Again the sample is naphtha, the stationary phase in the first packed column is CEF and the second Apiezon L. The two compounds of interest, benzene and toluene, can be seen clearly separated from the other compounds. It is in fact possible to separate completely all the aromatics in a system like this by taking more than one cut. The lack of interference from the non-aromatics is assured because of the polarity difference. A single capillary column cannot make use of polarity differences as two-dimensional GC does. The more complex the mixture the more a single-column system relies on efficiency for its separating power and the less important is the nature of the stationary phase. It is interesting to note that the capillary column which fails to achieve the separation of aromatics exhibits over 10,000 plates on the toluene peak. The two-dimensional system which gives more than adequate separation, exhibits just over 5000 theoretical plates on the toluene peak. The explanation of this is summarised in Table I.

The prime use of two-dimensional gas chromatographic systems is for analysis of complex mixtures where the analytical requirements are known. To set up a two-dimensional system to carry out a particular analysis takes some time and some experience. But, once the system is set up it can be operated either automatically or by

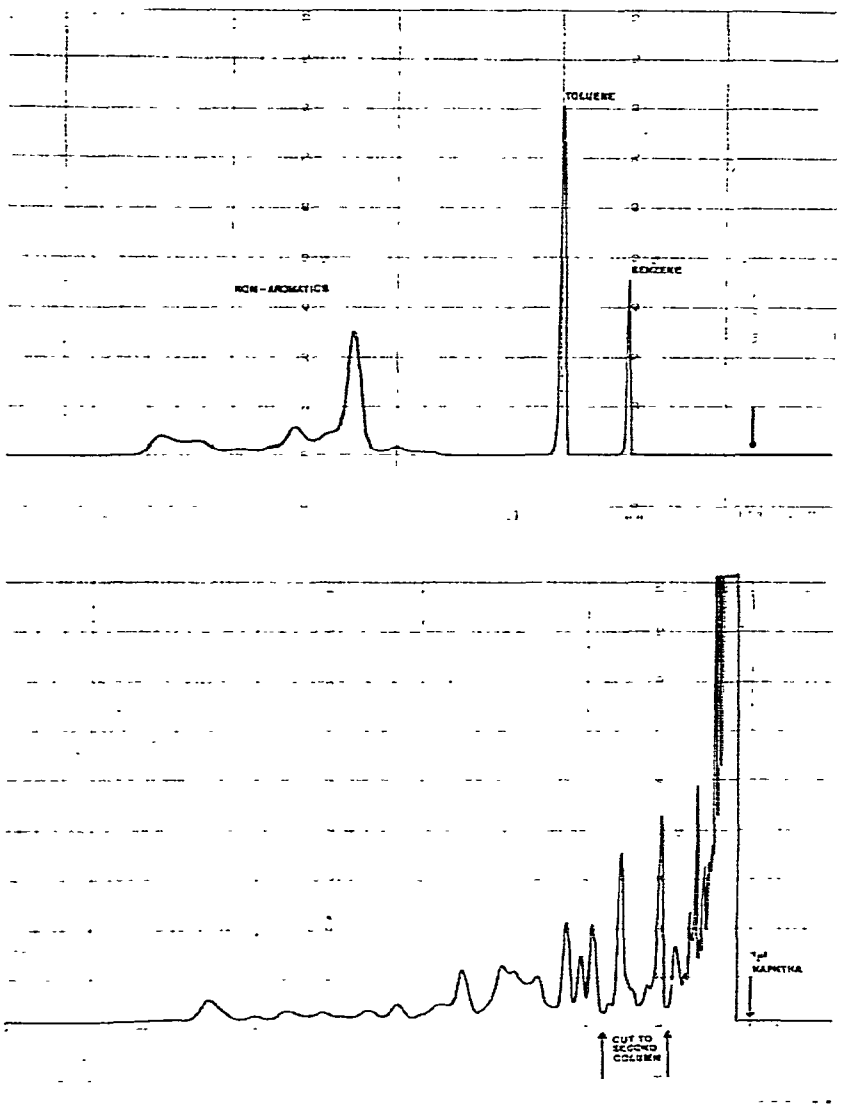

Fig. 3. Analysis of benzene and toluene in naptha. First column, 2 m × 2.4 mm I.D. 22.5% CEF; temperature, 90°C. Second column, 6 m × 2.4 mm I.D. 3% OV-17; temperature, 90°C.

inexperienced assistants. It is ideal for routine quantitative analysis for selected components. Because packed columns can be used in the majority of cases the problems of very small samples are avoided.

The use of packed columns generally has other advantages. Experience with operating both capillary and packed-column systems shows that the life of a capillary column is generally appreciably shorter than that of an equivalent packed column. Also replacement of a column with one of identical characteristics is more difficult with capillary columns, this is possibly because the high efficiency of the capillary

TABLE I

SOURCE OF SEPARATING POWER FOR COMPLEX MIXTURES

Single high-efficiency column	*Two-dimensional column system*
Number of plates	(1) The difference in relative retention times between two stationary phases.
	(2) The sacrifice of components of no interest*.
	(3) The number of plates.

* It is not necessary to sacrifice components, as each section of the first column effluent can be cut through on to the second column. This requires either several injections of the same sample or a "hold" system for the first column. The more cuts that are taken the longer the total analysis time.

makes criteria for identical characteristics more strict. A summary of the operating difficulties of the two systems is given in Table II.

Another difference in the characteristics of operation between a single-capillary and a heart cutting system is that a capillary system will normally require temperature programming for best results. Whereas a two-dimensional column system can use temperature programming it is rarely necessary because the isothermal conditions would be optimised for the selected peaks. Only when peaks of widely spread retention times are of interest would a temperature change during the analysis be worth considering. When a heart-cutting system is built it is usual to include a backflushing system for the first column at the same time[1]. This has the great advantage that temperature programming is not needed to remove the heavy ends in the sample from the column. Backflushing also serves to protect the second column and detector from these materials and consequently prolongs their life. Table III gives the author's view

TABLE II

DIFFICULTIES IN OPERATION OF SINGLE CAPILLARY AND TWO-DIMENSIONAL PACKED COLUMNS

Single capillary	*Two-dimensional packed columns*
(1) Precise injection of the small volume needed is not easy. Ensuring that the sample actually going on to the column is truly representative is a problem.	(1) Setting up to undertake heart cutting requires additional equipment.
(2) Accurate quantitative analysis is not easy to obtain, this is partly related to (1).	(2) Setting up the method and manipulating the controls requires some skill and experience.
(3) Short column life.	(3) Diagnosis of faults when something goes wrong is different from single-column systems and requires some experience.
(4) Poor reproducibility of columns.	

TABLE III

COMPARISON OF USES

Single capillary column	*Two-dimensional packed columns*
Sample identification or classification by pattern recognition or "finger-printing"	Quantitative analysis for selected compounds
Preliminary work to investigate the size of an analytical problem	In component identification systems together with *e.g.* mass spectrometry

of the appropriate use of single-capillary columns in comparison with two-packed columns and heart cutting.

THE USE OF HEART CUTTING IN EVEN MORE COMPLEX MIXTURES

Two packed columns do not always provide sufficient separating power to deal with very complex mixtures. When this happens there is a choice of techniques to solve the problem. It is only possible to mention these briefly in the limited space available.

The following systems, involving heart cutting between the columns in a two or more dimensional scheme, have all been used successfully. They are placed roughly in order of resolving power but the choice of technique depends on the nature of the problem and on the experience and skills available in the laboratory. Fig. 4 shows the geometry of the junction.

(1) A first packed column followed by a capillary. This has the advantage that a larger sample can be introduced. The first column effluent is then split before it enters the capillary column. The split ratio is precise and remains constant because the inlet to the capillary column is held at constant pressure. In order to make full use of the efficiency of the capillary either a high carrier velocity in the packed column has to be used to keep the peak widths narrow, or a trapping system at the inlet to the capillary has to be used as in (4) below.

(2) A first capillary column followed by a packed column. A slightly different gas control system is needed at the junction to maintain high efficiency. An example of the use is shown in Fig. 1.

(3) Two capillary columns with a specially designed junction to maintain high efficiency. Siemens manufacture a good example of this.

(4) Two capillary columns with trapping at the inlet to the second column followed by rapid vaporisation to give a sharp injection on to the second column. The first trapping system of this type was described by Schomburg and Weeke[2].

(5) Three or more packed columns. A good example of this, although it is used for a mixture of group analysis and selected individuals, is the paraffins–naphthene–aromatics (PNA) analysis that is routinely used in the European petroleum industry. Many people have contributed to the development of this system. The early work was done by Boer[3] and by Brunnock and Luke[4].

It is obviously possible to use capillary columns in three or more dimensional systems but packed columns are normally used. There are several reasons for this. Operation of such systems has to be automatic (*i.e.* timer controlled operation of

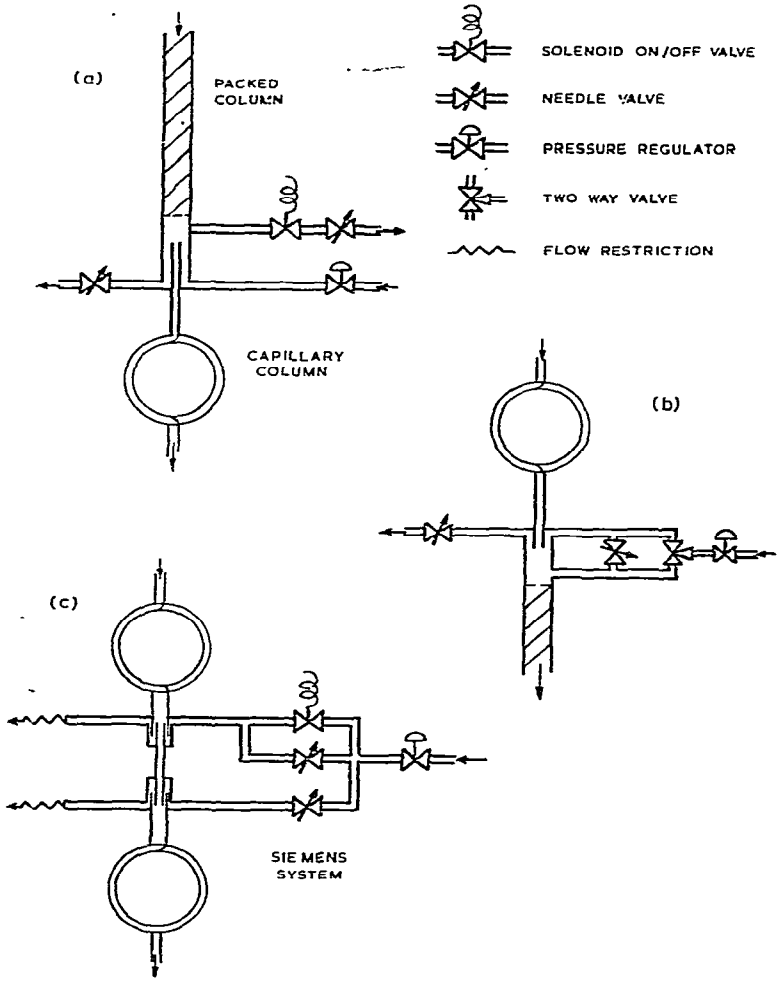

Fig. 4. Flow diagrams for heart cutting, (a) between a packed and a capillary column, (b) between a capillary column and a packed column, (c) between two capillary columns.

valves). Under these circumstances long stable life of the columns and reproducibility when they have to be replaced becomes of much greater importance. In multi-dimensional GC much use is made of differential selectivity of stationary phases and the high selectivity of molecular sieves and other specialised materials are only available as packings.

In the laboratories at ICI Petrochemicals Division many multi-column systems are used but each is designed to do a specific type of analysis and is operated automatically. Column-selection flow systems are often incorporated[5].

HEART CUTTING IN TRACE ANALYSIS AND ON SOLVENT TAILS

The problem and its solution are illustrated in Fig. 5. When a trace component is eluted on the tail of a major component or solvent peak, quantitative analysis

becomes difficult. In extreme cases the tail can be relatively so big that the trace cannot be seen at the sensitivity that allows it to be on scale, and data handling systems cannot produce a meaningful measurement. The source of the tail is mainly the Gaussian spread of the major component and the tail usually represents only a very small fraction of the total peak. Poor injection systems can also add to the tail of peaks.

Heart cutting is used to transfer a slice from the tail at the outlet of the first column on to the second column. The slice contains all the trace component and only the relatively small amount of the major component associated with it. Most of the

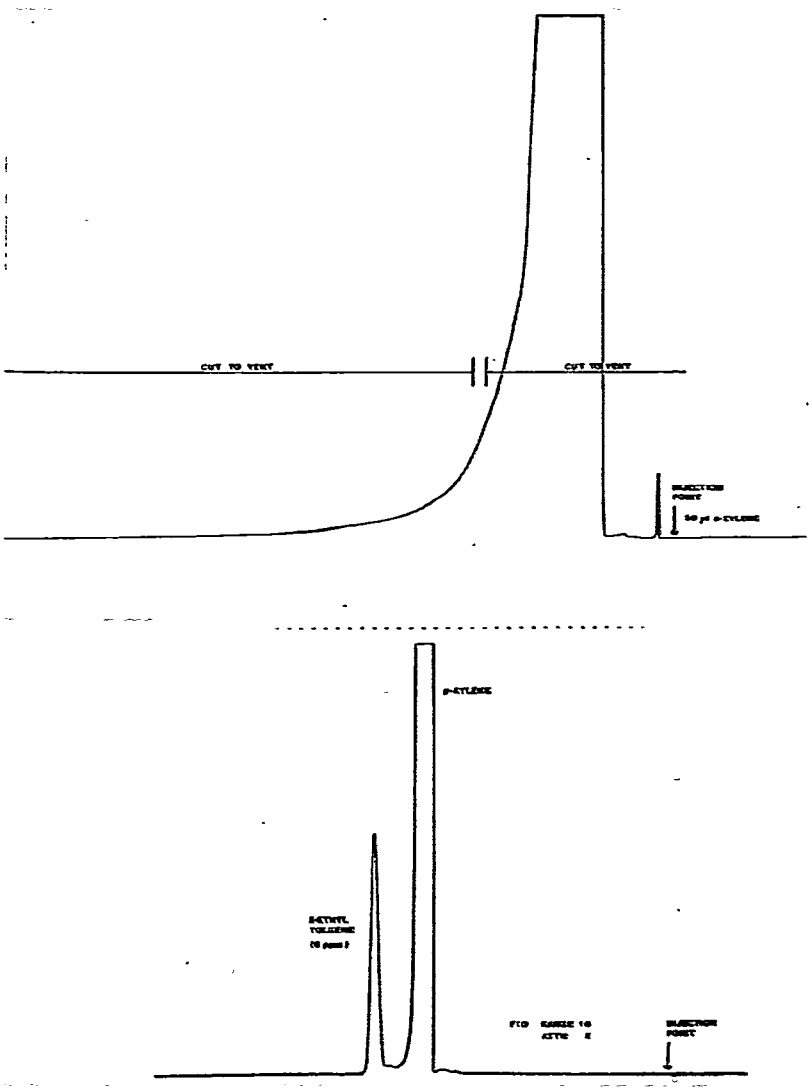

Fig. 5. Heart cutting to measure a trace component on a tail. Two 3 m × 2.4 mm 10% Apiezon L; temperature, 100°C.

major component is vented to atmosphere. The function of the first column is to separate enough of the major component from the trace components so that overloading of the second column is avoided, the use of the same stationary phase in both first and second columns is often appropriate. If there are a number of trace components on the tail it may be possible to cut each one onto the second column separately. If this is not possible, venting most of the major component at the end of the first column and allowing the whole of the tail with the trace components of interest onto the second column, produces a great improvement on a single column system.

If a heart cutting system is used for trace analysis it is often possible to increase the sensitivity of the system above that of a single column system. This is done by grossly overloading the first column under appropriate conditions where the sample acts as its own stationary phase and produces a sharp trace component peak on the back edge of the major component[6]. This can then be heart cut onto the second column. Sample sizes of up to 400 μl on 2.4 mm I.D. first columns have been used successfully in this way.

A final, but by no means the least important, use of heart cutting is at the end of a single-column system where the second column is replaced by a mass spectrometer inlet. The simplest method of operating this is to have the mass spectrometer inlet at a pressure controlled by PR2 in Fig. 2. The rate of flow into the mass spectrometer is then set by a restriction in the inlet. If the flow from the column is greater than the flow taken by the mass spectrometer a splitter-needle valve can be used to vent the excess from the line from the PR2. A monitor detector at the end of the first column is also needed. Using this system only the peaks of interest and carrier gas enter the mass spectrometer.

A two-column heart cutting system can be used as the inlet to the mass spectrometer in a similar way. This has the advantage that in addition to the mass spectrum, retention data on two different stationary phases are available to assist in the identification.

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