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POTENTIAL OF CAPILLARY GAS CHROMATOGRAPHY IN INDUSTRIAL RESEARCH LABORATORIES

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SUMMARY

The pros and cons of the application of capillary gas chromatography in an industrial research laboratory are discussed. The consequences of using a capillary instead of a packed column are dealt with, especially with respect to the injection technique and detection. Examples of separations in the fields of product evaluation and trace analyses are discussed.

INTRODUCTION

Since the first papers dealing with capillary gas chromatography (GC) were published[1,2], the applicability of this technique has widened tremendously. When the literature on the preparation of capillary columns became more explicit with respect to the experimental details, especially after the first "Hindelang" conference in 1975, the use of glass capillary chromatography was no longer restricted to a few, highly skilled chromatographers. Moreover, the improved situation which has developed during the past few years with respect to the commercial availability of both GC apparatus dedicated to capillary GC and high-quality glass and fused-silica capillary columns has led to the rapid expansion of the use of capillary GC.

The chromatographer's primary incentive to use capillary columns is undoubtedly the expectation of obtaining improved separations of complex mixtures. Those chromatographers who usually solve their separation problems satisfactorily by using packed columns are inclined to believe that they can do without capillary GC. In this paper, a number of considerations are dealt with that illustrate that, in general, it is preferable to use a capillary GC column, irrespective of whether a high separation efficiency is desired or not.

Especially for industrial research laboratories, in which a wide variety of samples often have to be analysed in a short time, capillary GC offers great advantages over packed column GC.

CHOICE OF CAPILLARY *VERSUS* PACKED COLUMN GC

Without going into theoretical details of a comparison of packed and capillary GC columns, a topic which has been dealt with in several textbooks (*e.g.*, ref. 3.), some

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general statements can be made with respect to the use of capillary columns (I.D. 0.1–0.5 mm, film thickness d_f = 0.1–1.0 μm): much higher separation efficiencies can be obtained; by using a capillary column with a resolution comparable to that of a packed column, much faster analyses are obtained; owing to the smaller peak width, a lower detection limit can be achieved in trace analyses; a capillary column offers various possibilities of optimization of analyses by changing parameters such as the column diameter, film thickness and column length.

SEPARATION EFFICIENCY

The high separation efficiency, together with the more recently achieved low adsorptivity, make capillary columns very suitable for the analysis of a wide variety of samples. Especially by applying capillary columns coated with apolar stationary phases, which can withstand temperatures up to 370°C, a very versatile general-purpose GC separation system has become available. The lack of selectivity for polar compounds of this column type is often offset by its high separation efficiency.

In research laboratories, such a general purpose GC system is very useful for screening complex mixtures of various origins (*e.g.*, organic synthesis, trace analysis, pyrolysis studies).

Fig. 1 shows the separation of a reaction mixture obtained from the ethoxylation of a fatty amine. It is obvious that without the high resolution of a capillary column it would have been impossible to obtain detailed information on the ethylene oxide (EO) distribution and the EO chain length in such a short time.

Fig. 2 shows an example of the separation of the pyrolysis products of a polymer by capillary GC. The very good separation efficiency offers the possibility of studying, in addition to the large peaks originating from the monomeric units, also smaller peaks which often contain information with respect to additives, modifiers or sub-structures in the polymer.

SPEED OF ANALYSIS

From theory, it can be derived that when $k > 0.5$ capillary GC columns allow a much faster analysis with the same or a higher resolution than can be obtained with packed columns. This feature of capillary columns is often overlooked, although it is sometimes of much greater importance than the high-resolution aspect. In those cases, for instance, where a large number of samples have to be analysed, a reduction of the analysis time by a factor of 2–3 cannot be ignored. Under these circumstances it is undoubtedly advantageous to use capillary columns, even for the separation of only three components, as shown in Fig. 3.

Especially in today's practice, where automation has become the password for time saving, one has to realize that in this respect speeding up the separation often may be more profitable than the installation of a faster output device, etc. On the other hand, the required reduction of the analysis time must be chosen carefully. If sample preparation, filling the autosampler tray, injection and data handling take several minutes, it is normally not worthwhile trying to achieve the separation within a few seconds.

In general, we feel that the use of capillary instead of packed columns is a very

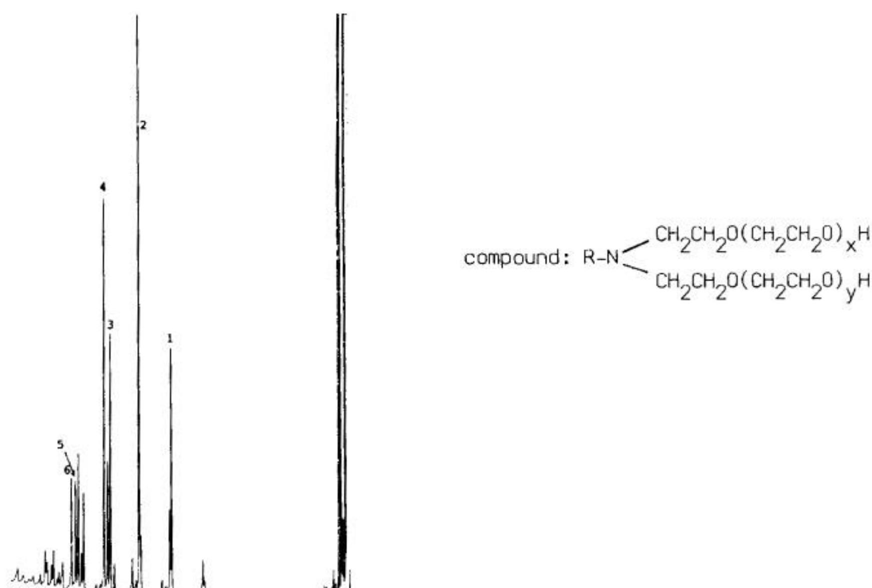

Fig. 1. Separation of a mixture obtained after ethoxylation of a fatty amine. Column: 20 m × 0.28 mm I.D. SE-30; d_f, 0.2 μm; carrier gas, hydrogen; pressure, 0.2 bar; on-column injection; total analysis time, 22 min.

Peak No.	*Compound*	
	x	*y*
1	0	0
2	1	0
3	1	1
4	2	0
5	2	1
6	3	0

attractive way of reducing the analysis time. Separations on packed columns with siloxanes or Carbowax as the stationary phase can be performed very easily on capillary columns.

LIMIT OF DETECTION

When equal amounts of a component are injected into both a capillary and a packed column, owing to the smaller peak widths the peak heights are much higher for a capillary column, resulting in a lower limit of detection. In principle, this feature makes a capillary column much more suitable than a packed column for trace analyses. However, the sample capacity of a capillary column is much lower than that of a packed column (capillary column of 0.28 mm I.D., d_f 0.2 μm; maximum concentration/peak *ca.* 10^{-7} g). This is an unsurmountable disadvantage when, apart from

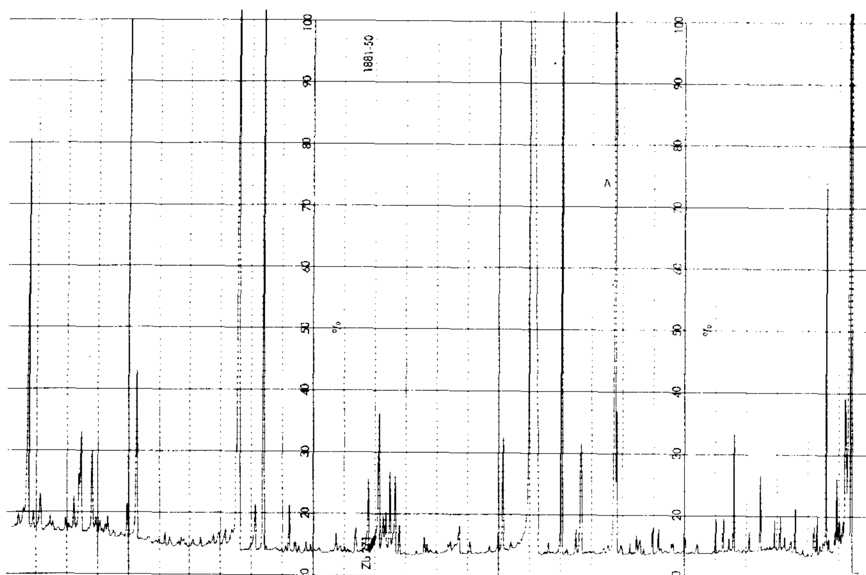

Fig. 2. Pyrogram of a PETP polymer, modified to improve its stability against hydrolysis. Separation conditions as in Fig. 1. Injection via splitter. Peak A: a stabilizer, identified as a substituted aromatic diisocyanate.

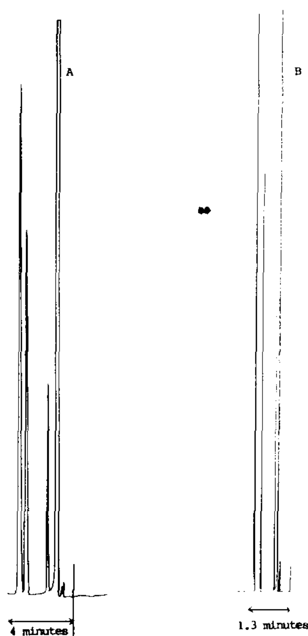

Fig. 3. Improvement of the speed of analysis by using a capillary column. (A) Separation of toluene, chlorobenzene and styrene on a packed column (1 m × 1/4 in. I.D., Carbowax 20M, 10% on Chromosorb W HP). (B) Same separation on a capillary column (20 m × 0.28 mm I.D., Carbowax 20M; d_f, 0.2 μm).

traces, the concentrations of the main components must also be determined in one GC analysis. When experimental conditions are used which enable the traces to be detected and quantified, the main component will overload the column and perhaps even the detector. Although overloading does not harm a capillary column, the quantification and resolution in that part of the chromatogram will be adversely affected.

However, if the aim of the GC analysis is the determination of traces, the application of a capillary column has distinct advantages over a packed column. In environmental analysis, for instance, a capillary column gives a high selectivity owing to its high separation efficiency and, in addition, an increased sensitivity.

When traces must be determined, obviously the same advantages are obtained as described above if their retention times differ appreciably from those of the main component. In those instances where the trace component is eluted in the vicinity of the main component, one obtains acceptable quantitative data only when the trace component is eluted before the main component (Fig. 4). Both the retention times and the determined amounts of small peaks eluted just after overloaded peaks are not very reliable.

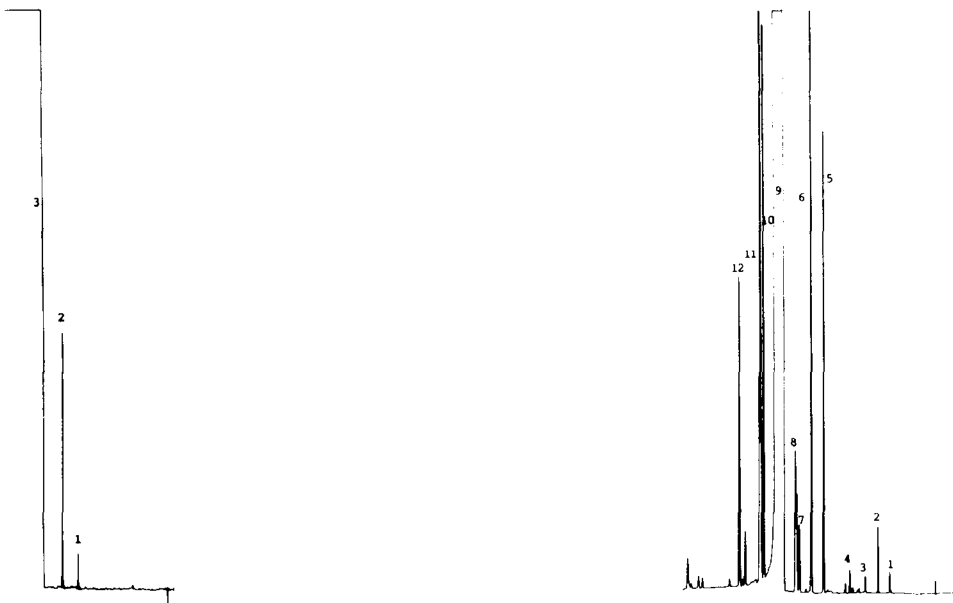

Fig. 4. Determination of traces of tetrachloromethane in chloroform. Column, 50 m × 0.28 mm I.D., OV-275; d_f, 0.2 μm; carrier gas, nitrogen; electron-capture detector (attenuation 8 ×). Peaks: 1, unknown; 2, tetrachloromethane, concentration $5 \cdot 10^{-4}$ g/l; 3, chloroform.

Fig. 5. Separation of chlorinated hydrocarbons. Column, 50 m × 0.28 mm I.D., SE-30; d_f, 3 μm; carrier gas, hydrogen; flame-ionization detector. Peaks: 1 = vinyl chloride; 2 = chloroethane; 3 = a chloropropylene; 4 = 1,1-dichloroethylene; 5 = 1,1-dichloroethane; 6 = 2-chlorobutadiene; 7 = chloroform; 8 = isomer of chlorobutadiene; 9 = 1,2-dichloroethane; 10 = benzene; 11 = tetrachloromethane; 12 = trichloroethylene.

ADJUSTMENT OF THE CAPILLARY GC SYSTEM WITH RESPECT TO THE NATURE OF THE SAMPLE

Owing to the easy adjustment of the phase ratio (β) by changing either the film thickness of the stationary phase (d_f, 0.1–3 μm) or the inner diameter of the column (0.05–0.7 mm), capillary GC can be used for the entire range of volatile to high-boiling compounds.

For screening purposes we use capillary columns of length 20 m, I.D. 0.28 mm and d_f 0.2 μm. When volatile compounds must be analysed, columns with an increased film thickness (up to 2 μm) and, when necessary for resolution, an increased length (40–50 m) are used.

Although the decrease in β, necessary for the efficient separation of volatile compounds, can also be obtained by decreasing the inner diameter of the column (*e.g.*, 0.10 mm), in daily practice it is difficult to obtain reliable results with this type of column. For instance, it appeared that the resolution obtained is strongly affected by the injection technique when standard, commercially available GC equipment is used. Moreover, the available electrometer amplifiers, recorders and integration systems possess time constants too large to be useful for processing the very fast signals obtained with this type of column.

In order to obtain reproducible quantitative data easily we have so far preferred the use of "thick-film" capillary columns for the separation of volatile compounds, compensating for the lower separation efficiency of these columns by increasing the column length (see Fig. 5).

The separation of high-boiling components is accomplished on short capillary columns (5–10 m) with relatively thin stationary-phase films (d_f 0.1 μm). These separations are normally performed with linear gas velocities far above the optimum value.

To obtain the best resolution under these conditions, hydrogen, which possesses a smaller *C*-term than nitrogen in the Van Deemter equation, is used as the carrier gas. An example of the analysis of high-boiling components is shown in Fig. 6. The risk of thermal degradation of the sample during this type of analysis should not be neglected. However, within certain limits, capillary GC can be applied to the separation of compounds with molecular weights up to 900–1000, whereas packed GC is usable only for molecular weights up to 500–600. Moreover, although working with a low resolution, the separation efficiency achieved is often much better than that obtained by using liquid chromatography.

CONSEQUENCES OF THE USE OF CAPILLARY COLUMNS WITH RESPECT TO INJECTION AND DETECTION SYSTEMS

Once it has been decided to use a capillary instead of a packed column, some unwelcome complications must be faced. Compared with packed columns, the injection of the sample into a capillary column is far more complicated and subject to error. First, it must be decided which type of injection system will be used, *i.e.*, split, splitless, cold on-column or solid-sampling (falling-needle) injection. The quantitative aspects of a split injection have been dealt with by Schomburg *et al.*[4]. The advantages

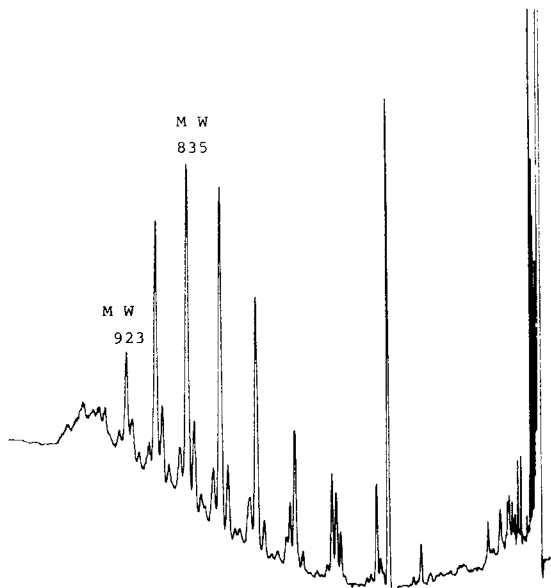

Fig. 6. Separation of compounds with a high boiling point. Column, 8 m × 0.28 m I.D., SE-30; d_f = 0.1 μm; carrier gas, hydrogen, p = 1.2 bar; on-column injection; temperature programming up to 350°C. Compounds: ethoxylated fatty amines (see Fig. 1): molecular weight (MW) 835 corresponds to $x + y = 13$; MW 923 corresponds to $x + y = 15$.

and problems observed with cold on-column injection have been described by Trestianu *et al.*[5] and Grob and Müller[6].

Table I gives a survey of the applicability of these four injection techniques with respect to a number of practical criteria.

Because it is easy to use and gives excellent results for quantitative analyses, we prever cold on-column injection when there is no need for automation of the analysis. Otherwise one has to work with split or splitless injection. Contaminated samples can be analysed with an on-column injection system when column contamination is taken into account. Contaminants can be removed from the recently introduced chemically bonded stationary phases by rinsing the column with suitable solvents. Very often, however, it suffices to remove a few centimetres from the column entrance to restore the original separation performance.

With respect to the detection of the separated components there is no problem when the different species need not be identified. Modern GC detectors are very suitable for capillary GC. However, when unknown materials have to be identified, the use of a capillary column makes great demands on the identification instruments (*e.g.*, mass or infrared spectrometers). Apart from the interfacing problem, the spectrometers must be capable of giving reliable and interpretable results for nanogram amounts of compounds. In general, this requires the use of a high-performance and, consequently, expensive instrument, provided with a data system.

CONCLUSIONS

For a wide variety of samples, capillary GC is indispensable as a general-

TABLE I

APPLICABILITY OF VARIOUS INJECTION TECHNIQUES

Application	*Injection system*			
	Split	*Splitless*	*Cold on-column*	*Falling-needle (solid-sampling)*
Qualitative analysis	–/+*	–/+*	++	–/++**
Quantitative analysis:				
Samples with wide boiling range	–	–	++	–/+**
Samples with narrow boiling range	+	+	++	–/++**
Trace analysis	–	+	++	–/++**
Compounds with high boiling point	–	–	++	++
Thermally unstable compounds	–	–	++	–/+
Contaminated samples	++	++	–	–/+***
Possibilities of automation	++	++	–	–

* Depending on the boiling points of the compounds to be separated.

** Ranging from – for compounds with a low boiling point to ++ for compounds with a high boiling point.

*** Needle can be cleaned easily.

purpose separation system. By simply varying the instrument settings (such as carrier gas flow-rate and/or temperature programming) on the same capillary column a fast separation can be obtained instead of a high resolution. Both aspects are very useful in the daily practice of gas chromatography.

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