Chromatographic Methods

V.G. Berezkin and J. de Zeeuw

Capillary Gas Adsorption Chromatography

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Preface

At present, capillary chromatography is the most widely used method for the analysis of volatile compounds. Two variants of gas chromatography (gas-liquid and gas-solid) are used in capillary chromatography. Gas-liquid chromatography employs an open-tubular column with the stationary phase film deposited on the inner wall. Many excellent books have been devoted to this variant of capillary gas chromatography.

For the first time, an attempt has now been made to present a consistent treatment of gas-solid capillary chromatography. This technique employs an open-tubular column with a solid sorbent layer present on the inner wall. Capillary gas adsorption columns are now in routine laboratory use. They are important for analysing gases (including isotopes) and light volatile compounds in chemistry, chemical engineering, petrochemistry, medicine, pharmacy, food science, environmental pollution control, and many more.

As authors, we tried to follow the familiar proverb: "A picture is worth a thousand words". In our book there are many chromatograms that graphically illustrate the analytical possibilities and the role of capillary gas-solid columns in gas chromatography.

We would like to thank all our colleagues at Chrompack International BV for their help with the development and application of the columns discussed in this book. We would like also to thank Chrompack International BV for support of our work on this book.

The support of our wives, Harriette de Zeeuw and Ludmila Berezkina, and of our children was very helpful in completing this work. We also wish to thank Mr. Jos Wessels for reviewing part of manuscript and Mrs. Ludmila Nowizkaya for her help in typing part of the manuscript.

We trust that the book will be of interest and of practical value to many chromatographers.

Chapters 1 – 6 were written by V.G. Berezkin and Chapter 7 by J. de Zeeuw.

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Contents

Chapter 1

Introduction

1.1 Advantages and Limitations of Gas-Solid Chromatography

The advent of chromatography completely changed the world of chemistry. According to Karrer [1] "no other discovery has exerted as great an influence and widened the field of investigation of the organic chemist as much as Tswett's chromatographic adsorption analysis".

At present, chromatography is one of the principal techniques of analytical chemistry, with numerous applications in industry, agriculture, environmental control, medicine, and research.

Chromatography has its origins in the twentieth century. It is both a separation technique and a scientific discipline and embraces a wide range of various separation methods based on different principles. Chromatography can be defined as a field of science studying the movement of substance zones in a flow of one or several phases moving relative to another phase or to several phases. One can consider chromatography also as a method of analytical and industrial separation (and estimation of physicochemical parameters) based on the different rates of movement and broadening of a chromatographic zone in the mobile phase (usually along a stationary liquid phase layer).

Classification of Gas Chromatography

One of the most important characteristics of certain variants of polyphase chromatography is the phase state of the mobile and stationary phases participating in the separation [2] (see Table 1-1 [3]). We note that gas [liquid-solid] chromatography can be arbitrarily divided into two basic, poorly defined types: first, gas chromatography with modifying adsorbent or gas [liquid-solid adsorbent] chromatography and, secondly, gas [liquid] or gas [liquid-solid support] chromatography. Gas [liquid-solid

Table 1-1.
Classification of various types of chromatography according to the state of aggregation of mobile and stationary phases [3].

Mobile phase	Stationary phase	
	solid	liquid-solid
Gas	gas [solid] chromatography [4-10]	gas [liquid-solid] chromatography [4-8]

adsorbent] chromatography is a hybrid variant of gas [solid] and gas [liquid-solid] chromatography.

Although gas [solid] chromatography is less popular than gas [liquid-solid] (or gas-liquid) chromatography, it is nevertheless used in such important fields as isotope separation and volatile compound determination, where it exhibits certain advantages over its gas-liquid counterpart. Analysis of volatile compounds is very important in many branches of industry and in research.

The advantages and limitations of gas [solid] chromatography are listed in Table 1-2. It is clearly characterized by a number of advantages that outweigh its disadvantages. Some of the disadvantages, for example, chromatographic zone broadening, irreversible adsorption of the chromatographed compounds, or their catalytic conversions, can be overcome by modification of the adsorbent used.

Comparison of capillary and packed columns

The columns used in gas chromatography can be divided into two types, viz. packed and open tubular. Packed columns are filled with the particles of solid sorbent. Open tubular columns are long capillary tubes having an open, unrestricted gas path along the column and the stationary phase is coated in the form of thin sorbent layer on the inner tube wall.

The advantages of gas [solid] chromatography, like those of gas [liquid-solid] chromatography, can be, as a rule, significantly increased by using open capillary rather than packed analytical columns (see Table 1-3). Gas [solid] open capillary columns

Table 1-2.
Advantages and limitations of gas-solid chromatography

Advantages	Limitations
1. High adsorbent stability over a wide temperature range	1. Real danger of asymmetric chromatographic zone as a result of nonlinear adsorption isotherm for a number of analyzed compounds
2. Reduced detector background noise (absence of "bleed" problems that occure with liquid phases)	2. Low reproducibility of chromatographic characteristics due to the fact that the properties of the adsorbents are not so readily standardized as compared with stationary liquid phases
3. Smaller HETP values than in gas-liquid chromatography (adsorption-desorption processes can be much faster than the corresponding diffusion process in liquid phase)	3. More probable losses of the analyzed compound as a result of irreversible adsorption or catalytic conversions in the separation process
4. Increased structural selectivity in the separation of geometric isomers (e.g., using molecular sieves or graphitized carbon black)	4. Limited number of commercially available adsorbents for gas-solid chromatography
5. High chemical selectivity when using complexing agent as an adsorbent (e.g., solid silver nitrate)	5. Strong dependence of the retention on the sample size is more common because of nonlinear adsorption
6. Enhanced adsorbent capacity permits separation of gases and volatile compounds at room temperature	
7. Enhanced chemical stability of a number of adsorbents, ensuring the analysis of agressive compounds	
8. Important tecnique for physicochemical studies of solid surfaces and adsorption phenomena	
9. Important technique for heterogeneous catalysis studies	

made it possible to combine the main advantages of selectivity of gas-solid chromatography and efficiency of capillary chromatography.

Since the selectivity of a solid adsorbent is independent of the type of column used (packed or capillary), we therefore considered it appropriate

Table 1-3.

Main advantages of capillary gas chromatography in comparison with traditional packed column gas chromatography

1. Increased efficiency (total efficiencies of capillary column and packed column are about 25,000 – 100,000 and 1,000 – 5,000 theoretical plates, respectively).
2. Increased separation rate as a result of higher mass transfer rate.
3. Small resistance to the carrier gas flow.
4. More reproducible temperature conditions owing to decreased size of column and apparatus.
5. Low consumption of carrier gas and sorbent owing to column miniaturization.
6. Field of applications of gas-[solid] and gas-[liquid-solid] (modifying) chromatography is becoming wider due to the decrease of separation temperature.

to include a short review of gas [solid] chromatography fundamentals in the present book.

1.2 Discovery of Gas-Solid Open Tubular Capillary Columns

The history of the discovery of gas-solid open tubular capillary columns is very interesting. V. Belinsky, a 19th century Russian literary critic wrote: "The content of history consists of ideas as well as facts".

M. Golay, the founder of capillary chromatography, was the first to propose open capillary columns with a sorbent layer on the inner column walls. In 1960 he made the following statement: "Why not make a semipacked column with a large open passage in the center, say, nine-tenths as large as the column inside diameter, and with a thin layer of packing material in the remaining space on the periphery? The answer is: why not indeed? I believe that such columns constitute almost ideal columns for a wider range of analysis than present-day smooth tubular columns" [11].

As Horvath noted, "Capillary columns have changed gas chromatography and with time capillary columns have also undergone changes. Golay recognized the major shortcoming of his columns, the low phase ratio that results in low loading capacity and low elute concentrations in the eluent, and in 1960 he proposed making columns with a porous

layer at the inner wall. Shortly thereafter, support-coated open tubular columns were introduced and thus columns with higher loading capacity became available" [12].

As correctly stated by Ettre [13], the idea of making a column with a porous sorbent layer on the inner capillary walls was implied in an early version of Golay's equation describing chromatographic zone broadening in an open capillary column, depending on the carrier gas velocity (the Amsterdam Symposium, 1958).

Experimentally, such a column was realized a few years later by the independent efforts of a number of researchers.

Thus in 1961 in a study of the "modification" of a glasses by trimethylchlorosilane during capillary drawing Kalmanovsky, Kiselev and co-workers [14] made the following observations: "On nonmodified capillaries the separation was poor (see Fig. 1-1a), the retention time for acetone was much greater than that for other components, and the acetone peak was sharply asymmetrical. This suggests the presence of a large number of polar sites on the capillary surface. The application of a silicone oil film on the surface of these nonmodified capillaries improved the separation (see Fig. 1-1b). The trimethylchlorosilane-modified capillary surfaces (Fig. 1-1c) are distinguished by better separation characteristics as compared with those of the nonmodified capillary of the same glass, with a changing elution order (acetone was the first elution compound). Such capillaries can be used for analytical purposes directly in gas-solid variant of capillary chromatography" [14]. Kalmanovsky and co-workers then noted that when the modified surface was coated with a silicone oil film, a better separation effect (Fig. 1-1d) was obtained as compared with that in the case of the nonmodified capillary (Fig. 1-1b). It should be noted that the modification was accomplished by the authors [14] in an unusual manner, i.e. in the process of drawing the capillary from a tube. The tube was initially filled with liquid trimethylchlorosilane; on drawing

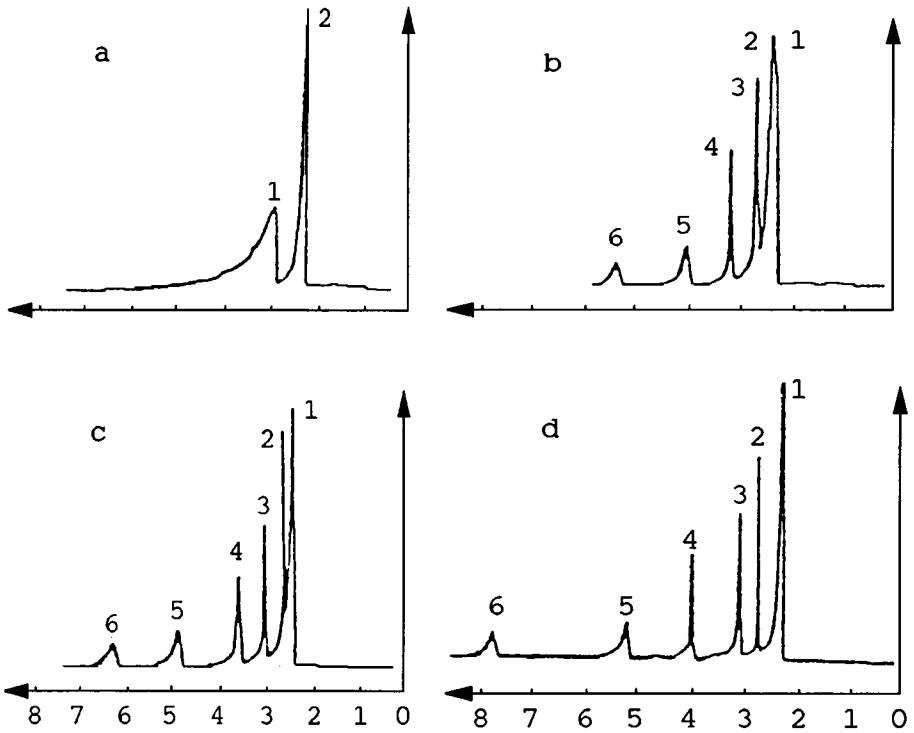

Fig. 1-1. Chromatograms for vapor mixtures of organic compounds on open glass capillary columns whose inner surface is modified by various methods [14].

(a) Unmodified capillary column; (b) unmodified capillary column whose inner wall surface is coated with a silicone oil film; (c) capillary column drawing from a wide glass tube with trimethylchlorosilane; (d) trimethylchlorosilane-modified capillary column whose inner wall surface is coated with silicone oil film. Peaks: 1 — acetone, 2 — n-hexane, 3 — benzene, 4 — n-heptane, 5 — toluene, 6 — n-octane.

formation of an adsorption layer took place on the glass surface of the capillary inner walls. The chromatograms shown in Fig. 1-1 [14] were obtained at 25 °C by chromatographic separation on capillary columns 15 – 20 m long and 0.3 mm i.d.

Separation of hydrogen isotopes and isomers

In 1961 — 1962 Mohnke and Saffert [16] obtained a silica layer on borosilicate glass capillaries after prolonged (30 h) etching of the inner surface of

the capillaries with aqueous ammonia solution at 170 – 180°C. The thickness of a resultant silica layer was 10 – 20 μm. It is interesting to note that their studies revealed a very important application of gas chromatography, viz., separation of gaseous isotopes and nuclear-spin isomers. Fig. 1-2 [16] shows a separation chromatogram for hydrogen isomers and isotopes, obtained on an open gas adsorption capillary column at low temperature. It is evident that a good separation of the hydrogen nuclear-spin isomers was attained.

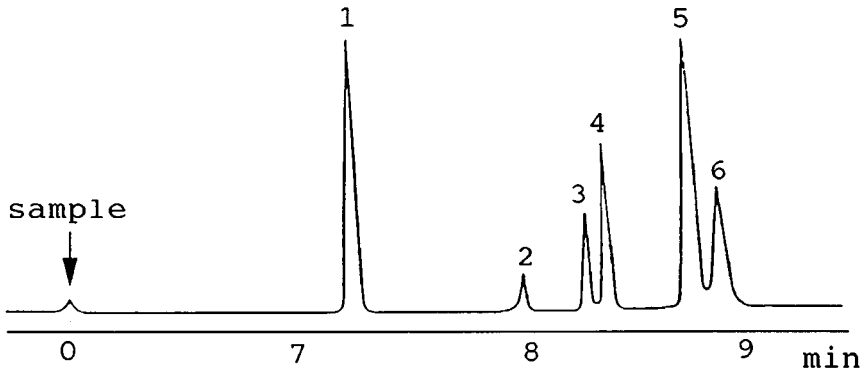

Fig. 1-2. Chromatogram of separation for hydrogen nuclear-spin isomers and isotopes on a capillary adsorption glass column [16].

Column length 30 m; adsorbent, dry silica, 20 μm thick; separation temperature 77.4 K; carrier gas neon.
Peaks: 1 — helium, 2 — paraprotium, 3 — orthoprotium, 4 — protium deuteride, 5 — orthodeuterium, 6 — paradeuterium.

Separation of aromatic hydrocarbons

A radically new method for preparing capillary adsorption columns, based on the application of an adsorbent layer on the inner capillary walls from a suspension, was proposed by Halasz and Horvath [17, 18]. In such columns the production of the adsorbent layer is independent of the material of the inner column walls, its modifications, etc. Fig. 1-3 [17] presents a chromatogram for a rapid separation of aromatic hydrocarbons on graphitized

Separation of some freons

carbon black, a layer of which was applied on the inner copper capillary walls. Fig. 1-4 [19] shows a chromatogram of a rapid separation of freons on a capillary column with a boehmite (Al_2O_3) layer. The separation was performed by Kirkland on 75 m × 0.5 mm column [19].

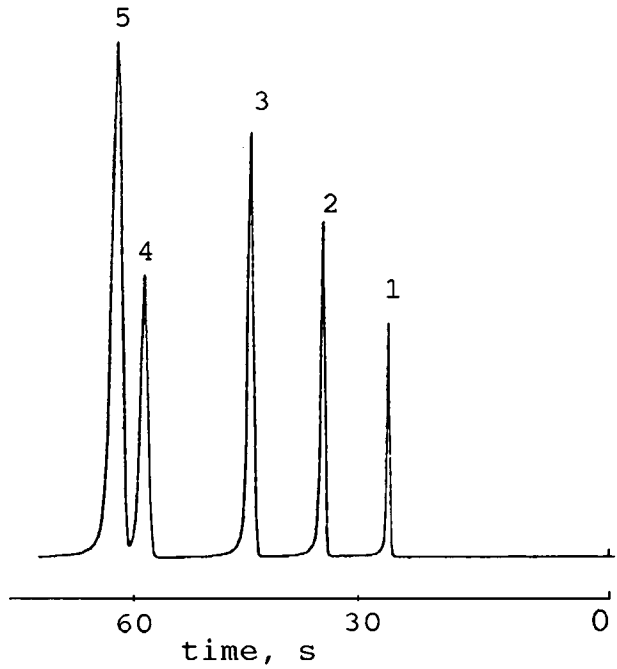

Fig. 1-3. Chromatogram of aromatic hydrocarbons separation on an open capillary column with graphitized carbon black [17].

Column silver-plated copper, 15 m × 0.25 mm; carbon black content, 5.4 mg/m; temperature 245 °C; carrier gas: hydrogen.

Peaks: 1 — benzene, 2 — toluene, 3 — ethylbenzene, 4 — *m*-xylene, 5 — *o*- and *p*-xylenes.

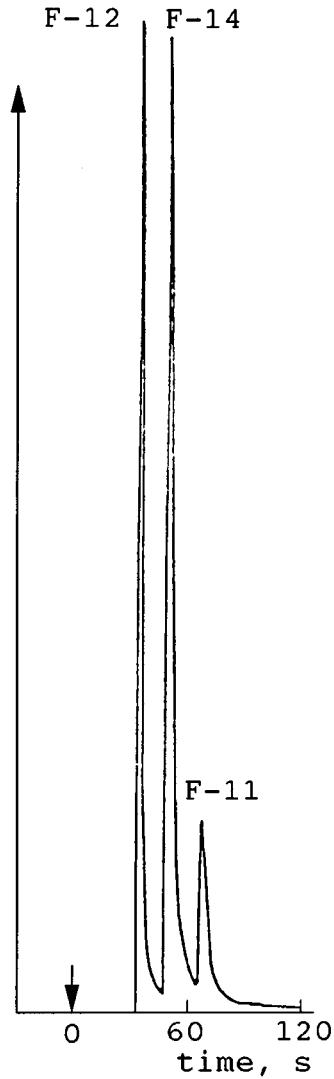

Fig. 1-4. Separation chromatogram for some freons on an open capillary column with a boehmite (Al_2O_3) layer [19].

Column 7.5 m × 0.5 mm; temperature 22 °C.

Separation of H_2, O_2, N_2

Purcell [20] was the first to suggest an adsorption open tubular capillary column with molecular sieves (see Fig. 1-5 [20]). The copper column (23 m × 1 mm) with roughened walls coated with pulverized molecular sieve 5A was used for separation of

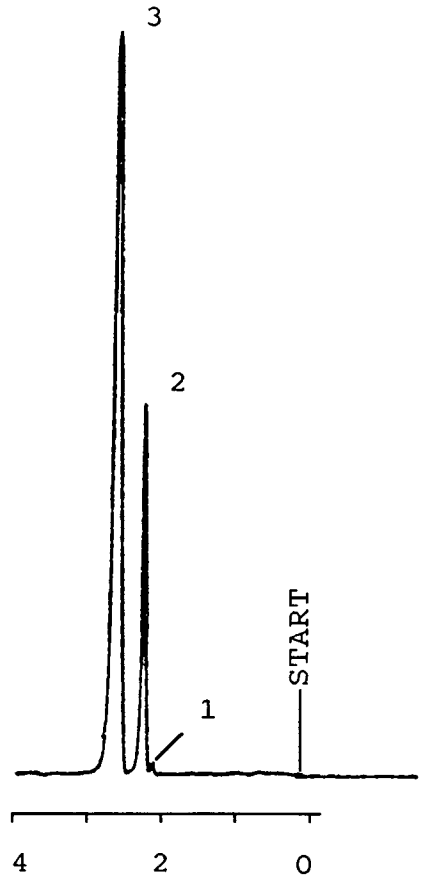

Fig. 1-5. Chromatogram of separation of hydrogen (1), oxygen (2) and nitrogen (3) on ALOT column with molecular sieve 5A [20].

Column 22 m × 1 mm; adsorbent molecular sieve 5A deposited on the inner wall;
temperature 26 °C; sample size and carrier gas (helium) flow-rate 10 μl, 12 ml/min, respectively.

permanent gases (hydrogen, oxygen, nitrogen and methane). The particle size diameter of the adsorbent was less then 20 μm. Elution times were unchanged, and no loss of adsorbent was observed. Peaks of oxygen and nitrogen were separated at sample sizes of 10 μl – 1 ml.

Separation of light hydrocarbons

The preparation of capillary columns with porous polymers was first described by Hollis [21] in 1973. The styrene-divinylbenzene polymers were synthesized in situ inside the capillary. An example of the gas chromatographic separation possible on such columns is shown in Fig. 1-6 [21]. These columns were usable for hydrocarbon separations (note the separation by carbon number) but polar molecules such as alcohols have the tailing peaks characteristic of adsorption. In Hollis' opinion, this is probably due to the same forces as are seen with a metal capillary column using apolar squalane without a tailing reducer [21].

Separation of unsaturated acids

Mention should be made of using a capillary column for separation of polar compounds on organic natural adsorbents. Fig. 1-7 [22] shows the separation of naturally occurring organic acids on a natural polymer, i.e., cells of *Staphylococcus aureus.* The use of such adsorbents holds good promise.

Petitjean and Leftault [23], Schwartz [24], and others also contributed to the early development of capillary gas-solid chromatography, and subsequent important contributions to this kind of chromatography were made by Liberti, Bruner, Cartoni, and co-workers [25 — 29] as well as Ilkova and Mistryukov [30].

An important contribution to the development of capillary chromatography using columns with inner walls coated with a porous layer, among which there are capillary columns with an adsorbent layer, was made by Ettre, Purcell, and co-workers [31–33]. Of special interest is their review [34] devoted to the theory, methods of manufacture, applications, and future of solid adsorbent coated open capillary columns.

Even the early work on capillary adsorption columns suggested, first, the remarkable resolving power of the method, especially as regards isotope separation capabilities, and, secondly, its high speed.

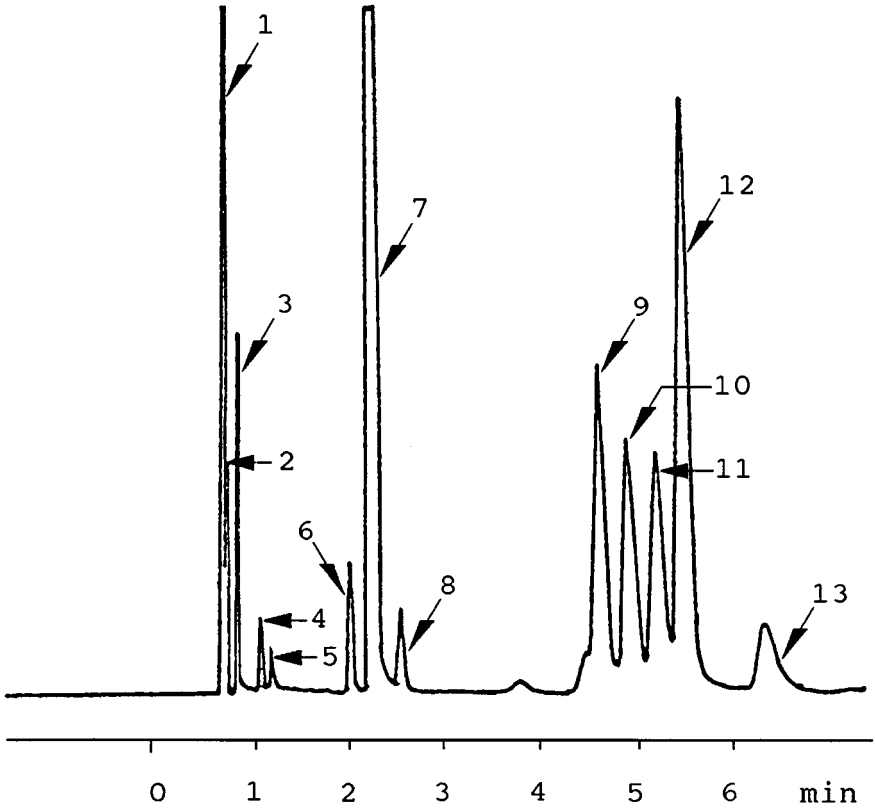

Fig. 1-6. Chromatogram of hydrocarbons on ALOT column with porous polymer adsorbent [21].

Column 7.5 m × 0.25 mm, temperature 150° C.

Peaks: 1 — methane; 2 — ethane; 3 — propane; 4 — isobutane; 5 — n-butane; 6 — isopentane; 7 — pentane; 8 — cyclopentane; 9 — 2-methylpentane; 10 — 3-methylpentane; 11 — n-hexane; 12 — benzene; 13 — cyclohexane.

In the last decade interesting studies have been performed, and further applications of open capillary gas adsorption columns have been suggested by de Nijs and de Zeeuw [35 – 37]. Chrompack (The Netherlands) has embarked upon the commercial production of some types of these columns, using alumina, molecular sieves, and polymer adsorbents [38 – 41].

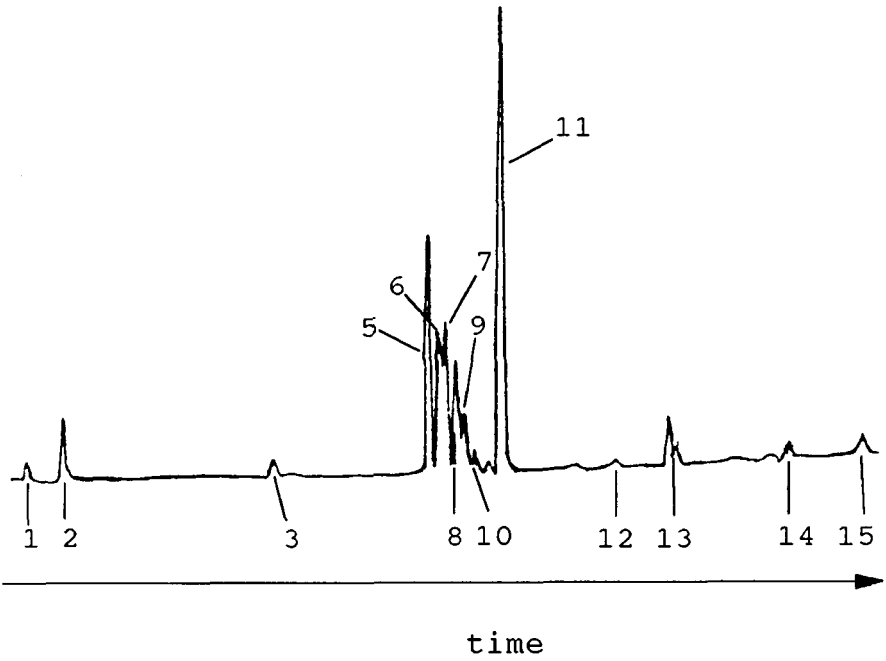

Fig. 1-7. Chromatogram for the separation of unsaturated acids on an open capillary column with *Staphylococcus aureus* cell as the adsorbent [2].

Peaks: 1 — 14:1 tetradecenoic, 2 — 14:0 myristic, 3 — 15:0 pentadecanoic, 4 — c-Δ^8-16:1 *cis*-hexadec-8-enoic, 5 — c-Δ^9-16:1 *cis*-hexadec-9-enoic, (palmitoleic), 6 — c-Δ^{10}-16:1 *cis*-hexadec-10-enoic, 7 — c-Δ^{11}-16:1 *cis*-hexadec-11-enoic and *trans*-hexadec-9-enoic, 8 — t-Δ^{10}-16:1 *trans*-hexadec-10-enoic, 9 — t-Δ^{11}-16:1 *trans*-hexadec-11-enoic, 10 — t-Δ^{12}-16:1 *trans*-hexadec-11-enoic, 11 — 16:0 palmatic, 12 — 17:0 *cis*-methylenehexadecanoic, 13 — t-Δ-17:0 *trans*-methylenehexadecanoic, 14 — 18:1 octadecanoic, 15 — 18:0 stearic.

1.3 Classification of Capillary Columns in Gas Chromatography

Classification of capillary columns seems to be a basic problem in gas chromatography [42–44]. Some authors believe that the terms "open capillary columns with a porous layer on the inner wall surface" and "open capillary columns with a solid carrier layer on the inner walls" are badly confused. One reason for this situation is an insufficiently strict classification of capillary columns. We proposed a more general (in our opinion) classification based on the following criteria: (1) the presence (or absence) of a porous layer on the inner capillary column walls and (2) the presence (or absence) of a stationary liquid phase layer on the inside column walls (see Table 1-4 [45]).

Nowadays only three of the four possible types of columns are mainly used: open capillary columns with a non-porous wall surface coated with a stationary liquid phase (wall-coated open tubular (WCOT); open capillary columns with a porous layer of adsorbent on the inside walls or adsorption layer open tubular columns (ALOT); open capillary columns with a porous layer impregnated with a

Table 1-4.
Classification of open capillary columns [45]

Classification criterion	Open tubular columns	
Presence (or absence) of a porous adsorbent layer or porous solid support layer on the inner column walls (smooth (nonporous) or porous inside wall surface).	1. Non (porous layer) open tubular column (NONPLOT) (open capillary column with smooth (nonporous) inside wall surface).	2. Porous layer open tubular column (PLOT) (open capillary columns with a porous inside wall surface).
	1.1 Adsorption (nonporous) wall open tubular column (AWOT) (open capillary adsorption columns with a nonporous wall surface).	2.1 Adsorption layer open tubular column (ALOT) (open capillary adsorption columns with a porous adsorbent layer on the inside walls).
Presence (or absence) of a stationary liquid phase on the inner column walls.	1.2 Wall-coated with film of stationary liquid phase open tubular column (WCOT).	2.2 Support-coated with stationary liquid phase open tubular column (SCOT).

stationary liquid phase layer (support-coated open tubular (SCOT)).

The adsorption (non-porous) wall open tubular column (AWOT) and the adsorption layer open tubular column (ALOT), both used in gas-solid chromatography, should be recognised as separate groups because their structure and chromatographic characteristics differ markedly from those of the other columns.

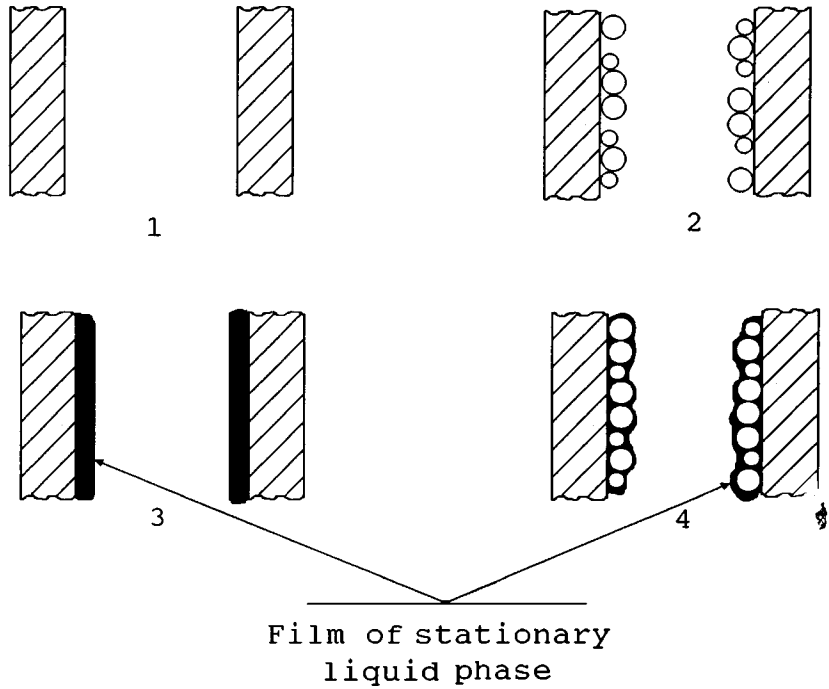

Fig. 1-8. Different types of open tubular capillary columns.

1 — adsorption wall open tubular column (AWOT column);

2 — adsorption layer open tubular column (ALOT column);

3 — wall coated with the film of stationary liquid phase open tubular column (WCOT column);

4 — support coated with the film of stationary liquid phase open tubular column (SCOT column).

In the chromatographic literature open capillary adsorption columns with a porous layer on their inner walls are frequently designated as PLOT columns, which does not seem to be well justified as this concept also includes capillary columns with a porous layer impregnated with a stationary liquid phase (SCOT columns). There is little or no published information on capillary adsorption columns with a non-porous (unextended) wall surface (AWOT).

The present book discusses open adsorption columns (mainly ALOT columns) (see Fig. 1-8) and compares their characteristics and analytical features.

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Chapter 2

Capillary Gas-Solid Chromatography (Advantages and Limitations)

2.1 On the Role of Gas-Solid Chromatography

Open capillary columns for gas-[liquid-solid] chromatography) are widely used in analytical practice (see, e.g. [18]). Separation of compounds on these columns is mainly based on differences in the interactions of the molecules of chromatographed compounds with a liquid stationary phase. However, gas-solid chromatography is equally expedient, and sometimes it is the only method available for solving a number of analytical problems [9–11].

Potential of GSC

The important role of gas-solid chromatography has been stressed by many researchers. Thus in the introduction to the book "Adsorption Gas and Liquid Chromatography" [11] Kiselev and Yashin wrote: "Significant progress has been attained in gas adsorption chromatography. The field of its usage has been materially extended to now embrace practically all compounds capable of converting to a gas phase without decomposition. Moreover, the adsorption effects are widely applied to gas-liquid chromatography as well as to enhancing the separation selectivity and column stability. Methods of modification of the adsorbent surface have resulted in the further development of absorption/adsorption chromatography, relying on the combined utilization of adsorption and dissolution (or partition) processes. New potentialities are offered now by adsorption chromatography due to the use of enhanced pressures and strongly adsorbable carrier gases".

A very interesting opinion on the evolution of gas-solid chromatography was expressed by Giddings about thirty years ago [10]. However, we think that

Comparison of GSC and GLC

this estimation of gas-solid chromatography is still generally correct today. Giddings wrote: "The spectacular advance of gas liquid chromatography in its first explosive decade (1952–1962) nearly obscured its somewhat less versatile companion technique, gas-solid chromatography. This relative obscurity now shows signs of yielding in the face of new breakthrough in knowledge and instrument technology. In some areas gas-solid chromatography now shows promise of exceeding the performance of gas-liquid system. Concrete progress in gas-solid chromatography (GSC), beyond the present art, will originate with numerous experimentalists who acquire new techniques and new solids with more versatile chromatographic value".

"It would be unreasonable to expect GSC to compete with GLC in overall simplicity and effectiveness, yet the practical problems of GSC (and thus the gap between GSC and GLC) have been reduced considerably in recent developments. With sensitive ionization detectors it appears that there is no major difficulty in operating GSC in the linear range of adsorption isotherm. In addition the recent work of Scott shows that GSC is no longer limited solely to low molecular weight compounds; hydrocarbons up to 45 carbon atoms were separated with specially modified solids [12]. The problem of obtaining reproducible adsorption surfaces is also found to be solved as more is understood about GSC".

"GSC has two immediate potential advantages over GLC which help to offset the latter's greater versatility. GSC also has a theoretical potential for handling very difficult analyses and high-speed analyses which, pending the solution of some complex technical problems, might provide up to a rather phenomenal 10^7 plates per second. The areas of immediate promise will be discussed first, followed by speculation concerning the use of GSC in providing the 'ultimate' column."

One immediate advantage of GSC resides in the fact that a surface with any reasonable degree

of uniformity will exhibit a C_K* value substantially smaller than the C_l of GLC".

"The second immediate advantage of GSC resides in the great potential selectivity of the adsorption process. Surface adsorption is potentially capable of offering the most versatile and selective characteristics of any of the known retention mechanisms" [13]. The rigidly fixed forces of a solid surface contrast sharply with the fluid forces of a liquid phase. As more is learned about the molecular-level detail of surfaces, it should be possible to use these rigid forces to enhance selectivity".

2.2 Comparison of Open Tubular and Packed Gas Adsorption Columns

The advantages of gas-solid chromatography are better realized if high-efficiency capillary columns are employed. Note the following general advantages of capillary columns over packed ones.

First, capillary columns are distinguished by higher separating power. Thus the specific efficiency of capillary columns is 2,000–5,000 theoretical plates per meter whereas for packed columns this value is far lower, i.e., 1000 theoretical plates per meter. The difference in the total efficiency owing to the greater length of the capillary columns is still more dramatic, being 25,000–100,000 theoretical plates for capillary columns.

The separation selectivity of capillary columns is also somewhat higher than that of packed ones. This is mainly attributed to the fact that the separation temperature of the former is significantly lower than that of the latter, and it is known that with decreasing temperature the selectivity is normally higher.

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* The efficiency of the chromatographic column is proportional to the reciprocal value of HETP. The mass transfer plate height contribution HETP is given by Cu (u is the linear velocity of the carrier gas, C is mass transfer resistance coefficient), C_k characterizes the C value in gas-solid (gas-adsorption) chromatography, and C_l that in gas-[liquid-solid] chromatography (see, for example, [1, 4]). (Authors' footnote.)

The higher efficiency (and selectivity) allows use of capillary columns to separate and identify 10–100 times more compounds than in the case of traditional packed columns with a specified diameter (24 mm). Thus capillary chromatography greatly improves "the chemical insight" of the investigator.

Secondly, using capillary columns extends somewhat the applications of gas-solid chromatography, which in turn permits the separation of heavier (high boiling) or thermally labile compounds. This is attributed to the fact that the total amount of adsorbent in open capillary columns is far smaller than that in packed ones and therefore the temperature of separation for capillary columns can be lower.

Thirdly, open tubular columns can speed up separation procedures. This is mainly explained by the simpler utilization of higher mass transfer and carrier gas rates.

Fourthly, column miniaturization provides improved temperature reproducibility in the separation process. This feature is due to a lower thermal time lag of capillary columns as compared with that of packed ones, and column miniaturization improves heat transfer conditions and reduces equipment size as well as sorbent and carrier gas consumption.

All these advantages have had a stimulating effect on the development of gas-solid capillary chromatography over the past years.

Experimental comparison between ALOT and packed columns

Franken and co-workers [14] separated nitrogen-containing compounds (see Fig. 2-1) on a sorbent composed of 3% phthalocyanine on graphitized carbon black. It is evident that using capillary-type chromatography improves separation (e.g., in the case of 2,3-lutidine, 2,4-lutidine, and 2,5-lutidine) and dramatically reduces the analysis time (by a factor of approximately12).

It should be pointed out that reducing the temperature to 137 °C permits complete separation of 2,4- and 2,5-lutidine during 90 s. The data pre-

sented suggest the suitability of capillary gas-solid chromatography for separating complex mixtures.

One important feature of a capillary column is the possibility of its use without a splitter to eliminate sample discrimination and to improve analytical characteristics. Therefore in the past few years chromatographers gave preference to wide capillary columns with a thick (a few micrometers) layer of immobilized stationary phase (see, e.g., [15, 16]).

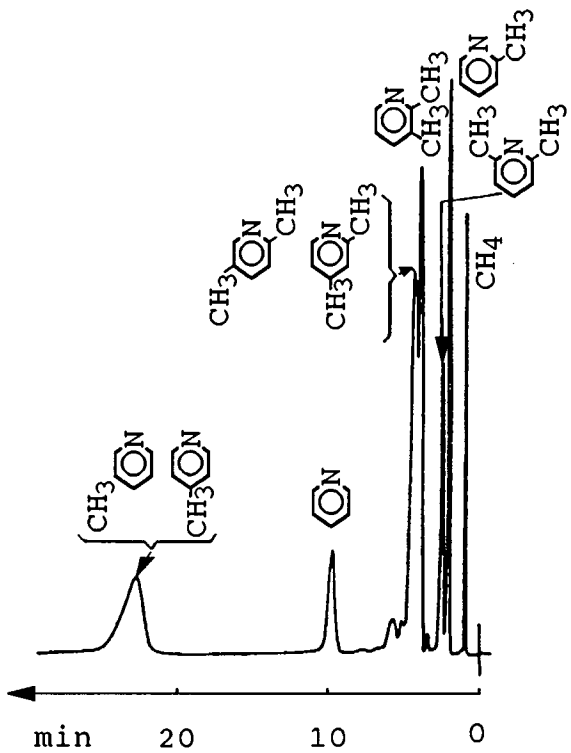

Fig. 2-1a Separation of nitrogen-containing compounds on a packed column [14].

Column 4 m × 2 mm, sorbent 5% cobalt phthalocyanine on Sterling MTG carbon black, temperature 178 °C,
elution order: methane, 2-picoline, 2,6-lutidine, 2,3-lutidine, 2,4-lutidine + 2,5-lutidine, pyridine, 3-picoline + 4-picoline.

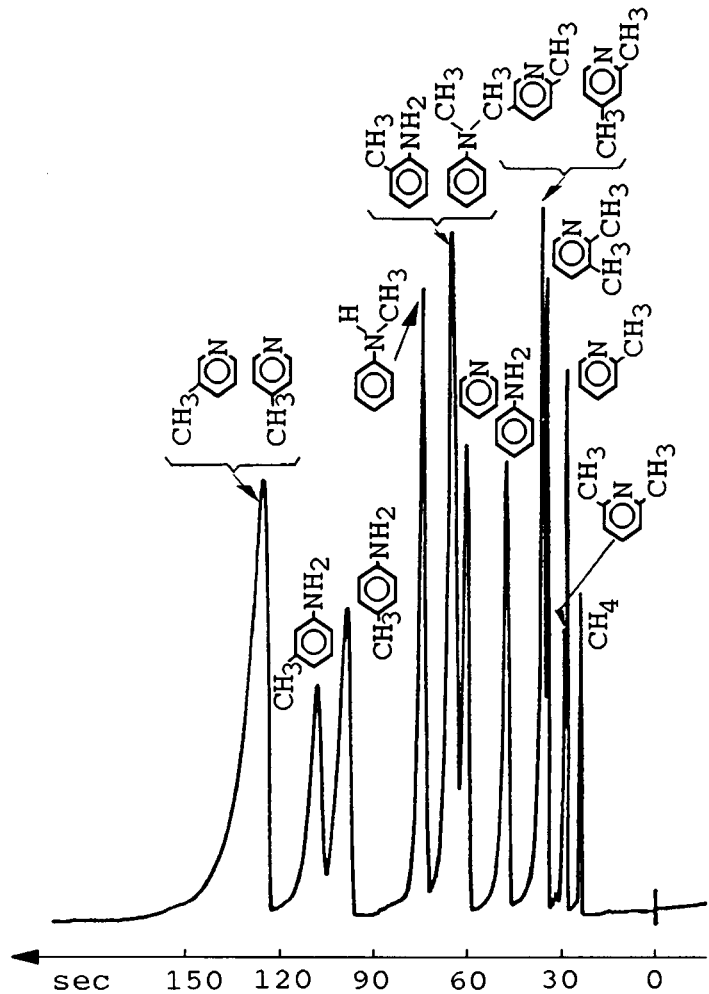

Fig. 2-1b Separation of nitrogen-containing compounds on an open capillary column [14].

Glass column 10 m × 0.5 mm, sorbent 5% cobalt phthalocyanine on Sterling FTG carbon black, temperature 178 °C, elution order: methane, 2-picoline, 2,6-lutidine, 2,3-lutidine, 2,4-lutidine + 2,5-lutidine, aniline, *o*-toluidine + *N,N*-dimethylaniline, *N*-methylaniline, *p*-toluidine, *m*-toluidine, 3-picoline + 4-picoline.

Capillary adsorption columns can be prepared with a relatively thick adsorbent layer (up to 50–100 μm). They are characterized by a high capacity per length unit and low mass transfer resistance to the adsorbent layer. The latter effect is due to the establishment of equilibrium of the chromatographed compounds in the gas-stationary phase (adsorbent) system, occurring, mainly, via diffusion in the gas phase, the rate of which is higher than that in the stationary liquid phase.

Wide-bore capillary column

Table 2-1 [15] compared characteristics of a packed column with those of a wide capillary column provided with a thick stationary liquid phase layer. The advantage of a wide-bore capillary column with a thick layer of stationary liquid phase is obvious.

It should be noted that the chromatogram in Fig. 2-1, obtained over 150 s, describes the separation of compounds for which the capacity factors are comparable with those listed in Table 2-1 (e.g., for 3- and 4-picolines the capacity factor is 4.25, for p-toluidine it is 3.12, and for m-toluidine it is 3.52). Therefore it is quite natural that open capillary adsorption columns can be usually used without a splitter. The porous-layer capillary adsorption column can be regarded as an efficient substitute for packed adsorption types. This property of such columns is discussed below in more detail.

Table 2-1
Characteristics of two types of analytical gas chromatographic columns: packed and wide capillary (with a thick layer of stationary liquid phase) ones [15].

Column	Length, m	Inner diameter, mm	Liquid-phase film thickness, μm	Phase ratio	Capacity factor	Number of theoretical plates, (N)
Packed	2	2.26	5	26	8.3	4500
Capillary	15	0.53	3	43	5.0	26000

Development of fused-silica GC capillary columns is the most important advance in the last decade [17–19]. Now fused-silica capillary columns are gaining widespread acceptance in most of gas chromatography laboratories.

Advantages of fused-silica capillary columns

The first advantage of fused-silica capillary columns as compared with glass columns is their inertness, although they still require deactivation.

The second major advantage is their flexibility, and especially the ease of column installation. Fused-silica capillary columns have virtually replaced glass columns for this reason.

The third advantage of fused-silica capillary columns is their commercial availability with a wide variety of inner diameters, film thicknesses and polarity ranges of immobilized and bonded stationary phases. Recent years are characterized by an increased application of fused silica capillary columns. Hyver [17] estimates that packed columns are used for about 20% of gas chromatography analysis, mainly for preparative applications, for simple and routine separations or those in which high resolution is not important, for fixed gas analysis, and for official methods that were validated on packed columns, when revalidation on capillaries would require costly and time consuming equivalency testing. In Thiele's opinion [18], except for the above-mentioned preparative applications or gas analysis, the generally acknowledged advantages of capillary gas chromatography will cause the technique to replace packed-column applications, even in official methods, over the next decade. Lee [19] also feels that capillary columns will replace packed columns in most cases.

In the opinion of Sandra and de Zeeuw [20], one of the further developments will concern new porous-layer open-tubular columns with various adsorbents and porous polymeric phases and their wide practical application.

To increase the field of applications and optimize accomplishment of practical tasks it was necessary to develop open fused-silica column with different

thickness of adsorbent layers and with adsorbents of different nature and to develop their use in multidimensional techniques [20]. Multidimensional methods are especially effective for separating mixtures with a wide range of boiling temperatures.

Development of gas adsorption fused-silica capillary column with adsorbent layer on inner wall is one of the promising directions of modern gas chromatography.

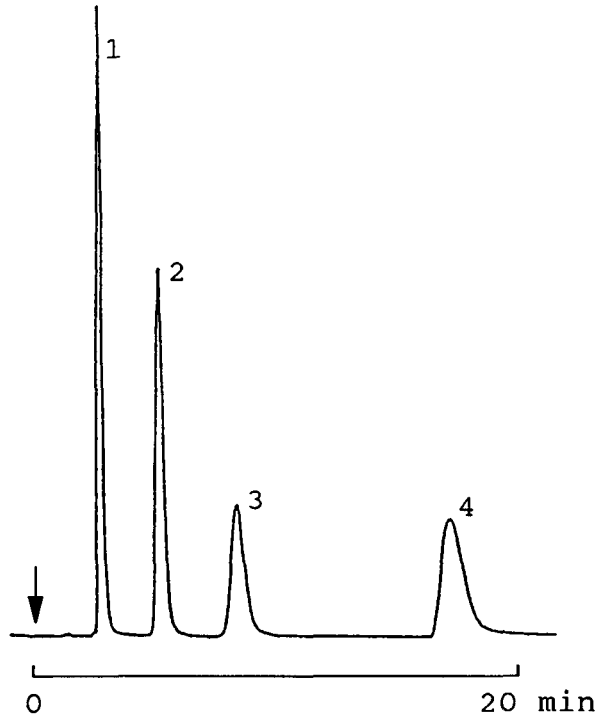

Fig. 2-2a Separation of permanent gases on packed column [24].

Packed column: 3.6 m × 3 mm, adsorbent: Molsieve 5A (60–80 mesh), temperature: 70 °C, carrier gas: helium, 20 ml/min, direct injection 10 μl, detector: TCD, sample: 5% components in helium.

1 — oxygen, 2 — nitrogen, 3 — methane, 4 — carbon monoxide.

Comparison of adsorbent layer open tubular and traditional packed columns shows the advantages of ALOT columns.

Permanent gas separation on capillary and packed columns

Separation of permanent gases on a molecular sieve column is shown in Fig. 2-2a [21]. Separation of oxygen, nitrogen, methane and carbon monoxide on a 3.6 m × 3 mm column at 70 °C is complete in less than 20 min. Fig. 2-2b [21] shows the same separation completed in 2.5 min using a wide-bore ALOT fused-silica column at 25°C. This chromatogram was obtained on a 10 m × 0.53 mm column with 50 μm layer of molecular sieve 5A using direct sample injection and a carrier gas flow rate

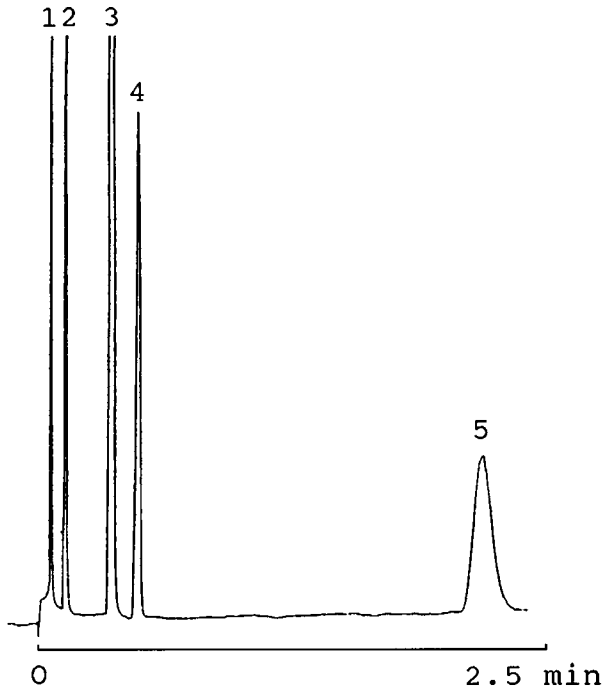

Fig. 2-2b Separation of permanent gases on ALOT column [24].

Capillary column: 10 m × 0.53 mm, adsorbent: Molsieve 5A, d_f = 50 μm, temperature: 25 °C, carrier gas: hydrogen, 35ml/min, direct injection 20 μl, detector: TCD, sample: 5% components in helium.
1 — helium, 2 — oxygen, 3 — nitrogen, 4 — methane, 5 — carbon monoxide.

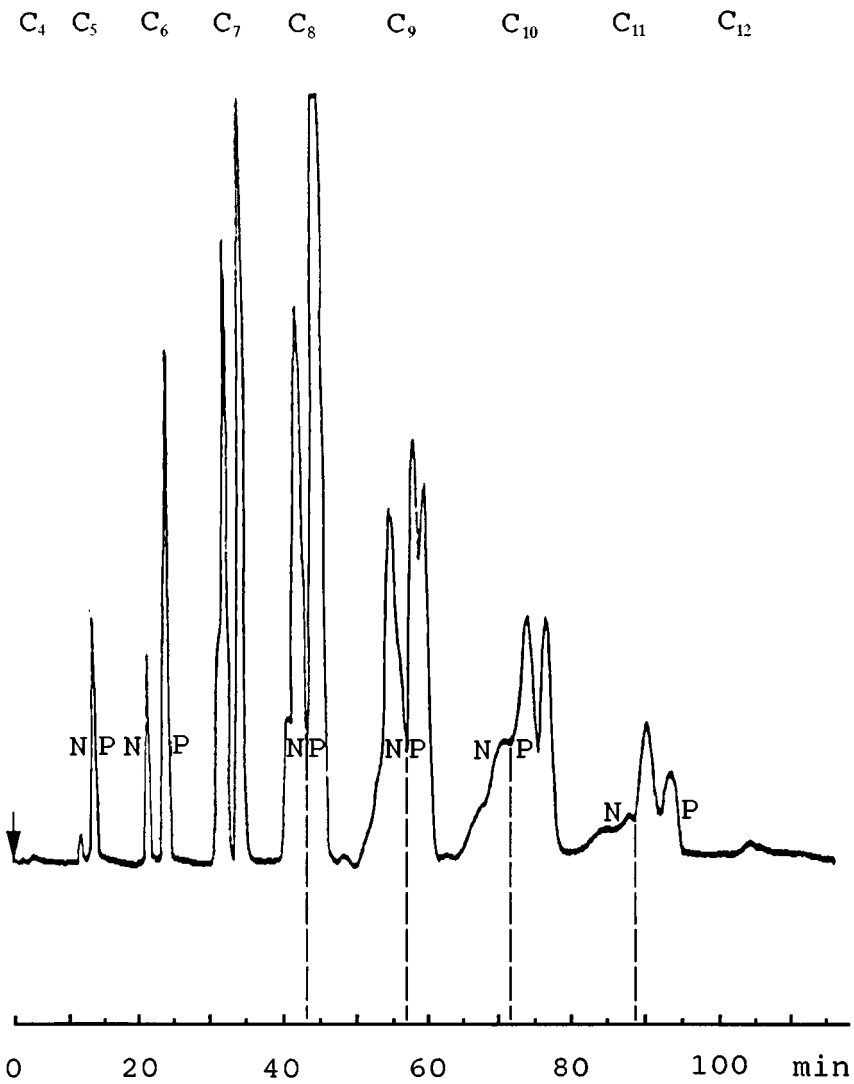

Fig. 2-3a Separation of naphthenic and paraffinic fractions in naphtha [21].

Column: 5 m × 3 mm, adsorbent: Molsieve 13X, temperature: 150 °C, then 4°/min to 500 °C, carrier gas: hydrogen, direct injection, detector: FID.

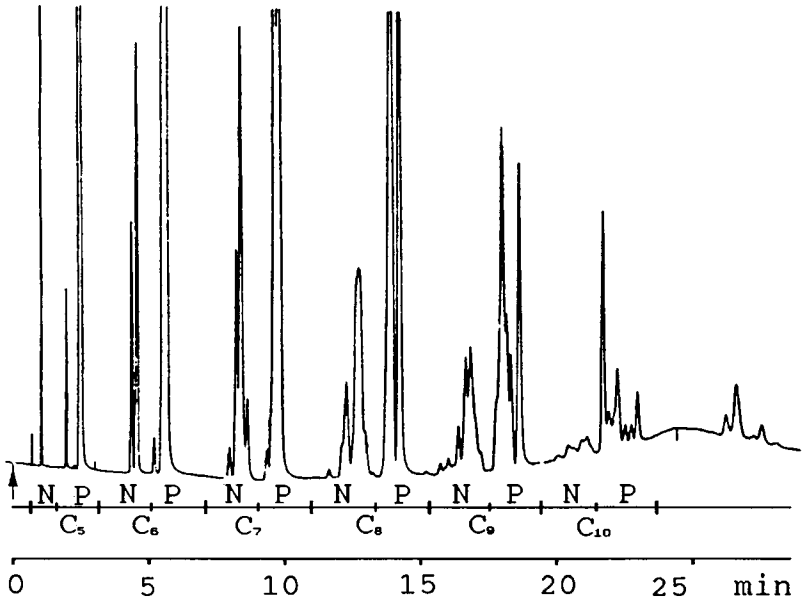

Fig. 2-3b Separation of naphthenic and paraffinic fractions in naphtha [21]

ALOT column: 10 m × 0.5 mm, adsorbent: Molsieve 13X, temperature: 150 °C, then 10 °/min to 400 °C, carrier gas: hydrogen, split injection, detector: FID.

of 35 ml/min. The separation of all components is very good and the analysis time is comparatively short (Fig. 2-2A).

Using molecular sieve 13X it is possible to separate paraffinic and naphthenic hydrocarbons according to carbon number [22]. However, the retention of high boiling hydrocarbons was very high. For example, the time required for the elution of hydrocarbons up to C_{11} in a typical naphtha sample on a packed column is 1.5 h (see Fig. 2-3a [21]). With 10 m × 0.5 mm stainless steel ALOT column with 0.3 μm porous layer, C_{11} hydrocarbons elute at 400 °C (see Fig. 2-3b [21]). ALOT column permits to decrease the maximal separation temperature (400 °C instead of 500 °C).

2.3 Some Peculiarities of Capillary Adsorption Columns

Fast analysis of volatile compounds is very important for chromatographic practice because permanent gases and low molecular weight organic compounds are frequently found in process steam and air-environmental samples.

Rapid analysis is a very important direction in gas chromatography [23–28]. ALOT columns can be used for fast gas analysis [23]. According to Tijssen and co-workers [23] the minimum analysis time can be determined with the following equation:

$$t_r \approx \frac{n_{reg}^{3/2}}{2} R\, f(k)\, (1+k) \left(\frac{\bar{\eta}}{D_m^0 P_0}\right)^{1/2} \qquad (2\text{-}1)$$

where

$$n_{reg} = 16(R_s)^2 \cdot \left(\frac{\alpha}{\alpha-1}\right)^2 \cdot \left(\frac{1+k}{k}\right)^2$$

is the well-known basic relation for chromatographic separations, R_S is the radius of a capillary column, k is capacity factor, $f(k)=(1+6k+11k^2)/(1+k)^2$, $\bar{\eta}$ is the dynamic gas velocity, D_m is the diffusion coefficient of the analyte molecules into the gaseous mobile phase under column outlet conditions, α is the separation factor, R_S is the peak resolution. As follows from this equation, the role of the column radius is rather important, being proportional to the time of analysis. Therefore fast analysis require small column diameter.

Examples of fast chromatographic separation are shown in Fig. 2-4 [23]. Columns were coated with submicrometer silica particles according to a slightly modified method originally developed by Schwartz and co-workers [24] and Cramers and co-workers [25].

Trace "a" (Fig. 2-4) was obtained with a virtually straight column, having a relatively wide inner diameter (0.54 mm). Trace "b" shows that the same columns but tightly coiled into a helical shape, performs much better. Thus the favorable coiling effects in high-speed chromatographic separation

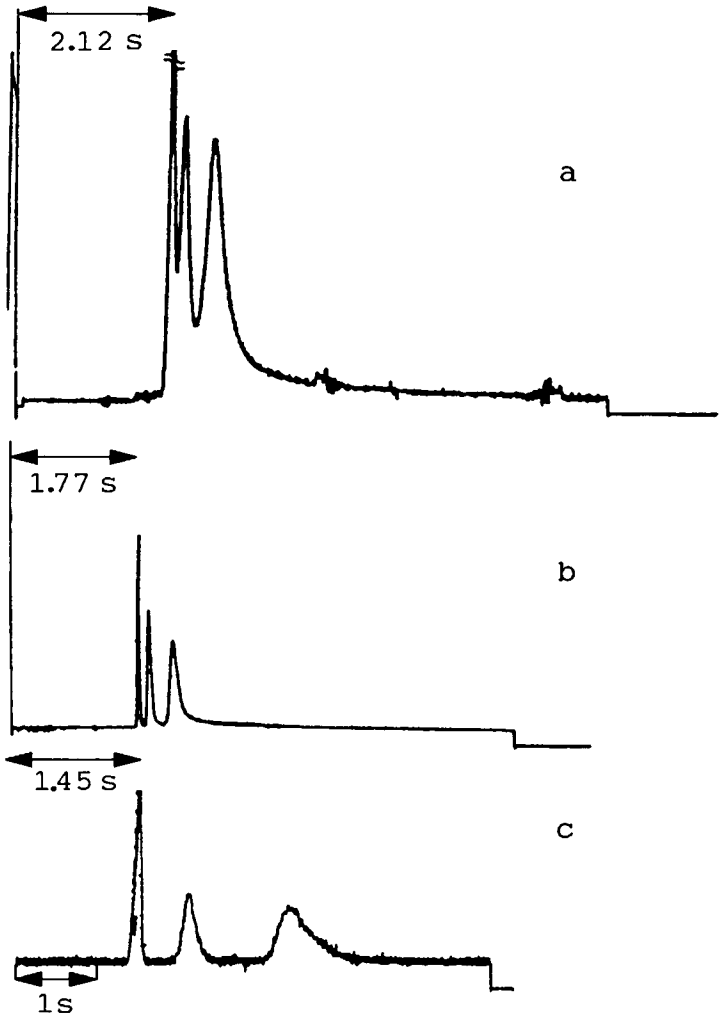

Fig. 2-4 Fast separation of some alkanes on ALOT columns with silica layer [23].

Mobile phase — nitrogen, temperature — 23°C, split ratio 1:1000.

Trace a: methane, n-hexane, and n-pentane in a straight column (0.027 cm radius, 501 cm length); pressure drop 0.5 bar. Trace b: same separation in the same column as under (a) but now tightly coiled 0.4 cm (coil radius); pressure drop 0.5 bar. Trace c: methane, n-pentane, and n-hexane in a microcapillary column (0.0082 cm radius, 299 cm length) tightly coiled into a coil of 0.1 cm radius; pressure drop 2 bar.

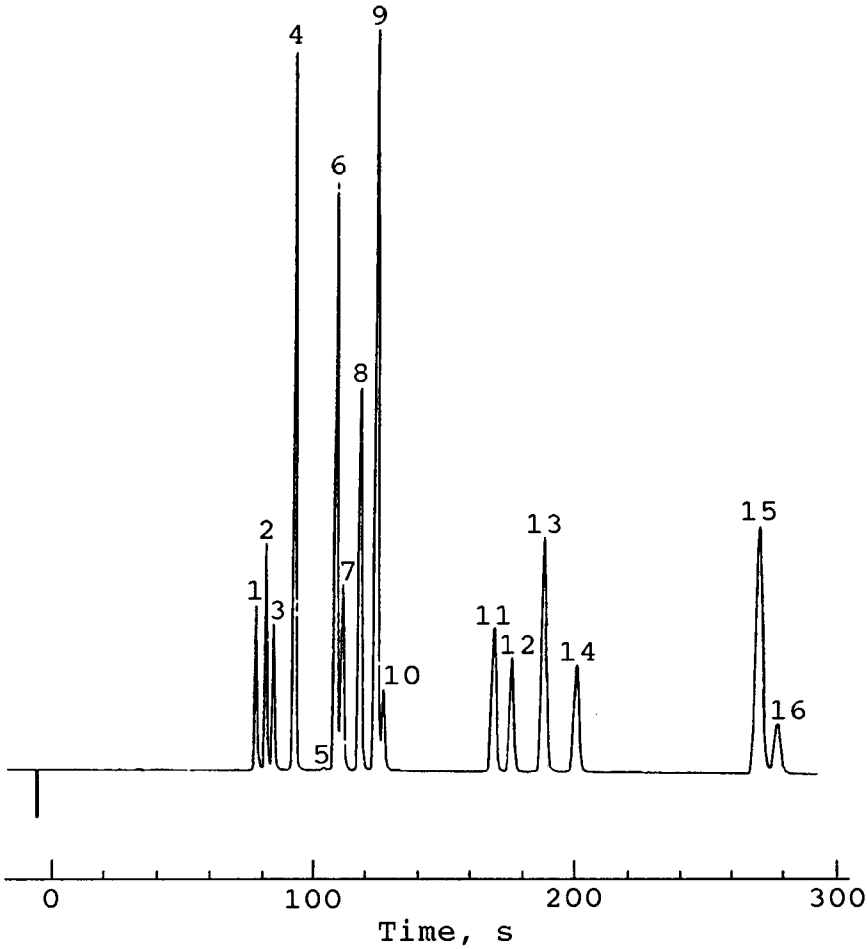

Fig. 2-5 Fast separation C_1–C_4 hydrocarbons [29].

Fused-silica aluminum oxide ALOT column 30 m × 0.32 mm; oven temperature 60 °C; detector FID; split ratio, split injection; 1:25 of 20 µl gas mixture of C_1 – C_4 hydrocarbons; water equalizer.

Peaks: 1 — methane, 2 — ethane, 3 — ethene, 4 — propane, 5 — cyclopropane, 6 — propene, 7 — ethyne, 8 — isobutane, 9 — n-butane, 10 — propadiene, 11 — 1-butene, 12 — *trans*-2-butene, 13 — isobutene, 14 — *cis*-2-butene, 15 — 1,3-butadiene, 16 — propyne.

are demonstrated. Trace "c" shows the result obtained with a 0.16 mm i.d. coiled column (inlet pressure 2 bar).

Therefore, using ALOT columns with small column diameter for high-speed analysis is very promising. ALOT columns can also allow faster chromatographic separations in routine analysis. For example, Fig. 2-5 shows the separation of 16 hydrocarbons C_1–C_4 within 300 seconds using ALOT column with alumina [29]. As can be seen from

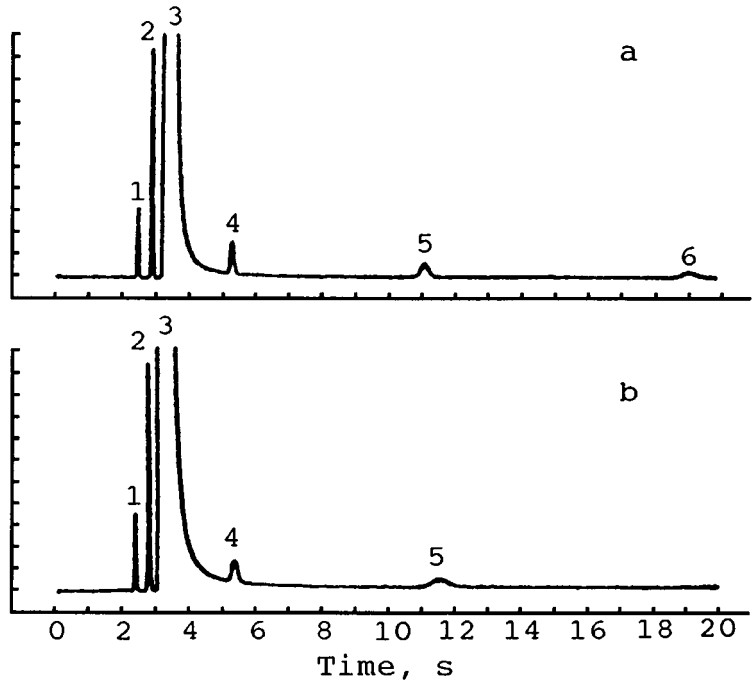

Fig. 2-6 Separation of impurities in ethylene [30].

Columns: 4.0 m × 0.32 mm (a) and 4.0 m × 0.53 mm (b), sorbent — alumina, temperature 40°C.

Peaks: 1 — methane, 2 — ethane, 3 — ethylene, 4 — propane, 5 — propylene, 6 — acetylene.

Fig. 2-5, the separation of all 16 hydrocarbons is fairly good.

High-speed gas chromatographic analysis of low molecular weight hydrocarbons and some chlorinated methanes with ALOT columns was investigated by Peters and Saks [30]. In their work relatively short length ALOT columns (2.0–4.0 m) are operated with hydrogen carrier gas at an average linear velocity of about 150 cm/s. A high-speed gas value inlet system is used to produce inlet band-widths of less then 5 ms. Also a high-speed electrometer is used for data collection. Alumina columns show greater selectivity, which makes them more attractive for some applications. 0.32 mm i.d. alumina columns show greater efficiency at higher temperatures than 0.53-mm i.d. alumina column (see Fig. 2-6). As can be seen, all compounds are well resolved on the alumina columns. Compounds with π-bonds are more strongly retained on the alumina columns. Peaks are broader on 0.53 mm i.d. alumina column than on the 0.32 mm i.d. column.

The utility of ALOT columns for high-speed analysis of some volatile aromatic compounds was also investigated by Peters and Saks [30]. Methane, benzene, toluene, *o*- and *p*-xylene are separated on capillary columns with alumina.

Decomposition of samples on alumina

Good separation of methane, methylene chloride, carbon tetrachloride and chloroform was performed on two alumina columns. The chromatograms are shown in Fig. 2-7 [30]. Note that this type of analysis is not recommended for alumina capillary columns because compounds which are not fully halogenated tend to undergo catalytic decomposition on the alumina surface [31]. The relatively small interaction time of analyte with the adsorbent surface may minimize catalytic decomposition.

There are some artifacts associated with the use of ALOT columns as compared to traditional forms of stationary phases for open tubular columns. An important example is the irreversible adsorption of water and other polar molecules on alumina

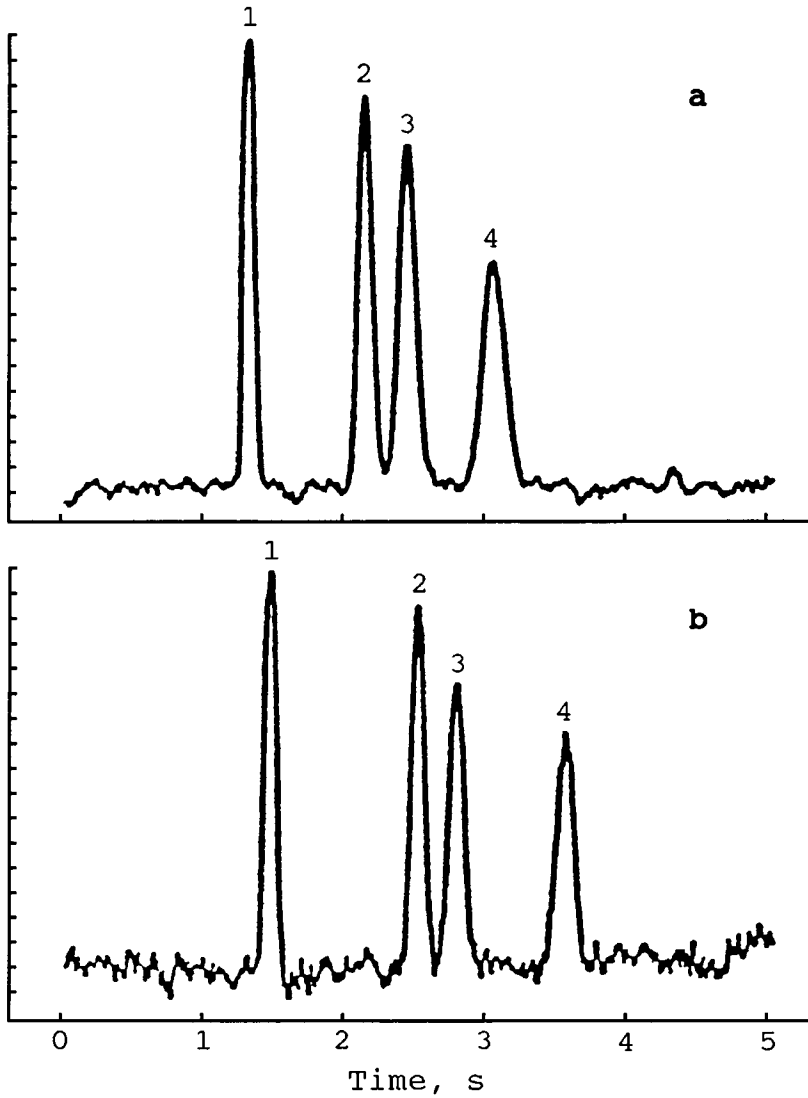

Fig. 2-7 Separation of chlorinated methanes [30].

Columns: 2.0 m × 0.32 mm i.d. (a), and 2.0 m × 0.53 mm i.d. (b), adsorbent — alumina, temperature 190 °C.

Peaks: 1 — methane, 2 — methylene chloride, 3 — carbon tetrachloride, 4 — chloroform.

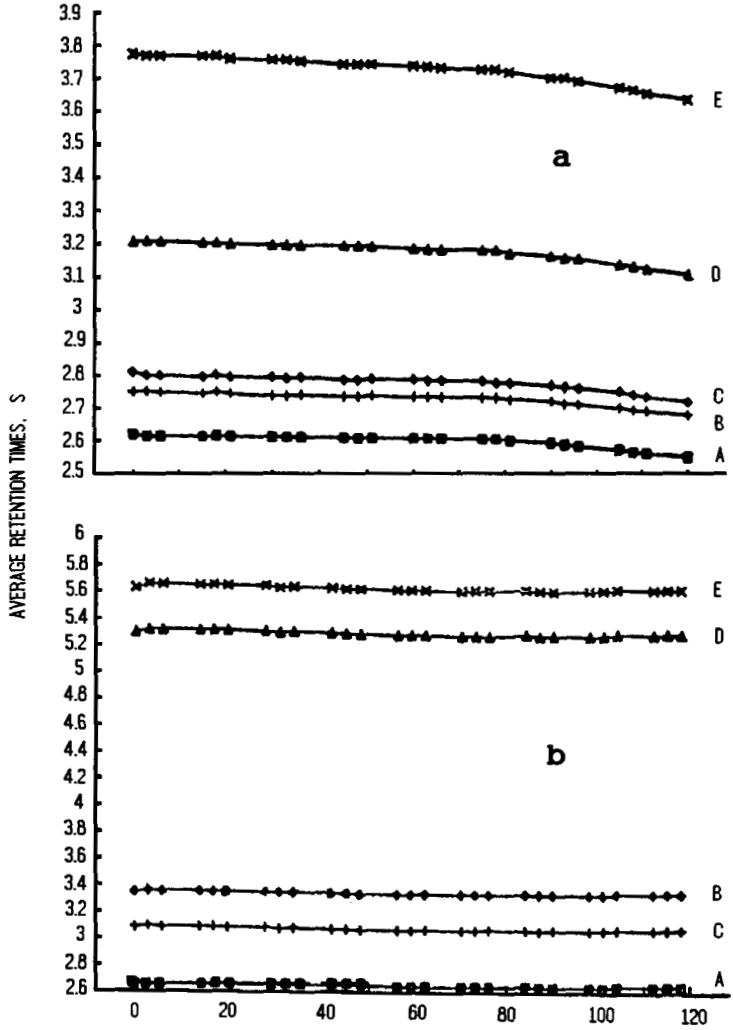

Fig. 2-8 Retention time stability in ALOT columns [30].

Columns: 4.0 m × 0.32 mm Al_2O_3 (a) and 4.0 m × 0.32 mm Pora PLOT Q (b), temperature 100 °C.

Peaks: A — methane, B — ethane, C — ethylene, D — propane, E — propylene (see explanations in text).

columns [30]. Adsorption leads to decreased retention times because there are fewer active sites available for components of interest. This effect can be seen in Fig. 2-8 [30], where average retention times are plotted versus time for a two-hour study involving 100 injections of ethylene mixture on 0.32 mm i.d. alumina column (a) and Pora PLOT Q column (b). In both cases, the average retention time in seconds is plotted versus time of experiment in minutes. On the graphs, each line represents a different component of the ethylene mixture, and each point is an average of four consecutive injections. During the course of a two-hour study a significant decrease in retention time for all components can be seen for the alumina column. No significant retention time changes are observed for Pora PLOT Q column because water and other polar components can elute from Pora PLOT Q column and retention times for other components are not affected. In our opinion, it will be possible to avoid changes in retention times using an aqualizer [29].

Limitations of Al_2O_3-ALOT columns

Analysis of volatile organic compounds by high performance capillary gas chromatography has become increasingly important, especially for environmental monitoring. ALOT columns with Al_2O_3 have proven to be suitable, for example, for separation of light hydrocarbons [29, 32–36], C_1–C_2 halocarbons [36, 37] and perfluorocarbons [38]. Al_2O_3-ALOT columns are used to great advantage for the analysis of volatiles because the capacity ratio and selectivity are increased (compared to WCOT column). Practical applications are limited to 1) relatively non-polar compounds with low boiling points (eluting before n-decane), 2) relatively stable compounds (for example, decomposition of certain compounds was observed).

Fig. 2-9 [9] shows the formation of reaction product (peak 3) when the temperatures increases. By using mass-spectrometry this peak was identified as CH_2CCl_2. An explanation for the presence of CH_2CCl_2 as a reaction product is the HCl abstraction from CH_3CCl_3 [31]. Similar reactions were

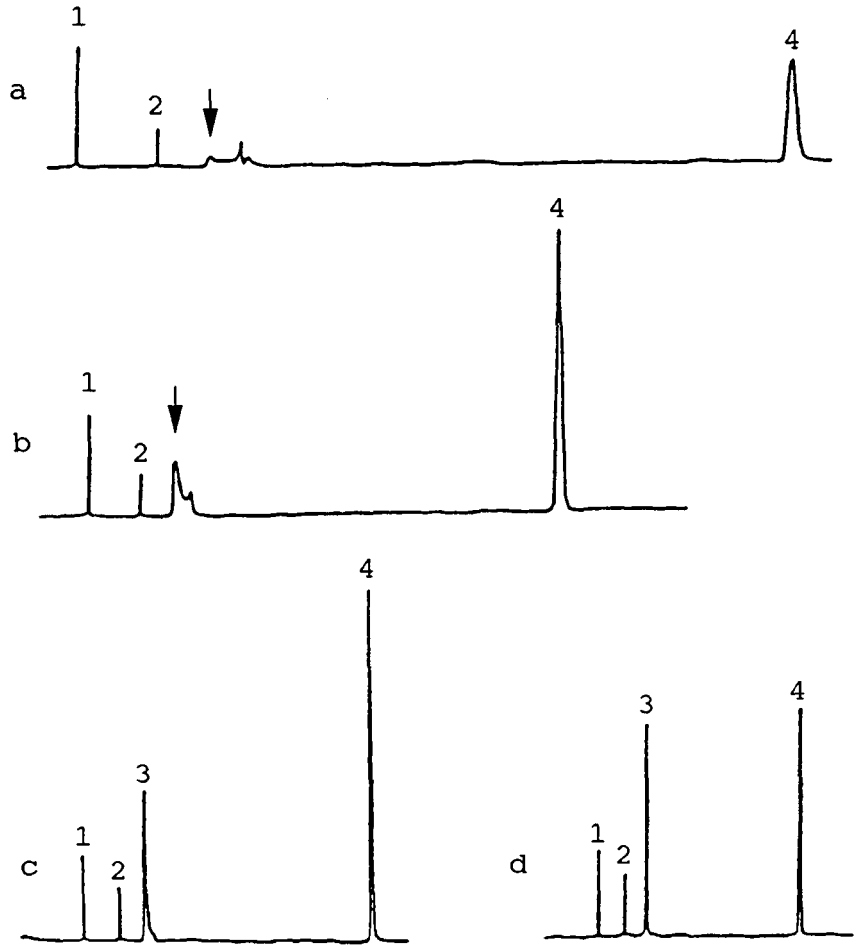

Fig. 2-9 Chromatograms showing CH_2CCl_2 formation from CH_3CCl_3 on Al_2O_3 at different temperatures [31].

Column: 50 m × 0.32 mm i.d.; adsorbent Al_2O_3/KCl;
temperature: a — 175°C, b — 200°C, c — 225°C, d — 250°C.
Peaks: 1 — CCl_2F_2 (strandard), 2 — CCl_3F, 3 — CH_2CCl_2, 4 — C_2Cl_4.

observed for $CHCl_2CH_3$ (to give $CHClCH_2$) and for $CH_2ClCHCl_2$ (to give CH_2Cl_2) [31]. Therefore at elevated temperature partly halogenated compounds are decomposed by Al_2O_3/KCl adsorbent.

Use of an aqualizer in GSC

Water is known [11] to be strongly adsorbed by the alumina surface. The capacity ratio and activity of the aluminum oxide surface decrease with increasing water concentration of this surface. Therefore for constant surface activity it is necessary to have constant water concentration in the carrier gas. De Nijs [29] suggested use of a column filter-aqualizer containing about 100 g of $CuSO_4 \cdot 5H_2O$. The aqualizer is used for carrier gas conditioning. The column is conditioned for 100 h at 60 °C (inlet column pressure 0.5 bar nitrogen, aqualizer pressure usually 5.0 bar nitrogen).

The partial vapor pressure of water in the columns is estimated from the equation [29]:

$$P_{(H_2O)} = \frac{P_{(CuSO_4 \cdot 5H_2O)}}{P_{(aqualizer)} / P_{(column)}} \text{ bar} \qquad (2\text{-}2)$$

where $P_{(H_2O)}$ — partial vapor pressure of water in the column; $P_{(CuSO_4 \cdot 5H_2O)}$ — water vapor pressure of $CuSO_4 \cdot 5H_2O$ = $22.7 \cdot 10^{-3}$ bar at 20°C; $P_{(aqualizer)}$ — pressure in the aqualizer; $P_{(column)}$ — pressure in the column. Thus, $P_{(H_2O)}$ in column after aqualizer at 20°C:

$$P_{(H_2O)} = \frac{22.7 \cdot 10^{-3}}{f(exp)} \text{ bar} \qquad (2\text{-}3)$$

where $f(exp) = [P_{(aqualizer)}/P_{(column)}]$ — expansion factor. The partial vapor pressure of water in the column and hence the amount of water adsorbed on the alumina surface is a function of the ratio of pressures in the aqualizer and the column. As an example, let us compare two chromatograms of hydrocarbons. These chromatograms differ in the separation of hydrocarbons as a result of differences in the concentrations of water in the carrier gas and on the alumina surface. In Fig. 2-10a 1,3-butadiene and propyne are not separated ($P_{(H_2O)} = 1.5 \cdot 10^{-3}$ bar), but in Fig. 2-10b 1,3-butadiene and propyne are well separated ($P_{(H_2O)} = 2.3 \cdot 10^{-3}$ bar). Therefore the water pressure in the

Modifying adsorbent by water

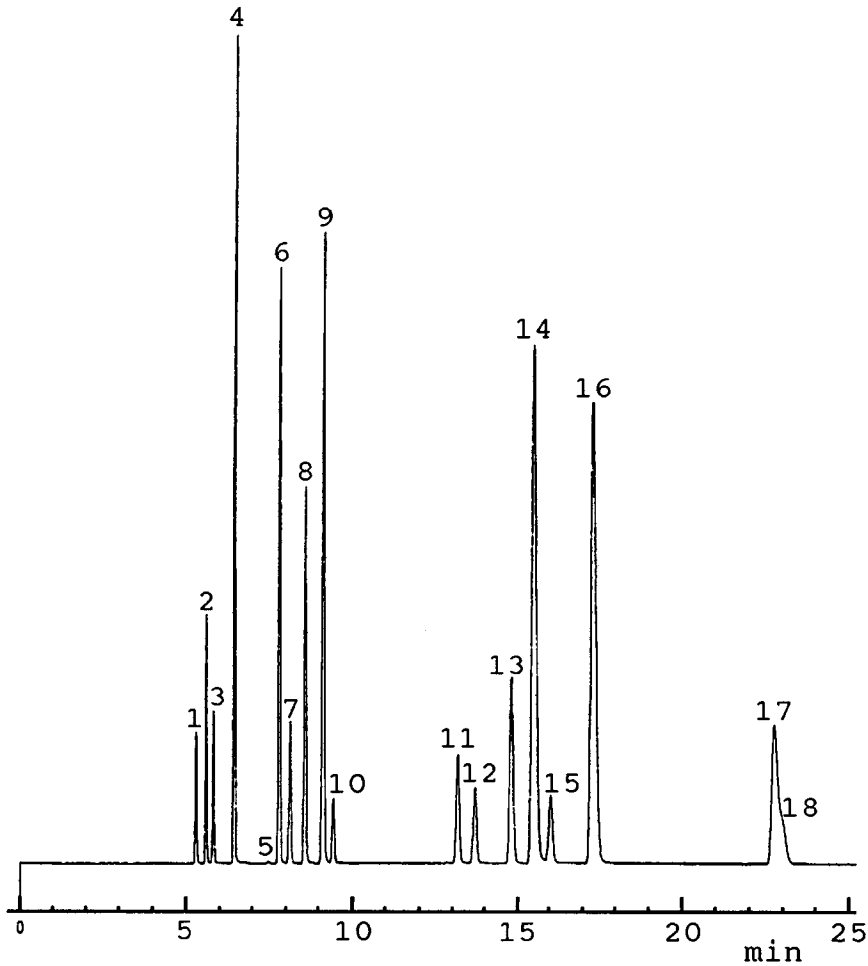

Fig. 2-10a Separation of hydrocarbons on ALOT column for water pressure $1.5 \cdot 10^{-3}$ bar H_2O [29].

Column 30 m × 0.32 mm, fused-silica alumina ALOT column, oven temperature 60°C, detector FID.

$P_{(H_2O)}$ — $1.5 \cdot 10^{-3}$ bar

Peaks: 1 — methane, 2 — ethane, 3 — ethene, 4 — propane, 5 — cyclopropane, 6 — propene, 7 — ethyne, 8 — isobutane, 9 — n-butane, 13 — isobutene, 14 — isopentane, 15 — *cis*-2-butene, 16 — n-pentane, 17 — 1,3-butadiene, 18 — propyne.

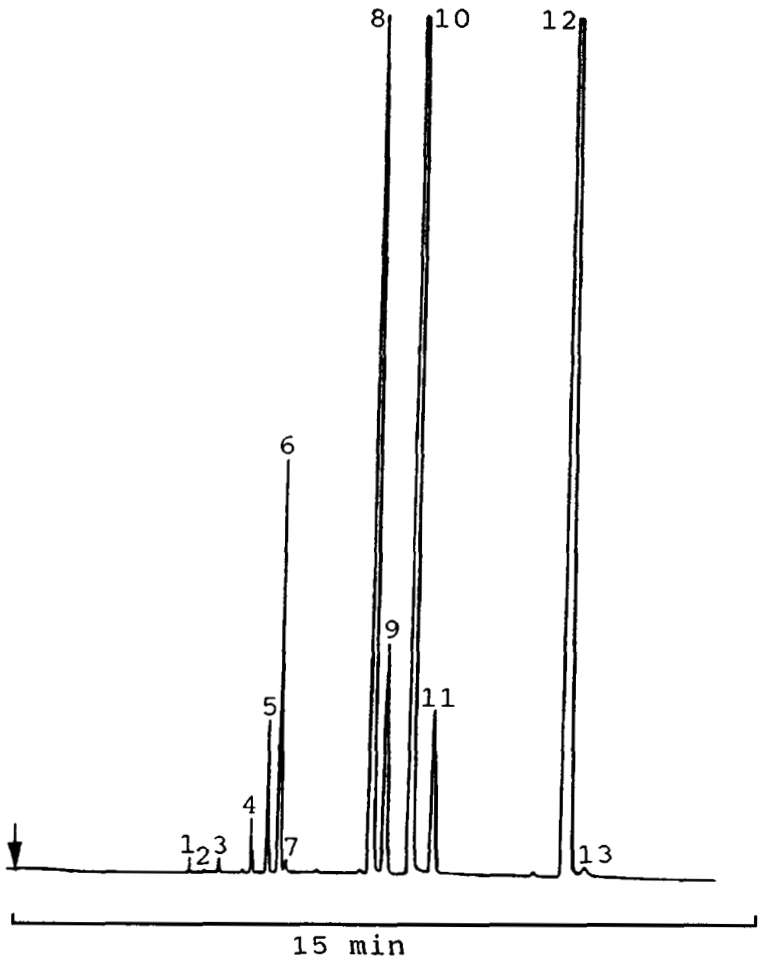

Fig. 2-10b Separation of hydrocarbons on ALOT column for water pressure $2.3 \cdot 10^{-3}$ bar H_2O [29].

Column 30 m × 0.32 mm, fused-silica alumina ALOT column, oven temperature 60 °C, detector FID.

$P_{(H_2O)}$ — $2.3 \cdot 10^{-3}$ bar

Peaks: 1 — methane, 2 — ethene, 3 — propane, 4 — propene, 5 — isobutene, 6 — n-butane, 7 — propadiene, 8 — 1-butene, 9 — *trans*-2-butene, 10 — isobutene, 11 — *cis*-2-butene, 12 — 1,3-butadiene, 13 — propyne.

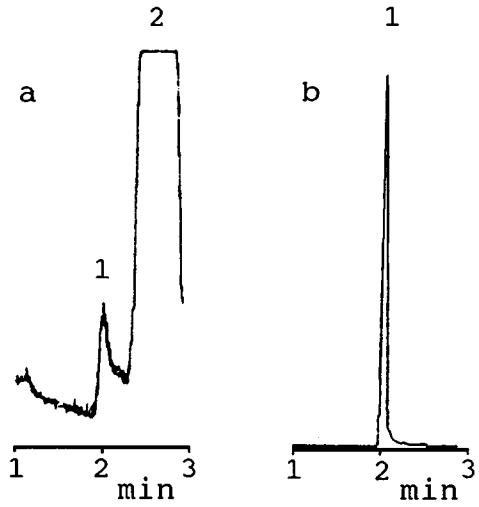

Fig. 2-11

(a) SIM chromatogram of hydrogen sulfide (1.4 ng/ml) (peak 1) in an aqueous sample (peak 2 — water).

(b) SIM chromatogram of hydrogen sulfide (1.6 μg/ml) in aqueous sample [56].

The equilibrium temperature was 25 °C and the sampled head-space volume was 100 μl. Ion of m/z = 34, corresponding to the molecular ion of H_2S, was monitored.

Column 10 m × 0.32 mm, Pora PLOT Q.

carrier gas can sharply change the separation of chromatographed compounds as a result of adsorbent surface modification.

The determination of traces of polar compounds is a very important application of adsorption capillary columns. For example, gas chromatographic analysis of hydrogen sulfide is often performed on polymer adsorbents (for example, Porapak Q, N or QS [39–44]). However, other adsorbents and stationary phases have been also used (Carbopack [45, 46], Triron X-305 [47–48], Tenax GC [49], polyphenyl ether [48, 50] and various methyl silicone phases [51, 52]). Determination of hydrogen sulfide on WCOT columns has been performed with non-polar or medium polar silicone phases at sub-ambient temperatures [53–55].

Jacobsson and Falk [56] suggested determination of low (ng/ml) concentrations of hydrogen sulfide in aqueous solutions with ALOT column (PoraPLOT Q). The detection limit is about 1 ng/ml (see Fig. 2-11 [56]). If greater sensitivity is needed stripping analysis in combination with a cryogenic focusing device should be used. A prerequisite of such a method, however, is that water has to be removed prior to the trap (for example, by calcium chloride [57]) in order to prevent plugging of the cold trap. Thus, ALOT columns can be recommended for trace analysis of polar compounds.

2.4 Uncoated Capillaries as Capillary Adsorption Columns.

The properties of uncoated fused-silica capillaries were investigated by some authors in connection with their adsorption activity. But we can also consider uncoated fused-silica capillaries as gas-adsorption columns. Therefore it will be interesting to estimate the results of these adsorption investigations.

Adsorption activity of glass or fused-silica capillary has always been an important topic in gas chromatography (see, e.g. [1, 4, 58]). The problem of column wall activity still remains important due to ever-increasing demands on column inertness in quantitative and qualitative analysis. An extended field of gas chromatographic analysis dealing with polar compounds of various classes such as underivatized drugs, pyridines, polynuclear aromatic hydrocarbons etc. requires particularly inert tubing.

Role of inner capillary wall

There are three different phenomena caused by solid support (inner capillary wall) activity: reversible absorption (or semi-irreversible adsorption), irreversible adsorption and catalytic reaction of chromatographed compounds with stationary liquid phase, and solid support (inner walls of capillary tube), see, e.g. [4, 59]. In order to obtain reliable quantitative and qualitative results a chromatographer must know for which compounds and under what chromatographic conditions the results will be influenced by these three types of activity and how to avoid its adverse influence. Column catalytic and adsorption activity is widely appreciated to be a function of temperature. Also, the thickness of

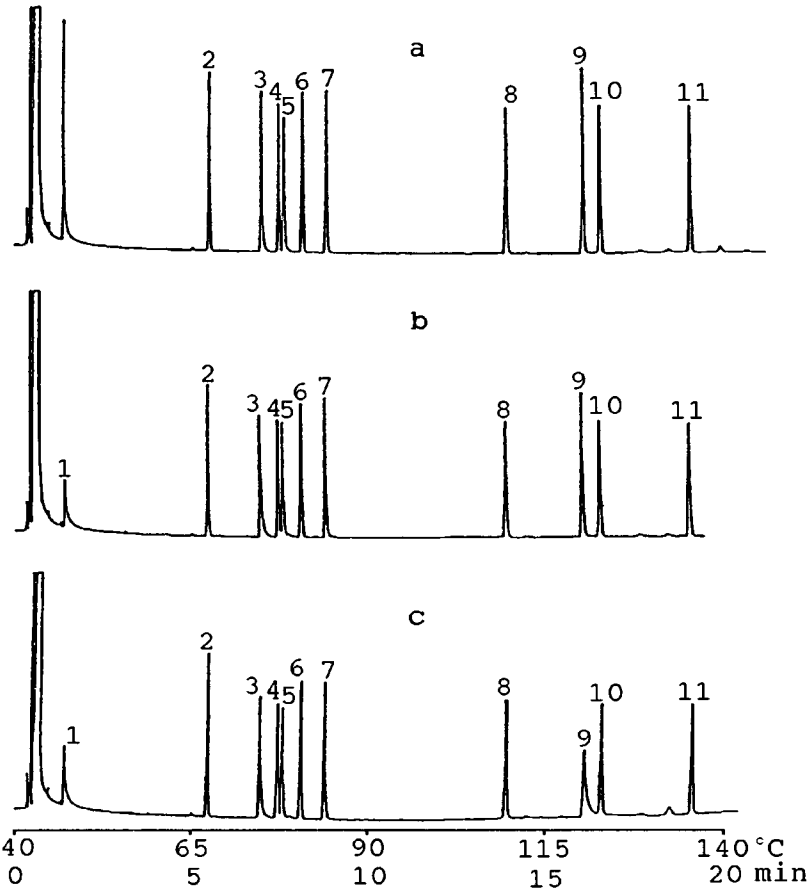

Fig. 2-12 Dependence of uncoated fused-silica capillary tube activity on oven temperature.

(a) Chromatogram of Grob test mixture on the separation column.
(b) The same but having uncoated capillary tubing between outlet and detector.
(c) The same but having uncoated capillary tubing between injection and column inlet [60].

Column: 12 m × 0.30 mm, coated with SE-30 methylsilicone. Uncoated tubing: 40 cm × 0.2 mm i.d. Column temperature: programmed from 40°C at 5°/min. Split injection, 1:25, injector temperature 280 °C. Carrier gas: hydrogen,50 cm/s.
Peaks: 1 — 2,3-butanediol, 2 — n-decane, 3 — 1-octanol,
4 — 2,6-dimethylphenol, 5 — nonanol, 6 — n-undecane,
7 — 2,6-dimethylaniline, 8 — decanoic acid methyl ester,
9 — dicyclohexylamine, 10 — undecanoic acid methyl ester,
11 — dodecanoic acid methyl ester.

the stationary phase film is an important factor affecting the activity of the capillary tubing inner surface. The thicker the film, the higher the elution temperature of a solute. Thus the column will exhibit more catalytic and sometimes less irreversible adsorptive activity.

Uncoated fused-silica capillary tubing has found use in gas chromatography, e.g. in splitless and on-column injection ("retention gap") and in hybrid (fused silica-glass capillary) columns.

Determination of adsorption activity of uncoated capillary column

Since uncoated capillary tubing is usually more active than coated tubing, it is very important to play sufficient attention to the deactivation of uncoated capillary [60]. Fig. 2-12 [60] illustrates the dependence of the activity of uncoated fused-silica capillary tubing (adsorption capillary column) on oven temperature. Fig. 2-12a is a chromatogram of a Grob test mixture [61] on a non-polar separation column. Fig. 2-12b and Fig. 2-12c were obtained under the same experimental conditions, but an uncoated fused-silica capillary tube (40 cm × 0.2 mm) was connected to the column outlet (Fig. 2-12b) or inlet (Fig. 2-12c). The fact that the height of peak 1 is lower in Fig. 2-12b and Fig. 2-12c than in Fig. 2-12a indicates the existence of adsorption activity of the uncoated tube toward 2,3-butanediol. The uncoated capillary tube shows a significant adsorption activity toward dicyclohexylamine at 40°C (peak 9 in Fig. 2-12c). Therefore, uncoated fused-silica capillaries in capillary chromatography practically play the role of gas adsorption columns and they are used in routine gas-liquid chromatography (for instance, as retention gap). The adsorption activity of these small capillary adsorption columns often exerts a negative effect. Consequently, an effective deactivation of the tubing used as the retention gap is indispensable for accurate quantitative work when dealing with polar samples [61].

On the other hand, the coating of capillary columns is a very complicated process and therefore the characteristics of open tubular column vary greatly, depending on the surface properties of the fused-

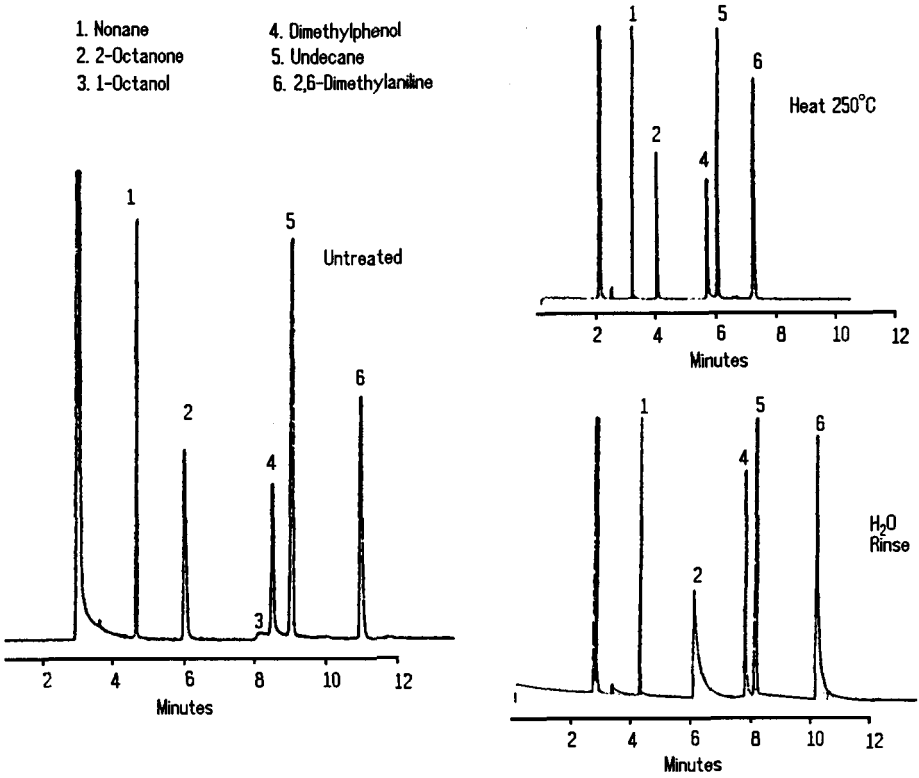

Fig. 2-13 Comparison of fused silica surface treatment [69].

silica, resulting in similar variations of chromatographic performance [1, 4, 62, 63]. To overcome these problems various processes have been used to modify the fused-silica surface. The so-called "hydrothermal treatment" was the most frequently used method for fused-silica capillary pretreatment. Other acidic methods were also described [64, 65]. Highly inert columns were then produced by reaction surface silanol groups [66] with any number of possible silylating agents [67, 68].

Estimation of pretreatment of fused-silica capillaries

Broske [69] investigated the correlation between the method of pretreatment of the fused-silica surface and the retention characteristics of components with different polarity. Broske used in his work the so-called dual column method (see, for instance, ref. [70]). This was accomplished by connecting a section of fused-silica tubing downstream to a standard 25 m× 0.32 mm capillary column. A direct correlation was found between the retention characteristics on uncoated tubing and the inertness measured on the chromatography column obtained.

After different pretreatment procedures uncoated columns were tested with test mixture [70]. Fig. 2-13 [14] shows representative chromatograms of untreated, water-rinsed and heat-treated surfaces. The capacity factor of 2-octanone shifted as a function of the treatment. More specifically, when the fused-silica surface was made more inert by heating, the retention time for the 2-octanone sample was shorter. Surface activation by water rinsing resulted in longer retention times. These changes in retention time were explained by the hydrogen bonding interaction of the carbonyl group of the ketone sample with surface silanols or adsorbed water [70].

Characteristics of AWOT column

As follows from the classification of open tubular capillary columns, capillary gas chromatography includes one more type of adsorption column, viz., an open capillary column with a nonporous (unextended) inner wall surface. This type of columns is distinguished by the following features: 1) low sorption capacity, which can be described, for example, by the $a_S = S/L$ value, where S is the total surface area of inner column walls and L is the column length; 2) high phase ratio $\beta_A = V_{tg}/S$, where V_{tg} is the gas-phase volume in the column and S is the total surface area of the inner column walls; 3) high rates of mass exchange between gas phase and inner column wall surface.

Such columns can only be used when samples are very small and the detectors used are very sensitive as large samples bring about column

overloading with a resultant fast drop in separation efficiency.

However, capillary adsorption columns with a smooth surface should have a fairly high efficiency (in the absence of overloading) and a moderate dependence on the carrier gas velocity.

Low specific sorption capacity suggested that these columns can be used successfully for separating high-boiling (nonvolatile) compounds. Small specific sorption capacity also allows reduction of the separation temperature and hence an increase in the number of compounds analyzed.

Scattered literature data as well as the results obtained by the authors [71] corroborate these considerations.

Fig. 2-14 exemplifies this situation by a chromatogram obtained by Corolla and Berezkin [71] for aromatic hydrocarbons with a fused-silica column after its dehydration at 300 °C in a stream of helium. The separation was effected under overloading conditions and the toluene peak is asymmetric. Nevertheless, this experiment suggests that even the inner fused-silica capillary column walls can serve as an adsorbent capable of separating a fairly simple mixture.

Separation of radioactive chlorides on AWOT columns

Fig. 2-15 [72] presents a chromatogram for analytical separation of radioactive zinc and indium chlorides (a) and indium and terbium chlorides (b) on an empty glass column (10 m × 1 mm). The separation was accomplished by using aluminum chloride vapors in a stream of helium as eluent.

Zvarova and Zvara [73, 74] have demonstrated that at moderate temperatures (under 250 °C) lanthanide chlorides, actinide chlorides, and other chlorides can be separated by gas chromatography if use is made of an inert gas and aluminum chloride vapor as components of the carrier gas. The method relies on aluminum chloride vapor forming gaseous complexes with rare-earth chlorides, which are then transported by the carrier gas. The excess of aluminum chloride inhibits dissociation of the

unstable molecular complexes and dynamically modifies the column surface [75].

Fig. 2-14 Hydrocarbon separation on a fused-silica capillary column [71].

Column 40 m × 0.19 mm, temperature 50 °C, sample size 10 ng/compound. The column surface was dehydrated at 300 °C in a stream of helium.

Peaks: 1 — methane, 2 — benzene, 3 — toluene.

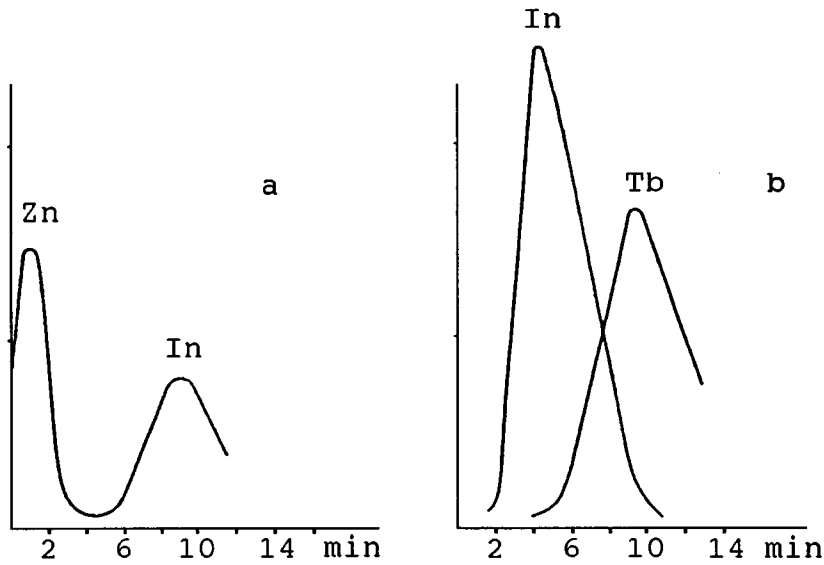

Fig. 2-15 Separation of nonvolatile chlorides on a glass column with helium/aluminum chloride vapor mixture as carrier gas [72].

(a) Separation of zinc and indium chlorides (temperature 170 °C).

(b) Separation of indium and terbium chlorides (temperature 200 °C).

Column 10 m × 1 mm, helium stream flow rate 7.0 ml/min, aluminum cloride vapor pressure, ca. 150 mm Hg.

Despite the low efficiency the column was used for the first time to separate a number of nonvolatile chlorides.

Thus open capillary adsorption columns with a nonporous (unextended) wall surface are also useful for separating high-boiling and unstable compounds.

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Chapter 3

Fundamentals of Gas-Solid Chromatography

Early investigations in GSC

Real development of gas-solid or gas-adsorption chromatography began in 1952–1969. However, the first pioneering work in this field was published earlier in 1930–1940. Important contributions to the development of gas-solid chromatography were made by Schuftan [1, 2] Cremer [3, 4], Turner [5], Damköhler and Theile [6], Janak [7, 8], Zhukhovitskii, Turkeltaub and co-workers [9, 10], Hesse and Tschachotin [11] and others. Important work on the history of chromatography has been performed by Ettre [12], Ettre and Zlatkis [13].

The discovery process of capillary gas-solid chromatography was presented in Chapter 1.

This chapter "Fundamentals of gas-solid chromatography" comprises four sections: 3.1. Retention in gas-solid chromatography; 3.2. Chromatographic zone broadening in ALOT columns; 3.3. Dependence of column efficiency on sample size and 3.4. Resolution of analyzed compounds. From a theoretical point of view, these topics are mainly of interest for capillary gas-solid chromatography.

3.1 Retention in Gas-Solid Chromatography

In general, the theory of gas-solid chromatography consists of two main parts, viz. theory of retention and theory of zone dispersion in gas-solid chromatography [14, 15].

At the low pressures usually typical of quasi-ideal gas chromatography, the moving phase is practically unadsorbed by the adsorbent (stationary phase). Therefore the adsorbent surface is free, and there is no competition of carrier gas with analyte for adsorption. Usually the partial pressure of the analyte in the gas phase is small compared

to the vapor pressure of this analyte, and its amount sorbed on the surface of adsorbent, a, is proportional to its concentration in the gas phase, c:

$$a = K \cdot c, \tag{3-1}$$

where K is Henry's coefficient.

$$V_g = K \cdot S_g, \tag{3-2}$$

or

$$V_N = K \cdot S, \tag{3-3}$$

where V_g is the specific retention volume, V_N is the net retention volume, S_g is the specific surface area, S is the surface area of adsorbent in the column.

Equations (3-1)–(3-3) are simple. The adsorption of carrier gas is much more important in gas-solid chromatography than in gas-liquid chromatography. In gas-solid chromatography part of the surface is occupied by the molecules of the carrier gas and consequently is not available to the analyte molecules.

The effects of non-ideal gas phase on the retention

The effects of the non-ideal behavior of the mobile phase and its adsorption on the surface of adsorbent are reflected in equation (3-4). Equation (3-4) relates the "pure" specific retention volume V_g^0 (which would be observed with an ideal non-sorbed gas or at zero gas pressure) and the measured specific retention volume, V_g [16];

$$\log V_g = \log V_g^0 + \frac{2B_{12} \cdot P}{RT}\left(1 - \frac{\Phi}{\Theta}\right) \tag{3-4}$$

where B_{12} is the mixed second virial coefficient of the adsorbate and the carrier gas, P is the average column pressure, T is the column temperature, Φ and Θ are the fractions of the adsorbate in the sorbed monolayer and in the gas phase at equilibrium, respectively. Φ/Θ is the column capacity factor for the carrier gas; this factor is assumed to be small and Henry's law is still valid

for the carrier gas under the conditions of investigation. The extent of carrier gas adsorption remains negligible. Gas phase non-ideality, adsorption of the carrier gas by solid stationary phase, surface heterogeneity and other factors influence solute retention [18]. A contemporary review of retention theory in gas-solid chromatography has been written by Rudzinski [18].

Kiselev's classification of sorbents and sorbates

Kiselev suggested classification of the sorbents and sorbates based on their main intermolecular interactions [14, 15, 19]. This classification is shown in Table 3-1 [14, 19]. Kiselev [14, 19] also suggested a classification of adsorbents based on the nature of the molecular interactions involved (see Table 3-2). This classification would help to indicate the various parameters that can be manipulated for the study of gas-solid chromatographic separations.

In practical gas-solid chromatography the homogeneity of the adsorbent surface is of great importance [21, 22]. Symmetrical peaks and good column efficiency can be obtained only if the adsorbents used have a homogeneous surface. When the surface of an adsorbent is heterogeneous, the elution bands become asymmetrical. Giddings [23] and Villermaux [24] have studied this phenomenon. They studied band profiles in cases where there were two different sites of adsorption (one type of site with a rather low adsorption energy, covering most of the surface, and the other one with a large energy, but covering a very small part of the surface). The band profile is then mostly Gaussian, but with a thin, long tail extending to a very long retention time and corresponding to the molecules desorbing slowly from saturated high energy sites. Methods of modified gas-solid chromatography made it possible to improve the homogeneity of the adsorbent surface using the so-called gas-adsorption layer chromatography or heavy carrier gases (see Chapter 5).

In some cases it is reasonable to use adsorbing carrier gases or those containing adsorbing component, thus decreasing retention time (and ca-

pacity factor). For example [25], when alkanes are eluted on Porasil C (50–100 m^2/g), using carbon dioxide as carrier gas at 80 °C, the logarithm of the column capacity factor is observed to decrease linearly with increasing average pressure. A considerable decrease of the column capacity factor

Table 3-1
Sorbate-sorbent interactions in chromatography [19].

Type of sorbate and adsorbent in chromatography	Non-specific interactions		Specific interactions		
	Dispersive interactions	Electrostatic induced interactions	Electrostatic orientated interactions	Hydrogen bond	Donor-acceptor complex (charge-transfer complex)
1. Chromatography of non-polar molecules on non-polar adsorbents	*				
2. Chromatography of non-polar molecules on polar adsorbents and chromatography of polar molecules on non-polar adsorbents	*	*			
3. Chromatography of polar molecules on polar adsorbents	*	*	*		
4. Chromatography of basic organic compounds on hydroxylic surfaces	*	*	*	*	
5. Chromatography of compounds forming charge transfer complex between corresponded functional groups of adsorbate and surface	*	*	*	*	*

Table 3-2
Kiselev's classification of adsorbents [19, 20].

Type of adsorbent	Nature of adsorbent surface	Examples
I	Surface of adsorbent is non-specific. It contains neither polar functional groups nor ions.	Graphitized carbon black, boron nitride, hydrocarbon polymers (e.g. polyethylene). Water is eluted close to methane.
II	Surface of adsorbent has polar groups (like hydroxyls) or small localized cations while the negative charge is distributed over a much larger volume, thus strong local electric fields appear near the surface.	The zeolites, on the surface of which small exchangeable cations carry the positive charge, while the negative charge is spread over the large aluminate ions in zeolite structure. These adsorbents have specific interactions with molecules having atoms, atomic groups or bonds on which the electronic density is highly concentrated (e.g. alcohols, ethers, ketones, amines, nitriles, thiols and so on).
III	Surface adsorbents have localized negative charges carried by isolated atoms of oxygen (ethers), nitrogen (nitriles), by carbonyl groups, by aromatic π-orbitals or by small localized exchangeable anions.	Graphitized carbon black with a monomolecular layer of a polar polymer (e.g. polyglycol or copper phthalocyanin) or, for example, silica with chemically bonded polar groups. These adsorbents may give strong selective interactions with alcohols and amines.

(30–40%) is measured when the inlet pressure is increased from 1.3 atm to 5.1 atm [25].

We have just the same situation in capillary gas-solid chromatography [26]. The replacement of a light carrier gas by a heavy one leads to dynamic modification of the sorbent surface, to the decrease of distribution coefficients in the solid-gas system, and, consequently, to the decrease of retention time. Table 3-3 contains data on capacity coefficient dependence on carrier gas nature using columns with an alumina layer (Chrompack, 50 m ×

0.32 mm, 100 °C). As can de seen from Table 3-3 capacity coefficients of hydrocarbons in helium and nitrogen are practically the same, but in the case of carbon dioxide they are noticeably lower. Figure 3-1 [26] shows chromatograms for some hydrocarbons separated on an alumina column using helium and carbon dioxide as carrier gases. As can be seen from adduced data, retention time, especially in the case of heavy hydrocarbons, decreases when the heavy carrier gas, carbon dioxide, is used.

The main retention parameter characterizing separation of two compounds is the relative retention (α) or the retention index (I). The relative retention is:

$$\alpha = t'_{R2}/t'_{R1} = k_2/k_1 = V'_{R2}/V'_{R1} \qquad (3\text{-}5)$$

where t'_{R1} and t'_{R2} are adjusted retention times of compounds 1 and 2, respectively ($t'_R = t_R - t_M$, t_M is mobile phase hold-up time); k_1 and k_2 are capacity factors of compounds 1 and 2, respectively ($k = [(t_R - t_M)/t_M] = t'_R/t_M$); V'_{R1} and V'_{R2} are adjusted retention volumes of compounds 1 and 2, respectively, α depends on the stationary phase used and is a function of temperature. α is also the separation factor.

Table 3-3
Dependence of capacity coefficient on carrier gas nature [26].

Carrier gas	Capacity factor of sorbate		
	propane	isobutane	n-butane
Helium	0.17	0.52	0.59
Nitrogen	0.18	0.53	0.60
Carbon dioxide	0.13	0.38	0.42

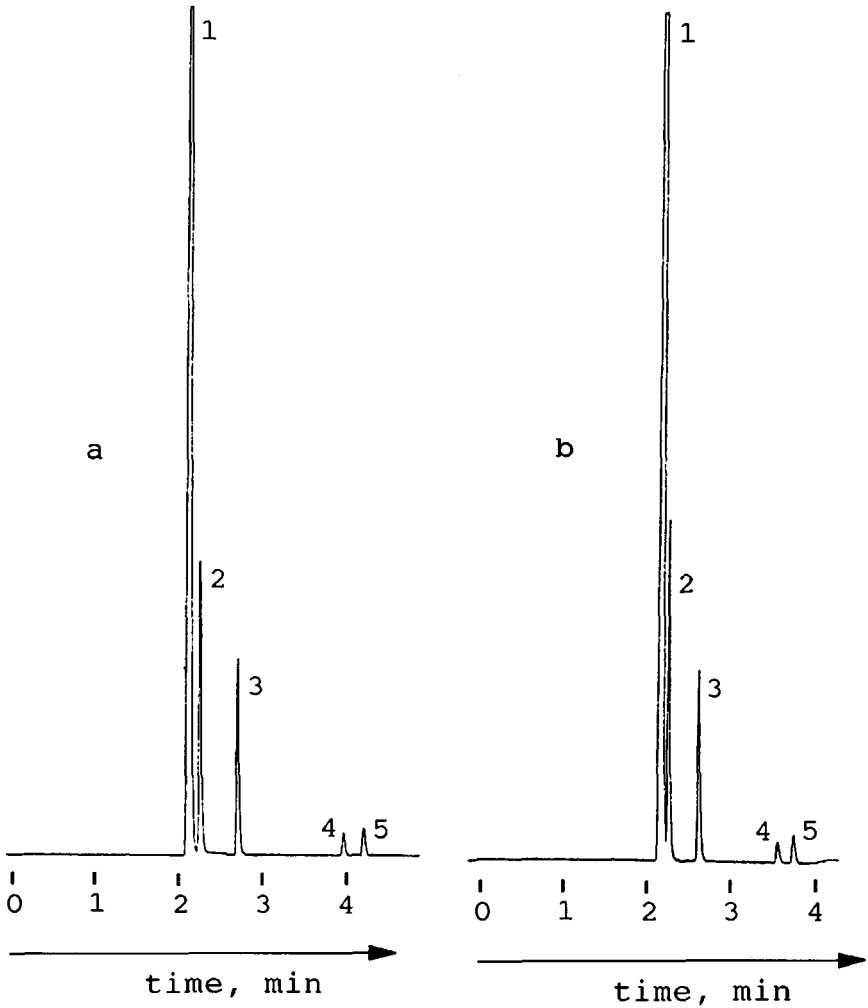

Fig. 3-1 Chromatograms for some hydrocarbons separated on an alumina capillary column using helium (a) and carbon dioxide (b) as carrier gases [26].

Fused-silica capillary column (Chrompack, the Netherlands), 50 m x 0.32 mm i.d., adsorbent Al_2O_3/KCl, temperature 100 °C. Peaks: 1 — methane, 2 — ethane, 3 — propane, 4 — isobutane, 5 — n-butane.

The retention index is:

$$I_i = 100z + 100\frac{\log(t'_i/t'_z)}{\log(t'_{z+1}/t'_z)} \qquad (3\text{-}6)$$

where t'_i is the adjusted retention time of the compound of interest, t'_z and t'_{z+1} are the adjusted retention times of normal alkanes with z and (z + 1) carbon atoms in the molecule, respectively. The retention index I_i is the most important retention parameter in practical gas-liquid chromatography, but in gas-solid chromatography this retention system is not often used.

It is interesting to note that the retention presentation systems know today in chromatography are actually a particular case of equation (3-7) [27]:

$$R_i = G[F + M\frac{f(t'_{R_i}) - f(t'_{R_m})}{f(t'_{R_g}) - f(t'_{R_m})}] \qquad (3\text{-}7)$$

where G, F and M are constants for a given system of retention values, and t'_{R_i}, t'_{R_m} and t'_{R_g} are adjusted retention times for compounds i, m and g, where m and g are known compounds.

The system of retention indices is also used for characterization of adsorbent selectivity (see Table 3-4). For example, Table 3-4 [28] provides values for McReynolds constants [29] at 200 °C using Chromasorb 106 as the reference adsorbent. The data in parentheses were obtained after aging the columns for 22 days. Polarity of polymer adsorbent changes greatly as follows from the data of Table 3-4.

3.2 Chromatographic Zone Broadening in ALOT Columns

Broadening of the chromatographic zones during separation depends on the type of carrier gas flow in the column, the diffusion characteristics of the compounds to be separated in the mobile and stationary phases, the interphase mass exchange rate and characteristics of the adsorbent layer used.

Table 3-4
McReynolds' selectivity constants for porous polymer beads[a] [28].

		Benzene	Butanol	2-Penta-none	Nitropro-pane	Pyridine
Porapak	N	50	108	83	126	98
	P	130	99	85	150	(176)
	Q	7	10	4	3	196
	R	32	77	46	74	15
	S	18	53	33	–[b]	69
	T	114	183	153	293	41
		(162)	(245)	(189)	(318)	187
						(273)
Chromosorb	101	107	76	66	122	144
		(100)			(114)	(138)
	102	32	25	21	40	50
	103	147	160	122	–[b]	212
		(140)	(167)			(203)
	104	246	330	314	467	405
					(476)	(415)
	105	31	62	45	72	74
			(71)	(55)		(98)
	106	0	0	0	0	0
	107	54	139	106	181	140
		(92)	(168)	(140)	(214)	(172)
	108	132	215	161	265	231
		(155)	(235)	(182)	(292)	(262)

a Values in parentheses refer to the value measured after aging the column for 22 days at 200 °C.

b Reacts with the phase, giving multiple or very broad peaks.

We have already mentioned that, even in his early work, Golay proposed [30–32] that in order to increase the column capacity ratio one should deposit a stationary liquid phase layer not onto the smooth inner walls of capillary columns but rather onto a porous layer of the solid carrier located on capillary walls. If this is done, the stationary liquid phase film thickness on the separate solid support particles can remain equal to that in the case of a smooth capillary wall (and, hence, resistance mass transfer of liquid phase layer remains practically unchanged), but the amount of stationary liquid phase per unit column length significantly

Golay's equation of HETP

increases due to the associated increase in the inside capillary surface. It results in a decreasing $\beta = V_g/V_l$ phase ratio (V_g is the volume of the gas phase in the column and V_l is the stationary liquid or solid phase volume in the column) and in an increasing capacity factor k and, hence, in better separation.

To describe the broadening process in open tubular columns with a porous layer on the walls, Golay theoretically obtained the following equation:

$$H = \frac{2D_g}{u} + \left[\frac{1 + 6k + 11k^2}{(1+k)^2} + \frac{(8+32k)a_2}{(1+k)^2} + \right. \\ \left. + \frac{8k^2}{(1+k)^2}\frac{a_1^2}{a_2}\right]\frac{r^2u}{24D_g} + \left[\frac{k^3}{6(1+k)^2}\frac{1+2a_2}{F}\right]\frac{r^2u}{K_D^2 D_1} \quad (3\text{-}8)$$

where H is the height equivalent to a theoretical plate (HETP), D_g and D_1 are the diffusion coefficients of the chromatographed compound in the gas and liquid phases, respectively, u is the linear velocity of the carrier gas, k is the capacity factor of the chromatographed compound, K_D is the coefficient of the compound distribution between the stationary and mobile phases, r is the inside radius of the capillary column, F is the ratio of the liquid phase to capillary wall surface, $a_1 = d_t/r$, where d_t is the average tortuous path length in the porous layer on the inside column walls, and $a_2 = d_g/r$, where d_g is the effective thickness of the gas layer in the porous layer on the inner column walls.

As follows from equation (3-8), the capillary column efficiency should grow with increasing porosity of the wall layer (H decreases with F). In other words, the idea of a capillary column with a solid support porous layer had been exploited as early as at the stage of the derivation of this equation, as pointed out by Ettre [33].

On our opinion, equation (3-8) can be used for adsorption capillary columns, if F is the ratio of the solid phase volume to the surface of the

capillary, D_i is the diffusion coefficient of the compound in the solid adsorbent layer.

An equation describing the dependence of HETP on the linear carrier gas velocity for gas-solid chromatography was also proposed by Giddings [34, 35]. The first terms of Giddings' equation are virtually identical to the first terms of Golay's equation. The main differences in Giddings' equation are that, first, it contains a term describing the mass transfer resistance in the adsorption layer on the inside capillary walls and, secondly, it includes the effect of the carrier gas pressure drop in the column on the broadening effect factor.

Giddings' equation of HETP

Giddings' equation can be written as follows:

$$H = \frac{2D_g}{u_0} + \frac{(1 + 6k + 11k^2)}{24\,(1 + k)^2} \cdot \frac{r^2 u}{D_g} f_1 + \\ + \frac{8}{a_k u_m}\left[\frac{k}{k+1}\right]^2 \frac{V_g}{S} f_n u_0 f_2 \qquad (3\text{–}9)$$

$$u_0 = L/(t_m f_2) \qquad (3\text{–}10)$$

$$f_1 = \frac{9}{8}\frac{(P^4 - 1)(P^2 - 1)}{(p^3 - 1)} \qquad (3\text{–}11)$$

$$f_2 = \frac{3}{2}\frac{(P^2 - 1)}{(P^3 - 1)} \qquad (3\text{–}12)$$

where $P = P_i/P_0$ (P_i and P_0 are the pressure of the carrier gas at the column inlet and outlet, respectively), a_k is the accommodation coefficient, u_m is the average velocity of the molecules of the chromatographed compound in the gas phase, V_g is the volume of the gas phase in the column, S is the total surface of the adsorbed layer in the column, and f_n is the adsorbent heterogeneity factor.

Let us write Giddings' equation for HETP in the capillary column in a different form, assuming that

the effect of pressure drop of the chromatographic zone broadening can be neglected, i.e., $f_2 \approx 1$ and $f_1/f_2 \approx 1$:

$$H = 2\frac{D_g}{u} + \left[\frac{C_{gp}}{D_g} + C_A\right] u = 2\frac{D_g}{u} + (C_g + C_A)u \qquad (3\text{–}13)$$

or

$$H = 2\frac{D_g}{u} + Cu \qquad (3\text{–}14)$$

where

$$C_{gp} = \left[\frac{1 + 6k + 11k^2}{24(1 + k)^2}\right] r^2 \qquad (3\text{-}15)$$

$$C_A = \frac{8}{a_k u_m}\frac{V_g}{S} f_n \left[\frac{k}{1 + k}\right]^2 \qquad (3\text{-}16)$$

$$C_g = C_{gp}/D_g \qquad (3\text{-}17)$$

$$C = C_g + C_A \qquad (3\text{-}18)$$

To test the compliance of equation (3-14) with experimental data, one can conveniently write it as follows:

$$Hu = 2D_g + Cu^2 \qquad (3\text{-}19)$$

D_g values can be estimated with the aid of the Fuller-Schettler-Giddings equation [36] or by some other calculation method (see, for example, [37]).

Estimation of accord between theory and observation

The C values for the chromatographed compounds, as found for two carrier gases on capillary adsorption columns, make it possible to determine separately mass transfer resistance coefficients for the gas phase (C_g) and for the adsorption layer (C_A). These methods were developed earlier for packed columns by Perrett and Purnell [38].

De Nijs and de Zeeuw [39] estimated the coefficients for 1,3-butadiene in a capillary adsorption (aluminum oxide) column. They used Giddings' equation (3-19). The coefficients were found to be

$C = C_{gp}/D_g$. The C value was also determined. With helium serving as the carrier gas, C_g (butadiene) = $1.3 \cdot 10^{-4}$ s, whereas with nitrogen, C_g (butadiene) = $4.6 \cdot 10^{-4}$ s. The same coefficient for the adsorption layer was found: $C_A = 1.8 \cdot 10^{-4}$ s. Thus, according to paper [39], C_g and C_A represent quantities of the same order.

For comparison we shall give similar coefficients for tridecane on fused-silica capillary column (24.7 m × 0.55 mm) with stationary liquid phase layer (dimethylsilicone CP-Sil5-CB) on its inner walls at 150 °C. Mass transfer resistance coefficients are as follows:

in the liquid phase, $C_g = 4.1 \cdot 10^{-4}$ s;

in the gas phase,

C_g (tridecane, helium) = $2.8 \cdot 10^{-4}$ s and

C_g (tridecane, nitrogen) = $10.6 \cdot 10^{-4}$ s.

These data for gas-liquid capillary chromatography were obtained by Cramers and co-workers [40]. Note that mass transfer resistance coefficients for gas-solid and gas-liquid types of capillary chromatography are of the same order (see Table 3-5).

Table 3-5
Coefficients of mass transfer resistance for adsorption layer columns (using Golay's equation: $H = B/u + (C_g + C_s)/u$).

Type of capillary gas chromatographic column	Analyzed compound	Mass transfer coefficients ($C = C_g + C_s$), s			C_g/C_s (He)	C_A/C_l
		in the gas phase		in the stationary phase		
		helium	nitrogen			
Gas-solid (Al_2O_3) [39]	1,3-butadiene	1.3×10^{-4}	4.6×10^{-4}	$C_A = 1.8 \times 10^{-4}$	0.7	
Gas-liquid (dimethylsilicone)-solid [40]	tridecane	2.8×10^{-4}	10.6×10^{-4}	$C_l = 4.1 \times 10^{-4}$	0.7	0.4

Table 3-6
Coefficients of Golay's equation ($H = B/U + CU$) [26]

Carrier gas	Compounds											
	Ethane				Propane				n-Butane			
	D_g (calc) cm^2/s	B (calc) cm^2/s	B (exp) cm^2/s	$C \cdot 10^4$ (exp) s	D_g (calc) cm^2/s	B (calc) cm^2/s	B (exp) cm^2/s	$C \cdot 10^4$ (exp) s	D_g (calc) cm^2/s	B (calc) cm^2/s	B (exp) cm^2/s	$C \cdot 10^4$ (exp) s
Helium	0.68	1.4	1.2 (0.07)	2.4 (0.2)	0.56	1.11	0.98 (0.04)	3.0 (0.3)	0.43	0.86	0.80 (0.04)	7.2 (1.04)
Nitrogen	0.22	0.44	0.45 (0.33)	6.8 (o.5)	0.17	0.34	0.36 (0.01)	8.6 (0.5)	—	—	—	—
Carbon dioxide	0.175	0.35	0.36 (0.02)	8.0 (0.7)	0.14	0.27	0.29 (0.01)	11.0 (1.0)	0.11	0.22	0.22 (0.01)	24.0 (2.0)

B = $2D_g$, D_g(calc) is calculated using Fuller-Schettler-Giddings' equation.
Standard deviations of B(exp) and $C \cdot 10^4$(exp) are given in parentheses.

The results of determining the coefficients of equation (3-19) are presented in Table 3-6 [26]. These data were obtained by Berezkin and Volkov [26] for a fused-silica column manufactured by Chrompack (Middelburg, The Netherlands); inner walls of the column are coated with adsorption layer composed of aluminum oxide and potassium chloride.

When studying the relation $H = f(u)$, one should consider the following factors. First, note that the experimental data for broadening of the hydrocarbon gases (methane, propane, and n-butane peaks) in two carrier gases such as nitrogen and helium are satisfactory described by linear equation (3-19). Secondly, the experimental diffusion coefficients for the analyzed gases, found in accordance with equation (3-19) and calculated by the equation proposed by Fuller, Schettler and Giddings [36], fit well.

Thus equation (3-19) fits the experimental data for open capillary adsorption columns well in terms of both the functional dependence and the diffusion coefficients of the compounds in the gas phase,

as determined from the experimental chromatographic data. The calculated coefficients for the chromatographed compounds were obtained by the Fuller-Schettler-Giddings equation [36]. Thus the diffusion coefficient for butane in helium as determined by simplified equation (3-19) was found to be 0.40 cm^2/s whereas that calculated according to Fuller-Schettler-Giddings was 0.43 cm^2/s (see Table 3-6).

Note that earlier Goretti, Liberti and Nota [41] reported agreement between the experimental data and equations (3-19) for glass capillary columns having a graphitized carbon black layer and found the values of mass transfer coefficients. These values are listed in Table 3-7 [41]. It follows from these data that the most important contribution to the broadening of the chromatographed compounds is made by a term describing transfer resistance.

The *B* term in capillary adsorption columns is smaller than in packed capillary columns and the minimum $HETP_{min}$ is lower for capillary columns.

Table 3-7
Data in agreement with Golay's equation for ALOT columns [41].

No.	Column			Compounds	*k*	B, cm^2/s	$C \cdot 10^3$, s	$HETP_{min}$, mm
	Length × diameter m×mm	Graphitized carbon black	Layer thickness, μm					
1	9.6 × 0.2	MT_2 7 m^2/g	100	isobutane	1.00	0.17	5.7	—
				n-butane	1.54	0.13	6.0	1.41
2	11.0 × 0.25	MT_2 7 m^2/g	65	isobutane	1.97	0.17	8.3	—
				n-butane	3.02	0.14	10.0	1.26
3	11.0 × 0.3	MT_2 7 m^2/g	45	isobutane	1.57	0.17	6.4	—
				n-butane	2.42	0.15	7.1	1.64
4	11.0 × 0.2	FT_2 15 m^2/g	100	isobutane	2.05	0.17	4.3	—
				n-butane	3.14	0.13	4.5	0.91

It is interesting to compare the order of the C_A value from Giddings' theory and corresponding experimental data. Let us estimate the value C_A in Giddings' equation (3-16). The mean velocity of the analyte molecules is approximately equal to the speed of sound (for example, for nitrogen this value is $\approx 3 \cdot 10^4$ cm/s). Thus if we assume that $u_m \approx 3 \cdot 10^4$ cm/s, $d_k \approx 0.1$,

$$8\left(\frac{k}{k+1}\right)^2 = 6, \text{ then } C_A \approx 2 \cdot 10^{-3}\frac{V_g}{S}.$$

Note, $V_g = 100 \text{ cm} \cdot 3 \cdot 10^{-3} \text{ cm}^2 = 0.3 \text{ cm}^3$,

$S = 10^{-4} g \cdot 10 \cdot 10^4 \text{ cm}^2/\text{g} = 10.0 \text{ cm}^2$,

and $V_g/S = (0.3 \text{ cm}^3/10.0 \text{ cm}^2) \approx 3 \cdot 10^{-2}$ cm.

Hence $C_A \approx 10^{-4}$ s. This value corresponds to the data in Tables 3-5 and 3-6.

Recently Ugrozov [42] suggested the following equation for describing HETP for open capillary column with layer of adsorbent (for $(\delta/r) << 1$, where δ is a thickness of porous adsorbent layer):

$$H = \frac{2D_g}{u} + \frac{(11k^2 + 6k + 1)}{24(k+1)^2} \cdot \frac{r^2}{D_g}u + \frac{1}{3}\left(\frac{k}{k+1}\right)^2 \frac{\delta r}{D_p \cdot \chi}u \qquad (3\text{-}20)$$

where D_p is the coefficient of analyte diffusion in porous adsorbent layer (note that $D_p \neq D_g$, as a rule $D_p < D_g$), $\chi = V_{pq}/V_p$ (V_{pq} is the volume of pores, V_p is volume of all porous layer). In estimating the last term of equation (3-20), we can a value equal to 10^{-3}–10^{-4} s. This is in rough agreement with the results given in Tables 3-5 and 3-6.

Note that the values of HETP decrease, first with decrease of the radius of capillary column and, secondly, with increase of adsorption layer porosity.

3.3 Dependence of Column Efficiency on Sample Size

At present, gas chromatographic analysis of impurities is an important area of gas chromatography because great importance attaches to trace analysis in many practical activities [17, 43–45].

One important characteristic of a column is the dependence of the efficiency (broadening of chromatographic zone) on sample size. The size or the quantity of sample introduced into the chromatographic column has a considerable influence on the resolution and other chromatographic characteristics (see, for example, [45–70]). This characteristic is essential to the application of chromatographic data for physicochemical and analytical measurement. When comparing the efficiency of different columns it is reasonable to use the ultimate values for the height equivalent to a theoretical plate (HETP) at a zero sample size (for a given detection system and in a given sensitivity range). It is important for impurities analysis to know the dependence of HETP on sample size. It is also important to take into consideration the possibility of using a column without a splitter and application of traditional methods of sample injection into capillary column. Thus a series of investigations are devoted to the discussion of the dependence of chromatographic zone broadening on sample size.

A quantitative study was performed on the relationship between the height equivalent to a theoretical plate (HETP or H) values and the sample size (W). Such a general equation has been proposed elsewhere [67]. Earlier it appeared to be in good agreement with the experimental data for open capillary columns with a stationary liquid phase layer (absorbent) and for packed capillary columns [69].

Equation of HETP vs. sample size

The dependence of column efficiency on sample size for capillary column with aluminum oxide layer on its inner walls has been studied by Berezkin and Volkov [26]. The initial experimental data were processed by the following equation:

$$\sqrt{H} = \sqrt{H_0} + \lambda W \qquad (3\text{-}21)$$

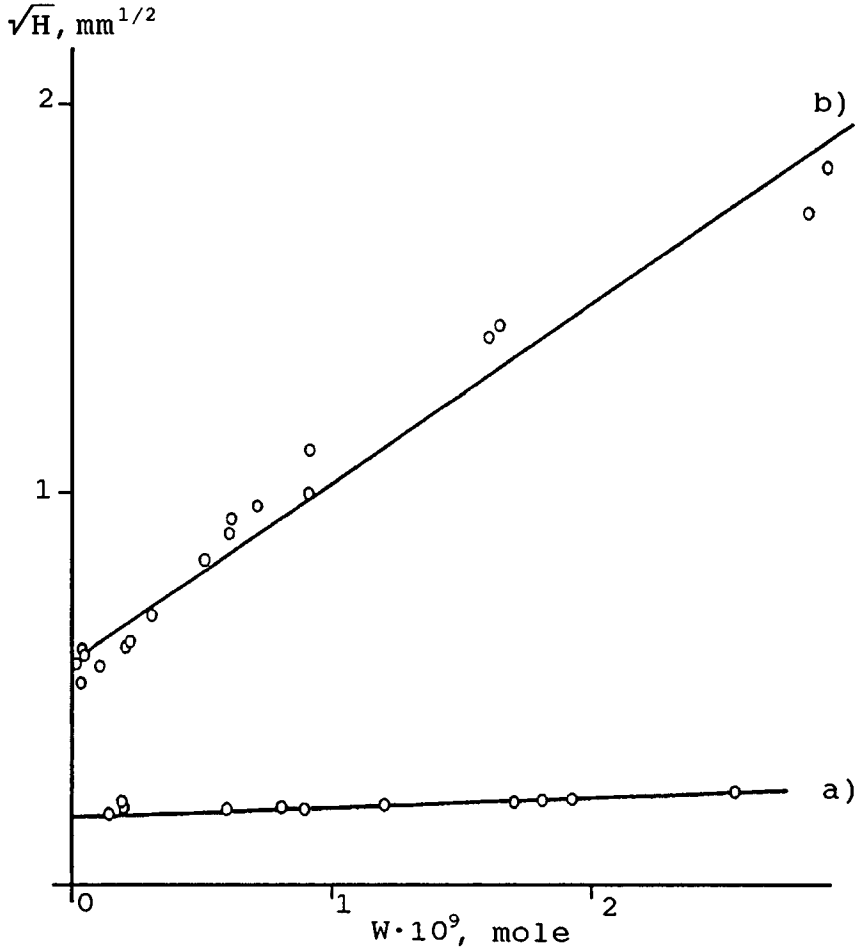

Fig. 3-2 Efficiency characteristic $\sqrt{H}$ vs. sample size for fused silica capillary micro-packed columns (a) and open tubular columns (b) [67].

a) Fused silica micro-packed column: 10 m × 0.2 mm, sorbent: Silasorb 600 (LC), 7.5 μm, chromatographic substance: n-pentane (k = 3.5), temperature: 95°C, carrier gas: nitrogen, inlet pressure, 15.6 atm.

b) Glass capillary column 37 m × 0.23 mm, stationary liquid phase: Apiezon L, sample compound: dodecane (k = 3.3), temperature: 100 °C, carrier gas: nitrogen.

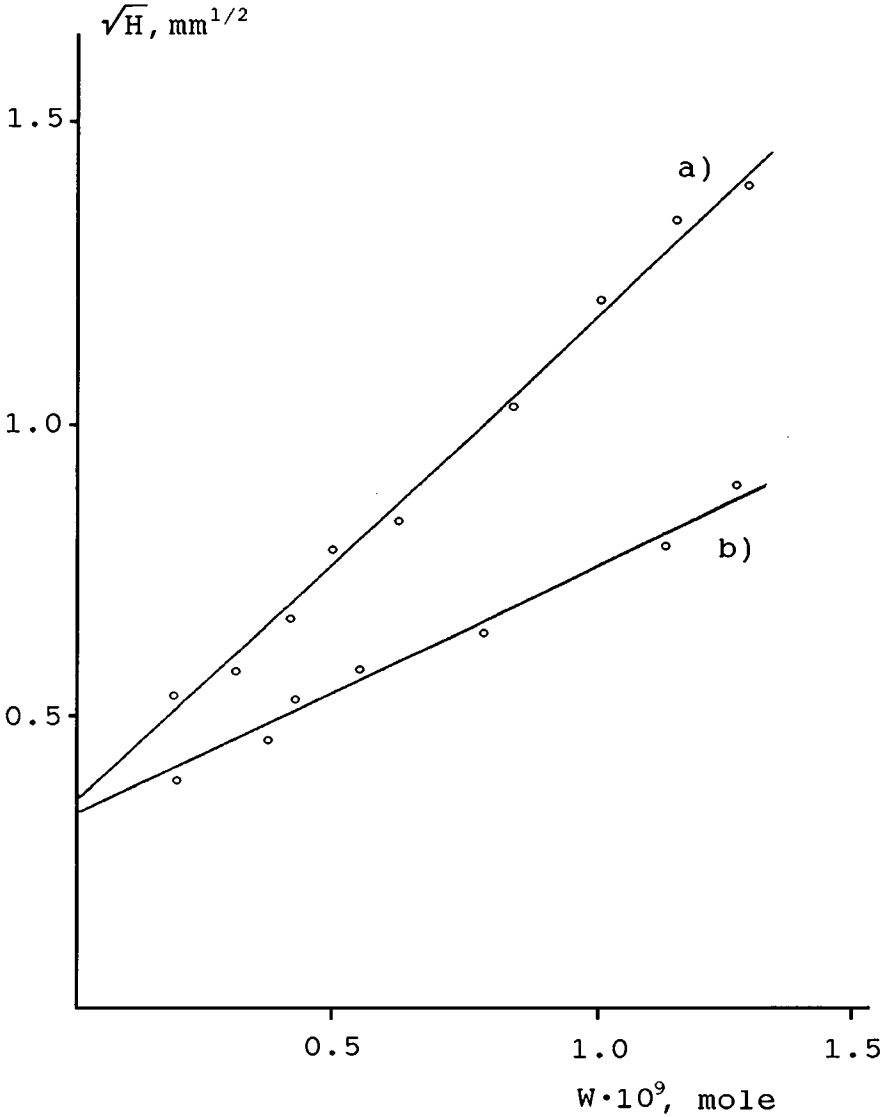

Fig. 3-3 Efficiency characteristic $\sqrt{H}$ vs. sample size for adsorption capillary column with aluminum oxide layer on the inner walls [26], splitless (a) and split-type (b) sample injection technique.

Fused-silica column (Chrompack, the Netherlands), 50 m × 0.32 mm with aluminum oxide, column temperature 100 °C, flame ionization detector, analyte n-butane.

where W is the sample size, H_0 is the limiting HETP value as the sample size tends to zero, and λ is a constant depending on the system studied. Note that it has earlier been shown (see Fig. 3-2 [67]) that the equation (3-21) is applicable not only to conventional packed columns [66] but also to fused silica capillary micro-packed columns and conventional open tubular columns [67]. Equation (3-21) allows one to determine both the minimum possible H value for a given chromatographic system (H_0) and the H value corresponding to a particular W value.

Fig. 3-3 shows the H-W dependence according to equation (3-21) for the same adsorption capillary column but with the use of different sample injection techniques, viz., split-type (b) and splitless (a). It is evident that the dependence of the HETP value on sample size in these coordinates is linear, which is corroborated by equation (3-21). When a splitter is used, the efficiency shows a market increase (the H value decreases).

Interestingly, the H_0 value is virtually the same irrespective of sample injection technique (split or splitless). This characteristic is an additional test of equation (3-21).

The results obtained suggest that an open capillary column with an adsorption layer on the inner column walls can be successfully used for gas chromatography without a splitter although with a noticeable efficiency drop. Using such a system permits a straightforward replacement of ordinary packed adsorption columns by far more efficient capillary adsorption columns in practically any gas chromatograph.

The possibility of using open capillary adsorption columns in gas chromatography without a splitter becomes obvious considering that the amount of adsorbent in such columns and its capacity per unit length are rather large. With respect to this characteristic capillary adsorption columns are very much like wide open capillary columns with a thick

layer of immobilized liquid stationary phase. At the same time, they have the advantage that the rate of the mass exchange between the loose solid

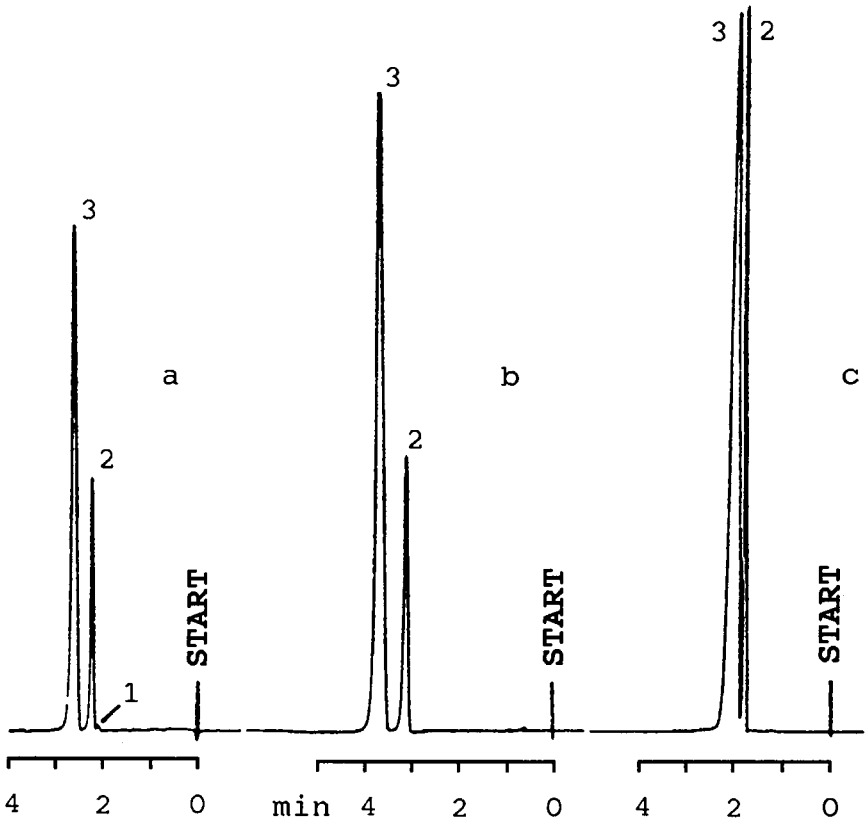

Fig. 3-4 Separation of hydrogen (1), oxygen (2) and nitrogen (3) [70].

Copper capillary column 23 m × 1 mm,
adsorbent: molecular sieves 5A, detector volume: 0.012 cm^3,
temperature: 26 °C, carrier gas: helium.

Sample sizes and carrier gas flow rates:

(a) 10 µl, 12 cm^3/min; (b) 10 µl, 1.5 cm^3/min; (c) 1 µl, 12 cm^3/min.

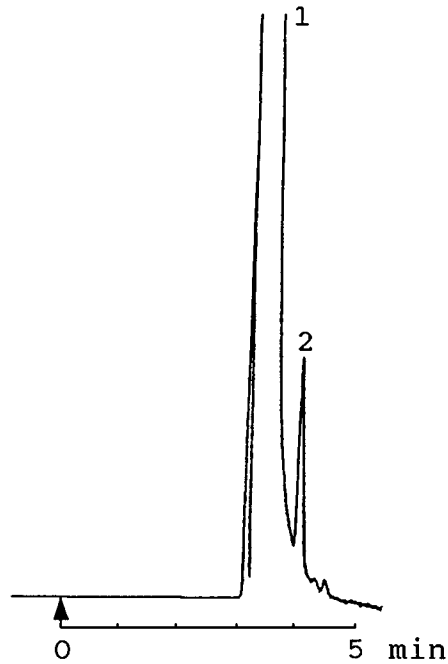

Fig. 3-5 Chromatographic determination of ethyne (10 ppm) in ethene [71].

Fused silica aluminum oxide ALOT column 30 m × 0.32 mm; oven temperature 60 °C; carrier gas: nitrogen, 0.5 bar; detector: FID; sample: 50 µl, splitless injection; aqualizer $CuSO_4 \cdot 5H_2O$.

Peaks: 1 — ethene, 2 — ethyne.

adsorption-active layer and the moving gas phase is higher than in the case of a thick layer of immobilized stationary liquid phase.

An example of the separation of a methane–isobutane–n-butane mixture with splitless injection of 0.5 ml of the sample into a glass capillary column with a silica layer is given in paper [26]. The analysis time is less than 1 min. Incidentally, splitless injection of a sample was already used in an earlier period of adsorption capillary column development (see, for example, Fig. 3-4 [70]).

De Nijs [7] showed experimentally the possibility of using ALOT column with aluminum oxide for trace determination (see, for example, Fig. 3-5, note: splitless injection).

In our opinion, it is possible to use adsorption capillary columns without a splitter to solve many practical problems.

3.4. Resolution of Analyzed Compounds

The principal aim of analytical elution chromatography is separation of an analyzed mixture into separate components. The degree of separation of two components is characterized, as a rule, by resolution (see, e.g., [17, 45]). Resolution (separation criterion) R is determined as the ratio of the distance between the centers of the chromatographic zones of the compounds separated to the mean width of the zones of these compounds:

Determination of resolution R

$$R_s = \frac{t_c - t_f}{1/2(\mu_c + \mu_f)} \qquad (3\text{–}22)$$

where t_c and t_f are retention times of components e and f, respectively, and μ_c and μ_f are the widths of the chromatographic zones of components e and f, respectively.

The equation reflecting the relationship of the resolution (separation criterion) and equilibrium and kinetic characteristics of the chromatographic process was derived by Purnell and is widely used in analytical practice [72, 73]:

Purnell's resolution equation

$$R_s = \frac{\sqrt{N}}{4} \frac{\alpha - 1}{\alpha} \frac{k}{k - 1} \qquad (3\text{-}23)$$

where N is the number of theoretical plates, α is the separation factor equal to the ratio of corrected retention times or net retention volumes of components e and f, $\alpha = V_{N_c}/V_{N_f}$ and k is the capacity factor of the second component e.

Thus resolution in chromatography is a function of three factors: selectivity (S), efficiency (E), and capacity (C):

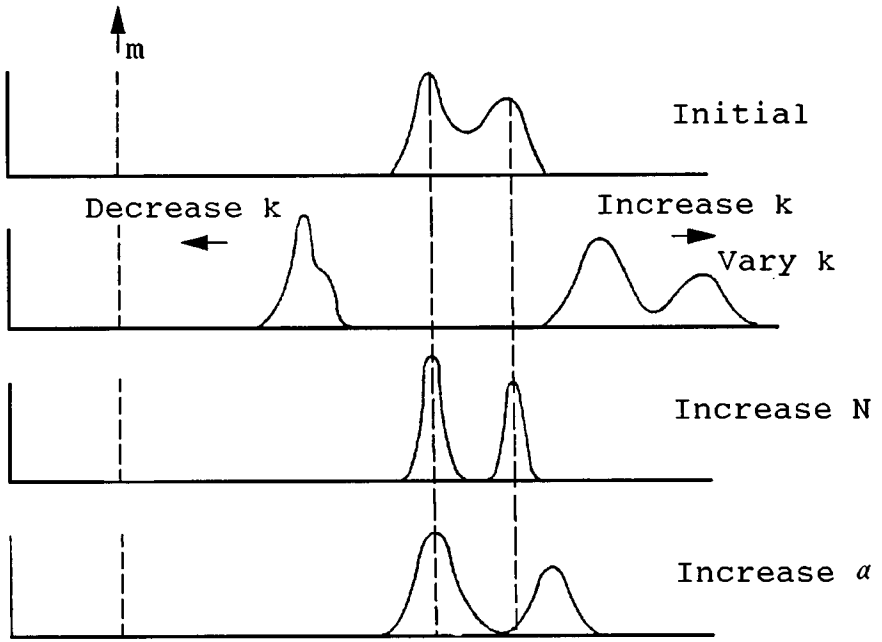

Fig. 3-6 Effect of changes in *k*, *N* and α on *R* [75].

$$R_s = SEC \qquad (3\text{-}24)$$

where

$$S = \frac{\alpha - 1}{\alpha}, \quad E = \frac{\sqrt{N}}{4}, \quad C = \frac{k}{k+1}$$

In gas-liquid-solid chromatography, in contrast to its idealized version, gas-liquid chromatography, a significant effect on the chromatographic process is exerted by adsorptional interactions of the compounds being separated with interphase surfaces of the gas-SLP and SLP-solid adsorption (SLP is stationary liquid phase) [74]. Adsorptional interactions of the separated compounds affect all factors determining the magnitude of separation: selectivity, efficiency and capacity. However, adsorption has a particularly specific and prominent effect on the selectivity of chromatographic separation.

Effect of S, E and C on resolution

The effect of varying terms *S*, *E* and *C* on resolution is illustrated in Fig. 3-6 [75]. Separation is known to be largely controlled by capillary column selectivity and efficiency. Especially selectivity can be increased by using the so-called selective phases based on the specific physical-chemical or specific geometrical interactions between the chromatographed compounds and the adsorbent. Application of ALOT columns shows interesting potential for using selective adsorbents in high efficiency capillary gas chromatography. Resolution will increase with increasing *N*. The overall efficiency of separation can be enhanced by adding "effective used lengths" of capillary columns in circulation schemes. Utilization of such schemes permits realization of an efficiency of about 20 million theoretical plates (see, e.g. [76]).

For low k values resolution increases very rapidly with increasing k. At large k values the term $C \rightarrow 1$ and a further k increase will not improve resolution. Thus, the optimum values of k lie in the range $1 < k < 10$. The minimum analysis time for open tubular columns is achieved under the conditions where k is about 1–2. As a rule, capacity is not a critical parameter in ALOT columns.

Separation is also characterized by separation number (*SN*) or Trennzahl (*TZ*). The latter is defined as the maximum number of peaks of equal heights one can place between the peaks of two reference compounds assuming a resolution of 1.0 between each of these peaks [77].

Separation number

Separation number is defined as the number of component peaks which can be placed between the peaks of two consecutive homologous standards with z and $(z + 1)$ carbon atoms and can be separated with resolution of $R = 1.77$,

$$TZ = SN = \frac{t_R(z+1) - t_R(z)}{w_h(z) + w_h(z+1)} - 1 \qquad (3\text{-}25)$$

where t_R is retention time, w_h is a peak width at half height. *TZ* and *R* are related by following expression:

$$TZ = \frac{(R-1)}{1.77} \tag{3-26}$$

The *SN* of a column is dependent on the nature of the stationary phase, on the column length, temperature and carrier gas flow rate. The separation number is the only parameter of column efficiency which can be determined under temperature programming conditions [50].

Equation (3-23) can be arranged for two peaks (located close to each other in the chromatogram) to predict the number of theoretical plates required to give the separation [78, 79]:

$$N_r = 16R_s^2\left(\frac{\alpha}{\alpha-1}\right)^2\left(\frac{k+1}{k}\right)^2 \tag{3-27}$$

or

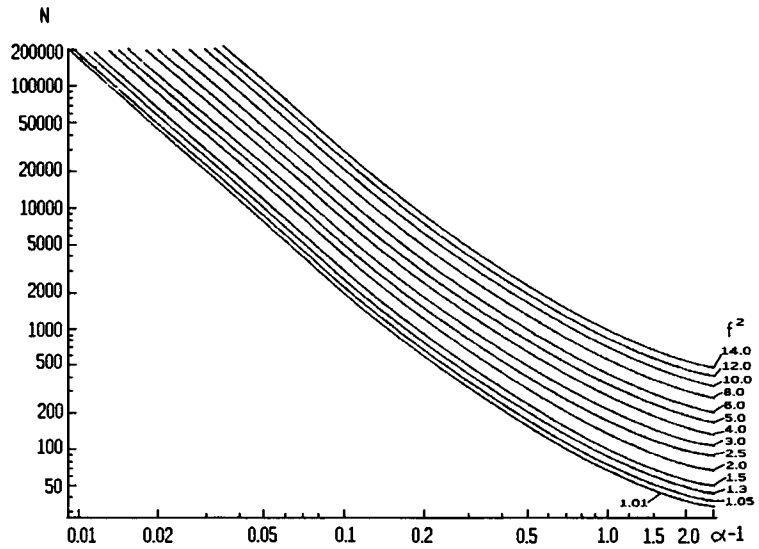

Fig. 3-7 Graphic determination of the number of theoretical plates, *N*, required for the separation (*R* = 1.0) of a pair of compounds, depending on the sorbent selectivity α and f^2 parameters, the values being controlled by the capacity factor *k* [79].

$$N_r = 16R_s^2\left(\frac{\alpha}{\alpha - 1}\right)^2 \cdot f^2 \tag{3-28}$$

Note

$$f^2 = \left(\frac{k+1}{k}\right)^2 = (1 + \frac{\beta}{K_D})^2 \tag{3-29}$$

where K_D is the distribution coefficient of the compound between stationary solid and mobile gas phases, and β is the phase ratio, i.e. the ratio of the volume of the mobile phase to that of the stationary one.

In practice a chromatographer usually has to consider the following two column characteristics: column efficiency and selectivity of the sorbent used. Such an approach naturally also holds for capillary adsorption columns.

Feasible alternatives can be selected by drawing a plot, from which the number of required theoretical plates and hence column length provided the selectivity and capacity of the adsorbent can be read off.

Graphical display N_r vs. $(\alpha - 1)$

Fig. 3-7 [79] shows the dependence of required plates (N) on the sorbent selectivity (α) for compounds with various capacity factors k. In this plot the role of the capacity factor is expressed by the function f^2. In Fig. 3-7 [79] each f^2 value has a definite dependence $N = 4(x)$, $x = \alpha - 1$.

Now we shall consider practical applications of the plot in Fig. 3-7. Suppose we have to find the required number of theoretical plates for a column with $\beta = 40$ for separating two components with $\alpha_2 = 1.05$ and $K_D = 100$. For these two components $f^2 = 2$. From the point on the x axis corresponding to $\alpha - 1 = 0.05$, we shall draw a vertical line until it intersects a curve corresponding to $f^2 = 2$. The ordinate corresponding to the point of interaction is equal to 16000 theoretical plates. This is exactly

the column efficiency necessary for the desired separation of the compounds.

Many chromatographers have used retention indexes in their papers and it is therefore useful to modify equation (3-27) by using retention indices to characterize the selectivity of a chromatographic system.

Purnell's modified equation of N_r vs. ΔI

Berezkin and Retunsky [80, 81] proposed a modified equation that approximates the Purnell equation (eq. (3-23)) with good accuracy (the relative error being less than 2% for both capillary and packed columns):

$$N_r = 16R^2 \frac{10^4 \log^2 e}{b_z^2(\Delta I)^2} + \frac{10^2 \log e}{b^2(\Delta I)} \qquad (3\text{-}30)$$

where $\Delta I = I_2 - I_1$ is the difference in retention indices of two sorbates, N_r is the effective plate number, e is the base of natural logarithms, $b_z = \log (t'_{z+1}/t'_z)$ and t'_z and $t'_z + 1$ are the adjusted retention times of two members of standard homologous series with carbon chain lengths z and $z + 1$, respectively. Note, that b_z is a coefficient linearly relating the logarithm of the adjusted retention time of a standard to the carbon chain length (z). Berezkin and Retunsky [81] published nomograms for rapid evaluation of the chromatographic conditions required for separation of two (or more) sorbates with known retention indices.

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Chapter 4

Chromatographic Adsorbents

4.1 Carbon Adsorbents

Active carbons are used in chromatography for the separation of inorganic gases and light hydrocarbons (see, for example, [1–8]). Active carbons have a heterogeneous geometric pore structure and chemical structure of the surface active sites. There are chemically and adsorptively active oxygen groups of different kinds on the surface of such adsorbents. As adsorption sites such groups cause a very strong adsorption of molecules capable of specific interactions whereas the geometric heterogeneity of pores leads to a low efficiency of chromatographic columns. The chromatographic characteristics of carbons differ greatly, due mainly to their different production procedures. Recent years have been characterized by a growing interest in carbon adsorbents [9–13].

Graphitized carbon black

Graphitized carbon black is one of the most reproducible of the known carbon adsorbents [4, 6]. However, at temperatures above 300 °C its surface becomes reactive towards oxygen. As result phenols, ketones, quinones, carboxylic groups and free radicals appear on the carbon surface.

Graphitized thermal carbon black (GTCB) was first used by Halasz and Horvath in 1963 [14] as a stationary solid phase in the form of a thin layer on the inner wall of capillary columns. Since then, many general investigations and analytical applications have been reported mainly by Kiselev and co-workers [6, 15–18], Guiochon and co-workers [4, 19, 20], Liberti, Di Corcia, Bruner and co-workers [21–26] and Engewald and co-workers [27–32].

The term carbon black refers to a wide range of products obtained by partial combustion or thermal decomposition of hydrocarbons under controlled

conditions (see, for example, [32]). Their properties depend on the raw material and the processing technology employed. All carbon blacks have a structure similar to that of graphite. However, in carbon black the carbon atoms are two-dimensionally arranged and the parallel layers are randomly oriented. The primary particles of carbon blacks are composed of 10^3 to 10^6 microcrystallites, which consist of about 60 to 120 condensed carbon hexagons per layer and 4 to 5 layers upon one another.

By prolonged heating at 2700–3000 °C in an inert atmosphere carbon blacks are converted into polyhedra having a homogeneous graphite surface.

Hydrogen treatment plays an important role in obtaining sorbents with a homogeneous surface. Hydrogen treatment improves the quality of Carbopack C as an adsorbent for general use, giving possibility of eluting polar compounds even though it is coated with a non-polar liquid phase. Carbopack C, once it has been treated with hydrogen at high temperature (more as 1000 °C) and coated with a liquid phase, yields lower retention times [33].

All carbon atoms in graphitized carbon black have the same electron sp^2-configuration that considerably simplifies the establishment of structure-retention relationships. Two different types of graphitized carbon black (GCB) can be distinguished with

Table 4-1
Types of graphitized carbon black (GCB) [32]

No.	Raw material	GCB	Specific surface, m^2/g	Field of preferred use
1.	Channel acetylene black	Carbopack B Graphon Spherochrom	80–100	Gas analysis, low boiling compounds, trace enrichment
2.	Thermal black	Carbopack C Carbopack F Sterling HT Sterling FT	6–12	Medium boiling compounds, structural and spatial isomers

respect to specific surface and fields of application (see Table 4-1 [32]).

Separation of organic compound isomers

GTCBs have a homogeneous, non-porous small specific surface. The intermolecular forces with the adsorbates belong to the non-specific dispersive type. In contrast to a non-polar liquid stationary phase, where the solute molecules are completely surrounded by the liquid phase molecules, the adsorbate molecules are only capable of interacting with the graphite surface from one side. Thus the adsorption energy is mainly determined by the distance of molecular force centers from the flat graphite plane. Retention strongly depends, therefore, on the geometrical configuration, the shape of the molecules and their arrangement on graphite plane surface, whereas the boiling points of adsorbates are of less importance. The distinct separation mechanism of GTCB as compared with non-polar liquid phases is illustrated by separation of *trans*-decalin (b.p. 185 °C) and *cis*-decalin (b.p. 194 °C) (see Table 4-2 [32]). *trans*-Decalin is eluted first according to its lower boiling point if liquid phases are used. In contrast, the flat *trans*-isomer, which is capable of being accommodated on GTCB more favorably, is eluted second on this adsorbent.

Table 4-2
Separation of *cis*- and *trans*-decalin on GTCB, squalane and OV-1 [32]

Stationary phase (temperature of separation)	Kovats index		$\Delta I = I_{trans} - I_{cis}$	First eluted isomer
	trans-decalin I_{trans}	*cis*-decalin I_{cis}		
GTCB (220 °C)	883	842	41	*trans*-decalin
Squalane (90 °C)	1064	1101	–37	*cis*-decalin
OV-1 (90 °C)	1046	1086	–40	*cis*-decalin

The retention indices for stereoisomeric 1,2- and 1,4-dimethylcyclohexanes and dimethylcycloheptanes (see Table 4-3 [32]) reflect the opposite

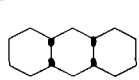
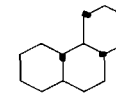
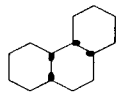
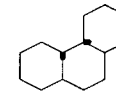
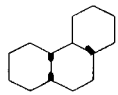
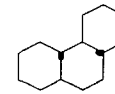
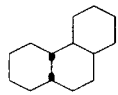
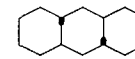
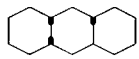
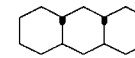
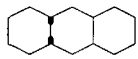
Table 4-3
Retention indices of isomeric dimethylcyclohexanes and dimethylcycloheptanes in GTCB and OV-1 [32]

Compound	GSC GTCB (140 °C)		GLC OV-1 (80 °C)	
	I	$\Delta I = I_{cis} - I_{trans}$	I	$\Delta I = I_{cis} - I_{trans}$
1,2-Dimethylcyclohexanes				
1,2 t (ee)	712	–38	798	28
1,2 c (ea)	674		826	
1,2-Dimethylcycloheptanes				
1,2 t	788	–22	931	19
1,2 c	766		950	
1,4-Dimethylcyclohexanes				
1,4 t (ee)	734	–64	779	23
1,4 c (ea)	670		802	

retention principle between GSC on GTCB and "pure" GLC. The large indices on GTCB for the *trans*-isomers indicate that these molecules possessing both methyl group in equatorial and pseudo-equatorial positions are more flattened than the *cis*-isomers. The smaller retention of the *trans*-isomers in GLC indicates that these compounds have lower boiling points. Most of all practical applications are connected with interactions between the 001 graphite facets of polyhedron particles and chromatographed molecules. Separation of *p*-dibutylbenzene isomers on packed capillary columns is shown Fig. 4-1 [34], and that of hydroanthracene and hydrophenanthrene stereoisomers is shown in Fig. 4-2 and Table 4-4 [35].

As follows from Fig. 4-1 and Fig. 4-2, the separation characteristics of graphitized thermal carbon black are unique. Graphitized carbon blacks are useful for analyzing *cis-trans* double bond isomers and positional isomers of multisubstituted aromatic (homo- and hetero-nuclear) compounds. Many examples of the separations are given in [36].

Table 4-4
Retention indexes of isomers of hydroanthracene and hydrophenanthrene on graphitized thermal carbon black at 250 °C [35]

#	Compound		Kovats index	#	Compound		Kovats index
	Formula	Name of isomer			Formula	Name of isomer	
1		*cis-syn-cis*	1125	7		*trans-syn-cis*	1263
2		*cis-syn-cis*	1156	8		*trans-syn-trans*	1290
3		*cis-anti-trans*	1179	9		*trans-anti-trans*	1302
4		*cis-anti-cis*	1196	10		*trans-anti-trans*	1310
5		*cis-syn-trans*	1207	11		*trans-syn-trans*	1336
6		*trans-syn-cis*	1241				

Engewald and co-workers [32] consider that preparation of high quality capillary columns with pure GTCB is a very difficult procedure because fine GTCB particles tend to conglomerate and, in turn, the suspension is destabilized during the evaporation process. Besides, some suspension liquids, such as 1,1,2,2-tetrabromoethane, decompose during the evaporation process, thus changing the adsorption characteristics of the GTCB. Similar effects were observed when using additional detergents to stabilize the coating suspension. In spite of their high performance and speed, ALOT columns with non-coated GTCB have not gained wide acceptance due to difficulties in preparation.

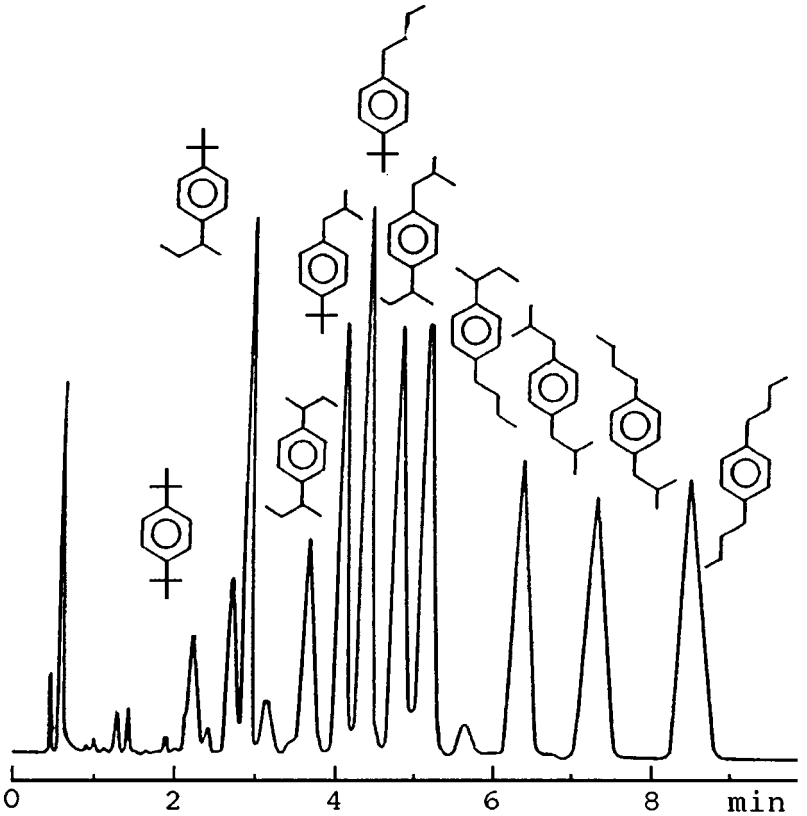


Fig. 4-1 Separation of p-dibutylbenzene isomers on graphitized thermal carbon black [34].

Packed column: 1.5 m × 0.8 mm, adsorbent: sterling MT (0.09–0.12 mm), carrier gas: hydrogen, column temperature: 310 °C.

They have not yet become commercially available. Bruner and co-workers [25, 37] showed that preparation of effective capillary columns with GTCB impregnated with a liquid phase is easier.

For analyzing complex mixtures consisting of a variety of components with widely distributed boiling-points, polarities and concentrations it is useful to use capillary gas chromatographic columns in series, one of which is a column with graphitized thermal carbon black [38].

Sometimes other type of graphite adsorbents can be useful. For example, Lopez-Garzon and co-workers [39] studied the adsorption of hydrocarbons and alcohols on mineralogical graphite. The Henry's law region of the adsorption isotherms was investigated by gas-solid chromatography. A non-specific interaction was shown between the graphite and adsorbates [39].

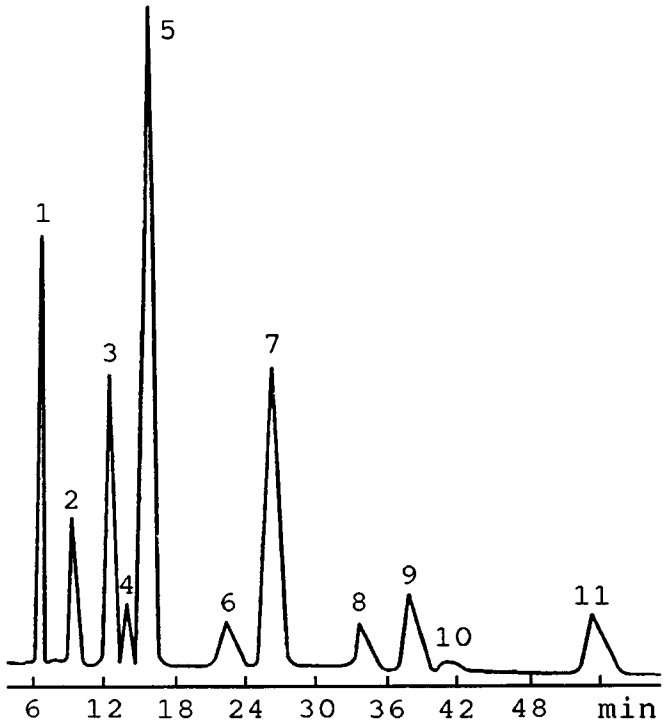


Fig. 4-2 Separation of hydroanthracene and hydrophenanthrene stereoisomers [35].

Packed column: 220 cm × 1 mm,
adsorbent: graphitized thermal carbon black (0.22–0.25 mm),
column temperature: 250 °C; carrier gas: hydrogen.
Peaks designations correspond to numbers shown in Table 4-4 [35].

4.2 Molybdenite (MoS_2)

The chromatographic properties of MoS_2 are similar to those of graphitized carbon blacks.

Investigation of the chromatographic properties of MoS_2 as adsorbent was described in [40]. The sample of MoS_2 adsorbent was introduced into the pores of Chromosorb W (MoS_2 content is 30% of the support weight). The specific surface area of the adsorbent was approx. 2 m^2/g.

A strong influence of the geometric structure of molecules on adsorption appears in the separation of *cis*- and *trans*-isomers. Isomers with *cis*-configurations have, as a rule, shorter retention times on MoS_2 then *trans*-isomers, as is also the case with separation on GTCB [40].

Fig. 4-3 [40] shows the separation of *cis*- and *trans*-4-methylheptene-3. Separation of naphthalene, tetralin and decalin (Fig. 4-4 [40]) indicates the predominant influence of geometric structure and the possible orientation of an adsorbed molecule on their retention times. The column with MoS_2 yields two peaks in exact correlation with the structures of *cis*- and *trans*-decalin. Tetralin is more strongly retained then decalin owing to its more planar structure. The most planar naphthalene

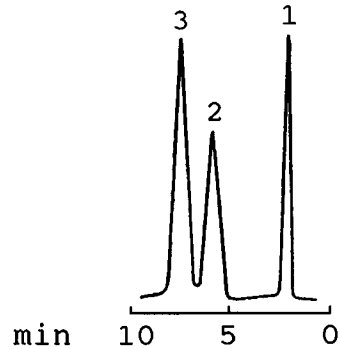


Fig. 4-3 Chromatogram of some hydrocarbon isomers on MoS_2 [40].

Column: 0.9 m × 0.4 mm; temperature 65 °C; carrier gas — helium; flame-ionization detector; Peaks: 1 — 2,2,4-trimethylpentene-3, 2 — *cis*-4-methylpentene-3, 3 — *trans*-4-methylpentene-3.

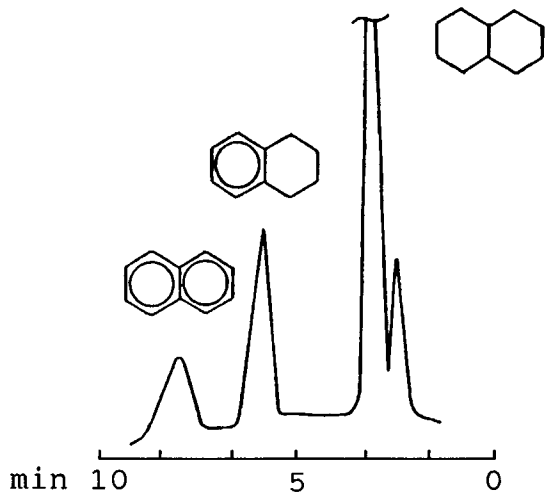


Fig. 4-4 Chromatogram of decalin, tetralin and naphthalene on MoS_2 [40].

Column: 1.2 m × 3 mm; temperature — 130 °C, carrier gas — helium; flame-ionization detector

molecules are the last to be eluted, although they contain fewer hydrogen atoms in the molecule.

Unfortunately, MoS_2 is easily oxidized by oxygen especially at high temperature. This fact restricts its field of application.

4.3 Porous Polymer Adsorbents

Porous polymer adsorbents are fairly popular as chromatographic adsorbents. In 1966 Hollis [41–43] suggested their use in gas chromatography.

Porous polymers are prepared by suspension co-polymerization of a large excess of monofunctional monomer (e.g. styrene, acrylic acid derivatives or vinylpyrrolidone) with a bifunctional monomer (e.g. divinylbenzene) in a suitable solvent. The cross-linking imparts the required rigidity to the bead polymer structure and, on drying, the solvent evaporates, leaving a porous framework. The choice of reagents, the solvent, catalyst and the reaction conditions determine bead size and porosity.

A review by Kiselev and co-workers [44] generally concerns sorption of gases (e.g., CO_2, NO_2, SO_2) by organic ionites. Since the adsorption of chemically active gases depends on the content of functional group accessible to the adsorbate molecules, synthesis of porous polymer adsorbents with a higher surface concentration of these groups presents one of the most important problems.

Presently the only popular organic sorbents are Porapaks and Chromosorb 100's (Johns Manville). Most of these commercial products are copolymers of styrene, ethylvinylbenzene and divinylbenzene. Some of them contain vinylpyrrolidone or other vinylic monomers. The specific surface areas of these organic adsorbents range from 15 m^2/g (Chromosorb 103) to 600 m^2/g (Porapak Q).

Now porous polymer adsorbents are widely used in routine analytical practice [45]. They have the following advantages as adsorbents: 1) high capacity, 2) homogeneous surface (and consequently symmetrical chromatographic zones), 3) hydrophobicity.

Porous polymeric beads have found many applications in the analysis of volatile inorganic and organic compounds, particularly for samples containing water, formaldehyde, carboxylic acids and inorganic gases [46]. Some general recommendations on the separation of different types of compounds are given in Table 4-5 [5, 42, 47, 48]. Physical properties of porous polymer beads, important for chromatographic applications, are presented in Table 4-6 [5].

Polymers with a pore size of less then 0.01 μm are used for separation of gases and higher boiling compounds such as alcohols, glycols, acids and amines. Note that the larger the pore size the faster is the analysis.

Porous polymers are an important group of chromatographic adsorbents. Important chromatographic separations can be performed using this group of organic adsorbents.

One of the principal practical applications of porous polymers in routine analysis is the analysis of traces of water [43]. Water is eluted very early on most organic polymer adsorbents. For example, water elutes just after ethylene, being totally resolved from it, on Porapak G. On the other hand,

Table 4-5
Samples suitable for separation on porous polymer beads [5, 42, 47, 48]

Porous polymer	Recommended for the separation of	Not recommended for the separation of
Chromosorb 101 Porapak P Porapak PS	Esters, ethers, ketones, alcohols, hydrocarbons, fatty acids, aldehydes, and glycols	Amines, anilines
Chromosorb 102 Porapak Q	Light and permanent gases, low molecular weight acids, alcohols, glycols, ketones, hydrocarbons, esters, nitriles, and nitroalkanes	Amines, anilines
Chromosorb 103	Amines, amides, alcohols, aldehydes hydrazines, and ketones	Acidic substances, glycols, nitriles, and nitroalkanes
Chromosorb 104	Nitriles, nitro compounds, sulfur gases, oxides of nitrogen, ammonia, and xylenols	Amines and glycols
Chromosorb 105 Porapak N	Aqueous mixtures of formaldehyde, acetylene from lower hydrocarbons, and most gases	Glycols, acids, and amines
Chromosorb 106 Porapak QS	Alcohols, C_2–C_5 carboxylic acids, alcohols, and sulfur gases	Glycols and amines
Chromosorb 107 Porapak T	Formaldehyde from water, acetylene from lower hydrocarbons	Glycols and amines
Chromosorb 108	Gases, polar compounds such as water, alcohols, aldehydes, and glycols	
Porapak S	Normal and branched alcohols, ketones, and halocarbon compounds	Acids and amines
Porapak R	Esters and ethers, nitriles, and nitro compounds	Glycols and amines
Tenax-GC	High boiling polar compounds, diols, phenols, methyl esters of dicarboxylic acids, amines, diamines, ethanolamines, amides, aldehydes, and ketones	

columns packed with porous polymers can be used for the analysis of organic pollutants in water, because water is much less retained than the light pollutants [47, 48].

Table 4-6
Physical properties of porous polymer beads [5].

Porous polymer	Type [a]	Physical Property			
		Free-fall density (g/cm^3)	Surface area (m^2/g) [b]	Average pore diameter (μm)	Temperature limit (°C)
Chromosorb 101	STY-DVB	0.30	50	0.3–0.4	275
Chromosorb 102	STY-DVB	0.29	300–500	0.0085	250
Chromosorb 103	Polystyrene	0.32	15–25	0.3–0.4	275
Chromosorb 104	AN-DVB	0.32	100–200	0.06–0.08	250
Chromosorb 105	Acrylic ester	0.34	600–700	0.04–0.06	250
Chromosorb 106	Polystyrene	0.28	700–800	0.5	250
Chromosorb 107	Acrylic ester	0.30	400–500	0.8	250
Chromosorb 108	Acrylic ester		100–200	0.25	250
Porapak N	Vinylpyrrolidone	0.39	225–350		200
Porapak P	STY-DVB	0.28	100–200		250
Porapak Q	EVB-DVB	0.35	500–700	0.0075	250
Porapak R	Vinylpyrrolidone	0.33	450–600	0.0076	250
Porapak S	Vinylpyrrolidone	0.35	300–450	0.0076	250
Porapak T	EGDMA	0.44	250–300	0.009	200
Porapak PS	Silanized P				250
Porapak QS	Silanized Q				
Tenax-GC		0.37	18.6		375

[a] STY — styrene; DVB — divinylbenzene; ACN — acrylonitrile; EVB — ethylvinylbenzene; EGDMA — ethylene glycol dimethacrylate

[b] Values for surface area vary widely in the literature

4.4 Silica Gels

Silica gel is a generic name for an adsorbent formed from silicon oxide. There are numerous different silica gels and batch-to-batch variations of product properties may also occur. Silica gels are characterized by their specific surface area (from 5 to 800 m^2/g), their pore volume or porosity (from 0.3 to 1 ml/g), the average pore diameter (from 10 to 200 nm), pore size distribution, the particle shape (spherical, ovoid or irregular), particle size (from about 1 μm to 500 μm), size distribution and the surface chemistry [4, 6, 49, 50].

Silica gels have extremely good mechanical properties. They can be packed with minimum attrition and can withstand considerable pressures. They resist many chemicals (especially oxygen) and easily withstand temperatures up to 600 °C without any structural changes. However, the surface chemistry of silica gel changes on heating.

The energy of adsorption depends on the number of silanol groups per unit of surface area and on the activity of these groups. The density of silanols groups on the surface of silica gels is approximately 5 groups per 100 $Å^2$ (after careful drying under partial vacuum at 150–200 °C). Therefore there is about 1 free silanol group per silicon atom on the surface [51]. There are four main kinds of silanol groups on the surface of silica gel: free silanols, geminal silanols, bound reactive silanols and siloxane groups [6, 49, 51–54].

As a rule silica gels are suitable for chromatographic analysis of group A and B molecules (according to the Kiselev classification). Use of silica gel for separation of light hydrocarbons (see Fig. 4-5 [55]) and more polar compounds (see Fig. 4-6 [56]) can be given as example.

4.5 Alumina

Alumina has been more rarely used in gas chromatography than silica gel (see, for example, [3, 5, 15, 35]). A very interesting review of alumina applications in liquid chromatography was written by Unger and Trüdinger [57] and is also useful for those who work in gas chromatography.

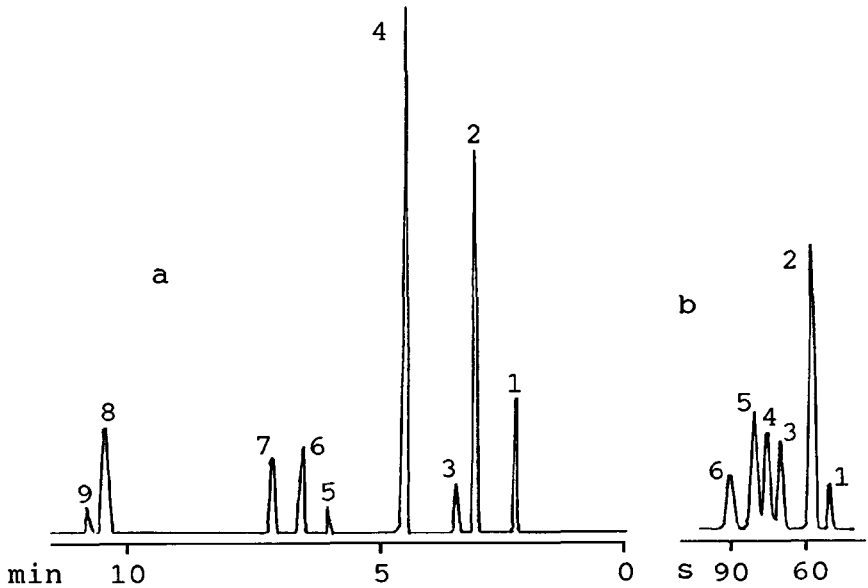


Fig. 4-5 Separation of light hydrocarbons [55].

a. Column 254 cm x 0.32 mm i.d., adsorbent silica gel (20 μm), temperature 52 °C.
Peaks: 1 — methane, 2 — ethane, 3 — ethene, 4 — propane, 5 — propene, 6 — isobutane, 7 — n-butane, 8 — n-pentane, 9 — isobutene.

b. Column 59 cm x 0.25 mm i.d., adsorbent silica gel (20 μm), temperature 80 °C.
Peaks: 1 — n-pentane, 2 — tetramethylbutane, 3 — 2,2-dimethylbutane, 4 — 2,3-dimethylbutane, 5 — n-hexane, 6 — cyclohexane.

The term hydrous alumina is commonly used for a variety of crystalline and amorphous products of composition $Al_2O_3 \cdot nH_2O$, where n varies between 3 and 0. Amorphous alumina gels are produced from aluminum salts, alkaline aluminates and aluminum alkoxides.

The major product of the thermal transition of alumina is γ-alumina. On dehydroxylation slit-shaped pores develop between the microcrystallites. γ-Alumina is a mesoporous material with some microporosity. Specific surface areas are about 200 m^2/g for the product obtained at low temperatures and drop to about 50 m^2/g as a

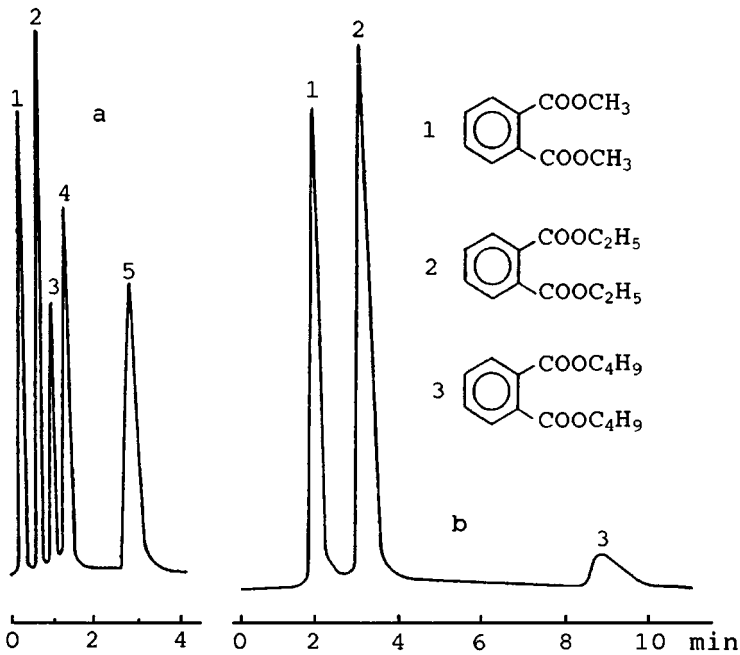


Fig. 4-6 Separation on silica gel (Silochrom-80) preheated at 350°C [56].

a. Column temperature 200 °C.
Peaks: 1 — cyclohexane, 2 — n-decane, 3 — aniline, 4 — nitrobenzene, 5 — acetophenone.

b. Column temperature 270 °C.
Peaks: 1 — dimethyl phthalate, 2 — diethyl phthalate, 3 — dibutyl phthalate.

result of heating at 1000 K. Similarly, the specific pore volume decreases from 0.6 to 0.2 ml/g.

On account of the high calcination temperature the surface bears Brönsted as well as Lewis sites. Five distinct acid-base sites were observed by Steyrer [58] (see Fig. 4-7 [58]). The total concentration of surface hydroxyl groups on γ-alumina activated at 470 K was 10 μmol/m^2, the amount of Lewis acid sites was assessed by means of pyridine adsorption as 0.6 μmol/m^2. The adsorption activity of alumina depends on the amount of adsorbed water [59, 60]. Alumina is suitable for separation of not too polar substances differing in steric arrangement or in the type of functional

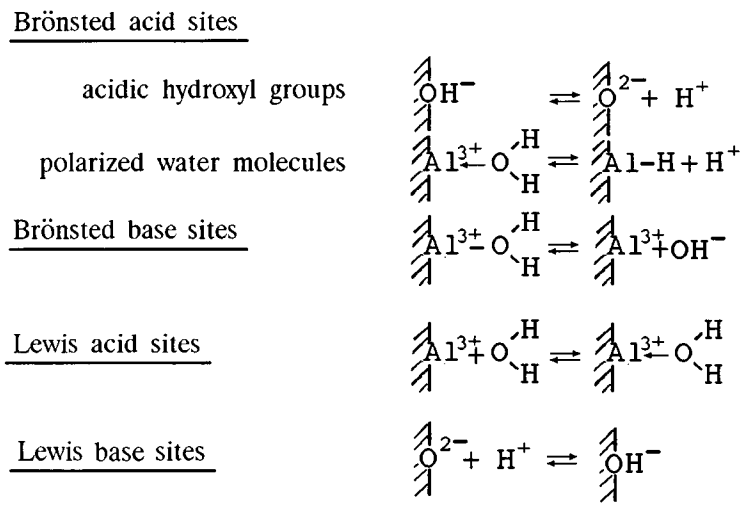


Fig. 4-7 Brönsted and Lewis surface sites on alumina surface [58].

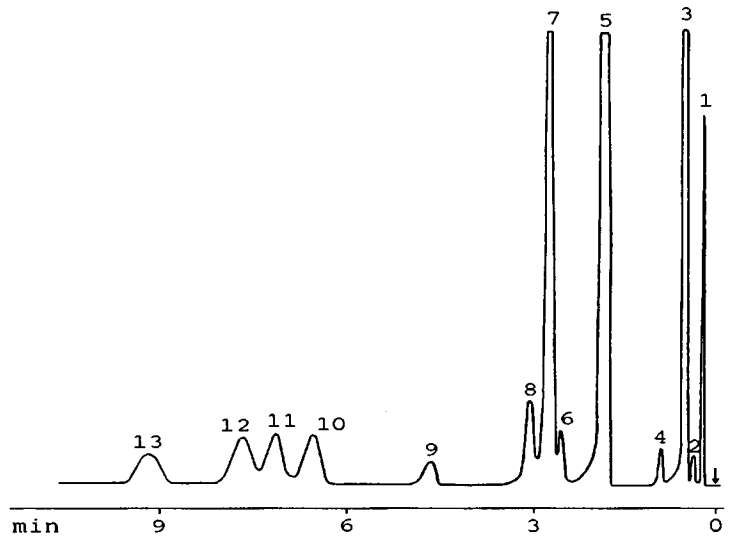


Fig. 4-8 Separation of saturated and unsaturated C_1-C_4 hydrocarbons on alumina.

Column, fused silica 115 cm × 0.32 mm i.d., sorbent aluminium oxide (40–50 μm), column temperature 45 °C; inlet pressure 1.0 MPa.
Peaks: 1 — methane, 2 — ethane, 3 — ethene, 4 — propane, 5 — propene, 6 — isobutane, 7 — cyclobutane, 8 — n-butane, 9 — cyclobutene, 10 — 1-butene, 11 — *trans*-2-butene, 12 — isobutene, 13 — *cis*-2-butene.

groups, especially those which are capable of intermolecular hydrogen bond formation. The presence of C=C bonds increases adsorption on alumina to a greater extent than on silica gel [61].

Alumina is often used for the separation of permanent gases or hydrocarbons C_1–C_4 [61]. Separation of light hydrocarbons is shown in Fig. 4-8 [62]. As can be seen, the separation selectivity of alumina is fairly good.

4.6 Molecular Sieves

Molecular sieves are natural or synthetic zeolites (alumina silicates of alkaline or alkaline earth metals, commonly, sodium or calcium). Their general formula is $M_{2/m}O \cdot Al_2O_3 \cdot n\ SiO_2 \cdot x\ H_2O$, where *m* is the cation valency. They have a well-ordered porous structure [4, 5, 15, 63]. The diameter of zeolite A cavities is 11.4 Å and of type X is 11.6 Å. Large cavities of A zeolites are connected by means of 8-membered oxygen windows with 4–5 Å diameters. Type X cavities are joined by 12-membered oxygen windows of 8–9 Å diameter. Cavities form the primary porous structure of dehydrated zeolite crystals. Molecules of substances with diameters smaller than those of the windows are easily adsorbed; when molecules are too large in

Table 4-7
Some physical characteristics of zeolites [64]

Type of zeolite	General formula	Density g/cm^3	Diameter of entry window, Å
4A (NaX)	$Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2 \cdot 4.5\ H_2O$	1.99	4
5A (CaX)	$CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.6H_2O$	1.98	5
10X (CaX)	$CaO \cdot Al_2O_3 \cdot 2.5SiO_2 \cdot 6.2\ H_2O$	1.92	8
13X (NaX)	$Na_2O \cdot Al_2O_3 \cdot 2.5\ SiO_2 \cdot 6\ H_2O$	1.93	9

size, the windows are no longer accessible and adsorption takes place only on external surfaces of the zeolite (≈10 m^2/g). Therefore, the selectivity of zeolites is generally due to the accessibility/inaccessibility of the porous structure (molecular sieve effect).

Some characteristics of channels (windows) are of the same order as the dimensions of small molecules. The diameter of the entry window determines the size of the molecules which can enter the pores of 4 Å, 5 Å, 8.0 Å and 9.0 Å (see Table 4-7). A molecular sieve of 5 A-type is the most commonly used adsorbent for separation of permanent gases, for example, nitrogen and oxygen. The elution order at room temperature is follows: neon, hydrogen, argon/oxygen, nitrogen, methane, carbon monoxide etc.

Zeolites were apparently used for the first time in gas chromatography by Andronikashvili, Kuzmina [65] and Janak [66]. Adsorption of gases on zeolites depends on the nature of the cations in zeolites. The zeolites are also ion-exchangers, making it possible to modify their adsorption properties by ion-exchange.

Habgood [67] studied the retention volume of oxygen, nitrogen, methane, ethane, propane, butane, ethylene and propene over a temperature range of 25 to 400 °C. He used lithium, sodium, potassium, magnesium, calcium, barium and silver ion-exchanged forms of zeolites X. The type of cationic form was found to greatly influence the retention of chromatographed compounds.

Andronikashvili [65] studied in detail the modification of zeolites by ion exchange and investigated the retention volume of gaseous compounds on rubidium, cadmium and other forms of zeolites. He found that the elution order of chromatographed compounds sometimes changed too. For example, if sodium ion in zeolite 13X (NaX) is exchanged by rubidium ion, the elution order of methane and carbon monoxide will be changed too.

4.7 Ionic Adsorbents

Some ionic adsorbents show unusual properties (see, for example, [15, 58, 68–70]). Belyakova and co-workers [68–70] have proposed barium sulfate as a selective adsorbent. They successfully used barium sulfate modified with sodium chloride for separation of some isomers of unsaturated, aromatic hydrocarbons, and oxygen- and nitrogen-containing heterocyclic compounds [68]. Barium sulfate was prepared by interaction of sodium sulfate and barium chloride solutions of various concentration present in equimolar proportions. The specific surface areas varied from 2.5 to 8 m^2/g.

Barium sulfate as adsorbent

To investigate this ionic adsorbent, glass capillary columns (1 mm i.d.) were packed with barium sulfate particles (0.16–0.20 mm). The maximum value of separation selectivity for all xylene isomers was observed on barium sulfate samples modified with 15% sodium chloride solution [69]. According to electron spectroscopy for chemical analysis these samples contained on the surface about 2% of

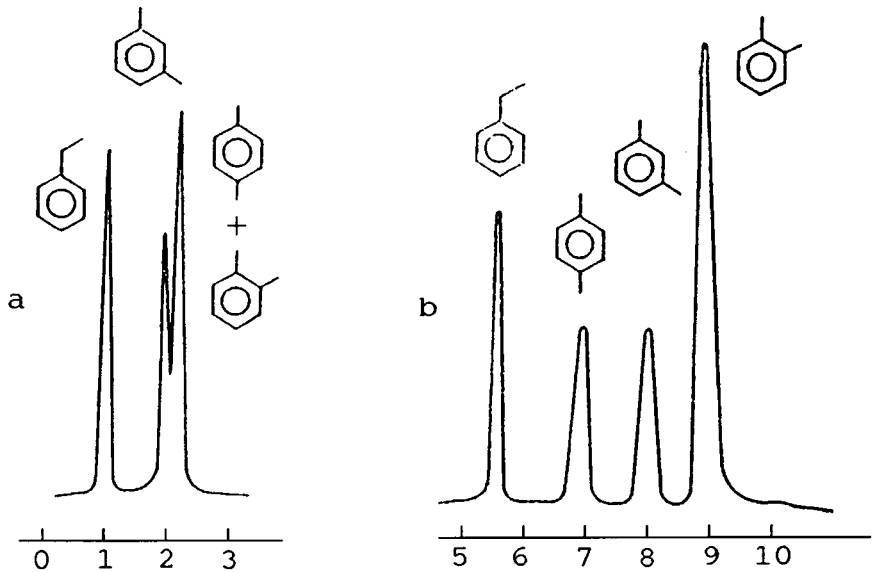


Fig. 4-9 Chromatograms of xylene isomers at 170 °C on graphitized carbon black (a) and barium sulfate (b) [56].

Column: 60 cm × 1 mm.

sodium ions. Belyakova et al. [68] compared selectivity (relative retention) of adsorbents of different natures for xylene isomers and showed that barium sulfate had better selectivity than graphitized carbon black. Fig. 4-9 [56] shows the chromatograms obtained for a mixture of aromatic hydrocarbons on graphitized carbon black and barium sulfate modified by sodium chloride. On a non-specific graphitized carbon black adsorbent the retention is generally determined by dispersion interaction, depending on the molecular geometry; hence the *meta*-isomer elutes first from the column, while *para*- and *ortho*-xylenes elute as one. The elution order on barium sulfate is different. It is explained by a strong specific intermolecular interaction between the dipole (electrostatically oriented) of the adsorbate and the ionic adsorbent. In our opinion, use of barium sulfate adsorbent in ALOT columns is very promising.

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Chapter 5

Modified Gas-Solid Chromatography

The solution of many difficult analytical problems of practical importance and the development of gas-solid chromatography can be achieved, in our opinion, by using modified gas-solid chromatography. Modified gas-solid chromatography is a variant of gas chromatography which uses an adsorbent covered by stable (under the experimental conditions) continuous or island-type layer of organic or inorganic volatile or involatile compounds, whose presence modifies the chemical or structural composition of the adsorbent surface, thus changing the nature and intensity of molecular interactions taking place between different analytes and the surface of the adsorbent. Fig. 5-1 shows the main variants of modified gas-solid chromatography. Of course, hybrid modified chromatography set-ups are some-times also useful (for example, simultaneous operation of both variant II and variant IV).

Variants of modified GSC

5.1 Solid Adsorbents Modified by Non-volatile Organic Compounds

In one of the versions of modified gas-solid chromatography, adsorbents covered by a stable layer of organic or inorganic compounds are used. The presence of modifier changes the chemical composition of the adsorbent surface and therefore the nature and intensity of molecular interactions taking place between the modified surface and the various analytes of a mixture under study. As a result, the adsorption energy of each component of the mixture usually decreases, permitting use of sorbent material at a much lower temperature. The selectivity of the modified stationary phase increases concomitantly. Finally, by changing the nature of the modifying compound and its surface concentration, it is possible to change the absolute and relative retention over a wide range.

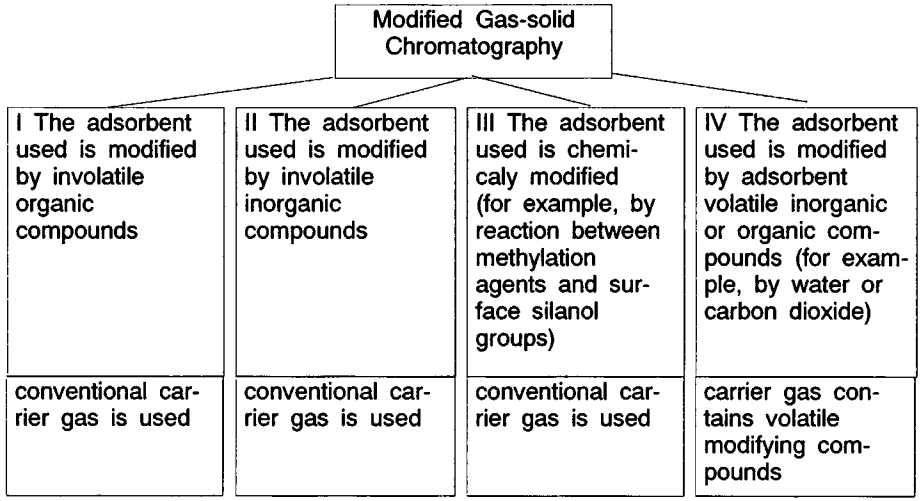

Fig. 5-1 Classification of the modified gas-solid chromatography variants.

The variants of modified gas-solid gas chromatography have been studied by numerous scientists, especially Scott [1], Halasz and Horvath [2], Vidal-Madjar and Guiochon [3], Kiselev and Yashin [4], Di Corcia and Bruner [5], Bruner, Liberti and Possanzine [6] Di Corcia and Liberti [7], Jonsson and Mathiasson [8], Berezkin [9] and others.

Main adsorbent types

Modification of solid adsorbent by stationary liquid phase is the most widespread variant of modified gas-solid chromatography. Three types of adsorbents have been used more extensively in the practice of modification [10]: 1) inorganic polar heterogeneous adsorbents (such as silica or alumina); 2) non-polar, homogeneous adsorbents (such as graphitized carbon black); 3) organic adsorbents (such as porous polymers).

Following an idea of Di Corcia and Liberti [7] led us to consider the model of adsorption of analyte on a liquid-modified solid modified by us. These authors suggested that this process is analogous to the adsorption of a particular binary gas mixture. Sketches of analyte (a) adsorption on an adsorbent containing some inhomogeneities at increasing surface concentration of modifying liquid (ML) are

shown in Fig. 5-2. Inhomogeneities are represented as discontinuities of the surface. Fig. 5-2A represents adsorption of analyte on the bare surface of adsorbent. In Fig. 5-2B, since inhomogeneities are preferentially occupied by molecules of ML, adsorption of analyte is shown to occur on the homogeneous part of the surface. In Fig. 5-2C, owing to the increased degree of surface occupation of ML, lateral interactions between two adsorbent molecules (ML and a) come into play. In Fig. 5-2D adsorption of analyte molecules is shown to occur on the monomolecular layer of ML. Note that adsorption of analyte on the surface of adsorbent is also possible. Fig. 5-2E illustrates the mode of adsorption of analyte when the surface coverage

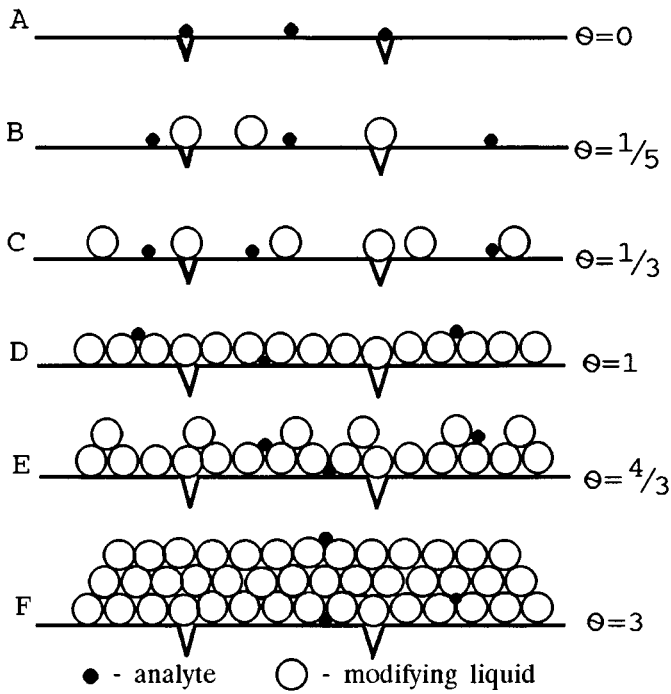

Fig. 5-2 Sketches of adsorption of analyte at varying degrees of surface coverage by modifying liquid.

A–F are variants of analyte adsorption on adsorbent surface coated by different amounts of modified liquid phase. Θ is a degree of surface coverage.

of ML is intermediate between Θ =1 and Θ = 2. Fig. 5-2F illustrates the mode of analyte adsorption when the adsorbent surface coverage of ML is more then two layers. In this case partition is also possible.

Retention time vs. amount of SLP

This model of sorption process corresponds to the effect of the coating ratio of stationary liquid phase (SLP) on the retention time of an analyte (see Fig. 5-3). The retention time decreases rapidly with increasing coating ratio (or specific amount of stationary liquid phase) if the coating ratio is low. A coating ratio increase leads to a surface energy decrease due to saturation of adsorbent active sites. Generally field A in Fig. 5-3 is mainly the

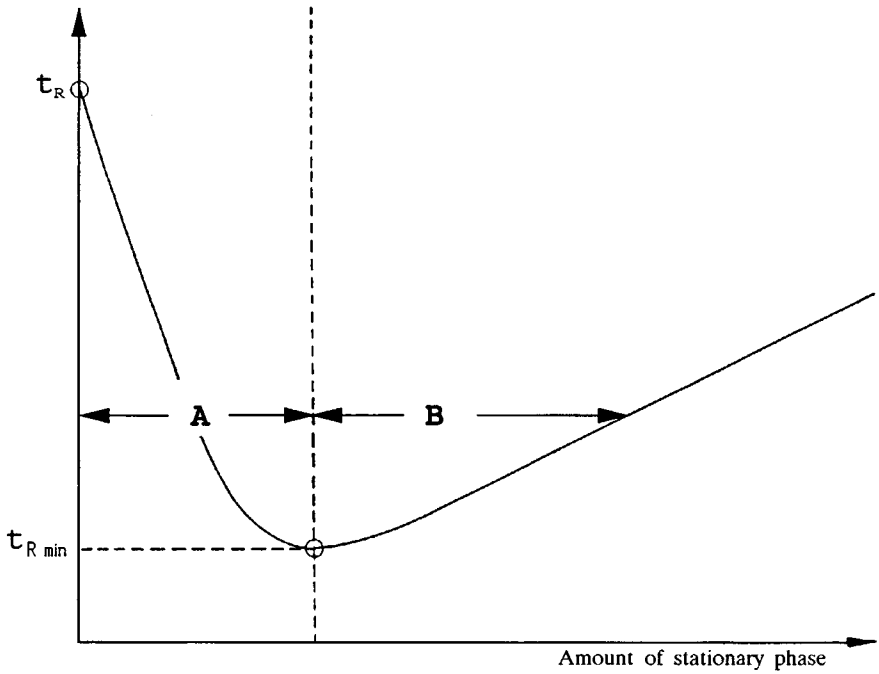

Fig. 5-3 Analyte retention time vs. the specific amount of stationary liquid phase.

A is a field of analyte adsorption on modified adsorbent.
B is a field of analyte adsorption and partition on modified adsorbent.

field of adsorption. After the minimum the retention time increases with increasing coating ratio. Field B in Fig. 5-3 is the field of partition in the system [stationary liquid phase–gas] and adsorption on solid-liquid and liquid-gas interphases.

Fig. 5-4 shows chromatograms of the same synthetic mixture on Spherosil (64 m^2/g) coated with different layer thicknesses of stationary phase (β,β-oxydipropionitrile) at 2%, 5%, 10%, 20% and 30% by weight with respect to the solid support.

All chromatograms in this Figure have the same general shape: retention firstly decreases with increasing thickness of stationary phase layer, then passes through a relatively well-defined minimum, and finally increases with further addition of SLP. Therefore for very small values of average layer thickness, gas-solid adsorption is still an important factor, giving rise to broad asymmetrical peaks. The presence of a retention minimum testifies to the gradual change of the nature of the separation mechanism. The intermediate transition region is characterized by the shortest retention time and by narrow, almost symmetrical, peaks. As shown in Fig. 5-4 the remaining weak asymmetry gradually disappears upon further addition of liquid phase, whereas the peak width increases slightly.

Model of sorbent in G[LS]C

Strictly speaking, if the adsorbent used is modified by organic compounds (for example, by a stationary liquid phase), we are working in the field of gas-[liquid-solid] chromatography [9]. If a simplest model of sorbent in gas-[liquid-solid] chromatography is fulfilled: (1) a sufficiently thick stationary liquid phase layer covers the entire surface of the solid adsorbent, and (2) the stationary liquid phase layer on the solid adsorbent is sufficiently thick. Under these conditions physicochemical properties of the stationary liquid phase layer are identical to those of the stationary liquid phase macrovolume.

The chromatographic properties of the sorbent discussed are determined approximately by the sorptional properties of the stationary liquid phase–gas surface, stationary liquid phase, and stationary

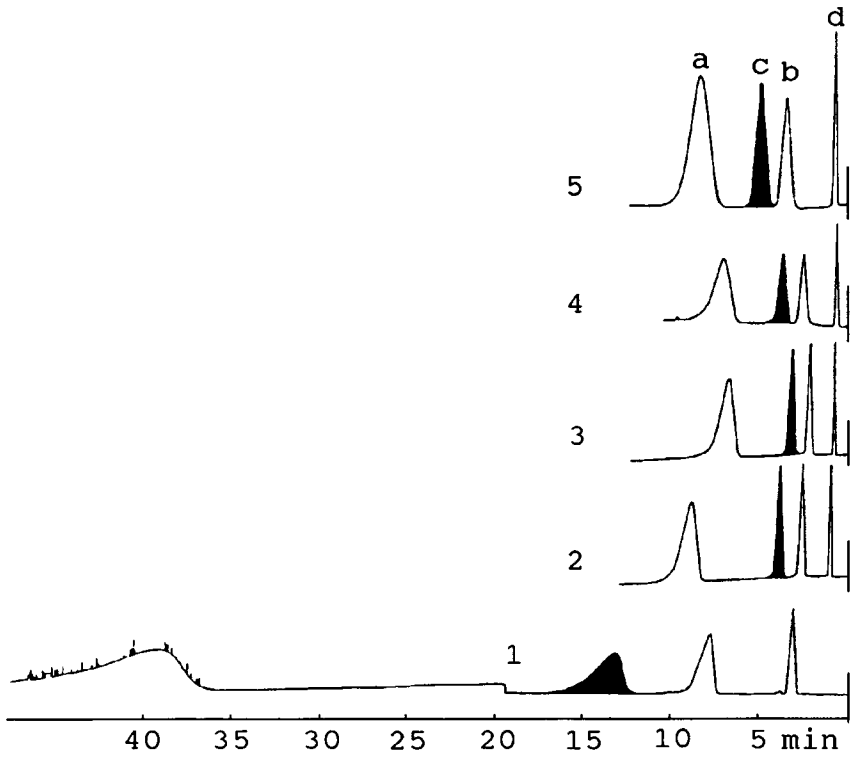

Fig. 5-4 Chromatograms of a mixture on Spherosil (64 m^2/g) with different average layer thickness of stationary liquid phase (β, β′-oxydipropionitrile) [11].

a — ethyl ether, b — acetone, c — methyl ethyl ketone, d — methyl isobutyl ketone. Operating conditions: sorbent Spherosil (64 m^2/g) plus various amounts of β, β′-oxydipropionitrile; particle size 200–250 μm; column: 100 cm × 0.4 mm, temperature 100°C; carrier gas: nitrogen, flow rate 3 l/h.

First use of modified GSC

liquid phase – solid adsorbent surface. Properties of polyphase sorbent are greatly affected by the stationary liquid phase/solid phase ratio. Active adsorbents (silica, carbon-containing, organic, polymeric, etc.) are widely used in gas-solid chromatography. However, adsorbents are often used not in pure form, but after modification by depositing low-volatile organic compounds on their surface (see, e.g. [4]). Such modification was first carried out by Eggertsen et al. [12] who significantly improved the symmetry of chromatographic zones by adding squalane (1.5%) to carbon black. The

first chromatogram [12] illustrating the positive effect of improved separation as a result of adsorbent modification was obtained in 1956 (Fig. 5-5). A large-scale application of solid adsorbents modification by stationary liquid phase appears feasible for the following reasons.

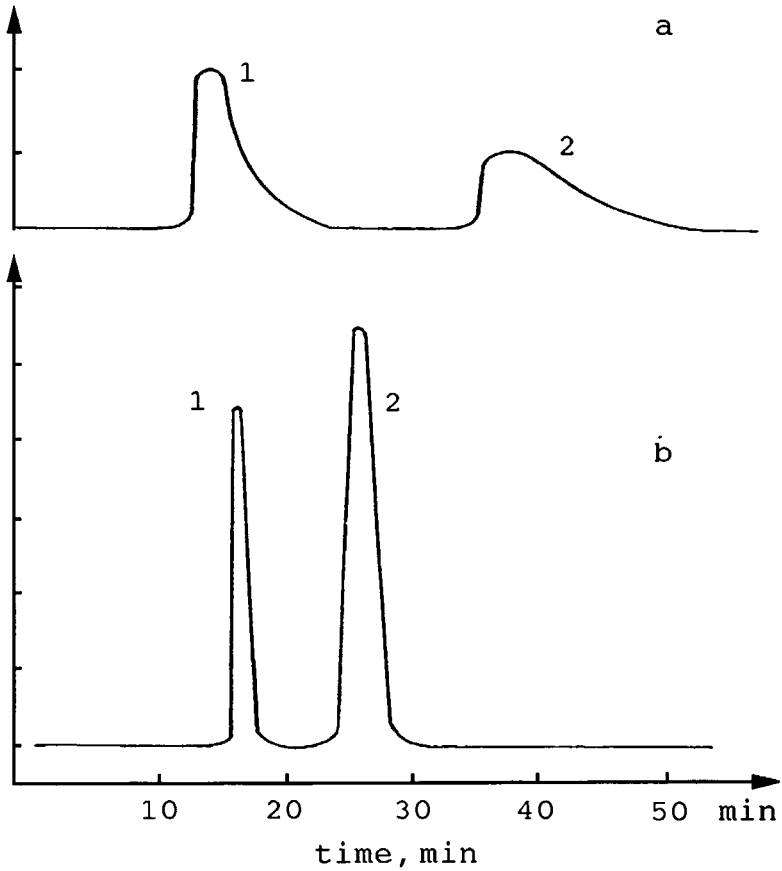

Fig. 5-5 Effect of furnace black (24 m^2/g) modification with squalane (1.5%) on cyclohexane (1) and 2,4-dimethylpentane (2) separation [12].

Column: 3 m × 6.25 mm; carrier-gas rate 20 ml/min.

a: sorbent: black Pelletex, temperature 120 °C.
b: sorbent: squalane-modified black Pelletex, temperature 40 °C.

Peculiarities of modified GSC

1. The character (and nature) of adsorptional retention significantly differs from retention in an ideal liquid-gas system (see, e.g. [9]). Therefore, the use of an adsorptional factor makes it possible to achieve separations that are impossible or very difficult to realize in an ideal version of gas-liquid chromatography.

Scott [1, 13], Hewett [14] and McKenna and Idleman [15] who modified aluminum oxide with silicone oil, liquid paraffin, and propylene carbonate were among the first to obtain positive results in separation improvement by adding stationary liquid phase to solid adsorbents. In all cases the separation of gases on a modified aluminum oxide was more complete compared to separation on a non-modified sorbent. We note that the separation of C_1–C_4 gases on aluminum oxide F10 modified with propylene carbonate (21%) is sufficiently complete for all the compounds. Separation was carried out at 26 °C in a 9 m × 5 mm column filled with a modified adsorbent (fraction 60 to 90 mesh) [15]. The chromatogram (see Fig. 5-6) shows separation of C_1–C_4 hydrocarbon gases.

Polymeric adsorbents modified with stationary liquid phase are widely used in chromatographic practice. Having proposed the use of porous sorbents based on styrene and divinyl benzene copolymers in gas chromatography, Hollis simultaneously demonstrated the feasibility of these sorbents modified with stationary liquid phase for GS separation of volatile compounds [16]. Studying water determination in various liquid specimens Hollis and Hayes found out [17] that the chromatographic properties of a modified adsorbent differ from both the pure initial polymeric adsorbent and the pure stationary liquid phase.

Thus adsorbent modification with stationary liquid phase permits us to obtain a new sorbent not just a superposition of retention on a pure support or a pure stationary liquid phase.

2. A considerable choice of SLP's of different selectivity and a limited choice of standard solid

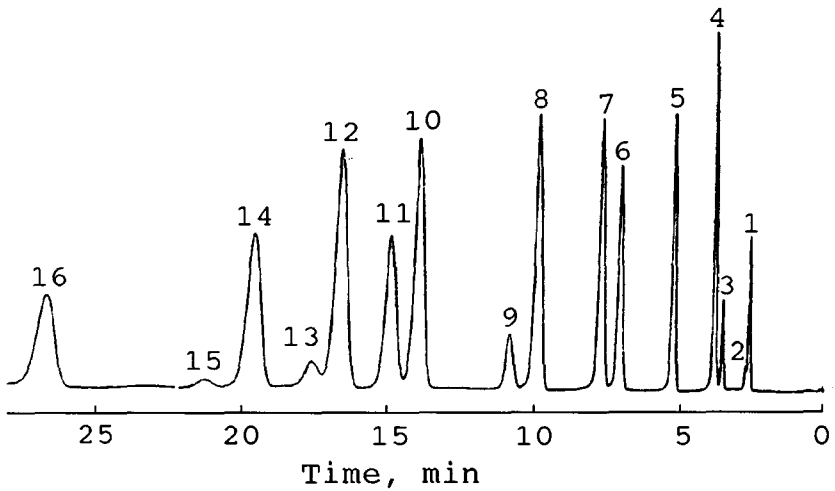

Fig. 5-6 Chromatogram of C_1–C_4 hydrocarbon gases at 26 °C on alumina modified with propylene carbonate [15].

Peaks: 1 — air, 2 — methane, 3 — ethane, 4 — ethene, 5 — propane, 6 — propene, 7 — isobutane, 8 — n-butane, 9 — 2,2-dimethylpropane (neopentane), 10 — 1-butene, 11 — isobutene, 12 — *trans*-2-butene, 13 — isopentane, 14 — *cis*-2-butene, 15 — n-pentane, 16 — 1,3-butadiene.

adsorbents, open broad opportunities for obtaining modified sorbents characterized by new properties different from those of the initial materials. Data for separation criteria obtained for separated compounds with similar properties and their dependence on the SLP content provide a valid approach to the choice of optimal separation conditions. Separation selectivity on modified sorbents is highly dependent on the content of the liquid modifying phase. Fig. 5-7 shows the selectivity coefficient vs. the squalane content on aluminum oxide [18].

As seen from the data cited, separation is highly dependent on the squalane content, and this dependence permits determination of the optimal modifier content.

3. A characteristic feature of modified adsorbents is their increased sorptional capacity. This enables the magnitude of the analyzed sample to be increased in both impurity analysis [19] and preparative separation [20]. Moreover, numerous investigators have focused much attention on the

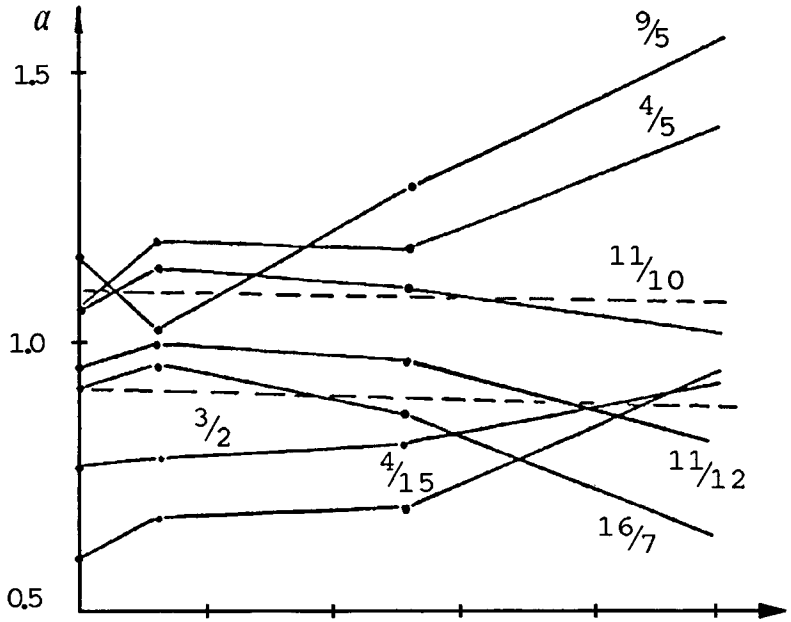

Fig. 5-7 Separation factor (α) variations for a number of not easily separable gaseous compounds C_1-C_4 with squalane on alumina (P) [18].

9/5 — cyclopropene/propylene, 4/5 — acetylene/propylene,
11/10 — isobutene/butene-1, 3/2 — ethane/ethylene,
4/15 — acetylene/isobutane, 11/12 — isobutene/*trans*-2-butene,
16/7 — 1,3-butadiene/propyne.

analysis of volatile compounds, particularly on the analysis of hydrocarbon and certain other gases on modified adsorbents [21] at 20 to 80 °C. The separation of light hydrocarbon gases on a highly efficient micropacked quartz capillary column filled with silica gel modified with crystalline hydrate salts was studied in [22]. Under temperature programming quite satisfactory separation of light hydrocarbons was obtained for a relatively short time.

4. Regularities underlying the retention of compound being chromatographed as dependent on SLP content are similar to those for solid support [9] in the region of SLP content from 3–8% to 50%. For the first time the applicability of the theory discussed earlier for modified adsorbents was demonstrated

for the polymer supports in paper [23] and for graphitized carbon black in paper [24].

Separation of cyclic hydrocarbons on Sterling MT 3000 graphitized carbon black, modified with squalane [24], was demonstrated. Note that, first, the retention of the compounds being chromatographed varies linearly with an increase in SLP content, in compliance with a theory discussed earlier [9], and, secondly, the contribution of adsorption to retention is significant. For instance, for the sorbent containing 9% squalane on Sterling MT 3000, the contribution of adsorption to retention varies for the C_6–C_8 cyclic hydrocarbons within 14 – 28%. Thus the theory of retention in gas-liquid-solid chromatography, elaborated earlier for solid carriers with a small surfaces (specific surface area 0.5 to 2 m^2/g), can also be applied to active adsorbents (specific surface 20 to 200 m^2/g). The known linear regularities underlying the variation of absolute retention values with SLP content on the adsorbent [9] and relative retention values (selectivity coefficient) with an inverse value of the SLP content [9] can be conveniently employed in determining optimal separation conditions.

5. The separation efficiency and the symmetry of chromatographic zones are observed to improve as a result of the particularly adsorptionally active centers due to the deposited liquid phase [12]. Modifiers obtained by addition of small amounts of polar surface-active substances to the main component can be useful [27]. It is interesting to note that the introduction of these substances will change not only absolute retention values, but also relative values, and sometimes even the order of compound elution. For instance, on a sorbent with 1% dinonyl phthalate, propane will elute after acetylene, while on the same sorbent with an addition of 1% stearic acid (by weight relative to dinonyl phthalate), propane will elute earlier than acetylene.

Therefore, changing the content of stationary liquid phase on a solid adsorbent proves to be a simple method for changing the selectivity of the chromatographic sorbent.

6. The vapor pressure of modifier deposited in small amounts (e.g., monomolecular layer) on the adsorbent surface is essentially below the equilibrium value of the SLP vapor pressure for a given temperature. This circumstance accounts in turn for an increase in the upper temperature limit of the modified adsorbent compared to that of the given SLP, and also for a decrease in detector noise due to SLP vapors. This characteristic of modified adsorbents was first pointed out in [4]. Discussion of this problem can be also found in reference [28].

7. The effect of a solid adsorbent on selective (structurally sensitive) SLP may significantly alter the properties of the latter. Thus Vetrova et al. [29] have shown that adsorptionally active macroporous adsorbents of Silochrome C-80 type have a perceptible effect on the orientation of adsorbed polar molecules of liquid crystals, and this accounts for displacement and variation of their phase transitions. The liquid crystal phases are endowed with a surprising selectivity and are widely used for separation of isomeric organic compounds [30, 31]. When a SLP, for instance, cholesterol pelargonate, is deposited on the solid support Chromaton N-AW, dependence of the logarithm of the retention volume on the inverse absolute temperature will be characterized by three distinctly marked regions, corresponding to the specific phase states of the substance: solid, liquid crystal (mesomorphous), and liquid. On heating, the transition from the solid state of the SLP to the mesomorphous state at 78 °C is accompanied by a substance being chromatographed. In the mesophase region (78 to 81.5 °C) a reduction of retention volumes with increasing temperature is observed. On transition to the isotropic liquid a jumplike and significant increase in retention volumes is again observed for cholesterol pelargonate. In the region of the liquid crystal state a complete separation of xylene isomers occurs, the maximum selectivity being observed at the SLP melting point. On depositing cholesterol pelargonate on a highly active adsorbent support no jumplike variation of the retention values

occurs while a selective separation of xylene isomers is observed over the entire temperature range under investigation. The results obtained, associated with an expansion of the region of liquid crystals specific selectivity, are explained by the fact that under the influence of the force field of the solid adsorbent an orientation of the molecules of the liquid crystal SLP in thick layers occurs, this orientation is observed within a wide temperature range. The effect of an active adsorbent on the properties of liquid crystals was also studied in papers [32, 33]. The positive features of modified adsorbents described above have accounted for their wide application in chromatographic practice for various analytical tasks [34–38].

The liquid film is selectively adsorbed by the most energetic adsorption sites of the solid adsorbent surface, being then practically unavailable to the analyte. The heterogeneous distribution of active sites is consequently reduced, providing a more energetic homogeneous surface (for interaction with the analyte). After modification both retention and peak asymmetry are drastically reduced. For the low levels of liquid phase it is assumed that adsorption interactions dominate in the retention mechanism. With increasing amount of liquid phase gas-liquid partition begins to contribute to the retention mechanism (see Fig. 5-3).

Separation of alcohols on modified carbon black

Experimental results described in many papers clearly show that GLSC is a powerful technique capable of solving analytical problems difficult to solve by either gas-liquid (partition) or gas-adsorption chromatography. Selectivity of GLS columns can be continuously varied by changing the liquid/solid ratio as well as by taking advantage of the large variety of stationary phases. For example, Fig. 5-8 [39] shows chromatograms of water mixtures containing small amounts of analyte (~ 30 ppm of each component). Separation of all components is achieved in 20 min by using Graphon (S = 110 m2/g) + 2% PEG-1500 as packing material (Fig. 5-8c).

With the same analysis time, neither the column filled with Graphon + 5% PEG-1500 (Fig. 5-8c), nor the column filled with Graphon + 0.6% PEG-1500 (Fig. 5-8b), where the liquid acts mainly as a "tailing reducer", is able to separate all the compounds. Note that column packed with Graphon + 5% PEG-1500, where the solid medium acts mainly as support (Fig. 5-8a), also cannot be used to separate all the compounds of the mixture.

Separation of organic acids and alcohols on modified carbon black

Di Corcia et al. [40] suggested a method for determining organic acids and alcohols. Vulcan (surface area 100 m^2/g) — a graphitized carbon black, commercially known as Carbopack B — is washed with an aqueous solution of H_3PO_4. After this chemical treatment chemisorption of acidic compounds was not observed on the graphitized carbon black surfaces. Indeed, acid-washed Vulcan allowed the separation of C_2–C_5 free fatty acids to be performed with untailed peaks at concentrations on the ppm level. Analysis of a complex dilute aqueous solution containing acids and alcohols was possible using acid-washed Carbopack B with 5% PEG 20M. Fig. 5-9 [40] shows a chromatogram of aqueous solution containing both acids and alcohols which can be encountered in the analysis of bacterial fermentation products. To obtain the desired separation graphitized carbon black Vulcan modified with 5% PEG 20M was suitable. The role of PEG 20M is also to eliminate nonlinear adsorption of very small quantities of alcohols occurring on the surface of Vulcan graphitized carbon black. The source of this anomalous adsorption of alcohols is probably the presence of surface chemical functional groups which are not removed or suppressed by acid washing.

Guillemin and co-workers have introduced spherical silica into gas chromatography practice [11, 43]. Application of Spherosil as an adsorbent for gas chromatography was particularly recommended for separation of saturated and unsaturated aliphatic hydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons [43]. In the separation of polar molecules modified gas-solid chromatography

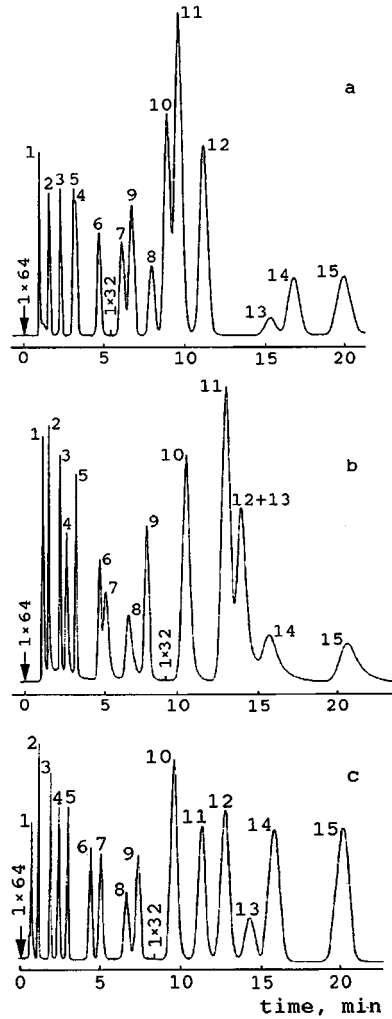

Fig. 5-8 Chromatograms of aqueous solution of C_1–C_5 aliphatic alcohols [39].

Column: 1.4 m × 2 mm, Graphon + PEG 1500 (5%, 98°C — a; 0.6%, 126°C — b; 2%, 131°C — c); sample size of each component: ~30ng; linear carrier gas velocity 10 cm/s.
Peaks: 1 — methanol, 2 — ethanol, 3 — 2-propanol, 4 — 1-propanol, 5 — 2-methyl-2-propanol, 6 — 2-butanol, 7 — 2-methyl-1-propanol, 8 — 1-butanol, 9 — 2-methyl-2-butanol, 10 — 3-methyl-2-butanol, 11 — 3-pentanol, 12 — 2-pentanol, 13 — 2-methyl-1-butanol, 14 — 3-methyl-1-butanol, 15 — 1-pentanol.

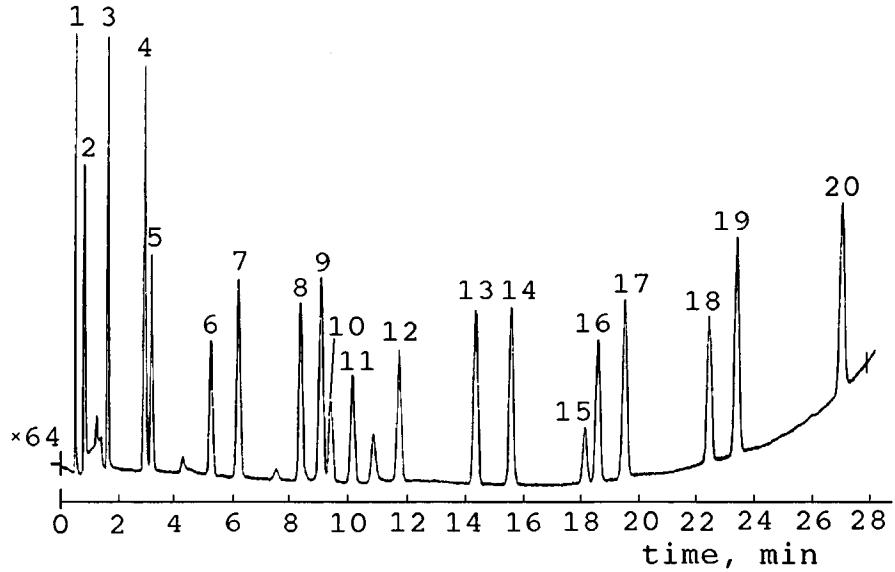

Fig. 5-9 Chromatogram of aqueous complex mixture of acids and alcohols [40].

Column: 1.8 m × 1.5 mm; adsorbent A.W. Vulcan + 5% PEG 20M; injected amount: 1 μm of water containing 50 ppm of each component; temperature 80 to 220 °C, 5°/min; carrier gas hydrogen.

Peaks: 1 — acetaldehyde, 2 — methanol, 3 — ethanol, 4 — ethyl acetate, 5 — propanol, 6 — isobutanol, 7 — butanol, 8 — acetic acid, 9 — 2-methyl-1-butanol, 10 — 3-methyl-1-butanol, 11 — 1-pentanol, 12 — propionic acid, 13 — isobutyric acid, 14 — butyric acid, 15 — 2-methylbutyric acid, 16 — 3-methylbutyric acid, 17 — valerianic acid, 18 — isocapronic acid, 19 — capronic acid, 20 — enanthic acid.

is more useful. The work by Guillemin and co-workers [43] was devoted to the systematic study of Spherosil coated with a small amounts of stationary phases.

Physical characteristics of commercially available Spherosils are given in Table 5-1 [11]. Spherosil comprises pure silica, and is available in the form of Spherosil beads. Each type of Spherosil is characterized by total pore volume, specific surface area, and mean pore diameter independent of the particle size. Spherosil beads are perfectly rigid

Table 5-1

Physical characteristics of Spherosil (Pechiney-Saint Gobain) [11]

Type of Spherosil	Specific surface area, m^2/g	Pore diameter, Å	Porous volume, cm^3/g
Spherosil XOA 400	400	80	1
Spherosil XOA 200	200	150	1
Spherosil XOB 075	100	300	1
Spherosil XOB 030	50	600	1
Spherosil XOB 015	25	1250	1
Spherosil XOB 005	10	3000	1

and incompressible despite their considerably porosity; they are resistant to attrition and do not swell in any liquid. The different grades of Spherosil may be subjected to temperatures up to 600 °C without any change of texture.

5.2 Adsorbents Modified by Inorganic Salts

Use of inorganic salts for deactivation of solid adsorbents surface is very promising, because inorganic salts have very high temperature limits. For instance, the actual mechanism of alumina deactivation can be illustrated qualitatively by Fig. 5-10 [44] where the number of active sites is plotted against the alumina surface activity. The distribution of active sites on the pure alumina surface is shown in a plot A. Most of the sites have an average activity. However, there are sites with higher and lower activity. Deactivation generally leads to a lower average activity level, lower number of active sites, and elimination of sites with extremely high activity. On treatment with KCl, the active sites with relatively high activity are covered first. This results in a more linear adsorption and more symmetrical peaks. The number of active sites is also reduced, leading to a capacity ratio reduction (see plots B and C on Fig. 5-10). One must find the optimal amount of deactivating agent in order to prepare a solid layer with sufficient

Deactivation of alumina by inorganic salts

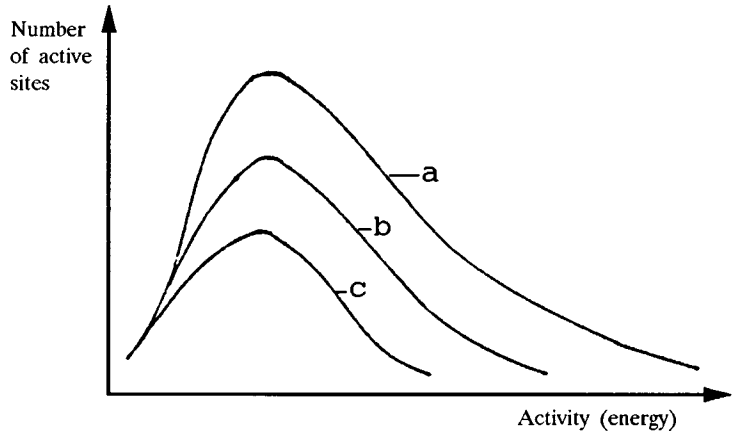

Fig. 5-10 Change of the number of active sites plotted vs. activity (energy) of each adsorption site for alumina surface [44].

a — pure Al_2O_3 surface; b — deactivation with 1% KCl; c — deactivation with 10% KCl.

amount of active sites to provide rather good retention with a small deviation in activity.

Aluminum oxide (alumina) has a very strong retention with respect to polar compounds (alcohols, aldehydes, ketones and others) (see, for example, [28]). Interaction of these compounds with active sites on the alumina is so strong that they will not elute at 200 °C. Therefore, it is important to keep the concentrations of polar impurities and high-boiling materials introduced onto the column as low as possible [44, 45].

Even though alumina is deactivated with potassium chloride, water can still adsorb, leading to a decrease in retention time for many compounds [44, 45]. Water can be desorbed by column heating to 200 °C. Regeneration takes from a few minutes to a few hours.

Coating of adsorbents with inorganic salts as a method for adsorbent modification is a well known approach in gas-solid chromatography (see, for example, [4, 28, 41, 46–56]). It is reasonable to note [56] that, depending on the salt loading, the original adsorbent is, as a rule, converted into a

less active one. The active adsorption sites are increasingly occupied by the salt dispersed in the form of ions and/or ion-pairs or shielded with a new layer formed by reaction or with fine particles or thin films of the salt crystals. Of course, specific

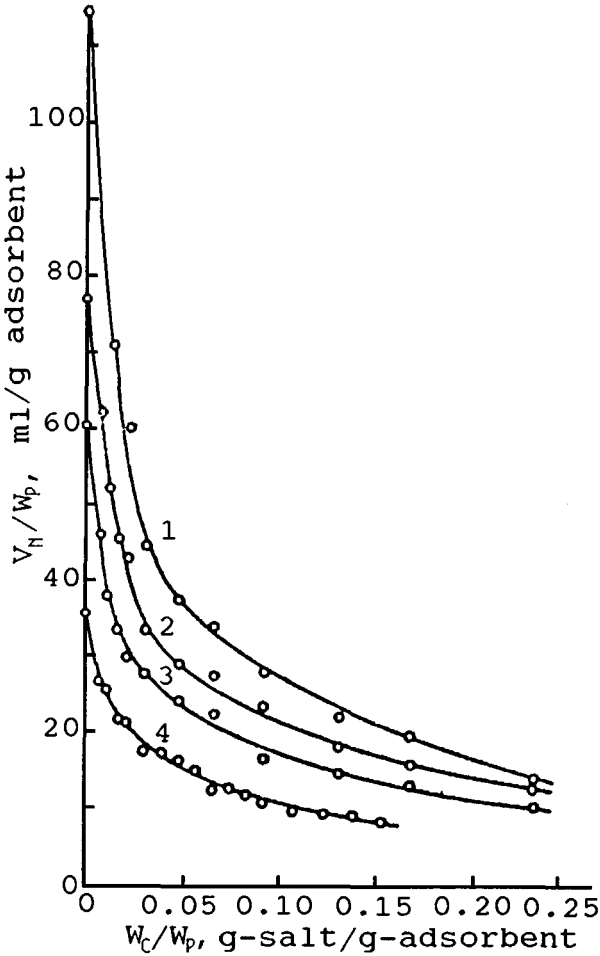

Fig. 5-11 Retention volume of toluene on alumina adsorbents salt-modified with potassium carbonate [56].

Adsorbents pre-heated at 500°C (1), 700°C (2), 900 °C (3) and 1000 °C (4). Column: 100 cm × 3 mm i.d., column temperature 180 °C.

surface area and surface adsorption activity will reflect different distributions of the salt on the adsorbent surface [56]. Detailed investigation of retention mechanism in gas-solid chromatography has been carried out by Naito and co-workers [56] for alumina adsorbents modified by pre-heating and subsequent coating with various amount of potassium carbonate. Retention volume of toluene on salt-modified alumina adsorbents coated with potassium carbonate is shown in Fig. 5-11 [56]. The retention volume decreased especially strongly at lower salt loadings. Interpretation of these results is very important for analytical applications [56].

Some separations of hydrogen isotopes were investigated using modifying solid adsorbents. For example, coating of alumina adsorbents with $MnCl_2$ rendered the surface deactivated, and it was elu-

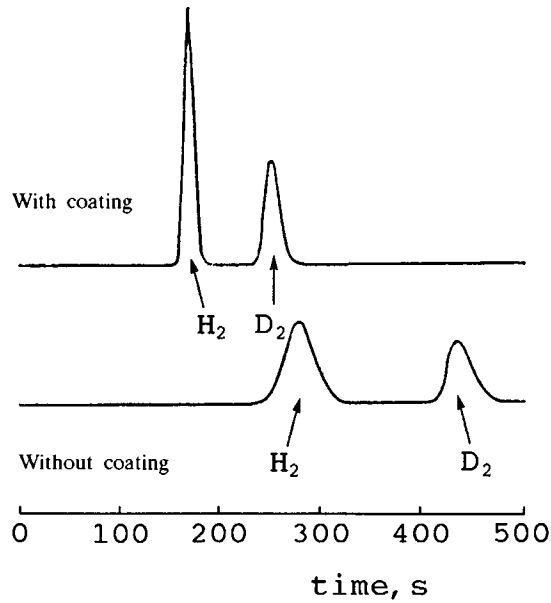

Fig. 5-12 Separation of H_2-D_2 mixture [57].

Column: 2 m × 3 mm i.d., adsorbent: alumina coated with $MnCl_2$ (19% w/w), carrier gas: neon, flow rate 1.933 cm^3/s, temperature: liquid nitrogen.

cidated that such adsorbents were suitable as column packing materials at the temperature of liquid nitrogen for separation of hydrogen isotopes by GSC. Separation of hydrogen isotopes is shown in Fig. 5-12 [57]. However the deactivation effect disappeared when alumina adsorbent was dried at a temperature above 473 K.

Gas chromatographic separation of hydrogen isotopes on different types of molecular sieves at the temperature of liquid nitrogen has been also investigated. Common molecular sieves 5A, 13X are not suited to this purpose. Ion-exchanged or ion-coated molecular sieves (4A, 5A, 13X) in the partially dehydrated state separate the isotopic mixtures H_2, ^2HH, $^2H_2$, and H_2, ^3HH, and $^3H_2$. The resolution varied with ion content and the residual moisture content in the molecular sieves. Good separations were obtained on 15% ion-coated molecular sieve 5A and 5% ion-coated molecular sieve 4A.

5.3 Chemically Modified Adsorbents (Bonded-Phase Silica as Adsorbent in Gas Chromatography)

A wide variety of modified adsorbents now available for HPLC also includes a number of new adsorbents useful for gas chromatography. Chemical modification of adsorbent surfaces may be necessary for the following reasons: 1) support surface may have some sites with high energy strongly adsorbing one or several components of the sample, resulting in a very long retention and/or tailing peaks; 2) some sensitive components may also undergo catalytic reactions during their elution. To overcome these difficulties chemical treatment can be effectively used to deactivate the adsorbent surface. Silanol groups and other groups on the surface of silica gels having a reactive hydrogen moiety can be eliminated by reaction with chlorosilane or aminosilane (see, for example, [4, 59–61]). Chemically bonded silicas include alkyl-bonded (C_4–C_{18}), perfluoropropyl-, cyanopropyl-, aminopropyl-, diolphenyl- and other radicals [4, 60–62]. Most chemically bonded silicas can be used up to stationary temperatures of about 250 °C. HPLC sorbents of this type are successfully used in capillary micropacked columns (see, for example,

[55, 63-68]). For instance, Takeuchi and co-workers [63] investigated application of bonded-phase sorbents for liquid chromatography in gas chromatography. Fused-silica capillary columns of 0.3–0.35 mm i.d. and 0.3–7.7 cm length, packed with octadecyl silica stationary phases (3–30 μm) used for liquid chromatography, were employed in gas chromatography for separation of low boiling hydrocarbons. Rapid separation of components of natural gas is shown in Fig. 5-13 [63].

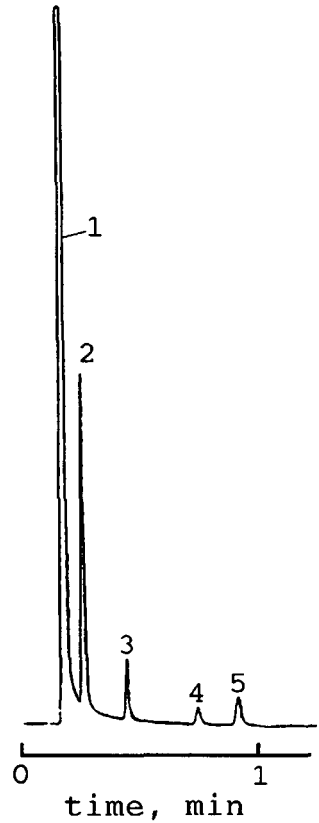

Fig. 5-13 Rapid separation of natural gas [63].

Fused-silica column 30 cm × 0.3 mm i.d., adsorbent — Develosil octadecylsilica ODS-5; carrier gas — nitrogen, inlet pressure — 100 kg/cm^2, column temperature — 35 °C.
Peaks: 1 — methane, 2 — ethane, 3 — propane, 4 — isobutane, 5 — butane.

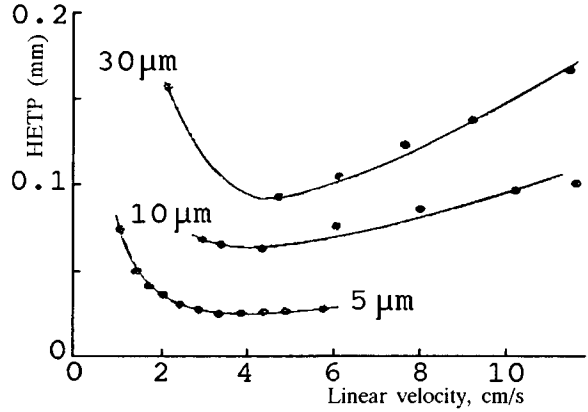

Fig. 5-14 HETP vs. linear velocity of carrier gas [63].

Fused-silica column — 30 cm × 0.3 mm i.d., packed with 5, 10 and 30 μm Develosil ODS; carrier gas — nitrogen, column temperature — 50 °C, sample — heptane.

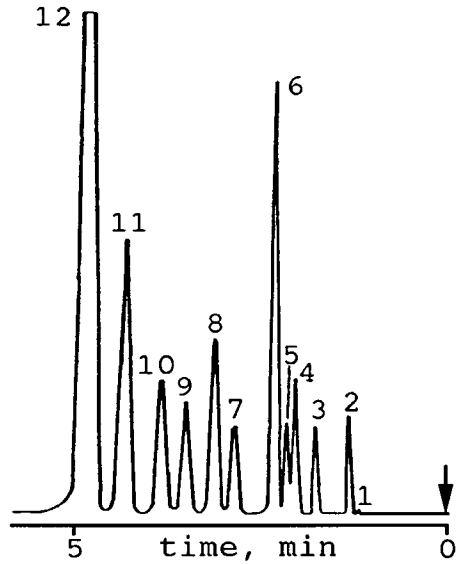

Fig. 5-15 Chromatogram of aliphatic and aromatic hydrocarbons [65].

Fused-silica column 45 cm × 0.38 mm, sorbent — Silasorb C18, ΔP = 24 atm, temperature — 100 °C.
Peaks: 1 — isopentane, 2 — n-pentane, 3 — 2,2-dimethylbutane, 4 — 2-methylpentane, 5 — 3-methylpentane, 6 — n-hexane, 7 — cyclohexane, 8 — benzene, 9 — 3,3-dimethylpentane, 10 — 3-methylhexane, 11 — 3-ethylpentane, 12 — n-pentane.

Fig. 5-14 [63] shows van Deemter plots obtained for columns packed with 5, 10 and 30 μm octadecylsilica. The smaller the particle the less was the dependence of linear velocity on the theoretical plate height. Chromatograms of aliphatic and aromatic hydrocarbons are shown in Fig. 5-15 [65]. Use of the octadecylsilica in micropacked columns allows improvement of the efficiency of capillary packed columns. No tailing was observed. Application of these sorbents to gas chromatography, especially in packed capillary columns, is, in our opinion, a very promising direction [55, 63-69]. We also think that this type of modified adsorbents can be successfully used in gas adsorption on open capillary columns.

5.4 Adsorbents Modified by Volatile Compounds

5.4.1 The Role of Volatile Modifier in Gas Chromatography

The molecules of modifying compound from the carrier gas are adsorbed on the adsorbent surface and can form a film of variable thickness. Surface sites of highest energy are saturated with the molecules of modifying agent, so the adsorbent surface is essentially transformed into a modified surface, which is much more homogeneous energetically than the original one. The properties of the modified surface (for example, thickness of the modifying agent layer) strongly depend on the column temperature and the partial pressure of modifying agent decreases continuously from the column inlet to the outlet. The surface properties also change regularly from the co-lumn inlet to outlet. Retention and column capacity factor, as well as selectivity of the modified adsorbent, usually increases continuously from the column inlet to the outlet. This peculiarity may result in difficulties for the elution of some polar and heavy compounds, i.e. strong retention and tailing [10, 41].

The role of volatile modifier in gas chromatography is very complicated. Volatile modifier changes the interactions of the analyte with both adsorbent and moving (gas) phase. Using the gas-liquid chromatographic system, Laub [70, 71] investigated the role of gas phase non-ideality on the selectivity of gas chromatographic separation. Selectivity of gas chromatographic column can be altered by varying

Second interaction virial coefficient vs. composition of carrier gas

carrier gas (or) its composition, thus causing a change in the solute–carrier virial coefficients. In order to take advantage of these nonideal gas-phase effects, a prediction of the second interaction virial coefficients of vapors of potential interest as carriers in gas chromatography is required [70]. Fig. 5-16 [70] presents plots of a portion of the data for hydrogen with helium, nitrogen, argon, methane, carbon dioxide, ethane, fluorotrichloro-methane, water (dashed curve) and carbon tetra-chloride. As expected the first of these plots, hydrogen with helium, is nearly horizontal, while the later combinations deviate increasingly strongly and negatively from ideality. Experimentally derived pure component virial coefficients B_{ij} for all species except water and hydrogen chloride are shown to fit quadratic equations [70].

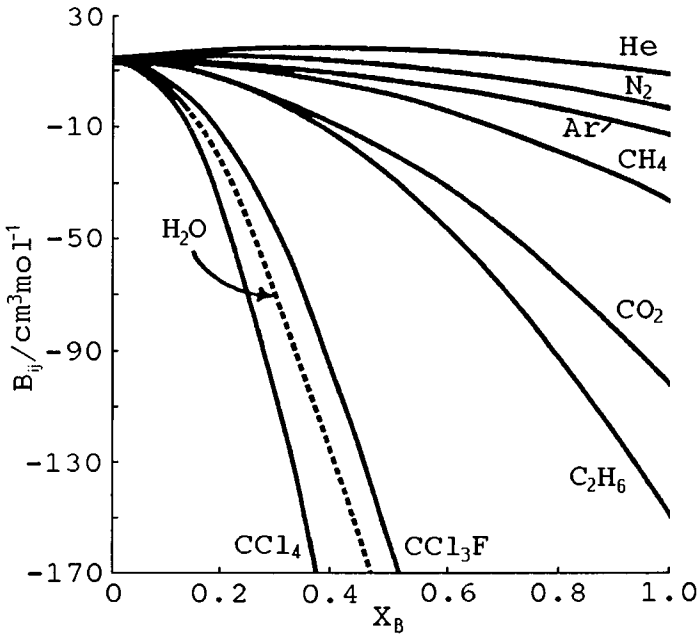

Fig. 5-16 Plots of second-interaction virial coefficients B_{ij} against mole fraction X_B for hydrogen with the indicated gases (B) at 323.15 K [70].

log V_g^0 vs. nature of carrier gas

Fig. 5-17 [71] illustrates variation of $\ln V_g^0$ of some solutes for a transition from one pure carrier to another calculated for 5 (a) and 10 atm (b) column inlet pressure (with 1 atm assumed at the outlet),

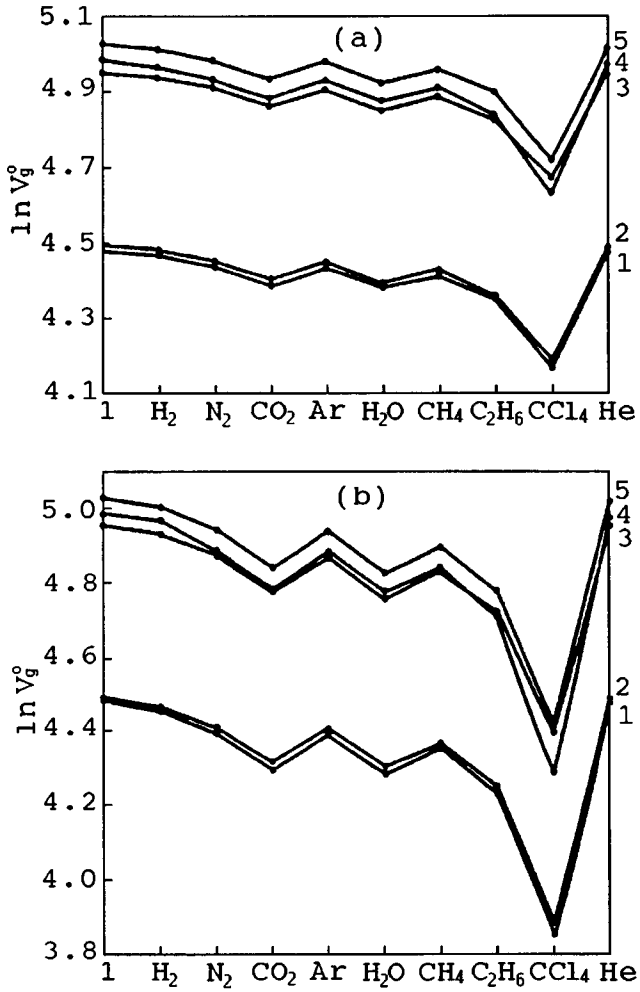

Fig. 5-17 Plots of ln V_g^0 (323.15 K) against indicated carrier gas at (a) 5 atm and at (b) 10 atm column pressure drop [71].

Peaks: 1 — n-hexane, 2 — *trans*-3-hexene, 3 — benzene, 4 — 3,3-dimethylpentane, 5 — cyclohexane.

where straight lines have been drawn between each data point without regard to intermediate compositions. Note that in addition to considerable changes in absolute retentions, the order of elution is altered too when passing from one carrier to another. For example, reversals are found for analyte 3 and 4 (benzene and 3,3-dimethylpentane) on transition from ethane to carbon tetrachloride and then to helium in (a), while inversions occur in (b) for the same analytes on going from methane to ethane and from carbon tetrachloride to helium.

Fig. 5-18 [71] provides an example of the results for five analytes with (hydrogen + Freon 11), where the primed numbers indicate column inlet pressure of 10 atm, while those without primes refer to

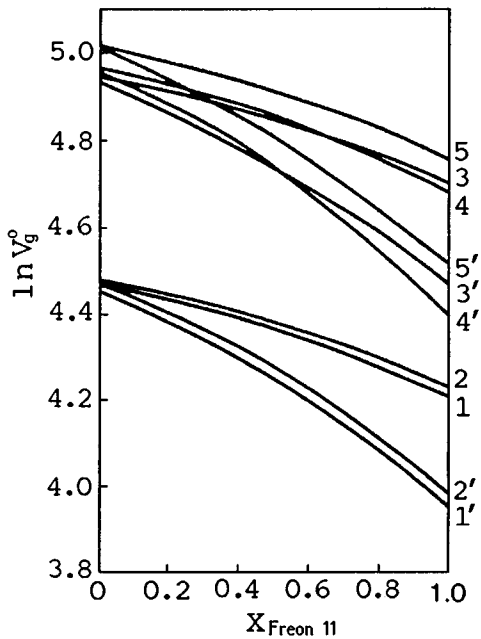

Fig. 5-18 Plots of $\ln V_g^0$ against mole fraction of Freon 11 admixture with hydrogen (gas carrier) at 323.15 K. Primed numbers indicate 10 atm, those without primes refer to 5 atm column pressure drop [71].

Peaks: 1 — n-hexane, 2 — *trans*-3-hexene, 3 — benzene, 4 — 3,3-dimethylpentane, 5 — cyclohexane.

5 atm. Absolute retentions decrease sharply on transition from pure hydrogen to pure haloalkane. Note that the retention order of solutes 3 and 4 inverts, the points of cross-over occurring at X = 0.5 (10 atm) and X = 0.6 (5 atm) [71].

Fig. 5-19 [71] illustrates variation of the specific retention volumes (right-hand ordinate) and the inverse of V_g^0 (left-hand ordinate) of n-hexane as a function of Freon 11 mole fraction as admixture in hydrogen at inlet/outlet pressure ratios of 1.1,

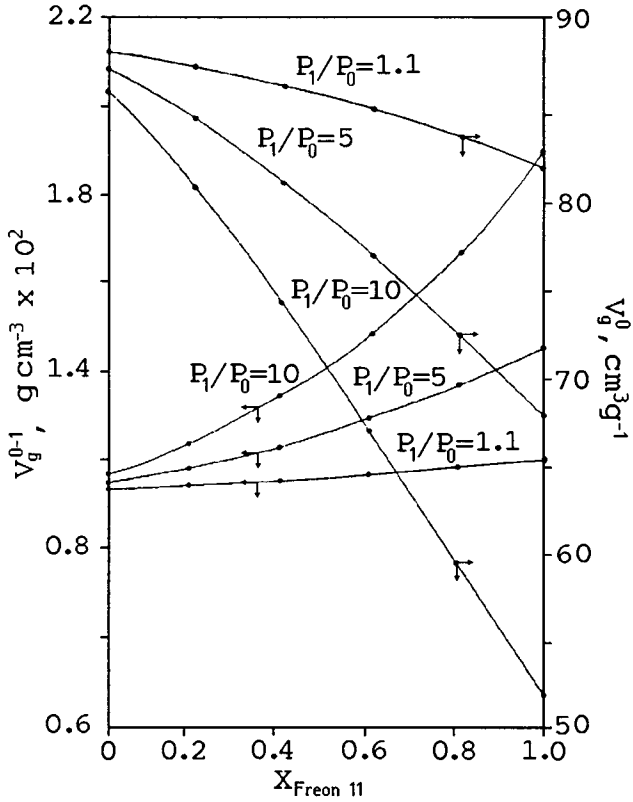

Fig. 5-19 Plots of V_g^0 (right-hand ordinate) and $(V_g^0)^{-1}$ (323.15 K) against mole fraction of Freon 11 in admixture with hydrogen carrier gas for n-hexane solute at indicated column pressure drops [71].

5 and 10. Curves for P_i/P_0 = 1.1 are almost linear, and they are indeed linear at column pressure drops close to zero. At moderate column inlet pressure, both retentions and inverse retentions may regress approximately linearly against mole fractional composition of the mobile phase [71, 72]. Thus the influence of non-ideality of the gas phase containing volatile modifier (for example, carbon dioxide, water), on the chromatographic process is very important in gas chromatography.

As a rule, a modifying agent is both a component of the carrier gas and a constituent of the stationary phase (surface layer of adsorbent). The situation is somewhat reminiscent of the retention in liquid chromatography, where the surface properties depend on the concentration of the modifier in the mobile phase. Analyte retention volume depends on the nature and partial pressure of the carrier gas additive as well as on the nature of adsorbent surface. Therefore the use of a phase system composed of a (modifier–carrier gas) mixture as mobile phase offers the possibility of fine tuning of selectivity and retention by adjusting the modifier content of both phases [10].

The idea of gradient elution (and pressure programming) for gas chromatography have been proposed and discussed for many years (see, for example, [10, 41, 73–80]). This method would involve the use of condensable vapor of "modifiers" in the carrier gas. Modifiers would adsorb in or on the stationary phase, altering the properties of the phase and, consequently, the selectivity of the system and the resolution of the analyzed mixture (see, for example, [10, 41, 72–75, 81–84]).

Although both temperature and volatile modifier programming can be used in practice, the volatile modifier programming techniques would have some advantages over temperature programming, e.g. milder thermal condition, symmetric peaks at low temperature, and shorter cycle times. The method has more significant potential for gas-solid chromatography [76] because of the greater selectivity range achievable by modification of solid surfaces

compared to the polarity range available with a liquid mixture composed of a vapor adsorbed in a high molecular weight liquid phase. In the case of gas-solid chromatography, another possible advantage of the use of such surface modifiers would be an ability of these components to block and deactivate the small number of physical and chemical heterogeneities, the so-called "active sites" present on many adsorbents (e.g. on graphitized carbon blacks too). An additional advantage would be possible manipulation of the retention of different solutes by fractional surface coverage control. That is, the possible utilization of steric or blocking effects observed on solid adsorbents can be useful for altering and controlling chromatographic selectivity. The major experimental disadvantage of the proposed methods is the need for a selective detection system that would not be adversely affected by vapor component in carrier gas; however, some proposals have been made [74].

It is very interesting to compare the modifying effects observed by Kiselev and Yashin [4] and Bruner et al. [83, 85] for systems with nonvolatile modifiers, i.e. common stationary liquid phases. These modifiers block and deactivate the active sites on graphitized carbon blacks, and also alter the selectivity of the stationary phase with adsorbent. On the other hand, Lin and Parcher [76, 77] have also observed the same effects with volatile modifiers. However, volatile modifiers offer the significant possibility of continuous, external control of chromatographic selectivity.

Retention mechanism in GSC

The retention mechanism in gas-solid chromatography with vapor mobile phase is complex. Interfacial adsorption processes, influenced by cooperativity and steric effects are the predominant mechanisms; in addition, the bulk solubility may operate at high pressures (multilayer adsorption) of modifiers. Parcher, Lin and Johnson [75] suggested the specific retention volume equation, which provides the first quantitative description for retention of one solute as a function of the surface coverage by a second component (modifier):

$$V^{o}_{g,i}(\eta) = K_i \cdot 273 \cdot R(1-\eta) \cdot$$
$$\cdot \exp\left[\frac{2\alpha_{ij}}{\beta_j RT} - (1 + 2\frac{\beta_i}{\beta_j})\frac{\eta}{1-\eta} - \frac{\beta_i}{\beta_j}\left(\frac{\eta}{1-\eta}\right)^2\right] \quad (5\text{-}1)$$

where η is a fixed surface coverage by component *j*, α_{ij} is the interaction term for unlike pairs *ij*, β_i and β_j are the size parameters of sorbate *i* and sorbate *j*, respectively, K_i is the adsorption coefficient, which represents in this equation the limiting value of the ratio $\eta_i(ads)/P_i$ when limit $P_i \rightarrow 0$ and $P_j \rightarrow 0$ (P_i and P_j are equilibrium pressures of solutes *i* and *j*, respectively), $\eta_i(ads)$ is the amount of component *i* adsorbed on the stationary phase.

This equation gives a quantitative relation for the retention volume of an infinite dilution solute, *i*, as a function of the surface coverage by a second adsorbate *j*.

If no modifier is present, the carrier gas is not adsorbed on the adsorbent, the specific retention volume can be related directly to the adsorption coefficient by the equation:

$$V^{o}_{gi} = 273\, R \cdot K_i \quad (5\text{-}2)$$

The main demands on modifying agents are listed below: 1) as a rule the modifying agent is a polar compound, capable of strong interactions with active sites of adsorbent surface; 2) the modifying agent is a thermally and chemically relatively stable compound; 3) sensitivity and response factor of the detector used to modifying agent are very small; modifying agent is practically "transparent" to the detector.

Several modifying agent are known, but application methods are well developed for water only.

5.4.2 Water Vapor as Carrier Gas and Modifying Agent

Water vapor (steam) can be used as a mobile phase. This variant of chromatography was originally suggested by Dumazert and Chiglione [86], who used pure water steam as moving phase,

and Turketlaub et al. [87], who used water vapor in air (carrier gas) as modifying agent.

Further important steps were developed by Nonaka [73, 88], Vigdergauz and co-workers [81] and other researchers (see, for example, books [4, 10, 41] and papers [73, 89]).

In many cases application of carrier gas containing water vapor is useful. For instance, Goretti, Liberti and Nota have used inert carrier gas with water [90]. By analyzing a mixture of methane, propane, isobutane, and n-butane they obtained gas chromatographic characteristics of columns with graphitized carbon black (Stirling MT and FT). Measurements have been made with a flame ionization detector. Tailed peaks were produced for many compounds. Tails were eliminated by continuous feeding of water vapor into the carrier gas. This was achieved by bubbling the nitrogen through a water trap which was kept at a temperature slightly less than the column (for example, if the column temperature is 60 °C, then the water trap temperature is 58 °C).

Using water vapor as carrier gas and modifying agent has certain merits compared with traditional carrier gases. In our opinion, the main advantages of water vapor and other similar media lie in the fact that the mobile vapor phase can play an active role in the chromatographic process. It can significantly influence not only the column efficiency, but also the selectivity of chromatographic separations. It becomes reasonable to use gradient techniques for this form of gas chromatography [10, 74, 91, 92]. We have already shown [93] that water steam can be used successfully as carrier gas in capillary gas chromatography, but it will be especially promising in adsorption capillary gas chromatography.

Methods for obtaining water vapor as mobile phase

Methods for obtaining water vapors as mobile phase are not complicated. Usually, production of water vapor, or a carrier gas containing some water vapor, consists in the following steps: 1) production of vapor in a heated evaporator containing

the liquid (see, for example, [94, 95]); 2) production of vapor in a heated evaporator into which water is fed at a given rate [95], and 3) production of a mixed carrier gas by gas flow saturation with water vapor, for instance, by bubbling the gas through a water layer (see, for example, [10, 81]). As already indicated, such devices are simple in design and provide means of supplying water vapor at a required rate, thus producing the necessary mobile phase flow. Several systems have been described for steam production where steam was used as the only component of the mobile phase [87, 88, 94], or as one of the components of mobile phase [10, 96, 97].

Fig. 5-20 [10] shows one of the instrumental designs for producing steam at the pressure controller (1) on the inlet of the gas stream. The carrier gas bubbles through water in water tank (4) and goes to the sampling port (6) and then to the column (7).

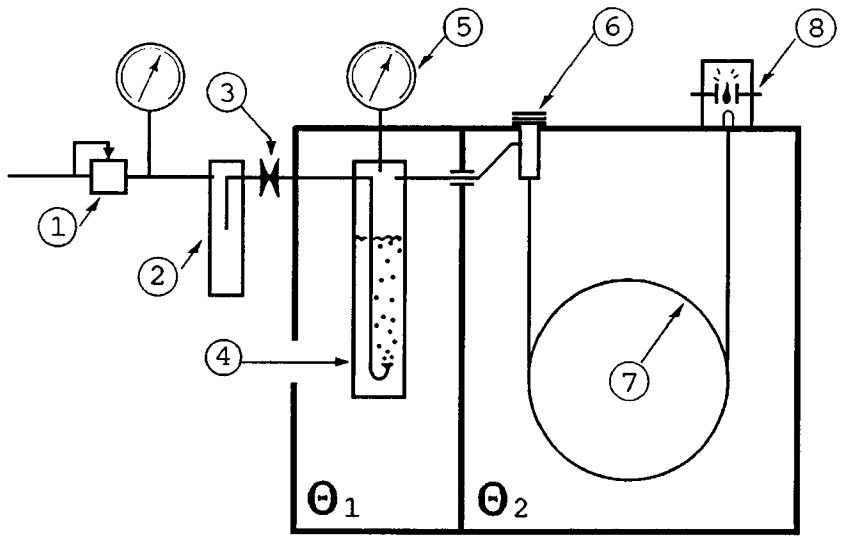

Fig. 5-20 Scheme of the carrier gas flow for gas chromatograph with steam as a carrier gas component [10].

1 — pressure controller of the inlet gas, 2 — safeguard tank for water from 4, 3 — stop valve, 4 — water tank, 5 — pressure gauge, 6 — sampling port, 7 — column, 8 — detector. Θ_1 — thermostat 1, Θ_2 — thermostat 2.

The water tank (4) is placed in a temperature controlled oven, separated from the column oven. Noise resulting from the formation of bubbles in the water tank (4) can be considerably reduced by use of metal frit with 10 to 20 μm porosity. The sampling port, the chromatographic column and the detector should always operate at a temperature higher than that of the water tank. In most applications a flame-ionization detector is used.

The hydrogen flow rate to the detector must be slightly higher than for conventional analyses, in order to keep the flame sufficiently hot. In these applications hydrogen flow rate is typically 3 l/h, while the air flow rate is 15 l/h. A large excess of air is required to avoid condensation of water in the detector [10].

Retention vs. water content in the mobile phase

The influence of water content in the carrier gas on the retention of chromatographed compounds is rather strong. Fig. 5-21 [98] shows the dependence of capacity factors of analytes on the water content in the mobile phase. The increase in water content decreases the sorbent activity, since the surface become increasingly water coated and homogeneous. As follows from Fig. 5-21 the column capacity factor decreases exponentially with increasing water content. Retention changes are especially sharp for polar compounds (for example, for acetone and methyl ethyl ketone). Fig. 5-21 can be useful for the selection of the optimum water steam content.

The retention time of chromatographed compounds changes significantly with increasing temperature (see Fig. 5-22 [98]). The order of elution (for example, for 1,2-dichloroethane and methyl ethyl ketone) also changes, as can be seen from Fig. 5-22. This type of function can be used for separation optimization.

Analysis of water samples

Using water as a component of carrier gas makes it possible to extend the field of application of adsorbents for more polar compounds. However, the most important field for this technique is the analysis of organic pollutants in water samples [10]. A very large injection volume is required for

trace analysis, but it makes quantitative analysis both less accurate and less reliable when dry carrier gas is used. Injection of large water samples (20–200 μl) results in the production of large volume of mobile phase (25–250 ml NTP, respectively). To avoid spurious detector signals and baseline drifts, as well as other complications and mistakes, the flow-rate controller on the inert carrier gas line is replaced by a pressure controller, operating at the pressure required for maintaining

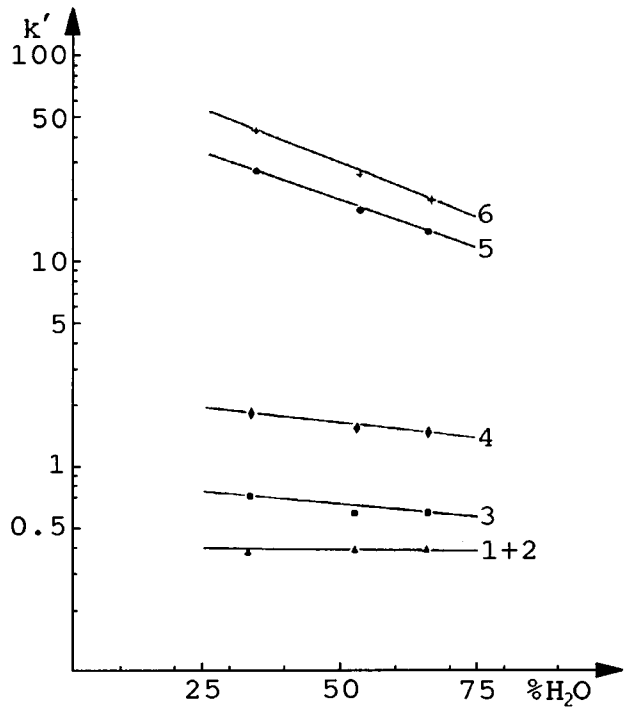

Fig. 5-21 Plot of logarithm of column capacity factor versus water content in the mobile phase [98].

Column: 2 m × 4 mm i.d., adsorbent Spherosil, 32 m^2/g; particle size 150–200 μm; column temperature 115 °C; carrier gas nitrogen and steam (33%, 52% and 60%); flow rate 3 l/h.

Peaks: 1 — 3-methylpentane, 2 — cyclohexane, 3 — n-heptane, 4 — 1,2-dichloroethane, 5 — acetone, 6 — methyl ethyl ketone.

the desired flow rate through the column [10]. A one-way valve, placed between the sampling port and the pressure controller, prevents back flow of steam with subsequent flooding of the upstream gas line. Thus, when the large water sample is injected and vaporized abruptly, giving rise to a strong pressure rise in the sampling port, the inert gas flow rate is reduced and the total flow rate through the detector is kept nearly constant. The migration of the large band of steam-enriched carrier gas does not seem to create changes in the retention pattern serious enough to result in

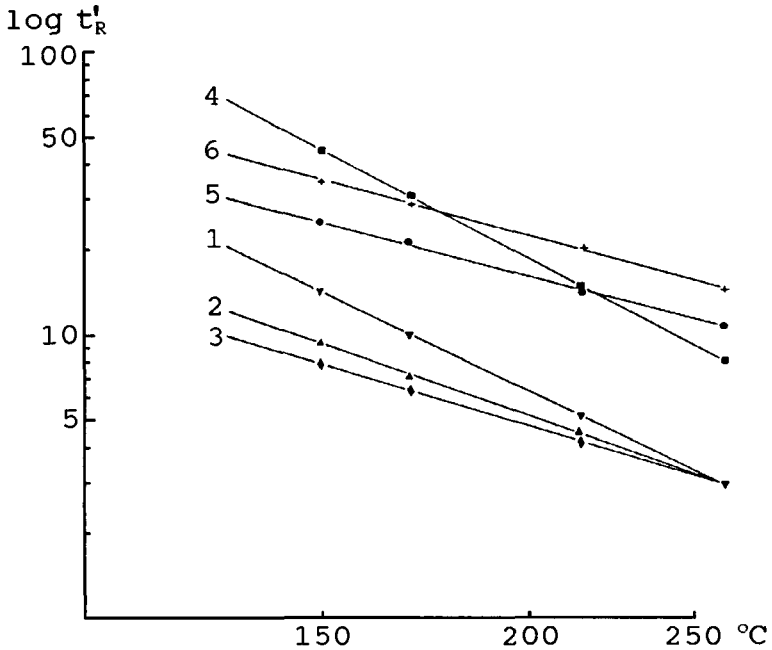

Fig. 5-22 Plot of logarithm of the corrected retention time versus column temperature [98].

Column: 1 m × 4 mm i.d., adsorbent Spherosil, 50 m^2/g, coated with pyrocarbon, particle size: 150–200 μm, carrier gas: nitrogen 56%, steam 44%, flow rate 3.06 l/h, temperatures: 150 °C, 170 °C, 216 °C and 260 °C.

1 — 3-methylpentane, 2 — cyclohexane, 3 — n-heptane,
4 — 1,2-dichloroethane, 5 — acetone, 6 — methyl ethyl ketone.

significant errors on either the determination of the retention times (qualitative analysis) or the peak area (quantitative analysis) [10]. As example, chromatogram of trace amounts of organic compounds in aqueous samples is shown on Fig. 5-23 [98].

Modification of molecular sieves by water vapor

Very interesting results are obtained on zeolites using a moistened carrier gas [99]. A systematic study has been made on the chromatographic properties of a KY zeolite using a moistened carrier gas at a partial water vapour pressure (from 0 to 2.35 kPa) over a wide temperature range (40–300 °C) [99]. Plots of the specific retention volume versus the partial water pressure in the carrier

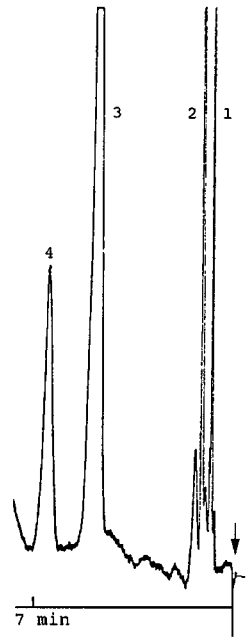

Fig. 5-23 Chromatogram of organic compounds trace in aqueous sample [98].

Column: 2 m × 4 mm i.d., adsorbent Spherosil, 32 m^2/g, particle size 150–200 μm, column temperature 160 °C, carrier gas: nitrogen 35% and steam 65%, flow rate 3 l/h, detector: FID, hydrogen flow rate 4 l/h, air —20l/h, sample 25 μl. Peaks: 1 — 0.6 ppm cyclohexane, 2 — 0.8 ppm heptane, 3 — 6 ppm acetone, 4 — 1 ppm methyl ethyl ketone.

gas are shown in Fig. 5-24 [99]. The specific retention volume strongly depends on the partial water pressure in the carrier gas in the area of medium temperatures. The use of a moistened carrier gas provides more efficient separation of gases on zeolites [99].

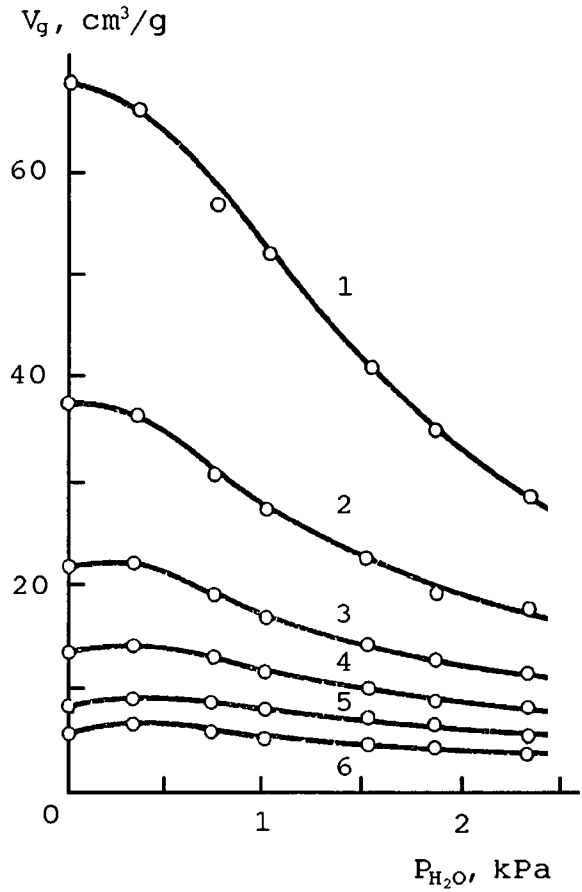

Fig. 5-24 Plots of specific retention volume of ethane versus partial water pressure in carrier gas [99].

Column: 100 cm × 3 mm, adsorbent — molecular sieve KY, temperatures: 1 — 60 °C, 2 — 80 °C, 3 — 100 °C, 4 — 120 °C, 5 — 140 °C, 6 — 160 °C.

5.4.3 Water Vapor (Carrier Gas) and Inorganic Salts (Stationary Phase) in Gas Chromatography

Modification of the solid support (adsorbent) by inorganic salts (water vapor mixed with nitrogen or pure water vapor are used as carrier gases) is, in our opinion, a very promising field [91, 92, 100–104].

The main task of analytical gas chromatography is separation of complex mixtures into their individual components; the resolution achieved is critically dependent upon the correct choice of stationary liquid phase. Although hundreds of commercially available stationary liquid phase are known, intensive searches for novel phases and further study of those already in use continue. Crystal hydrates undergo dynamic dehydration in a stream of dry gas.

To ensure long life and stable performance of a gas chromatographic column, carrier gas should contain water vapor. The partial pressure of water vapor in the carrier gas above the crystal hydrate should not be less than the equilibrium water vapor pressure at the separation temperature. If the vapor pressure of water in the carrier gas is higher than the equilibrium water vapor pressure of the crystal hydrate, then a solution of crystal hydrate in water "automatically" takes over as stationary liquid phase, and the water vapor pressure above this solute coincides with the water vapor pressure in the mobile phase. That is why increasing the column temperature leads to the decomposition of the phase, and consequently to large changes in the retention characteristics.

Using salts as stationary phases with water mobile phase

The selectivity of crystal hydrates used as stationary liquid phase in gas chromatography could have the following origins:

1) Interaction of the separated compounds with water and water-containing complexes. A certain analogy is observed between the chromatographic properties of pure water and molten crystal hydrates used as stationary liquid phases.

2) Interaction of the separated compounds with the salt components of crystal hydrates or with the salts dissolved in molten crystal hydrates.

Alcohols characteristically undergo specific hydrogen bonding interactions with molten crystal hydrates. The heats of solution of the crystal hydrate $Mg(NO_3)_2 \cdot 6\ H_2O$ are 7 kcal/mole for butyl alcohol, 6.4 kcal/mole for propyl alcohol, 3.6 kcal/mole for acetone and 3.6 kcal/mole for ethyl acetate. The energy of the hydrogen bonds usually lies within the range of 3 – 8 kcal/mole.

Melts and aqueous solutions of crystal hydrates exhibit unusual retention characteristics (see Fig. 5-25 – 5-27).

Fig. 5-25 [91] shows a separation of polar and non-polar compounds. Inorganic salts impregnated

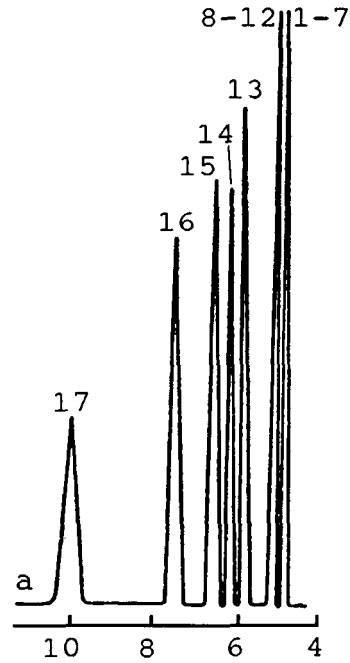

Fig. 5-25 Group separation of aromatic and aliphatic hydrocarbons and alcohols [91].

Liquid phase — water solution of $Zn(NO_3)_2$, carrier gas — steam, column temperature — 120 °C.
Peaks: 1–7 — methane, ethane, hexane, *trans*-hexene-2, *cis*-hexene-2, cyclohexane; 8–12 — benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene; 13 — pentanol, 14 — butanol, 15 — propanol, 16 — ethanol, 17 — methanol.

Unusual separation of hydrocarbons and alcohols on aqueous salts

on a solid support with steam as the mobile phase can be used to obtain highly selective packed columns. Separation of polar compounds on a sorbent coated with lithium chloride is shown in Fig. 5-26 [102]. The separation is very selective. Thus the use of inexpensive and accessible inorganic salts allows selective resolution of complex organic mixtures which can be obtained, as a rule, only by use of highly efficient capillary columns.

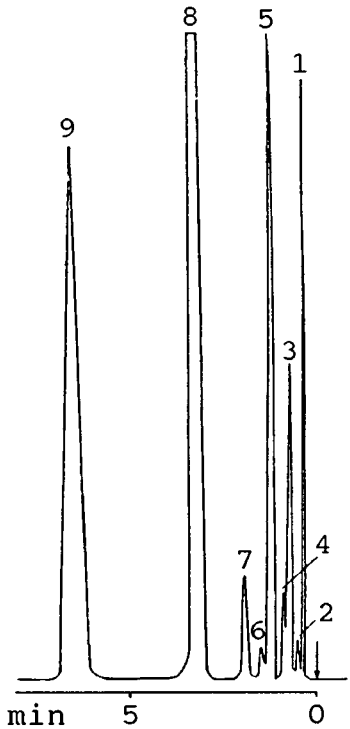

Fig. 5-26 Chromatogram of polar organic compounds on lithium chloride [102].

Column — 190 cm × 2 mm I.D., sorbent — 7% lithium chloride on Inerton N-AW (0.125–0.16 mm), temperature — 119 °C, inlet pressure — about 1.9 atm, carrier gas — water vapor.
Peaks: 1 — diethyl ether, 2 — ethyl acetate, 3 — methyl propyl ketone, 5 — acetone and n-butanol, 6 — isobutanol, 7 — n-propanol, 8 — ethanol, 9 — methanol.

Olefin separation on $AgNO_3$ in steam (mobile phase)

The chromatogram of dissolved C_{10}–C_{13} is shown in Fig. 5-27 [103]. Almost all the peaks are symmetrical. The stationary phases investigated (20% $AgNO_3$ on Celite C-22) are highly selective towards alkenes. The difference in the retention indices for decene isomers ΔI=I(*cis*-5-decene)-I(*trans*-5-decene) is 76 units, i.e., the selectivity towards these isomers is essentially higher than that with known polar and non-polar stationary phases. For example, with squalane, Apiezon, dibutyl tetrachlorophthalate this difference is 3, 2 and 6 units, respectively.

Retention on inorganic salts (steam–carrier gas) has the following features:

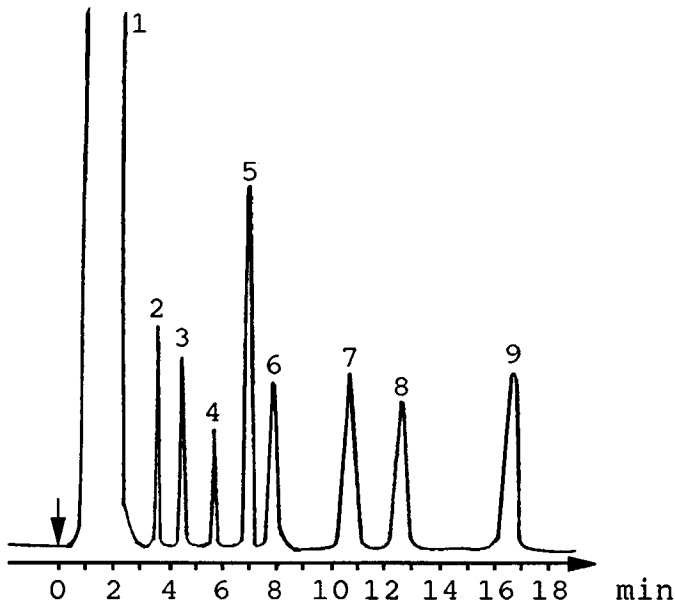

Fig. 5-27 Separation of C_{10}–C_{13} olefins on $AgNO_3$ using steam as the mobile phase [103].

Experimental conditions: stationary phase — 20% $AgNO_3$ on Celite C-22, stainless-steel column (2 m × 3 mm i.d.), temperature: 108 °C.
Peaks: 1 — hexane, 2 — *trans*-5-decene, 3 — 1-decene, 4 — *cis*-5-decene, 5 — *trans*-6-dodecene, 6 — 1-dodecene, 7 — *cis*-6-dodecene, 8 — *trans*-5-tridecene, 9 — *cis*-5-tridecene.

1) A very strong retention of compounds which undergo hydrogen bonding (alcohols, etc.).

2) Poor retention of aliphatic and aromatic hydrocarbons.

3) Reverse elution order, of homologous alcohols, nitroalkanes, etc. compared to conventional stationary phases.

If we use inorganic salts in minor concentrations together with water steam as carrier gas, inorganic salts can play the role of modifiers in usual sense.

5.4.4 Carbon Dioxide as Carrier Gas and Modifying Agent

Gas phase non-ideality and carrier gas adsorption influence analyte retention [41, 10]. The influence of carrier gas adsorption is often more important. For example, when alkanes are eluted on Porasil C (50–100 m^2/g) using carbon dioxide as carrier gas at 80 °C a considerable (30–40%) decrease of column capacity factor is measured if the pressure is raised from 1.3 atm to 5.1 atm [105]. It can be estimated that about 15% of the silica surface is covered with carbon dioxide at corresponding average pressure [106].

Application of carbon dioxide as carrier gas can also decrease band broadening for the following reasons.

1. Axial molecular diffusion can be decreased by increasing the molecular mass of the carrier gas. Under some circumstances this phenomenon can have beneficial effects. Carbon dioxide as carrier gas leads to a decrease in the minimum HEPT as compared to hydrogen [107, 108].

2. Heavy carrier gas may have a profound effect on the adsorptivity and separation of gases and volatile compounds in gas-solid chromatography, especially when using molecular sieves. Incidentally, carbon dioxide is "transparent" to the flame ionization detector. Therefore it is convenient to use carbon dioxide in quasi-displacement chromatography [10, 107–110]. In gas chromatography on zeolites "active" carrier gases (such as water vapor and carbon dioxide) are rarely used because they are selectively and strongly adsorbed on

Separation of hydrocarbons on zeolites in CO_2 (carrier gas)

zeolites. Andronikashvili, Berezkin and co-workers [109] showed that carbon dioxide as carrier gas allows good separation of some hydrocarbon gases mixtures on zeolites at lower column temperature and faster that with the use of conventional inert carrier gases such as helium (see Fig. 5-28 [109]).

The nature of the carrier gas strongly affects the separation of model mixtures. A six-component mixture of hydrocarbon gases can be separated completely on sodium zeolite at a column temperature of 20 °C with carbon dioxide, whereas the conventional carrier gases such as hydrocarbon and helium are not able to separate this mixture (see Fig. 5-28). It is interesting to note that, in contrast to carbon dioxide, use of helium or nitrogen as carrier gas with this form of zeolite does not result in a temperature inversion of the elution order propane-ethylene and butane-propylene, i.e., an unsaturated compound is eluted after the corresponding saturated compound at any column temperature.

Mixtures of C_1–C_4 hydrocarbon gases were found to be separated on zeolites of type Y in sodium, cadmium and silver forms at column temperatures of 25–100 °C.

When columns filled with NaY and also with CdY zeolite were used with carbon dioxide as carrier gas, a considerable decrease in specific retention volumes of hydrocarbon gases was obtained, especially at low temperatures typical of carbon dioxide adsorption on zeolites, screening of cations and partial deactivation of the adsorbents. Use of carbon dioxide as carrier gas improves the separating ability of zeolites without complete suppression of the cation effects on the separation and widens the range of zeolite applications in gas chromatography [109].

Andronikashvili, Berezkin and co-workers [110] studied the effects of carrier gas, adsorbent type (volumetric or surface layer) and the nature of the zeolite cation on the chromatographic process. By use of a model mixture, consisting of hydrocarbons,

alcohols, ethers and ketones, they found that the use of carrier gases such as carbon dioxide and zeolites in the form of surface layer adsorbents increases the efficiency of the chromatographic column, decreases the analysis time, makes the peaks more symmetrical, allows separations at lower column temperatures and broadens the range of zeolite utilization in gas chromatography. Chromatograms showing separation of model hydrocarbon mixtures are presented in Fig. 5-29 [39]. As follow from these results, the use of carbon dioxide as carrier gas and surface layer adsorbent is very promising.

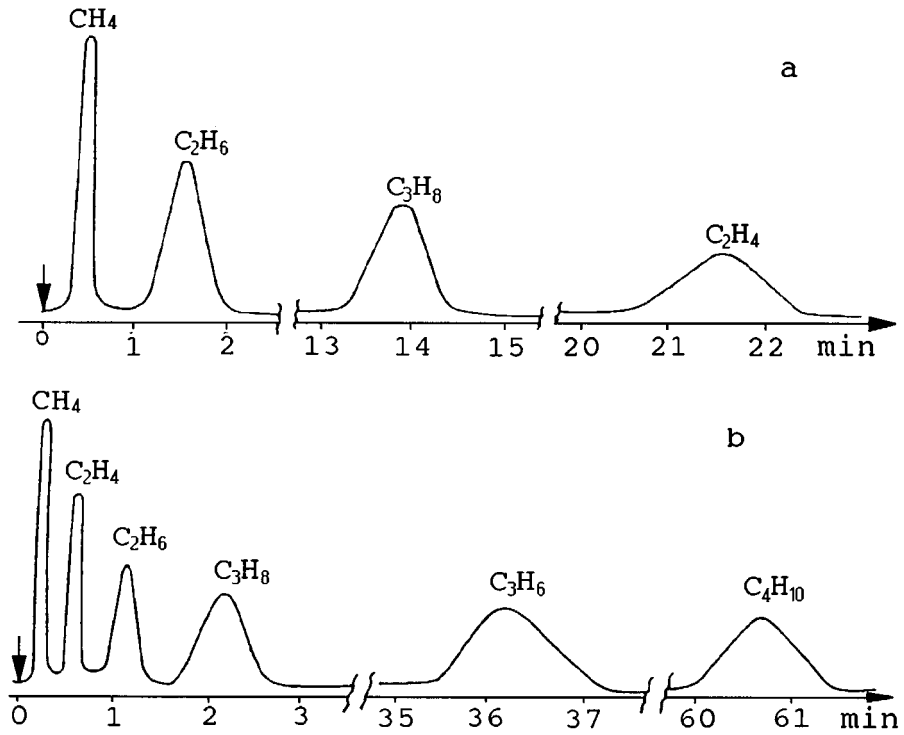

Fig. 5-28 Chromatograms of C_1–C_4 hydrocarbon gases [109].

Adsorbent: NaY, column: 0.5 m × 4 mm i.d., column temperature: 20 °C, carrier gases: (a) helium, (b) carbon dioxide.

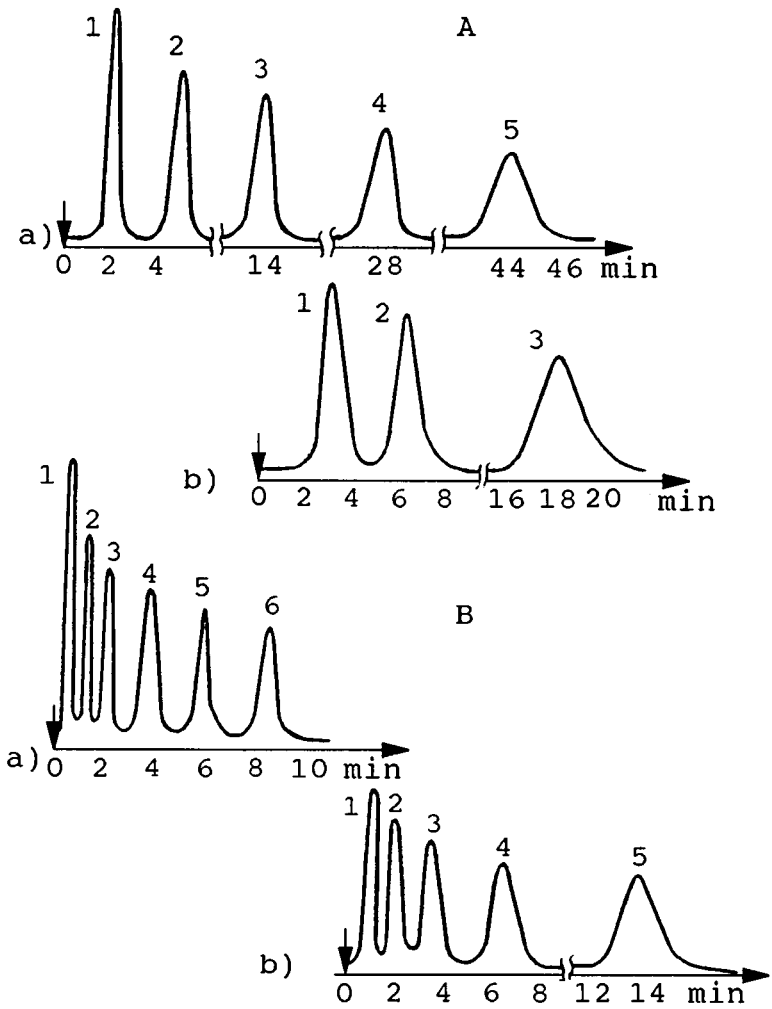

Fig. 5-29 Chromatograms of C_5–C_{10} hydrocarbon mixture on zeolite HY [110].

(A) volumetric adsorbent, column temperature 300 °C, (B) surface layer adsorbent, column temperature 225 °C.
Column 0.5 m × 4 mm i.d., carrier gases: (a) carbon dioxide, (b) helium.

Peaks: 1 — pentane, 2 — hexane, 3 — heptane, 4 — octane, 5 — nonane, 6 — decane.

5.4.5 Use of Volatile Modifier ("Transparent" to the Flame Ionization Detector)

In our opinion, the use of gas and volatile compounds (for example, ammonia and formic acid) of both basic and acidic nature as carrier gases and flame forming agents in gas-solid chromatography holds considerable promise.

The use of ammonia as carrier gas appears promising because: 1) the velocity of ammonia is much lower than that of widely used carrier gases such as nitrogen and helium, and, 2) ammonia readily forms hydrogen bonds with many active groups (for example, with silanol groups) at the adsorbent surface, and is likely to form stable complexes with a number of metals that can be present as surface contaminations (the second reason is more important). Consequently, through the use of ammonia as carrier gas (or as an additive to carrier gas) losses of polar compounds (especially amines) on column can be minimized. The symmetry of the chromatographic zones will be improved and the retention times shortened. A number of publications describe the use of ammonia as carrier gas [111–114].

Further application of ammonia in gas chromatography (and especially in gas-solid chromatography) appears appropriate. Formamide is also a compound of basic character and its use as carrier gas becomes beneficial in separating polar amines. Formamide has been shown to improve chromatographic zone symmetry for basic solutes and other polar compounds [115].

An acidic modifying agent is also available, namely, formic acid. It has been successfully used in gas-liquid-solid chromatography as a volatile "reagent" to suppress solute adsorption on the surfaces of apparatus and solid supports [116–119]. Formic acid is a relatively strong organic acid. It effectively suppresses adsorption of acidic and polar compounds on solid surfaces. The presence of formic acid vapor in carrier gas improves the symmetry of chromatographic zones, increases the chromatographic separation efficiency (through narrower zones), and even improves the separation selectivity.

It should be noted that the use of carrier gas containing formic acid vapor is advisable both in gas-liquid-solid and in gas-solid chromatography. Ackman [117] noted the beneficial effects of formic acid addition during the analysis of organic acids on porous polymers (Porapak and Chromosorb 101). Information on the improvement of analytical results with organic acids on Porapak N was reported in another paper [120]. The described procedure was based on a sequential injection of formic acid (5 ml) onto the column between the analysis. Therefore formic acid addition to carrier gas improves analytical results for organic acids determination. Formic acid can be also used directly as a flame-forming agent [74, 121]. Note that "neutral" carbon disulfide was also suggested as carrier gas and flame-forming agent in flame ionization detectors [74]. In conclusion, bilateral use of some compounds as mobile phases in gas chromatography and as flame-forming agents for flame-ionization detectors, provides considerable scope for individual analysis [74].

5.4.6 Using Volatile Modifier with Super-Selective Detector

Great investment in the development of gas chromatography with volatile modifier (or in vapor gas chromatography) was undertaken by Parcher and co-workers [75–78].

Chromatograms of n-pentane on Carbopack C with acetone (modifier) in the carrier gas over a wide temperature range are shown in Fig. 5-30 [76]. The main effect of acetone dopant consisted in diminishing the retention time of pentane at low temperatures. Thus the eluted peaks were sharper at the lowest temperature than at intermediate temperatures (30–40 °C). This effect is illustrated in Fig. 5-30 [76]. The loss of available adsorbent surface due to the preferential adsorption of acetone caused rapid elution of pentane and significant decrease of the peak width. Carbopack adsorbents are known to be very useful for polar sample separation. However, they must be deactivated with a small amount of a non-volatile liquid. Non-deactivated adsorbents are not suitable for polar solutes. As an example, Fig. 5-31 [76] illustrates

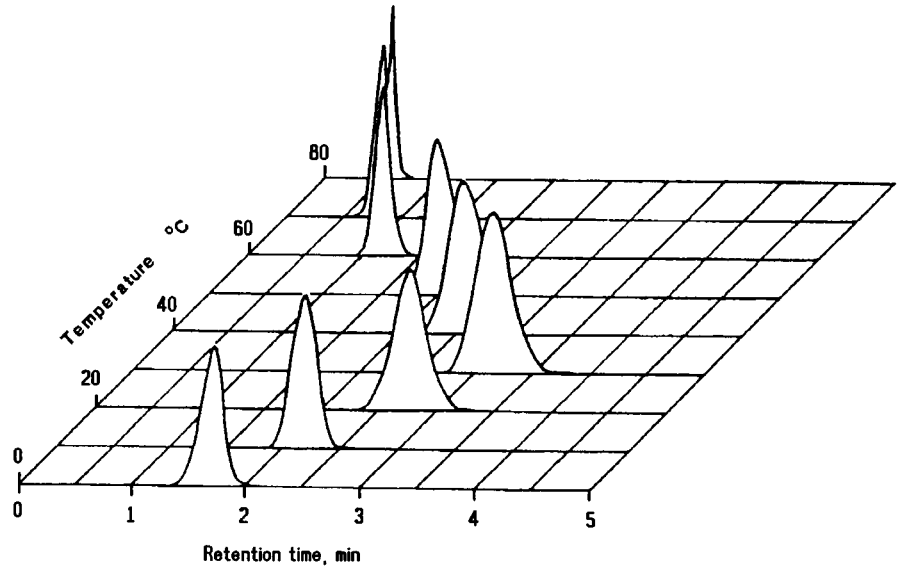

Fig. 5-30 Chromatograms of n-pentane on Carbopack C with acetone (19 torr) in the carrier gas over a wide temperature range [76].

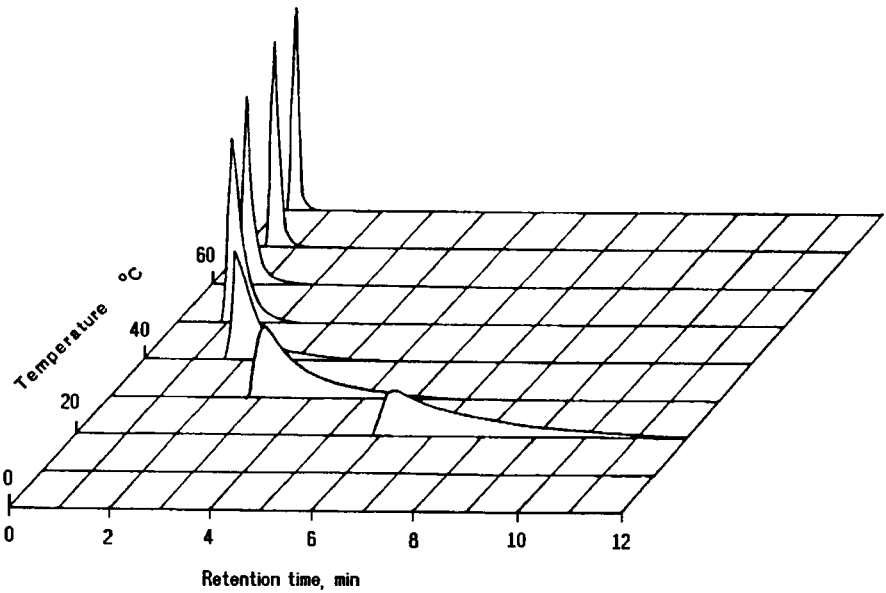

Fig. 5-31 Chromatograms of 1-propanol on Carbopack C with helium as carrier gas [76].

chromatograms of 1-propanol on untreated Carbopack C with helium as carrier gas. The chromatograms are bad, especially at lower temperatures. Peak tailing was caused by preferential adsorption on active sites of the unmodified adsorbent. Blocking the active sites with a small amount of polar stationary phase is an effective but inflexible deactivation method. In addition, liquid loading may be critical for selectivity and resolution of modified sorbent (for example, see [85]). A blocking effect, similar to that observed with nonvolatile adsorbates, can be achieved with volatile modifiers such as acetone. Adsorption of acetone on Carbopack C significantly reduced propanol retention time and peak width, as shown in Fig. 5-32 [76].

Chromatograms of propanol on acetone-modified Carbopack C are similar to those obtained on Carbopack C coated with 0.2% Carbowax. This elution curve is displayed as the solid peak in

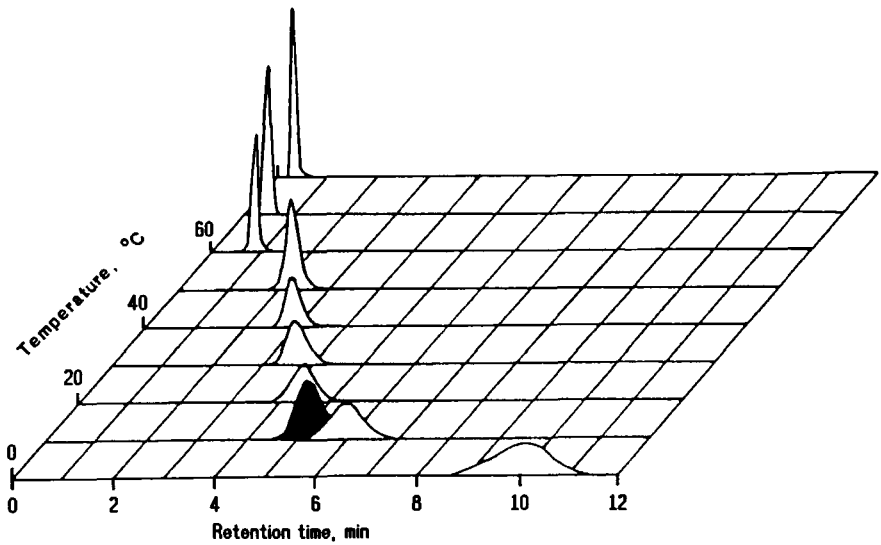

Fig. 5-32 Chromatograms of 1-propanol on Carbopack C with acetone (40 torr) in the carrier gas.

The solid peak is the profile for 1-propanol at 0 °C on Carbopack C, coated with 0.2% Carbowax-1500 [76].

Fig. 5-32 [76]. The chromatograms in the figure present the results for one acetone pressure. The effect of acetone dopant on peak shape and retention volumes persisted even at the lowest pressures investigated [76]. Therefore, the volatile modifier blocking process can be used to "mimic" (to simulate) the deactivation and to improve the chromatographic efficiency produced by low loading of non-volatile liquid on solid adsorbents.

Apparatus with super-selective detector for using volatile modifier

In our opinion, an experimental method, which allows use of methods with volatile modifiers is very important [76]. A mass-spectrometric (MS) detector can be "tuned" to measure retention time of a particular solute or group of solutes while ignoring other components including volatile modifiers [122]. The GS-MS method for adsorbable carrier gas is discussed in more detail by Parcher et. al. [51]. The instrumentation is shown in Fig. 5-33 [122] S_1 and S_2 are flow transducers, S_3 and S_4 are pressure transducers, R_1 and R_2 are flow control valves and GSV represents a gas sampling valve used for injection of gaseous solutes. The benzene

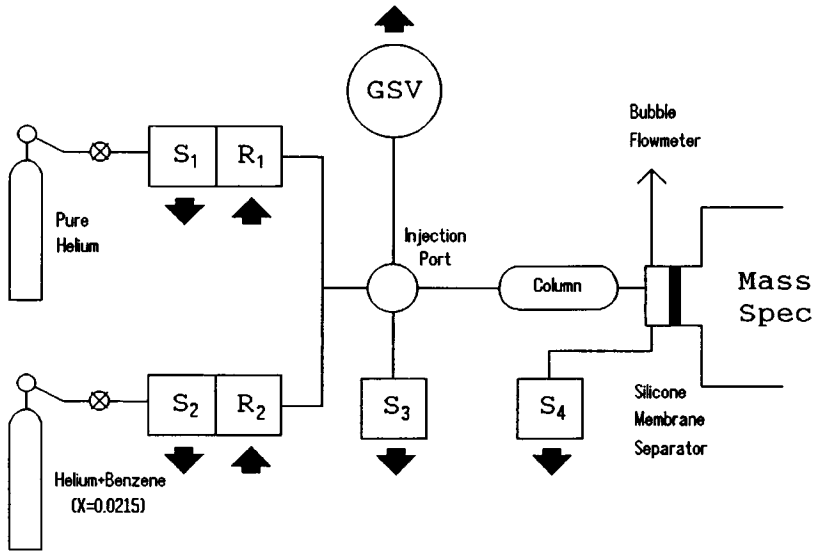

Fig. 5-33 Experimental apparatus with mass spectrometer (selective detector) for gas chromatography with volatile modifier [122].

mole fraction in the tank for mixed gas was X = 0.0215. Thus the benzene mole fraction in the carrier gas can be varied from 0 to 0.0215 by control of proportional flows from each source by the controllers R_1 and R_2. The entire flow and injection system was monitored and controlled by a microcomputer. The precise flow and pressure control provided by this instrumentation was necessary in order to accurately determine large variation in retention often observed for very small pressure variation, especially at low surface coverages.

This method is interesting for analytical and physicochemical investigation, for example, chromatographic methods similar to method of "molecular probes" can be used to isolate and quantify relatively weak but important interactions between adsorbates in two-dimensional adsorbed phase. Use of a mass spectrometer as detector is a more general approach but sometimes modifiers are more useful from a practical point of view since they are transparent to the detector used (see, for example, [74]).

5.5 Adsorption Open Tubular Columns with Modified Adsorbents

Active solid adsorbents are utilized not only in pure form but also after modification, usually carried out with low volatility organic compounds (see, e.g. [4, 9, 10]). This section contains some examples of the use of adsorption capillary columns with modified adsorbents.

Regularities underlying the retention of compounds being chromatographed as dependent on SLP (stationary liquid phase) content are similar to those for solid supports (see, e.g. [23]) and are described by additive absorption-adsorption theory [9].

Peculiarities of retention on adsorbent modified by SLP

Retention of volatile compound on adsorbent modified by SLP can be described by the following equation:

$$V_N = K_l V_l + K_{gl} S_{gl} + K_{ls} K_l S_{ls} \qquad (5\text{-}3)$$

where V_N is net retention volume of the chromatographed compound; K_l, K_{gl}, and K_{ls} stand for the distribution constants of the chromatographed

compound in the system gas-SLP (absorption), gas-liquid phase interface (adsorption) and liquid-solid support-adsorbent interface (adsorption), respectively; V_l is the SLP volume in the column, S_l denotes the area of the gas-liquid phase interface, and S_{ls} represents the area of the liquid phase-solid adsorbent (support) interface.

This equation corresponds to simplified model of sorbent in gas-[liquid-solid] chromatography. The sorbent in this model is a polyphase sorbent in which a thin film of the SLP covers the solid sorbent surface. If the chromatographed compound and SLP are compounds of the same type, then usually $K_{gl}\, S_{gl} \approx 0$, and the retention volume can be represented by the following relation:

$$V_N = K_l V_l + K_{ls} K_l S_{ls} \qquad (5\text{-}4)$$

This equation corresponds only to the simplified model of the sorbent where a thin film of the SLP covers the entire surface of a solid adsorbent (support).

We use data obtained by Bruner and Cartoni [124] to estimate this equation. They used glass capillary columns with modified internal surface. After treatment with alkaline solution (20% aqueous solution of NaOH) the columns were modified with squalane and were used for the analysis of low boiling hydrocarbons. After alkaline treatment a uniform white layer is observed over all the internal surface. For coating the columns with different amounts of liquid phase, a solution of squalane in ether (1% – 10% v/v) was used; a small amount of dye was added to the squalane solution to follow the filling operation.

A chromatogram of gaseous hydrocarbons on an alkaline treated column without squalane at room temperature is shown in Fig. 5-34. All peaks of light hydrocarbons were sharp and did not show any tailing, in spite of the fact that the column used was a pure adsorption one.

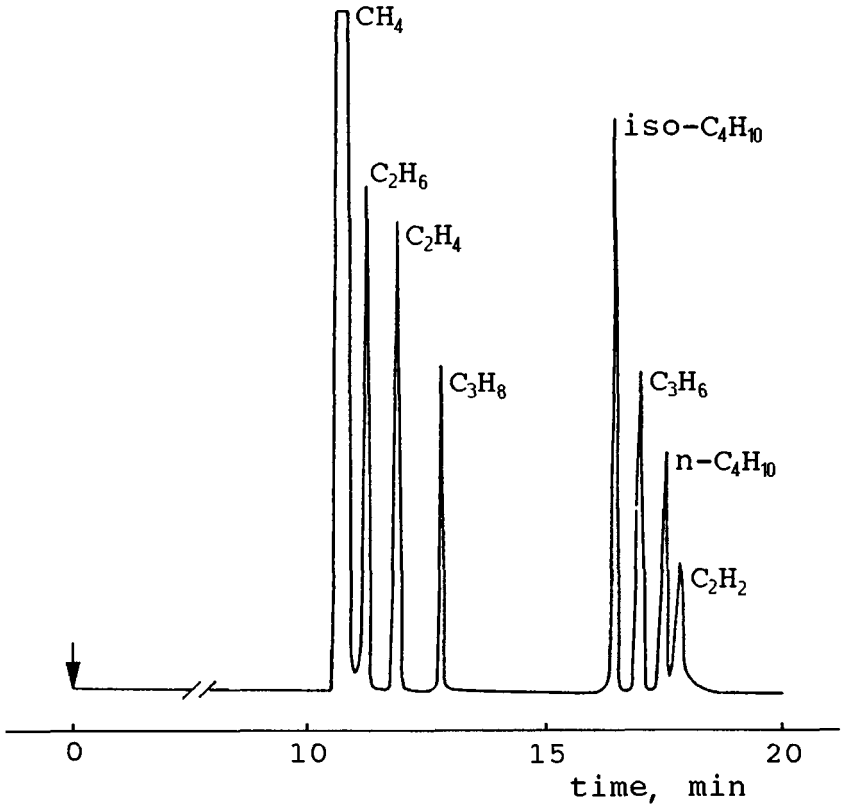

Fig. 5-34 Chromatogram of C_1–C_4 hydrocarbon gases on an adsorption capillary column with alkaline treated walls [124].

Net retention volumes for n-heptane measured for the various column and other characteristics are reported in Table 5-2. Using these we obtain function $V_N = f(W)$ in graphic form (see Fig. 5-35). The right part of this plot is linear in accordance with equation (5-4). As follows from this equation, in our case

$$V_N = \frac{K_l}{d} \cdot P + K_l K_s S_s \qquad (5\text{-}5)$$

or

$$V_N = V_{N\,ads} + V_{N\,ads} \qquad (5\text{-}6)$$

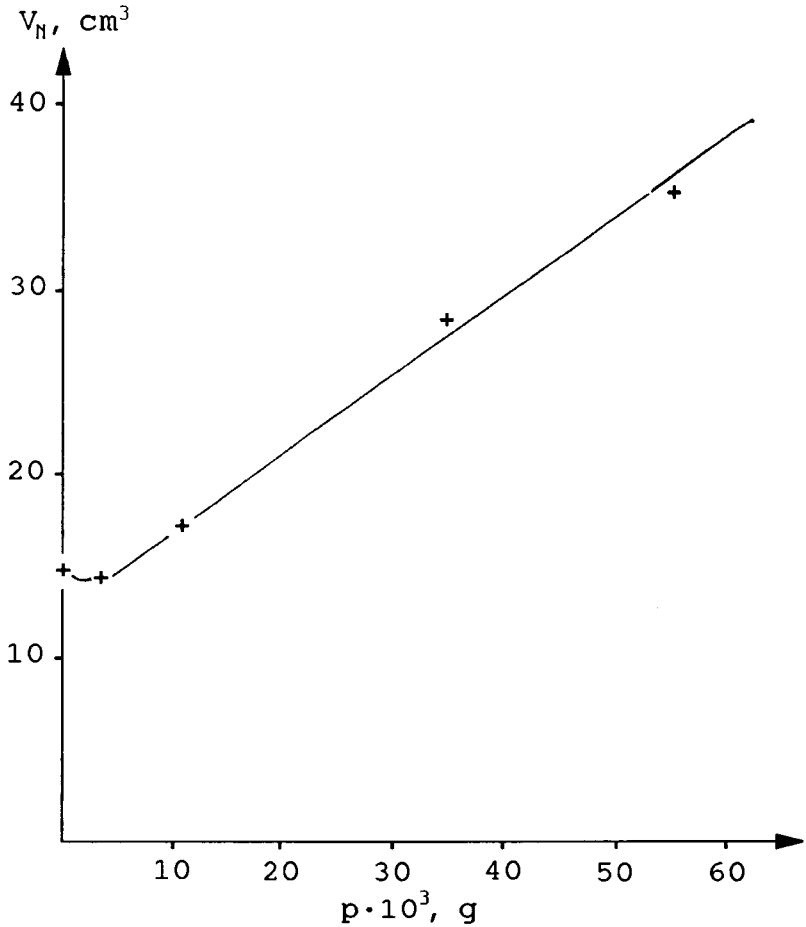

Fig. 5-35 Net retention volume (V_N) versus squalane (SLP) content on walls of capillary columns.

Table 5-2

Column characteristics and experimental data [124].

Column 38 m × 0.22 mm, S = 3750 cm^2, temperature 40 °C, liquid stationary phase — squalane, sorbate — n-heptane.

Column number	1	2	3	4	5
Stationary liquid phase, w, mg	0	3.14	11.2	35.1	55.6
V_N, ml (temp = 0°C, P = 1 atm)	14.72	14.57	17.31	28.22	35.54

where P is the mass of SLP, d is the density of squalane (SLP) , $d = 0.805\ g/cm^3$, $V_{N\,ads}$ is the net partial adsorption retention volume, $V_{N\,ads}=(K_l/d)P$; $V_{N\,ads}=K_lK_sS_s$. For Bruner and Cartoni's data [124]:

$K_l \approx 5.34$, $K_s \approx 6.1 \cdot 10^{-4}$ cm

The applicability of the additive retention theory to capillary chromatography with modified adsorbents was demonstrated for the first time in paper [125]. This work used experimental data [126] on n-heptane retention on an alkaline treated glass capillary column, the walls of which were coated with squalane, as reported by Bruner and Cartoni [126]. The dependence of retention volume on the liquid phase content was shown to be linear, being in complete agreement with additive absorption-adsorption theory.

Capillary columns with modified graphitized carbon black are used for separation of multicomponent samples. Guiochon and co-workers [126, 127], Liberti and co-workers [7, 128] suggested the use of graphitized carbon black for selective capillary columns production. In spite of the good selectivity results, the efficiency, in terms of HETP, was not entirely satisfactory in either set of experiments. Bruner and co-workers [129] showed that it is possible to obtain high performance fused-silica capillary columns. These columns are highly competitive with fused-silica gas-liquid capillary chromatography columns but have a higher selectivity and smaller HETP at high linear gas velocities.

Van Deemter plots of GLC and GLSC capillary columns

Fig. 5-36 [129] shows experimental Van Deemter plots for two fused-silica capillary columns of the same geometrical characteristics; comparative data are reported in Table 5-3. The two Van Deemter plots coincide in the left part (Fig. 5-36), as expected. The B term of the Van Deemter equation should have the same value if the same sample and carrier gas are used for columns of the same geometry. However, the right parts of the curves differ substantially, and calculation of the C term

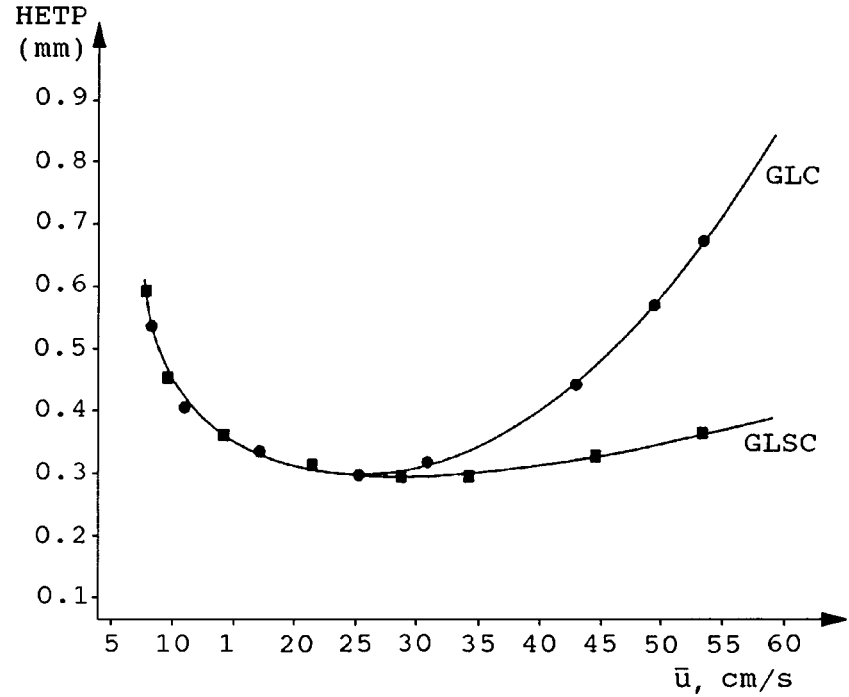

Fig. 5-36 Van Deemter plots obtained with two fused-silica capillary columns of the same geometrical dimentions (20 m × 0.25 mm) [129].

Coatings: modified graphitized carbon black,
GLSC — Carbopack F (6–6.5 m^2/g) + SP-1000 (10% w/w);
GLC — SP-1000, film thickness 0.25 μm. Sample: n-hexadecane.

Table 5-3

Comparison of chromatographic characteristics for two fused-silica capillary columns of the same dimensions (20 m × 0.25 mm) [129].

Column	HEPT$_{(min)}$, mm	$C10^4$, s	U_{min}, cm/s	TZ	Coating efficiency, %	$k'_{n\text{-}C_{16}}$ (105 °C)	$Q(n\text{-}C_{12})$,k cal/mol	Bleeding at 240 °C (% full scale)
"Pure" GLC	0.30	13.0	32	21.4	75	8.9	9.4	17
Active adsorbent: GLSC	0.30	2.3	34	31.5	75	5.7	14.1	5

yields values of $1.3 \cdot 10^{-3}$ s for the "pure" GLC column and of $2.3 \cdot 10^{-3}$ s for the adsorption column. The separation number (Trennzahl, TZ), which reflects both resolution and column efficiency, is 1.5 times higher for the adsorbent-liquid column. It is also interesting to compare the values obtained for stationary phase "bleeding" at the same temperature: this value is 3.4 times lower for the adsorbent-liquid column. The vapor pressure of the stationary liquid phase on the adsorbent is lower than in the bulk liquid (GLC).

In Fig. 5-37a and b two examples of the efficiency of active adsorbent–GLSC column and GLC columns are reported. The total analysis time is

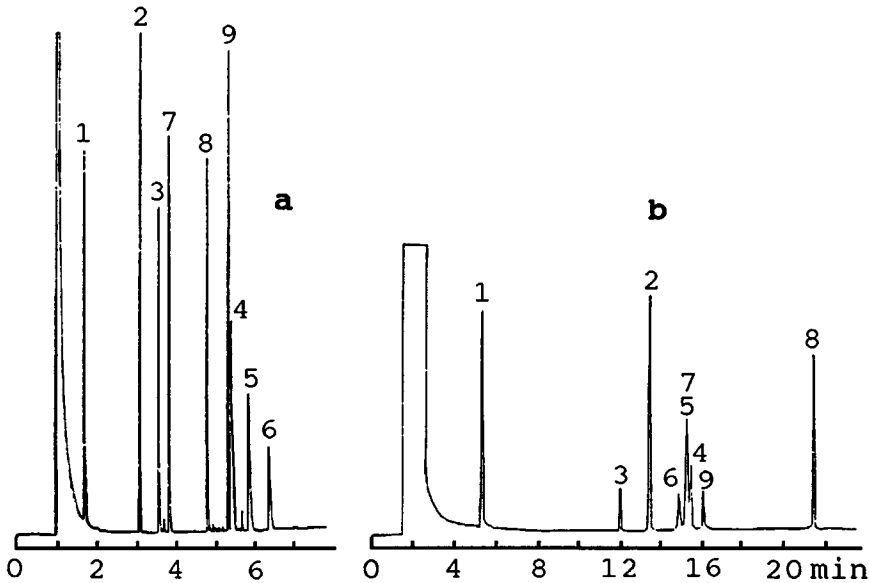

Fig. 5-37 Separation of some herbicides on GLC and GLSC capillary columns [129].

a. Fused-silica capillary column (20 m × 0.25 mm), coated with Carbopack F + SP-1000. Temperature program: 140 °C (for 2 min), then increased at 18 °/min to 230 °C.
b. SPB-5 fused-silica capillary column (30 m × 0.25 mm). Temperature program: 130 °C (for 2 min) then increased at 4 °/min to 230 °C.

Peaks: 1 — diclobenil, 2 — trifluralin, 3 — 2,4-DME, 4 — propazine, 5 — atrazine, 6 — simazine, 7 — silvex ME, 8 — 2,4-STME, 9 — DCPA.

3 times shorter when "pure" GLC columns are used for herbicide separation. We can also have better resolution and shorter analysis times if we use active adsorbent–GLSC column (b) for analysis of some pesticides (Fig. 5-38).

ALOT columns with molecular sieves

The ALOT column with molecular sieve 13X was suggested by Soulages and Brieva [130]. For the analysis shown in Fig. 5-39 [130] temperature programming started at 100 °C and increased slowly

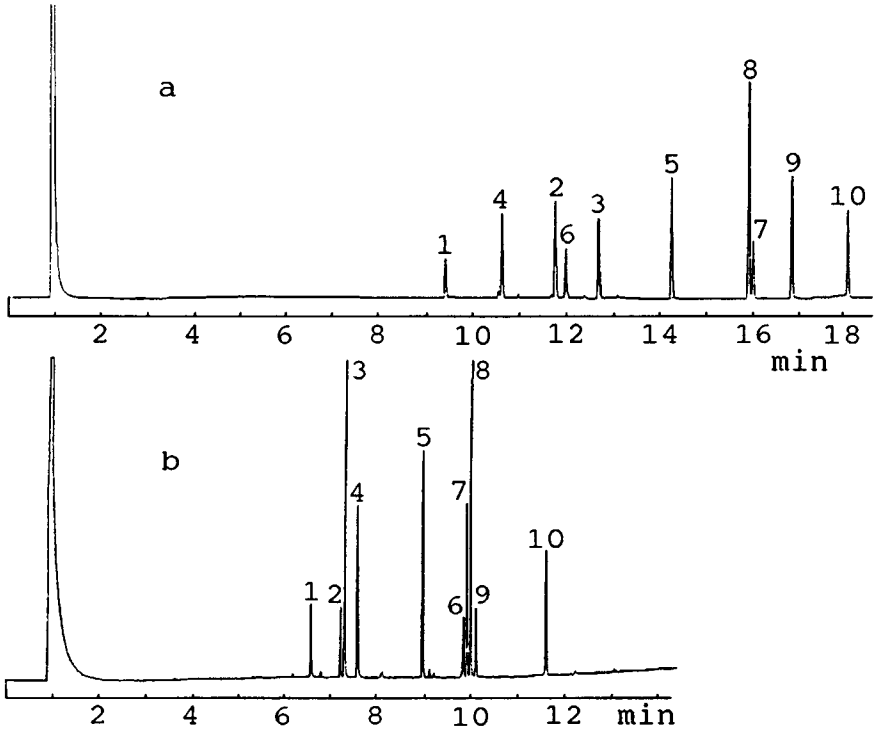

Fig. 5-38 Separation of some pesticides on GLC and GLSC capillary columns [129].

a. Fused-silica capillary column (20 m × 0.25 mm) coated with SPB-608.
Temperature program, 150 °C for 4 min, then increased at 8°/min to 290 °C.
b. Fused-Filica capillary column (20 m × 0.25 mm)
coated with Carbopack F + SP-1000.
Temperature program, 100 °C for 2 min, then increased at 13°/min to 240 °C.
Peaks: 1 — α-BHC, 2 — heptachlor, 3 — aldrin, 4 — lindane,
5 — heptachlor epoxide, 6 — δ-BHC, 7 — dieldrin, 8 — DDE,
9 — endrin, 10 — β′-DDT.

(4.5 °/min), so as to give a detailed resolution which would allow not only separation of paraffins and naphthenes, but also identification of individual hydrocarbons; cyclohexane and methylcyclopentane were completely isolated, and normal C_7–C_{11} paraffins were isolated from the corresponding branched chain isomers, thus allowing quantitative determinations.

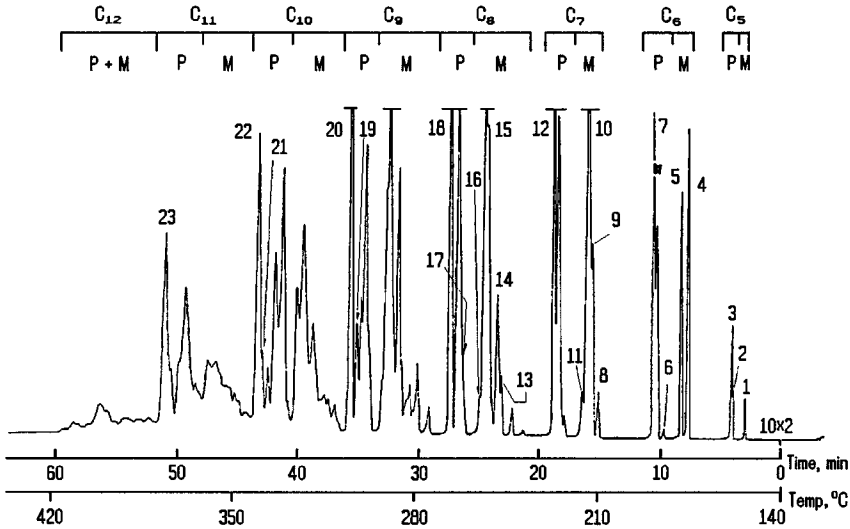

Fig. 5-39 Chromatogram of dearomatized naphtha on ALOT column with molecular sieve 13X [130].

Experimental conditions. Column: 5 m × 0.5 mm i.d.; temperature program: 140–450 °C at 4.5°/min; carrier gas nitrogen, linear velocity 10 cm/s; sample volume 0.2 μl; splitting ratio 1:50; detector FID.

Peaks: 1 — cyclopentane; 2 — isopentane; 3 — n-pentane; 4 — cyclohexane; 5 — methylcyclopentane; 6 — 2,2-dimethylbutane; 7 — n-hexane; 8 — 1,1-dimethylcyclopentane;
9 — 1-*trans*,3-dimethylcyclopentane, 1-*trans*,2-dimethylcyclopentane;
10 — 1-*cis*,3-dimethylcyclopentane, methylcyclohexane;
11 — 1-*cis*,2-dimethylcyclopentane; 12 — n-heptane;
13 — 1-*trans*,2-*cis*,4-trimethylcyclopentane, 1,1,3-trimethylcyclopentane;
14 — 1,1-dimethylciclohexane;
15 — 1-*trans*,4-dimethylcyclohexane, 1-*trans*,3-dimethylcyclohexane, 1-ethyl-*trans*,2-methylcyclopentane;
16 — n-propylcyclopentane; 17 — 3,3-dimethylhexane; 18 — n-octane;
19 — 2-methyloctane; 20 — n-nonane; 21 — 2-methylnonane;
22 — n-decane; 23 — n-undecane.

Powdered molecular sieves 13X were modified with sodium hydroxide in order to reduce their acidic activity and to improve selectivity for separation of saturated compounds into paraffins and naphthenes of the same carbon number.

Fig. 5-40 shows the results of a rapid analysis of the same sample. This analysis is recommended for routine determinations of paraffins and naphthenes. Thus the use of a molecular sieve 13X ALOT column permits determination of paraffins and naphthenes in dearomatized naphthas with boiling points up to 200 °C. Souleges and Brieva [130] established the practical possibilities and of this type of ALOT column, in which a porous layer adheres to the inner walls of the tube by natural cohesive forces only. The column was used for more then 100 analyses at different times and no sign of deterioration was observed. ALOT columns

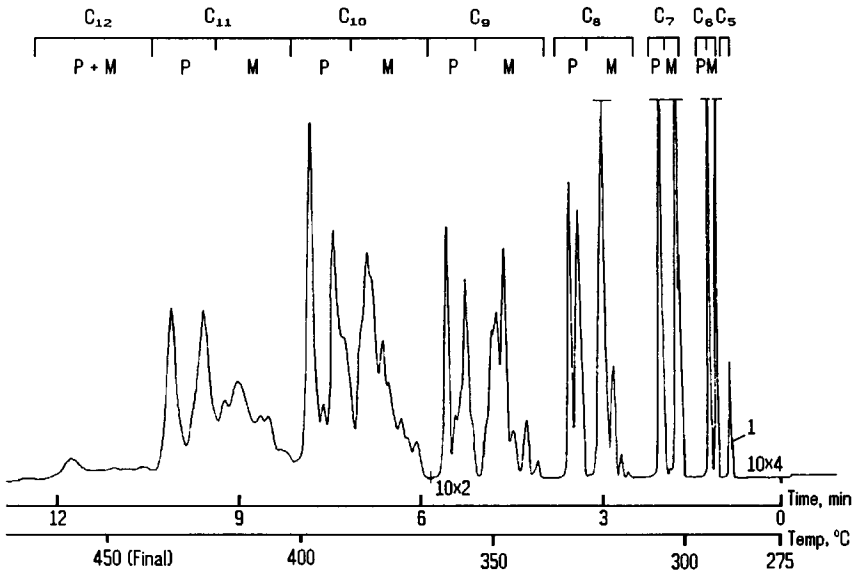

Fig. 5-40 Rapid analysis of paraffin/naphthene mixture [130].

Experimental conditions as on Fig. 5-39, except for the temperature program: 275–450 °C at 16 °/min.
Peak 1 – cyclopentane.

with molecular sieve 13X are characterized by a superior resolving power compared to that of classical packed columns. The analysis time for C_5–C_{12} saturated hydrocarbons is 12 min, which represents a five-fold increase in the speed of analysis [130].

* * *

There are many examples of successful application of modified gas-solid chromatography in scientific and technical literature. We agree with Guillemin et al. [11] that modified gas-solid chromatography is not a new method (see, e.g. [1–4, 10–12, 18, 41]), and that one can assert, by analogy with M. Jourdain in Molière's "Le Bourgeois Gentilhomme", that every chromatographer has practiced or still practices modified gas-solid chromatography without knowing it (see [11]).

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Chapter 6

Preparation of Adsorbent Layer Open Tubular Columns

Methods for the preparation of open tubular adsorption columns differ in some aspects from those used to produce absorption columns with a stationary liquid phase film.

Published data contain mainly descriptions of adsorption capillary columns covered with a porous adsorbent layer. Columns of this type are distinguished by high capacity and improved performance stability. Taking into account kinetic broadening factors, it is desirable that the adsorbent layer on the inside column walls is homogeneous in terms of coverage and thickness, that it is mechanically fixed on the wall surface, and that the layer structure is fairly "loose" in order to permit a high rate of mass exchange.

Classification of the methods for ALOT column preparation

A classification of the available methods for adsorption capillary column preparation is presented in Fig. 6-1 [1].

It is evident that three methods exist, namely the suspension, the chemical, and the dry sorbent method, the latter being realized in the process of glass capillary drawing.

6.1 Suspension Method

The method involves dispersion of the finished sorbent in a suitable liquid medium followed by filling of the column with the resulting suspension and subsequent removal of the volatile liquid. This method closely resembles that used for stationary liquid phase application during the preparation of "classical" capillary columns. In both cases use of either the dynamic or the static method is possible. The main difference consists in the heterogeneity (or microheterogeneity) of the system being introduced into the capillary during capillary adsorption

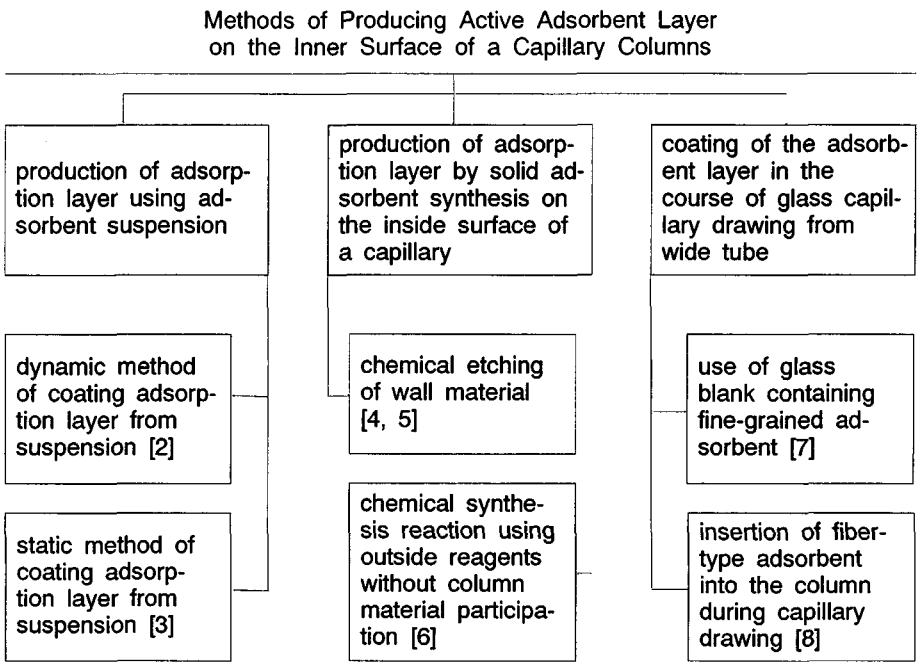

Fig. 6-1 Methods for producing active adsorbent layer on the inner surface of a capillary column [1].

column preparation. Here the suspension moving along the capillary represents a non-Newtonian fluid, frequently with distinct thixotropic properties. In the process of flowing the fluid particles are segregated in size according to the principles of FFF chromatography [9–12]. The rheological properties of the suspension undergo changes in the course of its application or column filling. Therefore, deposition of a sorbent layer that is homogeneous along the entire capillary length is complicated. Nevertheless, the suspension method for preparation of adsorption capillary columns was used even in the earliest work on capillary adsorption chromatography.

Usually ALOT columns can be prepared using dynamic or static coating techniques (classical methods, see, for example, [13, 14]). Static coating places considerable demands on adsorbent sus-

pension stability. It must be stable during the entire static coating process, which may take a few days. Suspension adsorbent stability is not so critical for dynamic coating. Columns are made in a few hours. However, reproducibility is a major problem and successful coating is only a result of accurate monitoring of coating parameters [15]. De Zeeuw, de Nijs and Henrich [15] recommended control of the following four factors when preparing efficient ALOT columns.

Main factors influencing preparation of ALOT columns

1. The surface upon which actual adsorption takes place should be homogeneous. Since the separation mechanism takes place at the active sites on the surface in the pores, the distribution of these active sites should be as homogeneous as possible. The number of active sites present in the pores is a function of the specific surface and the nature of the adsorbent. The distribution of these active sites depends on the chemical synthesis of the adsorbent and cannot be changed without chemical interference. There are several methods for decreasing the amount of active sites and reducing their individual activity by shielding with a non-removable compound that has a high affinity for the sites. In this way a more uniform distribution of the active sites is obtained.

2. It is advisable that the pore-size distribution of adsorbent used should be homogeneous. Characteristics of adsorbents used in GSC are generally a function of homogeneity of the pore distribution. Both the number of pores per unit area and the dimensions of those pores should be constant in order to give optimal interaction. Obviously, any deviation will contribute to extra peak broadening. Since it is very difficult to prepare these materials with a high degree of uniformity, reproducibility can only be obtained by using the same batch of adsorption material. This problem also occurs in gas-liquid chromatography.

3. The particle-size distribution should be uniform. To form a stable adsorption layer, all particles must be of the same size. The presence of small amounts of layer particles will result in non-uni-

formity and a decreased efficiency; in addition the mechanical stability of the adsorbent layer is reduced.

4. The adsorbent layer built up on the inner surface should be as homogeneous as possible. Any clots formed before, during, or after coating lead to a non-uniform film deposition and thus to a reduced column efficiency. The ultimate efficiency depends on the size of the clots and the distance between them. This could be compared with the influence of a droplet in liquid-phase coated capillary, where a few droplets cause large decreases in efficiency [15].

The static suspension method for preparing adsorption layer open tubular columns (ALOT) was suggested by Halasz and Horvath [16, 17]. The columns prepared by this method have been successfully used for many separations. Halasz and Horvath [16] filled stainless steel capillaries (50 m) with stable suspensions of many combinations of solid and liquid stationary phases, then closed the capillaries at one end and passed them through a furnace, where the solvent used to prepare the suspension evaporated through the open end. In this evaporation process the solid part of the suspension was retained on the capillary wall. This method was successfully used by Ettre and coworkers [18, 19] to produce efficient columns (a 45 m column has 57,000 theoretical plates).

Successful application of this method for preparing ALOT column requires the availability of suspensions with particle sizes 1–10 μm. The greatest problem encountered in preparing ALOT column is that the adhesiveness of these solid particles is partly based on adhesion between the particles and the wall surface and partly on cohesion between the particles themselves. With finely dispersed particles, effectively adhering coatings are obtained. Adhesiveness depends on the nature and pretreatment of the dispersed solid adsorbent, its grain size and the surface pretreatment of the capillary walls [20]. According to very interesting data reported by Rumpf [21], the tensile strengths

(up to 1 MPa) of particles sized 0.01–1 μm and at a grain distance of 0.01 μm result from van der Waals forces. In comparison, the tensile strengths of compact solids are more than 100 MPa. The durability of a settled layer of fine particles depends on the radius of curvature of the support surface (wall). As the radius of curvature is very small in capillary columns, a highly curved ring of highly stable adsorbent is produced. This ring will break down only if sections are removed from inside.

The thickness of the adsorbent layer is a very important characteristic of ALOT columns [22]. The minimum layer thickness required depends mainly on the distribution coefficient of the analyzed components and hence on the nature of the adsorbent and on the separation temperature. However, the adsorption layer should not be too thick, otherwise diffusion in its stationary phase will contribute to peak broadening, i.e. increase the height equivalent to a theoretical plate (HETP).

The layer thickness may be controlled via the solid concentration in the suspension. It is also possible to vary the radius of the uncoated capillary, R_k, since the column diameter influences the loading capacity. Mohnke and Heybey [22] deduced a formula for the estimation of solid adsorbent concentration in the suspension for ALOT columns.

$$C = 100\,[1 - \frac{(R_k - d_s)^2}{R_k^2}] \qquad (6\text{–}1)$$

where C is the solid adsorbent concentration (vol.%), R_k is the radius of the uncoated capillary, d_s is the adsorbent layer thickness.

A very valuable analysis of the suspension method was undertaken by Mohnke and Heybey [22]. Suspension must meet strict requirements for all coating experiments. It was observed than even fine solids, owing to their high surface energy and high collision density of particles, produce particle enlargement and consequently sedimentation at high solid concentration after various times. Particle

enlargement before evaporation results in solid layers with low packing densities and hence produces loose layers of low durability. To prevent particle enlargement, due to particle movement, and harmful consequences such as sedimentation, clogging, non-uniform layer thickness and poor durability of the layers, it is advantageous to add thickeners to suspensions. This greatly reduces the translational movements of the particles [22].

The suspension should meet the following demands: it must be "soluble" in the dispersion medium or be able to swell; the necessary concentration must be as low as possible; the micropores of the adsorbent must not be clogged; when the adsorbent is activated (200–500 °C), decomposition products must not affect the surface, or there must be no decomposition at all; and it should not have any tendency to foam during evaporation. Suitable substances are colloids, which in addition should be thixotropic. They make the filling of very long capillaries feasible.

The dispersion medium must meet certain demands: viscosity, density and polarity greatly influence sedimentation. A low boiling point of the dispersion medium and a high evaporation speed simplify evaporation; low surface tension and low foaming tendency prevent clogging. Many empirical experiments are necessary in order to select a suitable dispersion medium for a given solid because little experience has been gained in this field so far. In fact, the process of suspension preparation determines the success of the coating procedure [22].

Suspension methods for preparation of adsorbent layer open tubular columns with various adsorbents are described below.

Preparation of high efficiency fused-silica capillary columns coated with graphitized carbon black impregnated with liquid phases was proposed by Bruner and co-workers [23, 24]. This method is a modification of that described by Xu and Vermeulen [25] (free release static coating) for the preparation of glass capillary columns.

6.1.1 ALOT Columns with Graphitized Carbon Black

Preparation of the columns is based on a two-step procedure, namely: 1) preparation of a slurry where the adsorbent (graphitized carbon black) and the liquid phase (for instance, SP-1000) are mixed together in a suitable solvent and sonicated; 2) coating of the capillary columns by means of a static method using the prepared slurry.

It is necessary to use a slurry with a very small particle size during step (1). Carbopack B is wet-sieved via a multistage sieving cascade using water as medium. The material of finest particle size (<20 μm) is sonicated in water by means of high-power sonicator for 30 min. Water is the best medium for sonication. On using water, much greater subdivision of the carbon black particles is obtained, so that the slurry is more homogeneous. The slurry is then dried by means of a vacuum pump and methylene chloride–n-pentane (50:50), containing 35% (w/w) (with respect to the carbon black) of SP-1000, is added. The container is shaken and sonicated again for 30 min.

The coating step 2 does not differ substantially from that described previously [24, 25]. Essentially the slurry is pushed into the capillary by heating the slurry reservoir at 60 °C and the solvent is then evaporated while the column is kept at a temperature higher than the boiling point of the solvent mixture. Two types of columns with different i.d. (0.25 and 0.53 mm) were tested. A variant of this method was described in greater detail in paper [26].

The carbon black suspension (Carbopack F, 6.5 m^2/g) used to coat the column is prepared by the following procedure: 0.144 g of Carbopack F presieved to obtain dimensions lower than 120 mesh is added to 40 ml of a pentane–methylene chloride mixture (1:1 v/v) containing 10% w/w (with respect to carbon) of SP-1000 or Carbowax 20 M.

Sonication is carried out for 30 min by dipping the probe of an ultrasonic machine (Model 450, Branson, Duxbury, CT, USA) into the mixture. A suspension is obtained where the single carbon particles are reduced to an average size of 0.2 μm,

as can be inferred from the micrographs shown [26]. A static method is used to coat the column. The suspension is placed in a thick wall reservoir to which, after degassing, the fused silica capillary (20 m × 0.25 mm) is directly connected with a Swagelock reducing union by means of graphite ferrules. The capillary is quickly filled (10 min) by immersing the reservoir in a water bath kept at 70 °C.

Suspension coating apparatus

After the capillary has been disconnected, a 3 cm piece of 50 μm fused-silica is fitted into each end of the columns with a epoxy glue (Epotek 353 ND) and one end is flame sealed. Special equipment and procedures have to be used during the filling and sealing of the column to avoid formation

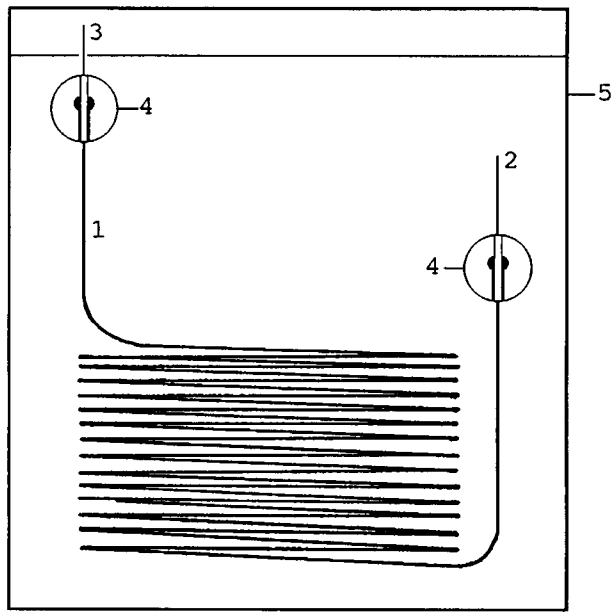

Fig. 6-2 Schematic view of the coating apparatus [26].

1 — 250 μm fused-silica capillary; 2 — open 50 μm fused-silica capillary; 3 — flame sealed 50 μm fused-silica capillary; 4 — magnified view of 50–250 μm capillaries union; 5 — water bath.

of air bubbles. The column is then completely immersed in the water bath with the exception of the sealed 50 μm capillary and kept at a temperature higher then the boiling point of the mixture. Fig. 6-2 [23] depicts a schematic view of the coating apparatus. Slow evaporation of the solvent takes place through the open end of the column (it is restricted by the 50 μm capillary). After the solvent has completely evaporated, the column is flushed with nitrogen for 2 hours and conditioned at the maximum operating temperature of the liquid phase.

Bruner and co-workers [27] investigated the reproducibility of the coating procedure. They prepared three columns under the same conditions to estimate the reproducibility of the coating method. The results are summarized in Table 6-1 [27]. The efficiency reproducibility is very good. The three columns show a maximum of ≈2600 theoretical plates per meter. The ratio of the retention volumes of n-heptanol (polar compound) and n-C_{18} (apolar compound) is a very good evidence of the surface coverage by liquid stationary phase. Of course, this parameter is critical. It means that very small variations in the percentage of stationary phase may lead to considerable differences in the relative retentions. The three columns show a difference

Table 6-1

Comparison of some parameters for three columns (A, B, C), prepared by the same procedure and for a column with a higher content of carbon black in the slurry (D) [23].

Fused-silica column: 7 m × 0.25 mm, stationary phase: Carbopack B + SP-1000

Column	Dead time, s	Flow-rate, ml/min	Capacity factor for n-C_{12}, k' (140 °C)	Separation factor $\left(\frac{\text{n-heptanol}}{\text{n-C}_8}\right)_{(90°C)}$	$HETP_{min}$, mm
A	18	1.5	49	3.8	0.40
B	18	1.5	52	3.8	0.38
C	18	1.5	56	3.7	0.40
D	18	1.5	125	4.0	0.40

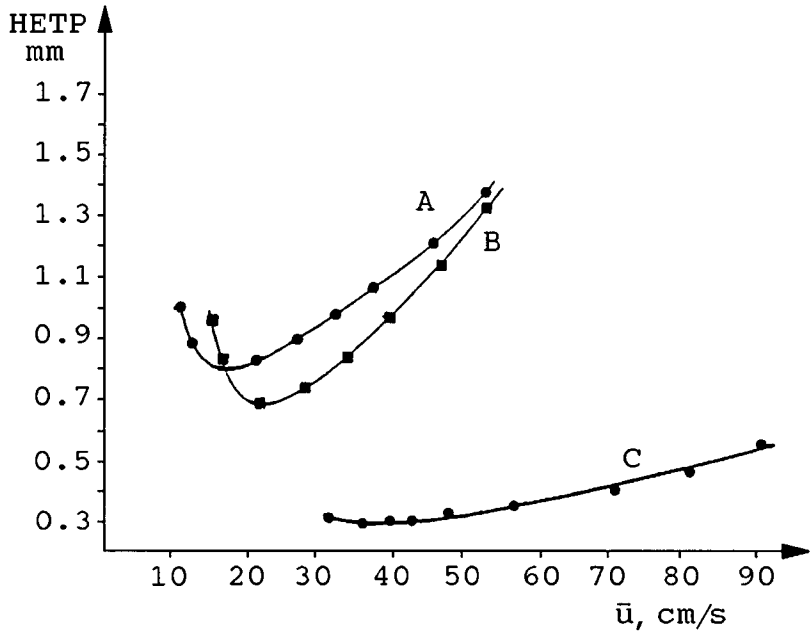

Fig. 6-3 Van Deemter plots obtained with three fused-silica capillary columns coated with Carbopack B + SP-1000 [23].

(A) 33 m × 0.53 mm (Q = 1.2), (B) 33 m × 0.53 mm (Q = 4.5), (C) 24 m × 0.25 mm (Q = 4.5).

Q is the value of surface coverage. Sample, n-dodecane (k' = 7), carrier gas hydrogen.

of about 10% in relative retention. In the opinion of Bruner and co-workers [27], this result is satisfactory and does not substantially affect the chromatographic characteristics of the columns. They found a reproducible method for preparing such columns, and their chromatographic properties can be predicted as a function of the various parameters investigated. These columns are advantageous as they combine the high selectivity and the high efficiency typical of capillary columns.

Van Deemter plots for ALOT columns with Carbopack B + SP-1000

In Fig. 6-3 [23] Van Deemter plots for three capillary columns with two different inner diameters (0.53 mm for columns A and B and 0.25 mm for column C) are shown. The columns contained Carbopack B coated with different amounts of SP-1000. The surface coverage values (that is effective number

of monolayers of stationary liquid phase on the surface of the adsorbent) are 1.2 for column A and 4.5 for columns B and C. The Van Deemter curve for column C (i.d. 0.25 mm) differs greatly from those for columns A and B (i.d. 0.53 mm). An obvious difference in the *B* and *C* terms in the Van Deemter equation for columns of different diameter is shown by the large difference in both the value of the minimum HETP and the resistance

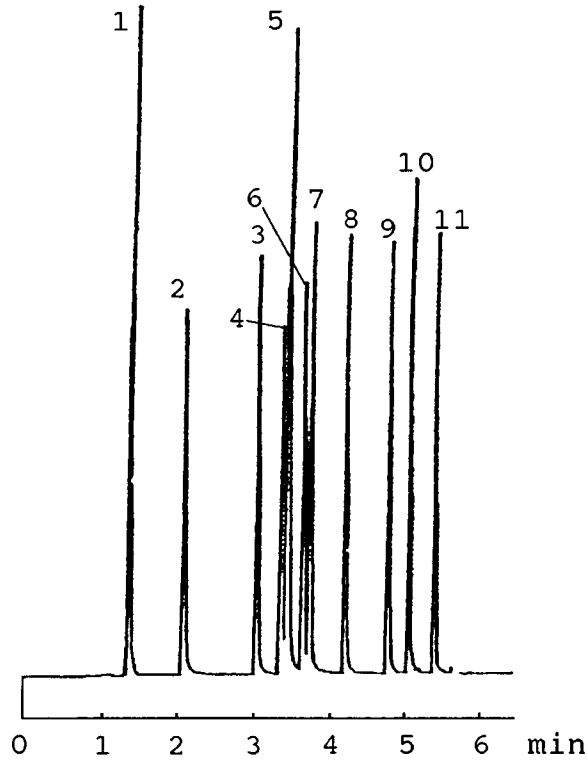

Fig. 6-4 Separation of aromatic hydrocarbons on fused-silica capillary column (24 m × 0.25 mm) coated with Carbopack B + 5% SP-1000 [23].

Column temperature: 1.5 min at 70 °C, then heated at 20°/min to 160 °C and held to the end. Carrier gas — hydrogen, linear velocity 40 cm/s, sample volume 0.1 μl, splitting ratio 1:100, flame ionization detector.

Compounds: 1 — benzene, 2 — toluene, 3 — ethylbenzene, 4 — *p*-xylene, 5 — *m*-xylene, 6 — isopropylbenzene, 7 — *o*-xylene, 8 — n-propylbenzene, 9 — 1,3,5-trimethylbenzene, 10 — *p*-cumene, 11 — n-butylbenzene.

to mass transfer term *C*. Column C shows good properties from the kinetic point of view. $HETP_{min}$ occurs at about 40 cm/s and shows a coating efficiency of about 80% with a measured $HETP_{min}$ of 0.29 mm. Fig. 6-4 [23] illustrates the separation of some aromatic compounds and the high resolving power of the GLSC capillary column is demonstrated. The separation of the three xylenes is good. In Bruner and co-workers' opinion [23], wide-bore columns do not belong to capillary chromatography.

By coating graphitized thermal carbon black (GTCB) on the walls of open tubular columns it is possible to obtain columns which permit very fast analysis [28] while offering the advantages of PLOT columns with GTCB modified by various polar liquid phases. Pyrex glass capillary columns of 0.50-mm i.d. were drawn using a machine similar to that described by Desty et al. [31]. A 5% (w/w) suspension of GTCB Sterling FTG (Cabot, Billerica, Mass., specific surface area 13 m^2/g) in 0.05% (w/w) squalane solution in methylene chloride is forced under pressure into the glass capillary column connected with a Swagelok fitting containing a metallic sieve. Squalane in solution acts as a dispersive material for carbon black particles and thus stabilizes the suspension for about 24 h.

Apparatus for preparation of adsorption capillary columns by the high-pressure static method

To increase the layer thickness, a static variant of the suspension method was attempted. For this purpose Horvath [3] designed a special device (see Fig. 6-5 [3]). The method involves completely filling the metal capillary column with a sorbent suspension in a volatile solvent, sealing one end of the column, and inserting the opposite end in an air oven heated to 90–150 °C through a metal block heated to 200–250 °C. The unit causes fast evaporation of the liquid, and a high oven temperature prevents vapor condensation. Using such a device modified by Mistryukov and co-workers [32] to accommodate glass capillary columns, Guiochon and co-workers [28] prepared a column with graphitized carbon black.

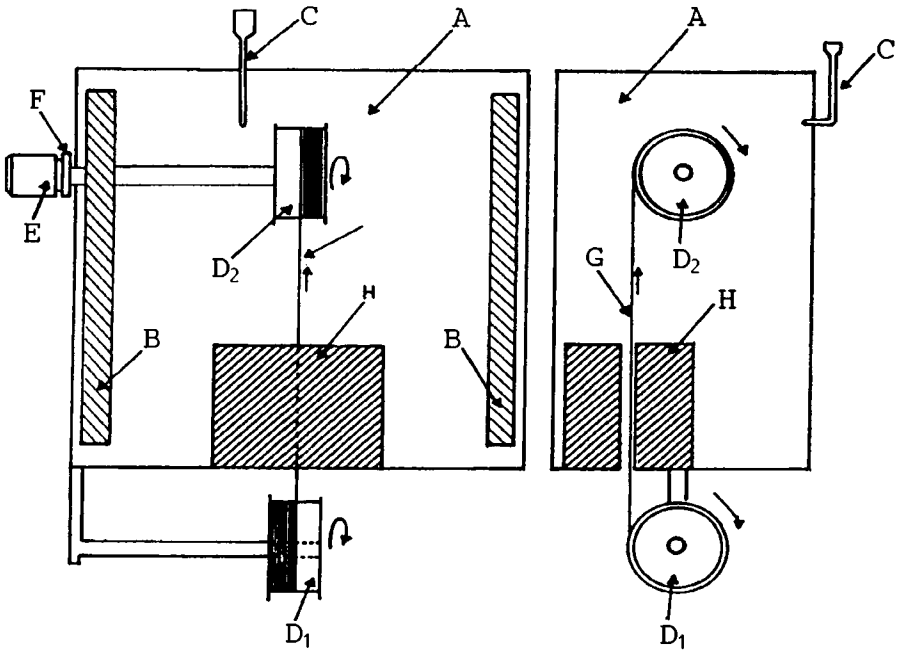

Fig. 6-5 Device for preparation of adsorption capillary column by the high-pressure static method [3].

(A) air oven; (B) heater; (C) thermometer; (D_1 and D_2) reels; (E) electric motor; (F) connection; (G) capillary tube; (H) heated metallic block.

When the column is filled with a suspension, one end is carefully sealed with a microburner. The open end of the capillary column is introduced into a drying apparatus similar to that described by Ilkova and Mistryukov [32], and the solvent vaporizes at 140 °C while the column slowly enters the oven. A thin carbon black layer is then formed on the walls of the column. The amount of GTCB Sterling FTG introduced into the column depends on the concentration of the suspension used. Most often it was about 10 mg/m of capillary column.

The column is heated overnight at 220 °C under a stream of nitrogen and washed with a slow stream of methylene chloride in order to completely eliminate squalane. This operation is easily carried out without destroying or appreciably disturbing the GTCB layer.

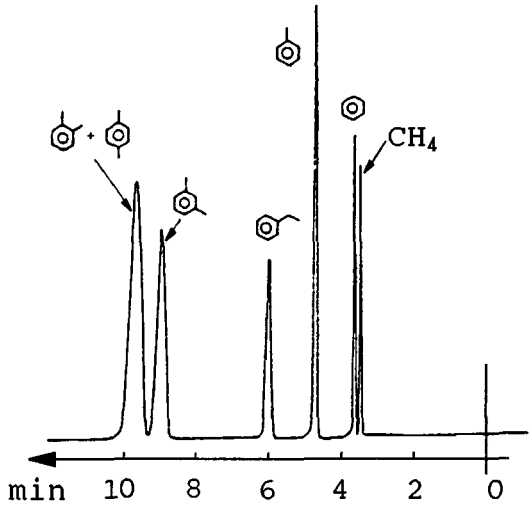

Fig. 6-6 Analysis of xylene isomers on unmodified GTCB [28].

Column: 19 m × 0.50 mm, temperature 165 °C, pressure drop 0.5 atm, carrier gas helium.

A GTCB capillary column is obtained, whose properties are similar to those described in paper [29]. Fig. 6-6 shows the separation of light aromatic hydrocarbons. The elution order of xylene isomers (*m* and (*o*+*p*) isomers) is characteristic of gas-solid chromatography on GTCB, and is different from that observed on most liquid phases.

The same static coating procedure has been used to coat the GTCB layer with a liquid stationary phase. The percentage of liquid phase coated on GTCB depends on the concentration of the solution. Without disturbing the carbon layer, the classical dynamic procedure can be also successfully used for impregnating GTCB with large amounts of stationary phase. Columns prepared by this method typically have 1000 plates per meter for retained compounds ($k' = 3$). This efficiency can be increased by using capillaries of smaller internal diameter.

The columns are connected to metal capillaries with a Kovar Pyrex type connection. The column is then easily connected to the gas chromatograph with Swagelok fittings.

Separation of xylene isomers on modified GTCB

The instrument has a flame ionization detector and a splitting system which allows injection of 0.1–10 mg of sample into the column as a narrow plug. Helium is used as a carrier gas.

GTCB has been modified with ca. 0.1% w/w of Carbowax 20 M coated from a diluted solution (0.004% w/w in methylene chloride). This low percentage of Carbowax is enough to change dramatically the adsorption properties of GTCB, as shown in Fig. 6-7a. The three xylene isomers are completely separated, whereas *p*- and *o*-xylene are not resolved on pure GTCB (Fig. 6-7b).

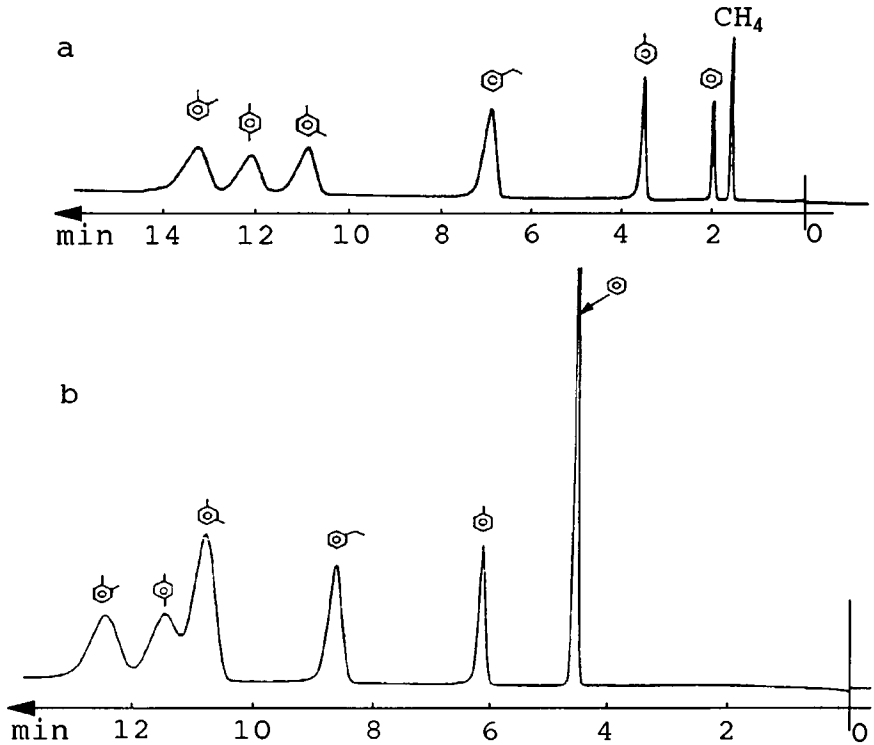

Fig. 6-7 Separation of xylene isomers on modified GTCB [28].

(a) Sterling FTG modified with ca. 0.1% Carbowax 20 m. Column: 7 m × 0.5 mm, temperature 91 °C, pressure drop 0.5 atm, carrier gas helium.

(b) Sterling FTG modified with ca. 0.4% Carbowax 20 M. Column: 19 m × 0.5 mm, temperature 90 °C, pressure drop 0.5 bar, carrier gas helium.

The primary retention mechanism on this modified adsorbent, however, still seems to be adsorption, as the retention pattern on this stationary phase is similar to that observed in gas-solid chromatography, with copper phthalocyanine on GTCB [33].

With a higher percentage of Carbowax 20 m (ca. 0.2% w/w), the adsorption properties are still the same and xylene isomers are well resolved. With an even larger amount of stationary phase (ca. 0.4% w/w), *m*- and *p*-xylene resolution decreases (Fig. 6-7b).

At low surface coverage ratios of the stationary phase (about 0.5% of Carbowax 20 M is necessary to form a monolayer [34]), the selectivity depends very much on the coverage ratio so that a wide range of selectivities can be observed. This is caused by the existence of two different adsorption mechanisms [28] which are superimposed: the first one is the nonspecific adsorption of molecules on GTCB which mainly depends on the molecular weight, the polarizability, and the geometrical structure of the molecule [35], while the second mechanism is the specific interaction between functional groups of the liquid phase and the molecule. The low amount of deposited stationary phase is not sufficient to deactivate appreciably either glass capillary surface or active sites of carbon black to obtain symmetrical peaks of polar compounds such as alcohols.

Aromatic amines, pyridine, picolines and lutidines have been separated as symmetrical elution peaks, using cobalt phthalocyanine on graphitized carbon black adsorbent [36]. A procedure for preparation of ALOT columns is not complicated [36]. The adsorbent (10 g of 5% cobalt on graphitized carbon black) is dispersed in high density liquid (for example, in trifluorotrichloroethane). To obtain a stable suspension, styrene (1 g) has been previously polymerized on the surface of the adsorbent by leaving both in contact for three weeks. The suspension is forced into a glass capillary column (10 m × 0.5 mm). A metallic sieve at the column inlet prevents large particles from plugging the

column. When the column is filled, the solvent is evaporated under vacuum from both ends. During vaporization, a thin layer of the adsorbent is deposited on the walls of the column. The column is heated overnight at 220 °C in a stream of helium to remove (as the authors think [36]) the styrene polymerized on the adsorbent surface [36].

Many investigators, and especially Italian scientists, have studied ALOT columns with internal walls modified by a thin layer of graphitized carbon black and stationary liquid phase (see, for example, [24, 28, 29, 37–43]). As a rule these researchers studied mainly columns of 200–500 μm i.d., with the exception of some promising work [39] perfomed on columns of less than 200 μm i.d.

These columns (i.d. < 200 μm) are characterized by a high specific efficiency (number of theoretical plates per meter and per second). Cartoni and co-workers [44] described the technique for preparing glass and fused-silica capillary columns (100 μm i.d.), which were precoated with a very thin layer of graphitized carbon black and then coated with polar liquid phases. The layer of carbon black increased the wettability of the capillary columns walls and a very uniform coating was obtained. Columns coated with Carbowax 20 M, 40 M and 600 M were prepared. Polar liquid phases were strongly retained on carbon black, and these column showed higher temperature stability.

The procedure for preparation of these columns is not complicated. The columns were precoated with a graphitized carbon black Carbopack A (S_g ≈ 12 m^2/g). The dynamically deposited carbon black increased the surface area and solid stationary phase wettability and consequently a very uniform coating was obtained [44]. Suspension of graphitized carbon black (GCB) was prepared with 50 mg GCB, 25 ml carbon tetrachloride, 25 ml dichloromethane and then exposed to an ultrasonic bath for about 30 min. Approximately 2 ml of this suspension were made to flow through the capillary four times at high speed (60 cm/s), reversing the flow direction each time and waiting for the solvent

to evaporate. Then the GCB layer was thermally treated with Carbowax 20 M (C 20 M). At first Carbowax was statically deposited from 0.2% solution in dichloromethane. After conditioning in a hydrogen flow for about 10 min at 240 °C, the column was kept overnight in an oven at 280 °C, after having had both ends flame sealed. Pretreatment with C 20 M probably increases the wettability of capillary surface walls for polar phases, deactivates the walls and makes the surface of graphitized carbon black more uniform. After this treatment the column was statically coated with the stationary phase. Use of a concentrated solution permitted attainment of the desired film thickness. The columns were conditioned by temperature programming from 50 to 240 °C (3°/min) and keep-

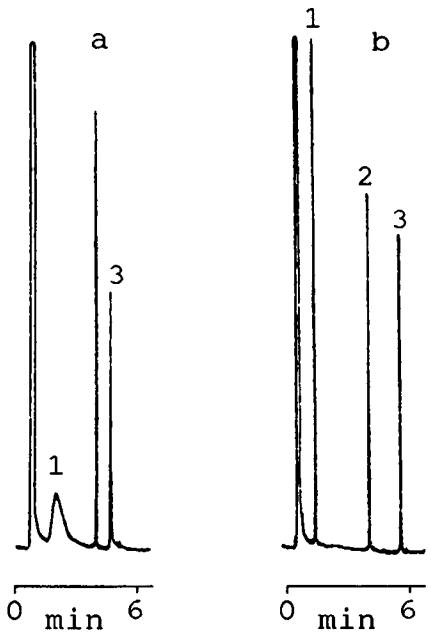

Fig. 6-8 Chromatograms of polar compounds on two microcapillary columns [44].

a — column with Carbopack C not pretreated by Carbowax 20 M;
b — column is pretreated by Carbowax 20 M.
Column i.d. — 100 μm, column temperature 90 °C.

Peaks: 1 — octanol, 2 — 2,6-dimethylpentol, 3 — 2,6-dimethylaniline.

Separations on microcapillary columns

ing the column at the latter temperature for 90 min in a hydrogen flow [44]. Fig. 6-8 (a and b) shows the role of pretreatment with Carbowax 20 M. The chromatogram in Fig. 6-8a was obtained on a column not pretreated with C 20 M, while the one in Fig. 6-8b was obtained on a column pretreated with Carbowax 20 M. In Fig. 6-8b all the peaks are symmetrical.

Van Deemter plot for a microcapillary column

Column characteristics for different phases and different test compounds are given in Table 6-2 [44]. The column characteristics are extremely good and the columns appear very promising for separation of polar compounds. Fig. 6-9 [44] shows the HETP dependence on the linear velocity to become stronger, while the efficiency still remains high. This characteristic is very important for fast analysis. Fig. 6-10 [44] shows two examples of amine separation, the first (a) for aromatic amines and the second (b) for aliphatic amines. Microcapillary columns offer good efficiency with symmetrical peaks, low analysis times and low operating temperatures, compared with classical capillary columns.

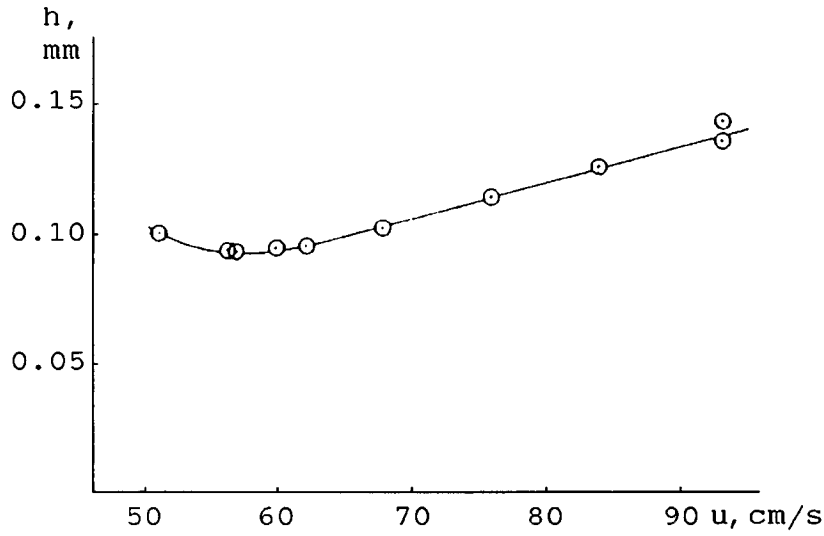

Fig. 6-9 Plot of HETP for 2,6-dimethylaniline vs linear gas velocity (*u*) [44].
Column 6.0 m × 0.1 mm, column temperature 90 °C

Table 6-2

Characteristics of microcapillary columns (i.d. 100 mm) with graphitized capillary black (GCB) modified liquid phase [44].

C — Carbowax, FFAP — free fatty acid phase, DMA — 2,6-dimethylaniline, DMF — 2,6-dimethylphenol, d_f — average liquid film thickness, N/s — number of theoretical plates per second, UT — utilized theoretical efficiency.

Column #	Phase	Length, m	d_f, (μm)	k'	U_{opt}, (cm/s)	H_{min}, (mm)	N/s	UTE, (%)	Test substance
1	C 20M	5.7	0.10	52.2	52.6	0.109	4830	87	DMA
2	C 20M	16.0	0.07	51.1	54.2	0.091	5960	100	DMA
3	C 40M	5.5	0.10	57.9	50.2	0.116	4330	82	DMA
4	C 40M	5.5	0.20	87.0	55.0	0.110	5050	87	DMA
5	C 40M	4.6	0.10	85.2	54.0	0.116	4660	81	DMF
6	C 40M	7.2	0.10	45.1	51.1	0.087	5870	100	DMA
7	C 600M	6.0	0.07	49.3	57.3	0.103	5560	93	DMA
8[a]	C 600M	15.0	0.07	49.3	56.6	0.094	6020	100	DMA
9[a]	C 600M	10.0	0.07	61.9	54.3	0.088	6130	100	DMA
10	FFAP	8.5	0.07	58.9	60.7	0.115	5280	82	DMF

[a] Fused silica

In our opinion, charcoal can be tentatively assigned to the group of carbon black adsorbents. The step of charcoal preparation for ALOT column is not very difficult [22]. In order to remove remaining metal oxides and sulfides, technical charcoal was boiled several times with concentrated hydrochloric acid, washed until neutral reaction and dried. After crushing by hand, the charcoal was dried for 24 h and pulverized in a vibration mill to a grain size of 1–3 μm. It was difficult to prepare stable suspensions. Aqueous systems, also with addition of wetting agents, have failed. Organic solvents, e.g. cyclohexane, led to stable suspensions but to adsorbent layers that adhered durably to the capillary. Good results were obtained by means of ethanol-water (4:1) mixture. Mohnke and Heybey [22] succeeded in coating about 30 m of an ALOT column with a stable 30 μm layer. Several sections of this type were joined manually by fusing under the microscope. Separation of single partially deuterated methanes is shown on Fig. 6-11 [22]. The separation is nearly complete at –9.5 °C.

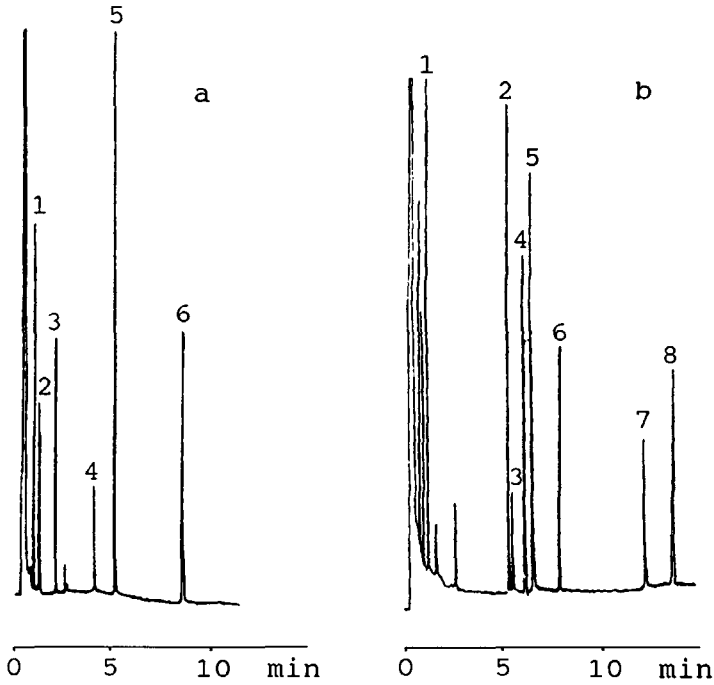

Fig. 6-10 Chromatograms of high-boiling amines on microcapillary columns [44].

Column 5.5 m × 0.1 mm; 3°/min; 200 °C (a) and 170 °C (b);

Peaks of aromatic amines (a): 1 — *o*-phenylenediamine, 2 — *p*-phenylenediamine, 3 — *o*-nitroaniline, 4 — *m*-nitroaniline, 5 — biphenylamine, 6 — *p*-nitroaniline.

Peaks of aliphatic amines (b): 1 — 4-methoxyphenyl-1,2-ethylaminopropane, 2 — *N,N*-dimethyl-1,2-diphenylmethoxyethylamine, 3 — *N*-methyl-3,3-diphenylpropylamine, 4 — ketocaine, 5 — *N*-methyl-1,2-diphenylmethoxyethylamine, 6 — cyclizine, 7 — 2-diphenylmethoxyethylamine, 8 — adiphenine.

In conclusion, we should like to note that use of ALOT columns with carbon adsorbents permits accomplishment of many difficult separations.

6.1.2 ALOT Columns with Alumina

Alumina has long been used in gas chromatography as separating adsorbent for hydrocarbons [45]. By modifying alumina with water [46–48], inorganic salts [49] or organic liquids [47], it is possible to achieve considerable improvements in the efficiency and in reduction of the tailing effect.

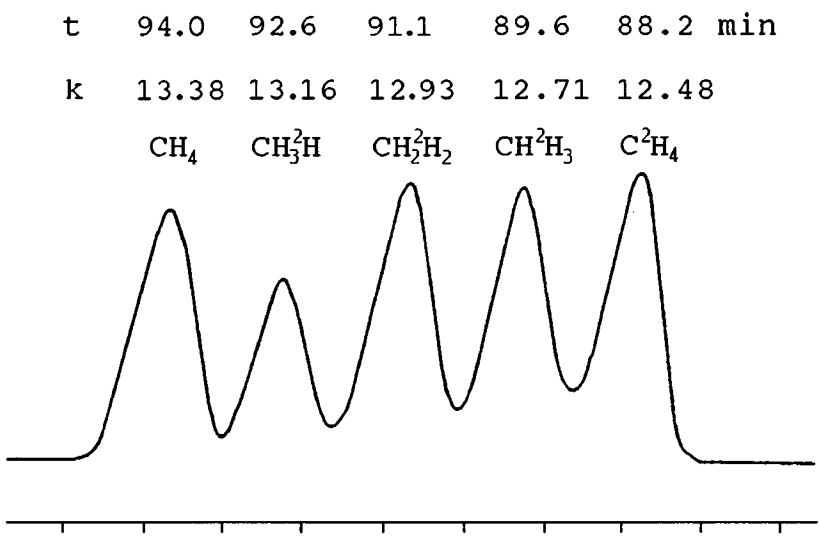

Fig. 6-11 Separation of deuterated methanes [22].

ALOT column 98 m × 0.28 mm i.d.; adsorbent active charcoal, layer thickness ~30 μm; temperature –9.5 °C; effective plate number — 66500.

The first attempt to use the dynamic method was undertaken by Kirkland [50] who used Al_2O_3 in the form of a fibrous mineral, i.e., boehmite. According to microscopic studies, the elementary fiber of this mineral is ca. 1000 Å long and 50 Å across. The fibers were aggregated to give a diameter of ca. 2 μm. The specific surface of such a sorbent is 275 m^2/g. A 7% aqueous boehmite solution was passed through a column (10 m × 0.25 or 0.5 mm i.d.) made of glass or stainless steel. The column was ready for use after the suspension had been coated and the adsorption layer was dried. The thus-prepared column was useful in separating a number of Freons and showed a moderate efficiency.

Some methods of ALOT columns preparation were based on generation of alumina layers in aluminum capillaries [51] and on coating the inner walls of

the tubes by using aqueous or organic dispersions [52–54]. Schneider and co-workers [55] emphasize the following advantages of glass columns coated with aluminum oxide: (1) the column walls have a low (as compared with metal capillaries) adsorption activity, (2) due to the presence of negative charge on the glass capillary walls, the layers of finely ground aluminum oxide stick well to the glass surface to form a thin layer without using any fixing agents, and the layers do not flake off the walls even in the case of capillary strain within the elastic limits, (3) the process of coating and the quality of the finished column can be controlled by visual inspection; (4) glass columns of any dimensions can be prepared in the laboratory. Fused-silica capillaries have practically the same advantages.

Advantage of glass columns

The aluminum oxide layer was applied to the inner walls of the glass capillary from an aqueous dispersion in the form of aluminum hydroxide and converted *in situ* into aluminum oxide by heat treatment. By varying heat treatment and by blocking unwanted activities with potassium chloride, adjustment to the desired separation characteristics can be achieved [55]. To prepare the coating suspension, aluminum oxide (particles <2 μm) obtained by calcination of hydroxide is heated for 24 h at 300 °C. 20 g of the alumina is mixed with 70 ml of 5% (w/w) Baymal solution (colloidal aluminum hydroxide) and with 0.3 ml of acetic acid (>96%) and stirred for about 10 min in an ultrasonic bath. Subsequently the mixture is filtered through a wire sieve of 300 mesh and allowed to stand for 24 h for aging. The suspension thus prepared shows thixotropic behavior.

Use of colloidal solutions of aluminum oxide for preparing ALOT columns

Use of an aluminum oxide colloidal solution allows preparation of a dispersion medium with an enhanced density and viscosity and thereby improves the suspension stability. Moreover, the colloidal aluminum oxide particles bind the large sorbent particles and additionally fix them on the capillary surface.

Before use the column is flushed with 1% acetic acid. The glass capillary tube is connected by a polyethylene capillary tube to the glass capillary tube of the same diameter to prevent draining disturbances. Then 0.6 ml of the suspension is forced into the capillary tube. The suspension is applied by forcing it through the capillary at 4 ml/min. To achieve complete coverage of a 65-m tube, this procedure must be repeated four times. To prepare longer columns, the authors recommended repetition of this procedure, considering, perhaps, that in this case the thickness of the layer on the initial portion of the column will remain the same. To complete the process of column preparation, the column is stored for 10 h after coating of the suspension and then dried under nitrogen at pressure of 0.3 MPa. A 65-m column, 0.4 mm i.d. can be dried in a week. After drying, the chromatography column is activated for 3 h at 300 °C. According to Schneider and co-workers [55] the thus-obtained columns contain ≈5.5 mg of Al_2O_3 per meter of length. The amount of sorbent can be widely varied by changing the suspension density, the rate at which it is forced through the capillary, or the volume of suspension portions injected per pass. To reduce column activity, it is twice flushed with 2 ml of 2% (w/w) potassium chloride solution. After drying and heating, the column is ready for use.

Reproducibility of column preparation procedure

The lifetime of alumina capillary columns can be several years. Kovats retention indices of several hydrocarbons on ten different separation columns prepared by the same procedure are satisfactorily reproducible (see Table 6-3 [55]).

The columns obtained in this way process a fairly high efficiency. For example, for trimethyl-1-butyne (capacity factor 7.1) the column efficiency amounts to 700 theoretical plates per meter. More than 50 light hydrocarbons were separated under isothermal conditions at a temperature of 130 °C, with their partial concentration in the gas mixture being equal to ca. 1 ppb.

Table 6-3

Kovats retention indices measured on ten different columns [55]

Test substance	Column									
	1	2	3	4	5	6	7	8	9	10
Acetylene	375	376	372	376	375	376	373	374	375	376
Isobutene	454	453	458	457	457	457	455	457	454	458
Pentyne	547	543	545	549	546	550	548	548	544	548
2-Hexene	625	624	623	626	625	626	625	624	626	626
Toluene	834	835	833	834	834	834	835	834	834	835

Separation of C_1–C_6 hydrocarbons on ALOT columns with alumina

The chromatogram of a C_1–C_6 hydrocarbon test mixture on an ALOT column with alumina is shown in Fig. 6-12 [55]. Fig. 6-13 and Fig. 6-14 show chromatograms of hydrocarbon test mixtures obtained with alumina capillaries additionally coated with squalane (Fig. 6-13) or polyethylene glycol (Fig. 6-14) [55]. The use of modified alumina allowed the range of analyzed mixtures to be broadened and the column temperature to be lowered.

In the course of recent developments in the field of fused silica capillary columns, this procedure has been extended by de Nijs [56] to commercial production by Chrompack [58–62]. The dynamic method requires a highly concentrated suspension as the column retains only that amount of sorbent which is present in the thin film appearing after passage of the suspension.

6.1.3 ALOT Columns with other Oxide Adsorbents

Schwartz and co-workers [52, 63] applied a silica layer on the inner surfaces of polymeric, copper, and steel capillaries of 4–400 m length and ≈0.5 mm inside diameter. The authors [62] ran into difficulties in using a suspension containing micron-size particles and therefore they decided in favor of true colloidal silica solutions. They used [52] 22% silica sol in [water–2-propanol] system commercially available under the trade mark Nalcoag 1092. Such colloidal silica sols are produced for preparing adsorption and antistatic impregnated systems. They have a low viscosity and therefore can readily pass through a capillary to form a thin

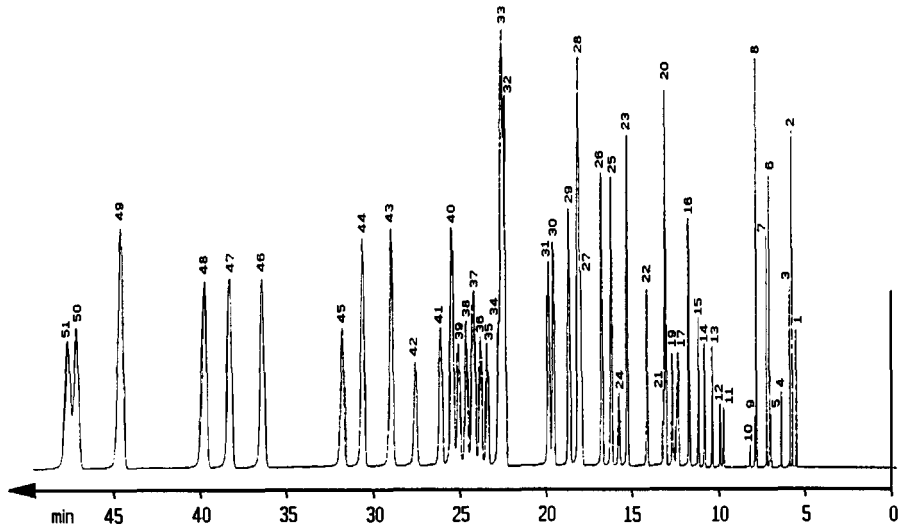

Fig. 6-12 Chromatogram of test hydrocarbon mixture using glass ALOT column coated with Al_2O_3 [33].

Column 71 m × 0.40 mm;
sorbent Al_2O_3, 5.1 mg/m;
temperature 130 °C;
inlet pressure 2 bar.

Peaks: 1— methane; 2 — ethane; 3 — ethene; 4 — propane;
5 — cyclopropane; 6 — propene; 7 — acetylene; 8 — propadiene;
9 — isobutane; 10 — n-butane; 11 — *trans*-2-butene; 12 — 1-butene;
13 — isobutene; 14 — *cis*-2-butene; 15 — 2,2-dimethylpropane;
16 — methylcyclobutane; 17 — cyclopentane; 18 — isopentane;
19 — 1,2-butadiene + propyne + *trans*-1,2-dimethylcyclopropane;
20 — 1,1-dimethylcyclopropane; 21 — n-pentane;
22 — *cis*-1,2-dimethylcyclopropane + 1,3-butadiene; 23 — ethylcyclopropane;
24 — 3-methyl-1-butene; 25 — cyclopentene; 26 — *trans*-2-pentene;
27 — 2-methyl-2-butene; 28 — 1-pentene + methylenecyclobutane;
29 — 2-methyl-1-butene; 30 — *cis*-2-pentene; 31 — 3-methyl-1,2-butadiene;
32 — 2-butyne; 33 — 2,2-dimethylbutane + 1,1,2-trimethylcyclopropane;
34 — methylcyclopentane + 3,3-dimethyl-1-butene; 35 — ethylcyclobutane;
36 — cyclohexane; 37 — 1-butyne+2,3-dimethylbutane; 38 — 2-methylpentane;
39 — 3-methylpentane; 40 — 1,2-pentadiene+2,3-pentadiene;
41 — vinylcyclopropane; 42 — n-hexane;
43 — *trans*-4-methyl-2-pentene+isopropylcylopropane;
44 — 2-methyl-1,3-butadiene; 45 — 1-methylcyclopentene;
46 — 4-methyl-1-pentene; 47 — *cis*-1,3-pentadiene;
48 — *trans*-1,3-pentadiene; 49 — 3-methyl-1-butyne;
50 — isopropylacetylene; 51 — 2-pentyne.

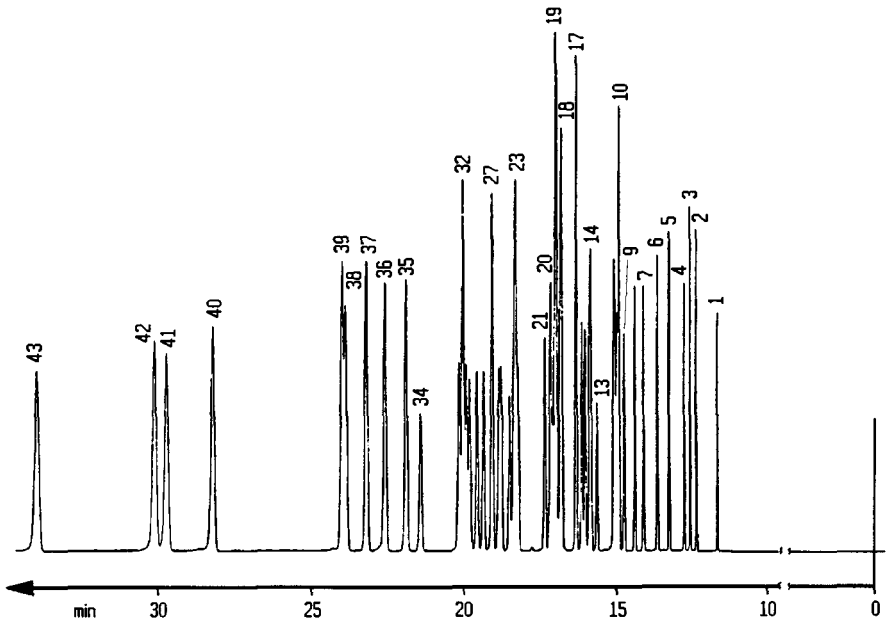

Fig. 6-13 Chromatogram of test hydrocarbon mixture using glass ALOT column coated with Al_2O_3 and squalane [55].

Column 129 m × 0.25 mm; sorbent Al_2O_3, 0.6 mg/m, squalane, 0.3 mg/m; column temperature 100 °C; inlet pressure 5 bar.

Peaks: 1 — n-pentane; 2 — 2-methylpentane; 3 — 3-methylpentane;
4 — n-hexane; 5 — 2,2-dimethylpentane; 6 — 2,2,3-trimethylbutane;
7 — 2-methylhexane; 8 — 3-methylhexane; 9 — *cis*-2,5-dimethyl-3-hexene;
10 — 2,2,4-trimethylpentane + *trans*-2,2-dimethyl-3-hexene;
11 — *trans*-2,5-dimethyl-3-hexene; 12 — benzene + n-heptane;
13 — 2,4,4-trimethyl-1-pentene;
14 — 2,4,4-trimethyl-2-pentene + 2,2-dimethylhexane;
15 — *cis*-2,2-dimethyl-3-hexene; 16 — 2,5-dimethylhexane;
17 — 2,4-dimethylhexane + 1,1,3-trimethylcyclopentane;
18 — *trans*-2-methyl-3-heptene + 2,2,3-trimethylpentane;
19 — *trans*-4-ethyl-2-hexene + 3,3-dimethylhexane + 2,5-dimethyl-1-hexene;
20 — 3,4-dimethyl-1-hexene + *trans*-6-methyl-3-heptene;
21 — *trans*-3,4,4-trimethylpentene; 22 — 3-methylheptane;
23 — *cis*-4-methyl-3-ethyl-2-pentene + 3,4-dimethylhexane;
24 — methyl-3-hexene; 25 — 2-methyl-1-heptene; 6 — 3-methyl-3-ethylpentane;
27 — 2-methyl-3-ethylpentene + 1-octene; 28 — *trans*-3-octene;
29 — 2-methyl-2-heptene; 30 — n-octane; 31 — toluene;
32 — *trans*-2-octene + *trans*-1-methyl-2-ethylcyclopentane;
33 — 1,1-dimethylcyclohexane; 34 — *trans*-1,3-dimethylcyclohexane;
35 — isopropylcyclopentane; 36 — *cis*-1-methyl-2-ethylcyclopentane;
37 — n-propylcyclopentane; 38 — 4-vinylcyclohexene; 39 — ethylcyclohexane;
40 — ethylbenzene; 41 — *p*-xylene; 42 — *m*-xylene; 43 — *o*-xylene.

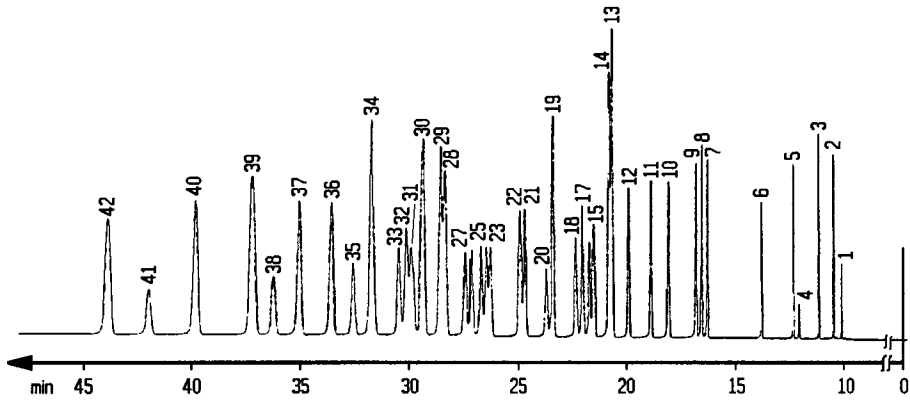

Fig. 6-14 Chromatogram of test hydrocarbon mixture using glass ALOT column with Al_2O_3 and Carbowax [55].

Column 125 m × 0.25 mm, sorbent Al_2O_3, 0.5 mg/m, Carbowax, 0.3 mg/m; column temperature 100 °C; inlet pressure 5 bar.

Peaks: 1 — n-heptane; 2 — n-octane; 3 — n-nonane; 4 — benzene; 5 — n-decane; 6 — toluene; 7 — ethylbenzene; 8 — *p*-xylene; 9 — *m*-xylene; 10 — isopropylbenzene; 11 — *o*-xylene; 12 — n-propylbenzene; 13 — 4-ethyltoluene; 14 — 3-ethyltoluene; 15 — tert.-butylbenzene; 16 — isobutylbenzene; 17 — 1,3,5-trimethylbenzene; 18 — sec.-butylbenzene; 19 — styrene+2-ethyltoluene + 1-methyl-3-isopropylbenzene; 20 — 1-methyl-4-isopropylbenzene; 21 — neopentylbenzene; 22 — 1,2,4-trimethylbenzene; 23 — 1,3-diethylbenzene; 24 — 1-methyl-2-isopropylbenzene + 1-methyl-3-n-propylbenzene; 25 — 1-methyl-4-n-propylbenzene; 26 — 1,4-diethylbenzene; 27 — n-butylbenzene; 28 — 1-methyl-3-tert.-butylbenzene; 29 — 1,3-dimethyl-5-ethylbenzene; 30 — 1-methyl-4-tert.-butylbenzene+ +1,3-diethylbenzene; 31 — α-methylstyrene; 32 — 1-methyl-2-n-propylbenzene+ + tert.-pentylbenzene; 33 — 1,2,3-trimethylbenzene; 34 — 1,3-diisopropylbenzene + 1,4-dimethyl-2-ethylbenzene; 35 — 1,3-dimethyl-5-isopropylbenzene; 36 — 1,2-dimethyl-4-ethylbenzene; 37 — 1,2-diisopropylbenzene+indane; 38 — 1,3-dimethyl-2-ethylbenzene; 39 — 1-methyl-3,5-diethylbenzene+1,4-diisopropylbenzene; 40 — n-pentylbenzene+1,2-dimethyl-3-ethylbenzene; 41 — 1,2,4,5-tetramethylbenzene; 42 — 1,2,3,5-tetramethylbenzene.

suspension layer on its inner surface. Such a layer on the inner surface of a capillary corresponds to the dynamic method of film coating. After evaporation of the dispersion medium, a thin solid silica layer remains on the inside capillary surface. Schwartz et al. [52] did not state whether the suspension stabilizer normally present in such sys-

tems remained on the silica particles after drying. Usually stabilizers are composed of surfactants modifying the surface and hence affecting the retention characteristics.

The size of the particles in such sols does not exceed 0.02 μm; therefore the adsorption layer should have a fairly significant specific surface, the capacity factor of the column with such a layer being as high as 1.0. A column prepared by this method was useful in separating pentane and hexane isomers. However, the specific column efficiency calculated from the chromatograms reported in this work [52] did not exceed 100 theoretical plates per meter. Such a low efficiency is most likely due to the inhomogeneous distribution of the solid sorbent particles over the column surface, which is caused both by the disadvantages inherent in the dynamic method (variations in the suspension meniscus motion velocity and instability of the resulting film) and by the rheological suspension properties that were discussed above. Moreover, the colloidal adsorbent appears to strongly resist mass transfer in the sorption layer. Starting with these considerations the authors [63–65] used large silica particles (ca. 4 μm) for preparation of adsorption columns [52]. In this case they used hydrophobized silica CD-100, which was replaced later by silica Siloid-144. Before coating, the silica was treated with the surfactant Igepal. *p*-Toluenesulfonic acid became covalently bonded to the silica surface to give a stable suspension in hydrocarbon dispersion media. However, in this case one can also speak of a modified sorbent, as the silica being treated by that method contained 23% of an organic phase, as determined from the mass loss on sintering.

The sorbent was coated by the dynamic method from a 7.5% suspension in n-heptane. The thus-obtained glass capillary column (120 m long × 0.5 mm i.d.) permitted separation of 13 isomers of C_5–C_7 hydrocarbons in 18 min. The efficiency as determined for 2,4-dimethylpentene was 550 theoretical plates per meter [63–65].

Early in the 1960s the dynamic silica gel coating method was employed by Perkin-Elmer for the commercial production of copper capillary adsorption columns. These columns were ca. 400 m long × 0.5 mm i.d. [66] and were designed for the rapid analysis of light hydrocarbons gases.

Halasz and Horvath [17] suggested a method for the production of ALOT columns with Fe_2O_3 and triethylene glycol as stationary phase. The procedure was not complicated. 20 grams of highly dispersed ferric oxide (specific surface 37 m^2/g) was suspended in 150 ml of trifluorotrichloroethane and 20 ml of chloroform with the aid of a high-speed stirrer. Afterwards 2 g of triethylene glycol dissolved in 20 ml of chloroform was added to this suspension with stirring. The suspension was then pressed through a sieve (mesh size 60 μm). The inner wall of a copper capillary (28.5 m × 0.25 mm)

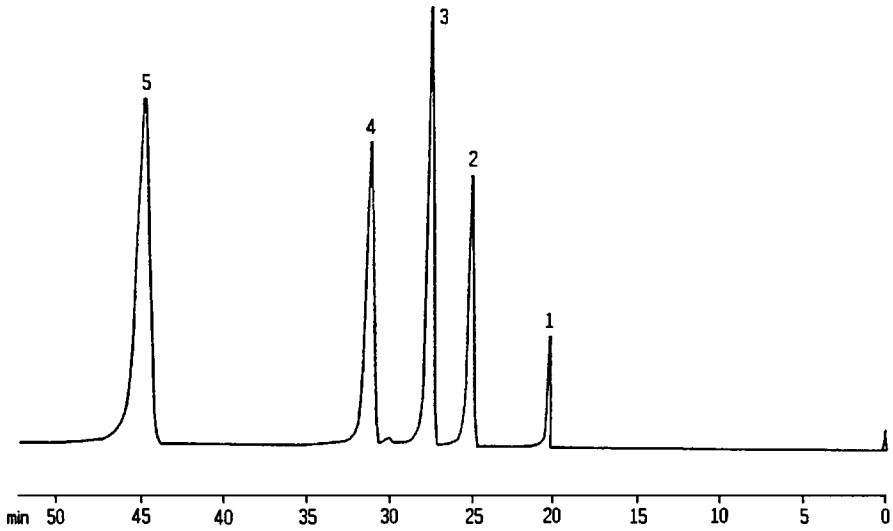

Fig. 6-15 Chromatogram of hydrocarbon mixture [17].

Column — 28.5 m × 0.25 mm i.d., adsorbent Fe_2O_3 (5.5 mg/m) coated with triethylene glycol (0.55 mg/m), temperature — 80 °C; Peaks: 1 — methane, 2 — n-pentane, 3 — 2,2-dimethylbutane, 4 — n-hexane, 5 — n-heptane.

was silvered over. Then the suspension was pressed into the capillary tube with the aid of nitrogen under high pressure (150 atm). After evaporation of the solvent, about 5.5 mg of β-Fe_2O_3 and about 0.55 mg of triethylene glycol per meter of the column remained on the inner wall. The separation of the hydrocarbon mixture is shown in Fig. 6-15 [17]. In some separation cases open tubular columns with impregnated thin layer of support are superior to conventional capillary columns.

6.1.4 ALOT Columns with Molecular Sieves

Open tubular adsorption columns with molecular sieves were suggested by Purcell [67]. This type of columns was used for separation of permanent gases [67].

The separation of hydrocarbons is a very important field of application of columns with molecular sieves.

Powdered molecular sieve 13X was treated with sodium hydroxide in order to reduce its acidic activity and to improve the separation of saturated hydrocarbons into paraffins and naphthenes of the same carbon number [68–70].

10 ml of molecular sieve 13X was mixed with 50 ml of 3% sodium hydroxide solution in a centrifuge tube for 15 min. Particles of molecular sieve 13X were then separated by centrifugation, sodium hydroxide was poured off and the residue was washed with distilled water as least five times. During each rinse, the suspension was thoroughly dispersed by shaking and was then centrifuged. The washed aqueous suspension was ground in a colloidal mill so as to give a particle size of 1–2 μm (by microscopic observation). The concentration of molecular sieve 13X in the suspension was assessed by evaporating to dryness an aliquot of solution and weighing the residue.

The columns prepared by the dynamic coating procedure behaved in a superior manner.

Soulages and Brieva [68] obtained good performance with columns prepared with suspensions in the 5–10% (w/v) range.

A stainless steel tube (5 m × 0.5 mm i.d.) was connected to a 10 ml reservoir with a side entrance connected in turn to a nitrogen cylinder via a needle valve to pressurize the filling tube. The molecular sieve suspension was thoroughly shaken and 5 ml thereof was added to the reservoir and forced to pass through the column in 2–4 min by applying pressure. Owing to the instability of the aqueous dispersion, it is important that the passage is effected in a short time.

Once the excess of the suspension had drained through, the nitrogen flow rate was adjusted to 5 ml/min and allowed to run overnight in order to dry the column.

The column was conditioned by temperature programming at 3 °/min up to 450 °C, this temperature then being maintained for several hours with a nitrogen flow rate of 1 ml/min [68].

Brunnock and Luke [69] suggested a technique employing a high temperature gas-solid chromatographic process using molecular sieve 13X modified by alkali treatment. Prior to packing, the molecular sieve was treated by percolating 3% caustic soda solution through a 3.0 m × 12 mm i.d. column filled with molecular sieve at 4 ml/min for 25 min. Then the sieve was washed with water, dried and heated to 450 °C for 3 hours. After treatment of the sieves in this manner, the reproducibility of the retention volumes appears to be as good as that obtained with conventional liquid or support packed columns.

Saturated hydrocarbons in petroleum distillates boiling up to ≈185 °C are quantitatively separated by carbon number or by bulk hydrocarbon type within each carbon number. Examples of analysis for individual naphthene and paraffin contents on capillary column are also given by Brunnock and Luke [69].

Application of columns with molecular sieves to the separation of molecules with different isotopic composition is a very interesting direction.

Separation of isotope-substituted molecules on ALOT column with molecular sieves

As an example, let us consider the characteristics of an ALOT column with molecular sieve 5A for separation of isotope-substituted molecules [22, 71]. Using the static method to apply an aqueous suspension containing molecular sieve crystals (about 1 μm) in size and at a concentration of 35 vol.%) a capillary column was coated with uniform, thick porcelain-like rigid layer (≈30 μm thickness) with good adhesiveness. Even at gas speeds of 1 m/s, blow-out of molecular sieves was not observed. It is necessary to start column heating carefully because molecular sieves contain a lot of water in the micropores and hollow spaces. At first heating proceeded from 20 °C to 100 °C at 1 °/min and was held at 100 °C for 8 h. Then the column was heated at the same rate to 350 °C and subsequently activated for 2 h, always in a stream of pure hydrogen. Fig. 6-16 [22] shows a typical chromatogram of gas sample. All the components are completely separated at room tem-

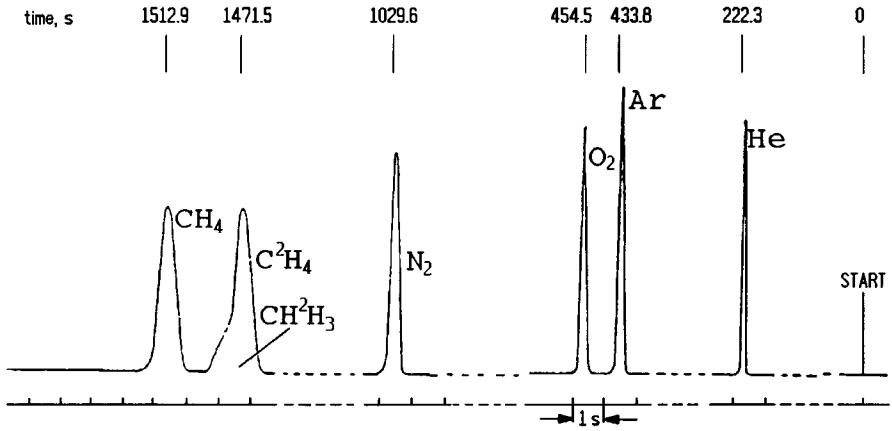

Fig. 6-16 Separation of some gases including CH_4 and C_2H_4 [22].

Column — 67 m × 0.33 mm, adsorbent — molecular sieves 5A, adsorbent layer thickness — 30 μm, temperature — 22.3 °C, carrier gas — hydrogen (1.4 bar), thermal conductivity detector.

$HETP_{eff}$ — 0.71 mm, capacity ratio CH_4 — 5.8, separation factor $\alpha(CH_4/C^2H_4)$ = 1.0336.

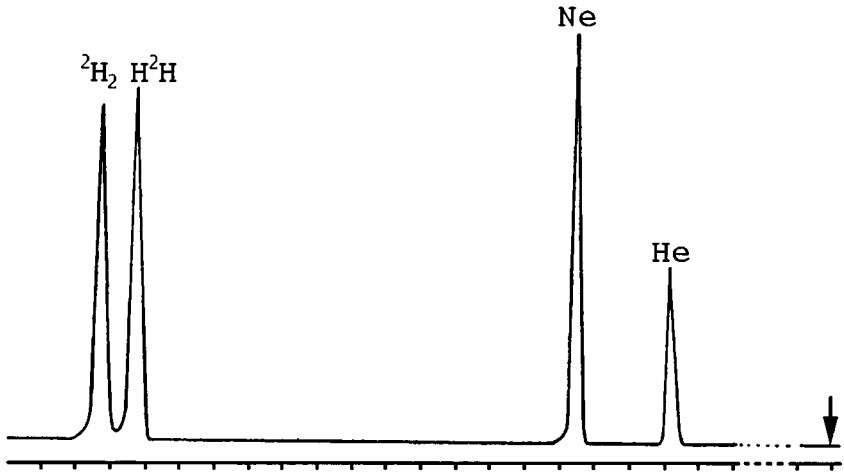

Fig. 6-17 Separation of H^2H and $^2H_2$ [22].

Column — 67 m × 0.33 mm, adsorbent — molecular sieves 5A, adsorbent layer thickness — 30 μm, temperature — –78.5°C, $\alpha(^2H_2/H^2H)$ — 1.0622, capacity ratio ($^2H_2$) — 0.574, separation time — 4.6 min.

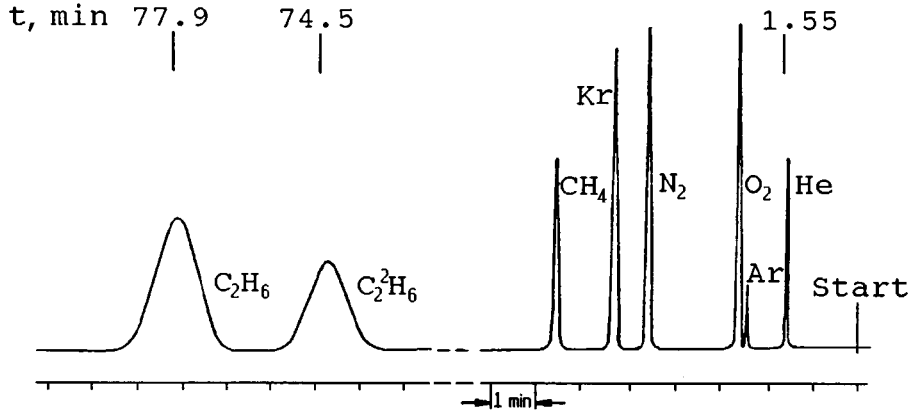

Fig. 6-18 Separation of C_2H_6–$C_2^2H_6$ [22].

Column — 18.8 m × 0.31 mm i.d., adsorbent — molecular sieves 13X, adsorbent layer thickness — 30 μm, temperature 44.5 °C, effective plate number — 29500, capacity ratio (C_2H_6) — 49.3, $\alpha(C_2H_6/C_2^2H_6)$ = 1.047.

perature. The peak symmetry is good. Tailing of C^2H_4 peak is due to CH^2H_3 still present in the sample. Argon and oxygen are completely separated.

Separation of H^2H and $^2H_2$ on an ALOT column with 5A molecular sieves is shown in Fig. 6-17 [22]. Separation of hydrogen isotopes is completed in a short time and at a high separation temperature.

ALOT columns with molecular sieves have now been successfully produced with fused silica.

The same method was used for preparing ALOT column with molecular sieves 13 X. Separation of some gases is shown in Fig. 6-18 [22]. C_2H_6 and $C_2{}^2H_6$ are completely separated.

6.1.5 SCOT Columns

Methods for preparation of SCOT columns are similar to those used for preparation of ALOT columns. Therefore it is interesting, in our opinion, to describe some of those methods.

The average thickness of the diatomaceous layer (Johns-Manville) produced by Ettre and co-workers with the aid of Horvath's device was 60 μm [18]. Since in this case a sorbent with 10-μm particles was used, it can be assumed that the authors were capable of producing at one pass a layer with a thickness equal to 6 times the particle diameter. Such a result is difficult to obtain in practice with the dynamic method. Nevertheless, the static method has some disadvantages. They are primarily connected with the necessity of filling capillaries with the suspension so that suspension traveling inside the tube cannot be avoided. This leads to disturbance of the suspension structure and to the formation of aggregated particles nonuniformly distributed over the column, thus resulting in an inhomogeneous layer and a decrease of the entire system's separating power. Moreover, the method is restricted to volatile dispersion media characterized, as a rule, by low densities.

Support-coated open tubular (SCOT) capillary columns with Alltech CS-10 on solid support silica T 40 and the procedure for preparation of this type of column were described in paper [72].

Soda-glass columns (100 m × 0.45 mm i.d.; coil diameter 130 mm) were washed with methanol, chloroform, diethyl ether and acetone (ca. 20 ml of each solvent), then dried under a stream of nitrogen and coated immediately to avoid exposure to air. Columns soaked overnight with 50% aqueous hydrochloric acid and then washed with water, methanol and acetone were also used.

A column was placed horizontally in a small container made of foamed polystyrene insulation. The upper end of the column was connected with heat-shrinking tubing to the coating reservoir, and the other end to a buffer column (15–20 m) in order to maintain the same coating speed in the last part of the column [73]. A lid was placed on the container to ensure a uniform temperature throughout the column for steady coating speed and uniform solvent evaporation and film spreading [74]. The column was coated at room temperature (approximately 25 °C).

Using SiO_2 as solid support in SCOT columns

Silica T40, a pure silicon dioxide of particle size 5–30 nm, was used as the solid support. Approximately 0.2 g of support was weighed into a 20 ml vial, 8 ml of acetone was added, and the suspension was sonicated for 1–1.5 h in an ultrasonic bath. During this time, the vial was taken out of the ultrasonic bath four or five times; and the suspension was decanted into a new vial to remove the particles that had conglomerated on the wall of the vial above the suspension. Then 0.8 g of Alltech CS-10 was added, and the suspension was further sonicated for ca. 30 min. After standing, the suspension was stable for some days.

A column was coated dynamically [75]. A wetting plug of acetone (3 ml), followed by the slurry (8 ml), was introduced into the column under nitrogen pressure. Both plugs were pushed through the column at a slow coating speed of 1–1.5 cm/s and a nitrogen pressure of 100–150 kPa. In fact a coating speed of 8–10 cm/s and a pressure of 350–400 kPa were also used for producing a thicker film [76]. The solvent was evaporated slowly from the slow-coated columns at 100–150 kPa.

Fast solvent evaporation was applied for fast-coated columns at 350–400 kPa [77]. The evaporation continued for 3–4 h. The column was conditioned overnight by running an oven temperature program up to 195 °C at a heating rate of 0.2–0.3 °/min with a carrier-gas flow-rate of 1–2 ml/min.

The object of the work [72] was to produce, for the authors' own use, highly polar SCOT capillary columns capable of separating isomeric fatty acid methyl esters; several solid supports and techniques were tested.

Columns washed with aqueous hydrochloric acid before coating were not better than non-washed columns, but acid-washed Silanox 101 (made hydrophilic) produced more efficient columns than Silanox 101 (hydrophobic) itself; in both cases the columns have a short life time. Although the hydrophobic properties of Silanox 101 are considered unsuitable for use with polar phases, it has been reported that Silanox 101 and polar phases can be directly coated on borosilicate glass. Chromosorb R-6470-1 produced unevenly coated columns with low efficiency, probably because of its large particle size. Acetone was found to be a better solvent for dispersing silica T40 than chloroform or acetonitrile. Other workers report that acetone is an excellent solvent for polar phases, and this was confirmed by our experiments. Slow coating of silica T40 slurry in acetone and slow evaporation greatly improved the uniformity of the liquid film. Columns produced as described had a useful life of ca. 2 months at oven temperatures of 170–180°C.

Compared with the other solid supports tested, Silica T40 gave the best performance.

An efficiency of 60,000–70,000 effective theoretical plates for methyl oleate was regularly attained and satisfactory separation of the four methyl octadecanoates (9-*trans*, 6-*cis*, 9-*cis*) was achieved (Fig. 6-19 [72]).

In principle the dynamic coating procedure is similar to that used for wall-coated open tubular col-

umns [78]. Kaiser [74] and Nikelly [53] used dynamic procedures for preparation of porous layer open tubular columns. A simple procedure for preparation of PLOT capillary column reported by Nikelly [53] is described below.

The coating procedure is relatively simple. Briefly, the dynamic technique consists of passing a plug of adsorbent suspension through coiled capillary tubing under gas pressure. The adsorbent suspension is a suspension of the solid support (solid adsorbent) in a solution of the liquid phase in a volatile solvent. The gas flow is continued until all the solvent is removed leaving a uniform porous layer covered with liquid phase on the inner walls of the tubing.

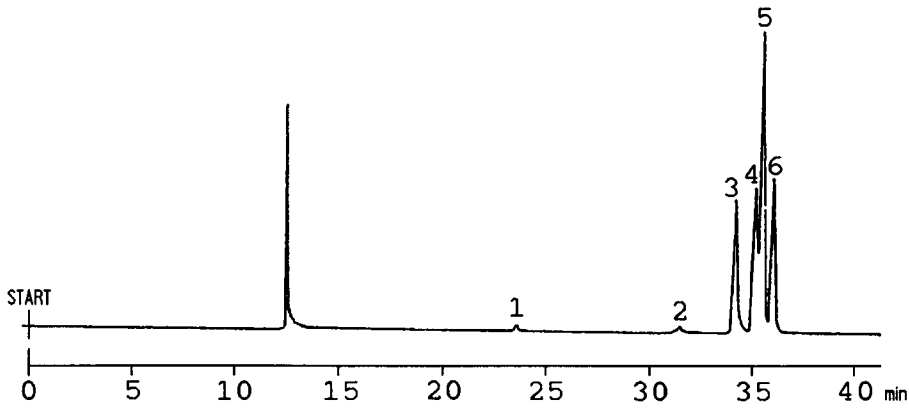

Fig. 6-19 Chromatogram of a mixture of fatty acid methyl esters [72].

Column coated with adsorbents Alltech CS-10 and silica T40. Carrier gas flow-rate, 3 ml/min. Oven, injector and detector temperature is 180, 260 and 280 °C, respectively.

Peaks: 1 — palmitate, 2 — stearate, 3 — 9-*trans*-octadecenoate, 4 — 6-*cis*-octadecenoate, 5 — 9-*cis*-octadecanoate, 6 — 11-*cis*-octadecanoate.

The reservoir (or filling tube) for introducing the coating mixture (plug) into the column tubing consists of a piece of metal tubing (10 cm length, 6.25 mm i.d.) connected to the column tubing by a Swagelok reducing union at one end. At the other end it is connected to the outlet of a nitrogen gas regulator. Since the gas delivery pressure required for some of the column coating procedures exceeds 5.0 kg/cm^2, a high pressure regulator is recommended. To prepare a solid support about 2 g of Chromosorb W is pulverized for about 3 to 5 min in a mortar, preferably made of agate or porcelain. Next, the finely ground material is sized by suspending it in ≈40 ml of relatively dry acetone using a 50 ml beaker and discarding the fraction that settles in the first 2–3 minutes. The suspended material is recovered by allowing it to settle over a period of a few hours or by evaporating off the acetone. The recovered fraction is then dried at 110 °C for about an hour and stored in a desiccator.

Using Chromosorb W as solid support in SCOT columns

Coating of a typical SCOT column (15 m × 0.5 mm), requires about 1.5 g of suspension. This is prepared by mixing 0.3 g of solid support and 1.2 g of liquid phase solution having a concentration of 2 to 10% in a small glass stoppered vial. A 15 m section of tubing coiled into a suitable shape and connected to the filling tube is flushed with a few milliliters of 1% solution of liquid phase in chloroform (or other high density solvent). The tubing is further flushed with nitrogen at a pressure of 0.7–1.4 kg/cm^2 for about 30 s after the above 1% solution had emerged.

With the aid of capillary pipet, the suspension is added to the filling tube and this is connected to the gas supply regulated at 1.4 kg/cm^2 or higher. Light tapping of the column is sometimes necessary to ensure continuous flow of the plug. After the excess suspension emerges (in about 3 min), the pressure is reduced to 0.07 or 0.14 kg/cm^2 and the gas flow is continued for 0.5 hour.

Table 6-4

Chromatographic characteristics of DEGS SCOT columns [79].

Column	length, m	15
	diameter, mm	0.75
Phase ratio		60
Temperature, °C		150
Flow rate, ml/min		2.0
Methyl oleate	capacity factor	5.3
	number theoretical plates	12500
	HETP, mm	1.2
	retention time, min	4.8
Methyl oleate/ methyl stearate	relative retention	1.13
	resolution	1.0

SN is separation number, N/m is a number of theoretical plates per 1 m.

Experimental conditions: glass capillary column (50 m × 0.27 mm) coated from suspension with different concentration of Cromosorb R and PPSEB, columns temperature — 125°C, carrier gas — nitrogen, 2 ml/min, sample size 0.3 μl with 30 ng of n-C_{15} and n-C_{16}.

Separation of methyl esters on SCOT columns

The column is conditioned in the same way as other open tubular columns [53]. As an example, Table 6-4 shows the main characteristics of SCOT capillary columns [79]. The separation of methyl esters is shown in Fig. 6-20 [79]. Conditions are as given in Table 6-4 [79].

Note that the important stearic-oleate separation, which required 12 min for complete resolution using a carefully selected and specially preconditioned packed column is accomplished in about 5 min on the DEGS SCOT column.

In Nikelly's opinion dynamically coated SCOT columns are almost equivalent to those made by the static method in terms of efficiency and capacity.

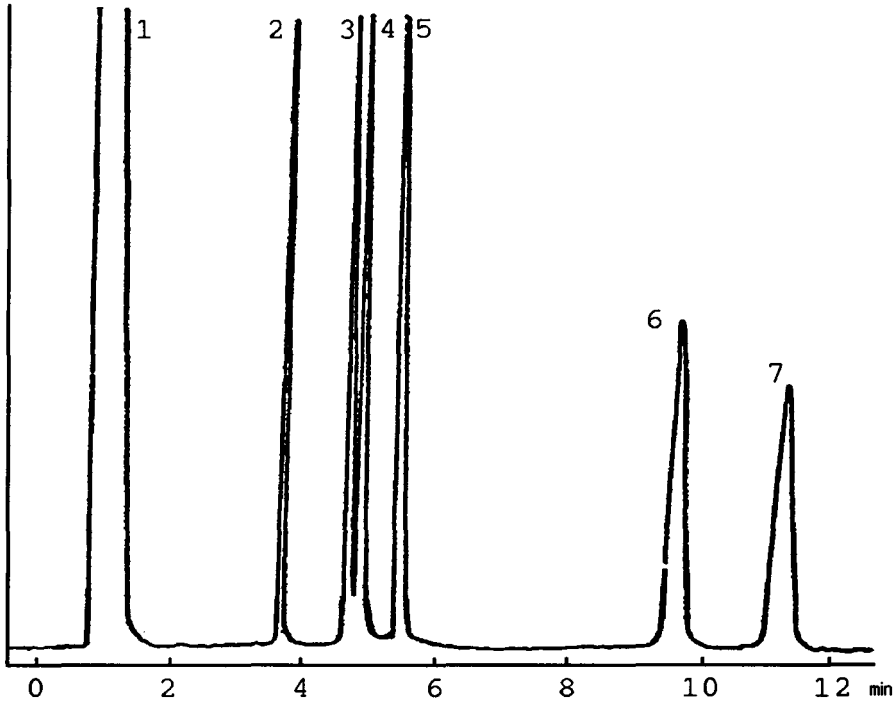

Fig. 6-20 Chromatogram of methyl esters [79].

DEGC SCOT column — 15 m × 0.75 mm I..D.; solid support (adsorbent) — Chromosorb W. Other conditions are given in Table 5-4 [79].

Peaks: 1 — solvent, 2 — palmitoleate, 3 — stearate, 4 — oleate, 5 — linoleate, 6 — behenate, 7 — arachidonate.

Compared to wall-coated columns, dynamically coated SCOT columns have higher capacity ratios.

A single-step coating method for preparation of glass capillary SCOT columns was proposed by Chanhan and Darbre [80]. They mentioned that SCOT columns have certain advantages over wall coated open tubular (WCOT) columns. Their values $\beta = V_m/V_l$ (V_m is gas phase volume in capillary column, V_l is liquid phase volume in capillary column) are usually much lower in comparison to

WCOT columns. This makes them more suitable for injecting large amounts of solutes and splitting can be avoided [80].

Chanhan and Darbre [80] developed a single-step coating procedure for SCOT column preparation. This procedure gives reproducibility and it is less time-consuming than another well known two-step coating procedure (see, e.g. [81, 82]).

The single-step procedure for SCOT columns

The single-step coating procedure is not complicated [80]. Coating was carried out on a 75 m length capillary tubing (0.27 mm i.d.). After coating, a 12.5 m length of capillary was cut from each end. The column was successively washed at room temperature with 5 ml of chloroform, a solution of benzyltriphenylphosphonium chloride (BTPPC)–1% w/v in chloroform:isooctane (1:1, w/v) containing liquid stationary phase (5% w/v) and Chromosorb R (5% w/v). This liquid plug was forced through the column at 4 cm/s. As soon as the plug left the capillary tubing, the nitrogen pressure was increased to 100 p.s.i. (gas flows 15 ml/min) and the column was dried for 4 h. As follows from SEM date [80], the sizes of the Chromosorb R solid support are changed from 1–2 μm to 6–8 μm. The best results were obtained with the liquid phase polypropylene sebacate (PPSEB). The column characteristics are given in Table 6-5 [80].

As follows from the data in Table 6-5, the column with 5% Chromosorb R and 5% PPSEB gave maximum efficiency (3400 theoretical plates/m). Other columns were prepared using 5% of Chromosorb R and 5% of liquid phase (Dexsil 300 GC, SE-52, SE-54, OV-101, SP-1000, SP-2250) and these columns gave 2,500–3,000 theoretical plates/m.

In our opinion, a single-step coating method was an important stage in developing methods for the preparation of SCOT columns. A particular feature of this method is the use of viscous suspensions containing liquid phases for coating, thus improving the stability of the coating phase.

Table 6-5

Characteristics values of SCOT columns prepared by the one-step coating procedure [80].

Chromosorb R, % (w/v)	PPSEB, % (w/v)	N/m (C_{15})	SN, (C_{15}–C_{16})	Coating efficiency, %
10	10	440	6	8.8
10	5	1700	15	38
5	5	3400	31	70
2.5	5	2200	17	40

6.2 Formation of Adsorbent Layer by Synthesis from Materials of the Inner Capillary Walls

Starting with the early attempts at adsorption capillary column production, adsorbents were obtained directly in the column by chemical reaction. The potential advantages of such a method are as follows: the adsorption layer can be prepared without using suspensions and with homogeneous reagents readily filling the entire column and being removable from it. Moreover, chemical reactions can be repeated in order to increase layer thickness.

Initially, researchers dealing with capillary columns attempted to obtain sorbents by chemical conversion of the column material. This method has been widely applied to glass columns by the use of various etching and leaching techniques to obtain, for example, active silica gel layers.

The first results of this kind were reported by Kiselev and co-workers [4, 83] and Mohnke and Saffert [5, 84, 85]. Kiselev managed to separate C_1–C_4 hydrocarbons on 10-m column (0.5-mm i.d.) after a short treatment of the capillary with 0.1 M HCl and subsequent flushing with distilled water.

Etching and leaching of glass as method of production of ALOT columns

Mohnke and Saffert filled a capillary 80 m long (0.27 mm i.d.) with 17% ammonia solution, sealed both ends of the column, and allowed it to stand for 70 h. Then the liquid was removed from the column, which was dried at 190 °C in a carrier gas stream. A microscope-discernible layer ca. 20 μm thick was formed on the inside capillary surface. The thus-obtained column was used for

separating hydrogen isotopes and spin hydrogen isomers.

Alkali etching of glass was also employed by Bruner and co-workers as well as by other researchers [86–89]. They etched the column walls with 20% NaOH solution for 6 h with subsequent activation in a nitrogen stream at 200 °C. The finished column was useful in oxygen and nitrogen isotope separation.

Below one of the procedures for etching glass capillary columns, which was worked out by Bruner and co-workers [90], is described as an example.

The glass capillary column was prepared from soft glass tubing and etched by passing a 10% solution of NaOH through the capillary which was heated on a water bath at about 100 °C for 8 h. After washing with water, alcohol, and ether, the column is dried in an oven at 120 °C under nitrogen. After this treatment a thin layer of active silica is formed inside the capillary column. In order to deactivate this adsorbing medium to a constant level, a flow of wet nitrogen, saturated with water vapor from a trap maintained at 0 °C, is passed through, until a constant value of the retention volume is observed. In this way columns of high efficiency are obtained (70,000 theoretical plates for a column 47 meters long), and methane shows symmetrical peaks even at a very low temperature [90].

The separation of isotopic methanes on etched glass capillary column was described by Bruner and co-workers [90]. All of the measurements were carried out on a gas chromatographic apparatus prepared for working at low temperatures. Hydrogen flame and ion chamber detectors have been used, the former as a general detector and the latter for the detection of radioactive compounds. Both detectors are connected to the column outlet through a T-tube. To avoid the influence of the large ionization chamber volume on peak shape, nitrogen is added as scavenging gas to the column effluent.

Separation of deuterated and tritiated methanes

A mixture of 70% N_2 and 30% He was employed as carrier gas. This mixture is recommended because use of helium alone at liquid nitrogen temperature causes a very strong retention of methane. With this mixture some nitrogen is adsorbed on the silica layer of the column. At values of the relative vapor pressures p/p_0 between 0.7–0.9 a polymolecular layer of N_2 covers all the surface, and pores with a radius below 80 Å are filled. In this way the most active sites of the adsorbent, which are located in the small pores, are blocked, and as a consequence retention volumes are decreased and symmetrical peaks are obtained. Separation of all isotopic methanes obtained on the glass capillary column at liquid nitrogen temperature is shown in Fig. 6-21 [90]. In the upper part of the chromatogram there are the radioactive compounds detected by the ion chamber and in the lower part there are the stable isotopes monitored by the flame ionization detector. These chromatograms do not refer to the same injection.

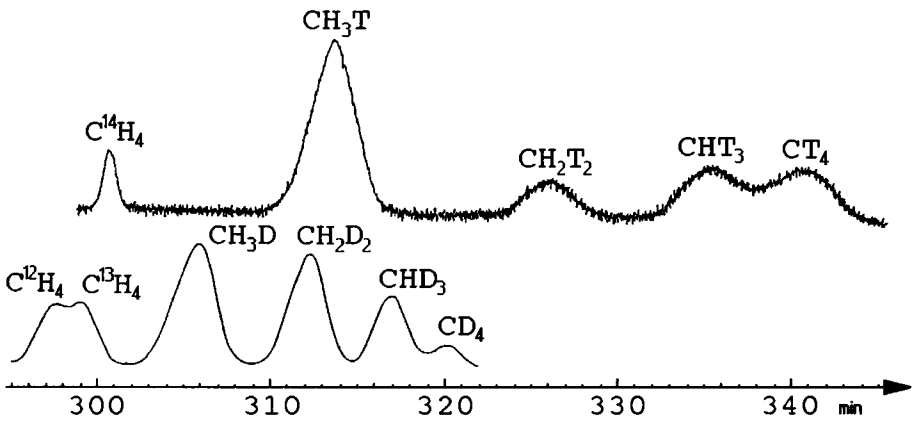

Fig. 6-21 Chromatograms of deuterated and tritiated methanes on an etched glass capillary column [90].

Separation conditions: column 47 m × 0.22 mm; temperature 77 K; carrier gas: 70% nitrogen, 30% helium, pressure 21 cm Hg, flow-rate 1 ml/min, detectors — flame ionization and ion chamber.

Some geometrical modifications of inner surface of glass capillaries are also interesting for the preparation of SCOT columns. A brief description of this treatment is given below.

Tesarik, Novotny [91] and Alexander, Rutten [92] proposed a static treatment of glass surfaces with gaseous hydrogen chloride. It reacts with sodium ions on the surface of the glass to form a layer of small crystalls on the inner surface. Note that silanol groups and water are also formed during this process. Some procedures have been proposed (see, for example, [93–95]).

Watanabe and Tomita [96, 97] described a procedure based on coating the column wall with sodium chloride. Similar procedures have been reported elsewhere [98,99].

Formation of porous silica layer in ALOT columns

"Whisker" growing is also a possible direction in preparation of APLOT columns. In an attempt to duplicate chemical treatment described by Tesarik and Novotny [91], Pretorius and co-workers [100] observed the formation of very fine needles or whiskers of silica in the glass capillaries.

Tock and co-workers [101] suggested a very interesting method for preparation of porous silica layers in open tubular columns. This method was worked out for fused silica capillaries used in liquid chromatography. However, in our opinion it is also promising for ALOT columns in gas chromatography.

The etching method [101] is not complicated. For fused silica capillaries, etching with a base is the only possible way of modifying the surface. Potassium hydroxide was selected as the base. A solution of potassium hydroxide was pumped through the fused silica column for several hours, using a reservoir as shown in Fig. 6-22 [101]. The column and reservoir were placed in an oven to control the temperature. The column outlet has to end under water to avoid blockage at that point by precipitate formation (probably silica). Then the column was rinsed at room temperature, first with water, then with 0.03 M HCl for 2 hours and finally

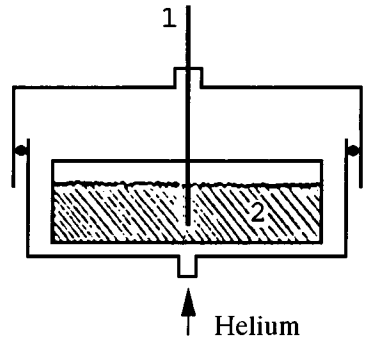

Fig. 6-22 Coating reservoir for filling capillaries [101].

1 — capillary column, 2 — glass vessel filled with coating or etching solution.

with water until the effluent became neutral. Next the column was dried at 200 °C under a stream of dry carrier gas for at least 2 hours [101].

From measurements of the internal diameter before and after etching, it was found that, in fact, about 1 μm silica was removed from the surface of the capillaries. This indicates that creation of a thick porous layer on fused silica capillaries by etching is not possible [101]. However, retention on an etched capillary compared to an untreated one is about twice as high (in LC). Etching of fused silica capillaries with 1M potassium hydroxide creates an activated surface, but the capacity of the silica layer (in LC) is too small. However, we think that this method may be useful for gas chromatography capillary columns.

Patents [102, 103] describe the preparation of open tubular columns with an inside thickness-fixed porous layer by etching. First, the authors prepared a capillary column from a two-layer workpiece composed of two concentric tubes, one of them (external) being made of sodium borosilicate glass. To obtain an adsorption layer of defined thickness, the inner layer of the two-layer capillary was entirely leached. The method relies on porous glasses as the adsorbents. Porous glasses have been successfully used in gas capillary (see, for example, [104]).

Similar methods were proposed for the preparation of aluminum oxide (by treatment of aluminum capillaries in an oxygen stream) [51] and copper oxide (by treatment of copper capillaries with 40% HNO_3 and subsequent oxidation with dry O_2) [105] layers.

6.3 Preparation of ALOT Columns by Sorbent Synthesis inside the Capillary Column

Although the known methods of chemical treatment of capillary walls are readily realizable, they have a serious disadvantage, namely, they are not universal and are restricted as a rule to glass and metal columns. Moreover, the composition and properties of the adsorption layer formed strongly depend on the composition of the column material, which may vary widely.

This disadvantage is non-existent with the sorbent synthesized by chemical reaction, which leaves the walls intact. This can be exemplified by the synthesis of crystalline barium carbonate on the capillary walls, proposed by Grob [106–108]. Although barium carbonate is not used as a pure adsorbent, it permits significant extension of the surface. The method can be also used for fused-silica capillary columns. In general the procedure consists in dynamic coating of the glass surface with barium hydroxide solution using carbon dioxide gas (there is a small volume of nitrogen between the plug of hydroxide solution and carbon dioxide gas) to push the plug of barium hydroxide solution through the column. During this procedure a barium carbonate layer is generated on the inner walls of the capillary.

Formation of barium carbonate layer in SCOT columns

This procedure was used by Berezkin and coworkers for flexible fused silica columns [109]. The results of comparison of two squalane-coated fused silica capillary columns, one of which had previously been wall-coated with barium carbonate crystals, are given in Table 6-6 [109]. The capillary column with rough inner walls has better chromatographic characteristics. This result was confirmed by comparison of two chromatograms obtained on these columns (see Fig. 6-23 [106]). Only 7 chromatographic peaks were separated on the column with smooth walls while all 12 peaks were separated on the column with walls covered by barium car-

Table 6-6

Chromatographic characteristics of two fused silica capillary columns with squalane [109].

Type of inner surface	Capacity factor, k' (n-C_{10})	Efficiency, theoretical plates/m
Smooth	2.6	1200
Rough (with barium carbonate layer)	4.0	2650

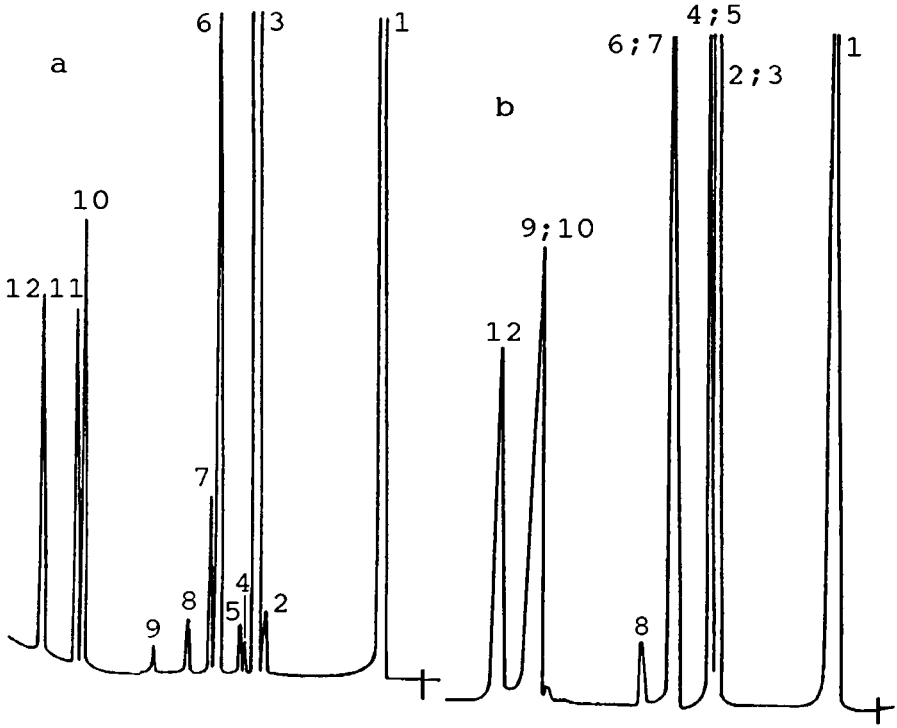

Fig. 6-23 Chromatograms of phenol alkylation products on fused silica capillary columns with smooth (a) and rough (b) inner walls [106].

Columns 25 m × 0.22 mm, stationary liquid phase OV-17, carrier gas He, temperature 70 °C → 340 °C (12 °/min).

Compounds: 1 — toluene, 3 — 1-methyl-3-phenyl-1-indene, 4 — 1-methyl-3-phenyl-2-indene, 6 — 1,3-diphenyl-1-butene, 2,5,8,9 — not identified, 10,11,12 — mono(1,3-diphenylbutyl)phenols.

bonate crystals. Therefore, a column with rough inner walls can have improved chromatographic characteristics.

Recently, a method was proposed for preparing a capillary column with a silica layer based on the hydrothermal treatment of silica sol inside the column [110]. According to this method, the capillary is filled with silica sol to 80% of its volume, sealed, and heated to 180–210°C for several hours. Under such conditions small silica particles dissolve and then polymerize on the surface to form layer particles. Thus an inside surface comprising a silica layer is formed. The thickness of the adsorption layer depends on the sol concentration and process duration. The optimum sol concentration is 0.1–0.5%, and the optimum treatment duration is 5–11 h. Columns prepared by this method were used for high-speed analysis of light hydrocarbons.

Formation of porous silica layer in ALOT columns

Tock and co-workers [101] suggested preparation of ALOT column by precipitation of a thick porous silica layer on the inner wall of fused silica capillaries. Precipitation of silica was from polyethoxysiloxane solution dynamically coated on the inner wall of the capillary. This investigation was carried out for capillary HPLC; however, the results are undoubtedly valuable for gas capillary ALOT columns too.

Deposition of a stable porous silica layer on the inner wall of fused silica capillaries was performed by precipitation of silica from a solution of polyethoxysiloxane (PES). PES was prepared by polycondensation of tetraethoxylane (TES) according to Unger's method [11, 112]. 5.7 ml of water (0.32 mole) containing 60 μmole of HCl was added to 50 ml of TES (0.22 mole) dissolved in 30 ml of dry ethanol. This solution was vigorously stirred for 1 h and then refluxed for 6 h. Then ethanol and HCl were evaporated in vacuum. Dried capillaries, treated with 1 M KOH at room temperature for 2 h and rinsed with HCl, were dynamically coated with PES by filling the capillary with a 25 cm plug of pure PES. The plug was pushed through the column by means of helium at a linear

velocity of 30 cm/h. The PES layer was converted into silica by treatment with gaseous ammonia in a helium stream for 1 day at room temperature. Then the capillary was flushed with 0.01 M ammonia for half an hour, rinsed with water for 3 h and finally dried for at least two hours at 200–250 °C while purging with helium.

The column performance in HPLC was good [101]. This type of column is also very promising for gas chromatography.

Preparation of Pora PLOT columns by copolymerization reaction inside ALOT columns

Using new techniques [113] it became possible to develop fused silica capillary columns with a porous polymer on the capillary inner walls. The porous polymer used in Pora PLOT Q columns is prepared by copolymerization reaction of styrene and divinylbenzene.

The preparation process is a two-step procedure. In the first step the porous pre-polymer is formed. This is important because the pore size, pore distribution and homogeneity of the inside pore surface are established during its course. The second step is *in situ* polymerization and stabilization of the porous pre-polymer. Special additives have to be used to stabilize the porous polymer on the inner walls of fused silica columns [113].

Table 6-7

Comparison of retention indices on columns with Porapak Q and Pora PLOT Q at 200 °C [113].

Compound	Retention indices		$\Delta I = I_2 - I_1$
	Porapak Q packed column 1 m × 2 mm, carrier gas — hydrogen, 25 ml/m	Pora PLOT Q capillary column 25 m × 0.5 3 mm, carrier gas — hydrogen, 14 ml/min	
	I_1	I_2	
Benzene	630	650	20
Acetonitrile	450	460	10
tert-Butanol	538	530	–8
Methyl ethyl ketone	580	581	1

The selectivity of Pora PLOT Q porous polymer is therefore slightly different from that of Porapak Q (see Table 6-7 [113]). The highest index deviation is obtained for benzene (ΔI = 20). Indices of the the other compounds show less deviation. Therefore, overall selectivity of the Pora PLOT Q porous polymer is comparable with that of Porapak Q.

The inertness of the Pora PLOT Q surface reflects the influence of water on retention. Water molecules can adsorb on the adsorbent surface, thus leading to a decrease of retention times. This influence of water on retention was tested by performing a five-fold splitless water injection (5 μl) at 60°C into 25 m × 0.32 mm fused silica column coated with Pora PLOT Q [113]. Comparing retention times before water injections and after them, we find that there is an ≈1% increase in retention for all compounds, the difference in relative retention being smaller.

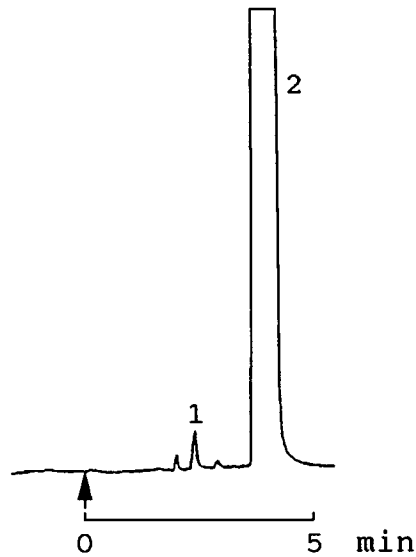

Fig. 6-24 Chromatogram of water impurities in ethanol [113].

Column: 10 m × 0.32 mm Pora PLOT Q; temperature 175 °C; carrier gas: hydrogen; injection: 1.0 μl, split; detector micro TCD.

Peaks: 1 — water, 2 — ethanol.

The surface of Pora PLOT Q is apolar. For example, Fig. 6-24 shows water analysis in ethanol. The water peak corresponds to 500 ppm, detected with a microthermal conductivity detector.

The sorbent surface area in a Pora PLOT column is rather high. It is enough for gas separation including permanent gases (see Fig. 6-25 [113]). Pora PLOT columns are thermally stable at 250 °C [114].

6.4 Formation of Adsorption Layer during Glass Capillary Drawing

Glass capillary production can be accomplished by incorporating the finished sorbent into a capillary without any need for its conversion into a suspension. The capillary is drawn from a comparatively wide tube; therefore it can readily accommodate the sorbent prior to drawing.

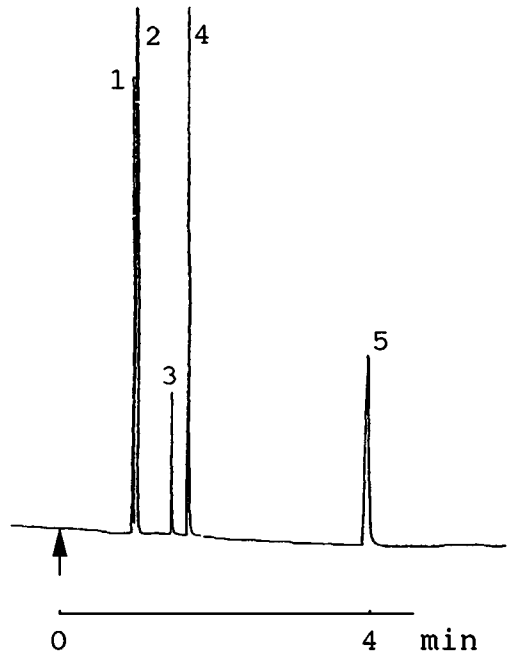

Fig. 6-25 Chromatogram of gases on Pora PLOT Q column [113].

Column: 25 m × 0.32 mm Pora PLOT Q column; temperature 30 °C; carrier gas: hydrogen; injection: 25 µl, split; detector: micro TCD.

Peaks: 1 — He, 2 — CO, 3 — CO_2, 4 — N_2O, 5 — H_2S.

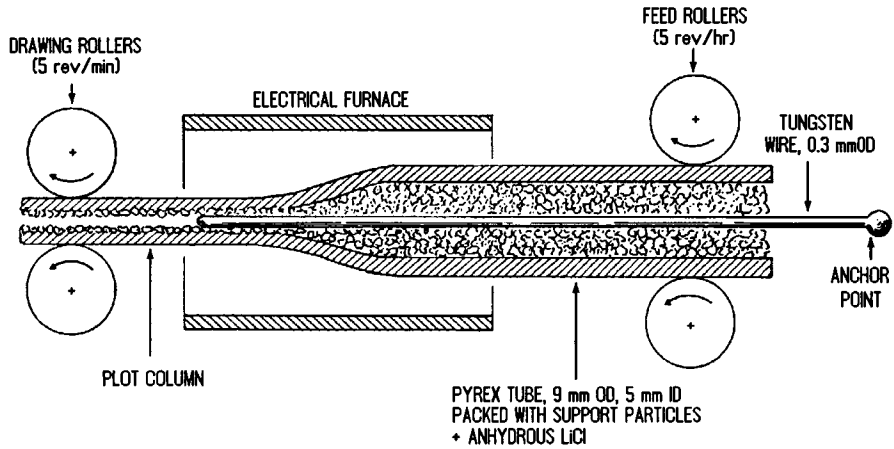

Fig. 6-26 A device for PLOT column preparation [7].

Halasz and Heine [115] used this method for the preparation of aluminum oxide columns. To retain an open passage inside the column, a steel wire with a diameter of 1 mm was inserted into the initial tube. In the course of drawing the softened glass carried the aluminum oxide particles away. The obtained 2-m column represented an intermediate variant of packed and open capillary columns with a fairly high efficiency (3500 theoretical plates per meter) with respect to ethylene.

Apparatus for PLOT column preparation

Later, the diameter of the wire was decreased to that of the inside channel. The wire passed through the softening (hot) zone and terminated in the capillary (Fig. 6-26). Such a system allows rigid specification of the inside column opening size and hence the layer thickness. Thus Grant [7] obtained a column with a 100 μm layer, 0.33-mm inner capillary diameter, and 0.1-mm tungsten wire. According to Grant [7], lithium chloride should be used as the binding layer. The height equivalent to a theoretical plate was 0.5 mm.

Since the sorbent is exposed to high temperatures (700–800°C) during the manufacturing process, the adsorbents should consist of heat-resistant packings that withstand temperatures at least equivalent

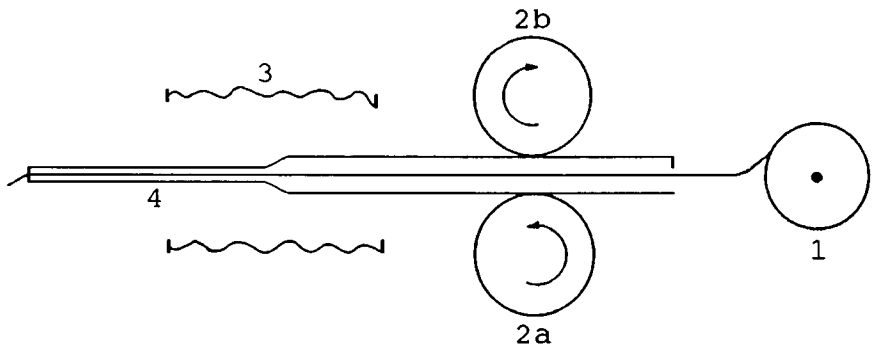

Fig. 6-27 Apparatus for sandwiched columns production [8].

1 — spool of carbon yarn, 2 — feed rollers, 3 — electric furnace, 4 — carbon yarn sandwiched into capillary tubing.

to the glass softening point. Therefore graphite was chosen as the only alternative to aluminum oxide. Goretti and co-workers [116] have thus made ≈10 m long columns with a 50–100 μm layer. The columns efficiency was ca. 1500 theoretical plates per meter with a fairly high permeability.

Apparatus for sandwich column production

The method of preparation of sandwiched adsorption ca-pillary columns for gas chromatography is similar to that used for adsorbent layer formation during glass capillary drawing. Liberti, Nota, Goretti [8] use the term "sandwiched capillary columns" to describe columns made of any material, in which the separating medium is a thread inserted inside the capillary. Of course, any material which is available as thread can be used for preparation of sandwiched capillary columns.

A modified version of the glass-drawing apparatus due to Desty et al. [31] was used. A piece of carbon yarn was inserted into the glass tubing (2.2 mm i.d. and 2.6 mm o.d.). The stretched glass tubing leaving the yarn hanging out was set in the apparatus and drawn out as usual (see Fig. 6-27 [8]). While the spool of column yarn

Table 6-8

Characteristics of carbon and graphite yarns used for preparation of sandwiched capillary columns [8].

Brand (Union Carbide)	Type of adsorbent	Surface area		Filament size, μm
		m^2/g	m^2/m	
1 WYB	graphitized carbon black (2800°C)	0.45	0.027	10
2 WYD	graphitized carbon black (2800°C)	0.75	0.028	7.5
3 VYB	carbon fibers (1300 °C)	154	12.8	7.5

unwound continuously the thread was sandwiched inside the glass capillary tubing. Columns of any length, in the form of spirals (12 cm diameter) can be obtained quite easily, their preparation is simple, and they give highly reproducible results, provided the surface of the yarn is not scratched when the glass tubing is drawn out. Before use, carbon and graphite yarns were washed several times with isopropyl alcohol to remove lubricant and dried in an oven at 300 °C. Characteristics of the used yarns are given in Table 6-8 [8].

6.5 Conclusion

Usually tailed peaks were obtained. Formic acid, water and carbon disulfide act as effective peak-tailing reducers [8]. In the authors' opinion [8], sandwiched capillary columns may be regarded as a set of equal micro-capillaries and specific gas permeability and other operational chromatographic parameters of sandwiched columns compare favorably with those of packed capillary columns. Fig. 6-28 [8] shows chromatograms of geometric isomers on WYB sandwiched columns. The results are promising.

Methods for the preparation of open capillary columns for gas-solid chromatography should meet very strict requirements: 1) a fairly uniform distribution of the adsorbent layer over the capillary surface; 2) rigid attachment of the adsorbent par-

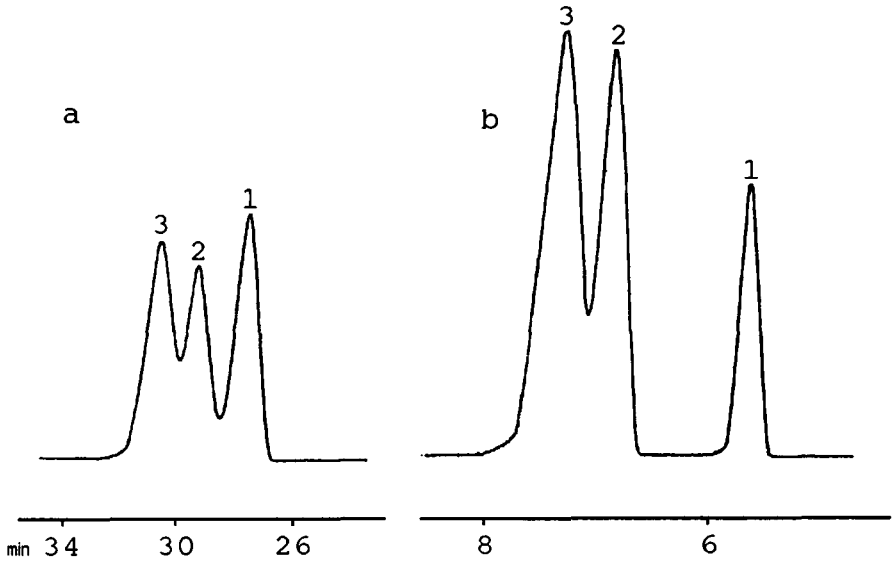

Fig. 6-28 Chromatograms of geometric isomers on sandwiched column [8].

Column length — 10 m.

a) Temperature — 124°C, $P(N_2)$ — 0.8 atm, peaks: 1 — *m*-xylene, 2 — *p*-xylene, 3 — *o*-xylene.

b) Temperature — 164°C, $P(N_2)$ — 0.8 atm, peaks: 1 — *o*-cresol, 2 — *m*-cresol, 3 — *p*-cresol.

ticles to the capillary surface; 3) sufficient reproducibility; 4) application of a variety of adsorbents for making the adsorption layer; 5) high speed of the preparation method.

The method of applying the adsorption layer during glass capillary drawing is one of the most promising. Nevertheless, it also has some shortcomings, namely: 1) the field of its application is restricted by thermostable sorbents (for example, polymeric sorbents cannot be used); 2) it is necessary to select a binding substance for producing the compact immobilized sorption layer individually for each kind of adsorbent and column material; 3) if adsorbents are not stable at high temperature in air, it is necessary to draw the column media in an inert-gas atmosphere, thus leading to complication of the apparatus.

The method of adsorption capillary column preparation by means of *in situ* synthesis of sorbents is only applicable to a limited number of adsorbents, but it does allow two problems to be solved simultaneously: 1) sorbent formation; 2) binding of a sorbent to the inside surface of capillary.

In our opinion, the suspension method is the most universal for gas adsorption capillary column production. The main unsolved problem is the binding of adsorbent to the capillary inside walls; methods of binding and binding agents must be selected individually.

Of course, the choice of optimal method depends on the kind of sorbent and column material.

Generally, the problem of preparing open tubular columns with adsorption layers on their walls has not yet been completely solved, and this fact is holding back wide application of adsorption capillary chromatography.

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Chapter 7

Applications of ALOT Columns

In this chapter the general applications of adsorption layer open tubular (ALOT) columns will be discussed. As the basic separation on adsorbents is realized by a gas-adsorption mechanism, the ALOT columns are generally used for relatively volatile compounds. Depending on the type of the adsorbent and its physical characteristics each adsorbent has its own specific retention behavior.

Advantages of adsorption capillary chromatography

The application of adsorbents in combination with high resolution capillary gas chromatography has several advantages over gas-liquid chromatography (see also Chapter 1).

1. High retention.

The high retentivity is very specific for adsorbents. Due to the adsorption mechanism the practical oven temperatures can be much higher compared with liquid stationary phases. The oven temperature can be adjusted above ambient which is a practical advantage for many applications. Higher temperatures are also more easily and more accurately controlled. Due to the high retention of for instance Molsieve 5A coated fused silica columns, the separation of permanent gases up to methane can be realized at temperatures of 40 – 70 °C or even higher. On using polydimethylsiloxane stationary phases, the operation temperature for this type of separation will be at least 100 °C lower and even then the separation is marginal.

2. High plate number.

The kinetics involved in adsorption chromatography are based on very fast adsorption-desorption kinetics which results in a small contribution in band broadening (see also Chapters 2 and 3). Typical theoretical plate numbers for ALOT columns are 1500 – 1800 plates/m

for 0.53 mm i.d. fused silica and 2500 – 3000 plates/m for 0.32 mm i.d. fused silica. The theoretical plate number for ALOT columns will therefore be very high compared with liquid or chemically bonded stationary phases.

Although it is possible to chemically bond polymethylsiloxane polymers on fused silica capillary columns with film thicknesses up to 5 μm (high capacity columns), these capillary columns provide a relatively low resolution.

3. Unique selectivity.

As the adsorption mechanism in gas-solid chromatography is basically different from the partition mechanism in gas-liquid chromatography, the selectivity of adsorption materials is therefore unique and very specific. For instance on Al_2O_3/KCl adsorbents the light hydrocarbons in the range of $C_1 - C_5$ are all baseline separated due to the high selectivity for unsaturated hydrocarbons. The molecular sieve adsorbent separates all permanent gases including argon and oxygen, while on porous polymer coated ALOT columns a range of compounds of different polarity can be separated.

4. Durability.

Practically it is quite difficult to destroy an ALOT-type of capillary column. The adsorbents are generally not sensitive to oxygen or moisture. Although the retention behavior of several adsorbents is influenced by moisture, columns can be regenerated by proper conditioning (see also Section 7.4.4 "Samples containing moisture").

7.1 The Carrier Gas

For the application of ALOT columns any carrier gas can be used. Mainly hydrogen, helium and nitrogen are employed. It is recommended that proper carrier gas purification is used since the adsorbent in the ALOT column will act as a "trap" for all volatile impurities introduced in the carrier gas lines. A typical practical experiment to verify whether the GC-system is clean is the following: Condition the ALOT column for 30 minutes on its maximal isothermal operation temperature, followed by cooling down to ambient.

The ALOT column is kept at ambient temperature for a fixed time interval (for instance 30 minutes), during which the contaminants or impurities in the gas lines will accumulate on the ALOT column. After the time interval the column is temperature programmed up again and a blank run is started. The presence of any peaks on the baseline indicates contamination of the system. To prevent these problems the carrier gas should be filtered with an active charcoal filter which will retain all organic impurities.

7.1.1 Use of Hydrogen

The application of hydrogen as the carrier gas is potentially most interesting since its optimal carrier gas velocity is very high and analysis times are the shortest. However, the use of hydrogen in combination with highly active adsorption surfaces could lead to hydrogenation reactions for the unsaturated hydrocarbons. Especially for aluminum oxide coated surfaces this would significantly limit the application field of these columns.

Experiments were performed with Al_2O_3 coated fused silica columns which had been deactivated with potassium chloride. At a temperature of 200 °C a certain amount of propadiene and methylacetylene together with propane was separated by using different linear gas velocities.

The different absolute retention times will be actual "reaction times" of a possible hydrogenation reaction in the column. The peak area of propyne was normalized to a saturated hydrocarbon, propane, and listed in Table 7-1. From the results it is easy to see that for unsaturated compounds no hydrogenation occurs at temperatures of 200 °C. On using hydrogen as the carrier gas hydrocarbons can be separated up to n-decane.

7.1.2 Optimum Carrier Gas Velocity

In general the ALOT column will have relatively high optimum carrier gas velocities due to the fast kinetics of the gas-solid adsorption mechanism and the relatively small compounds to be analyzed. This was also found on Al_2O_3 coated fused silica columns where the optimum carrier gas velocity was found to be a factor 2.5 higher than with normal gas-liquid capillary chromatography.

Table 7-1
Peak area of propyne relative to propane.

Column: 50 m × 0.32 mm, Al_2O_3/KCl; Carrier gas: H_2; temperature 200 °C.

Inlet pressure, kPa	Reaction time, min	propyne / propane	Relative standard deviation, %	*n*
200	1.301	0.22	2.2	4
100	2.625	0.21	2.7	4
50	5.393	0.21	3.9	4
25	9.717	0.21	10.1	5

An example of a Van Deemter plot on Al_2O_3/KCl fused silica is shown in Fig. 7-1. The test component was 1,3-butadiene and the oven temperature was 130 °C. Optimum carrier gas velocity for nitrogen is 24 cm/s, for helium – 45 cm/s and for hydrogen – 75 cm/s. The high optimal carrier gas velocity reduces the analysis time of light hydrocarbons considerably and is therefore recommended.

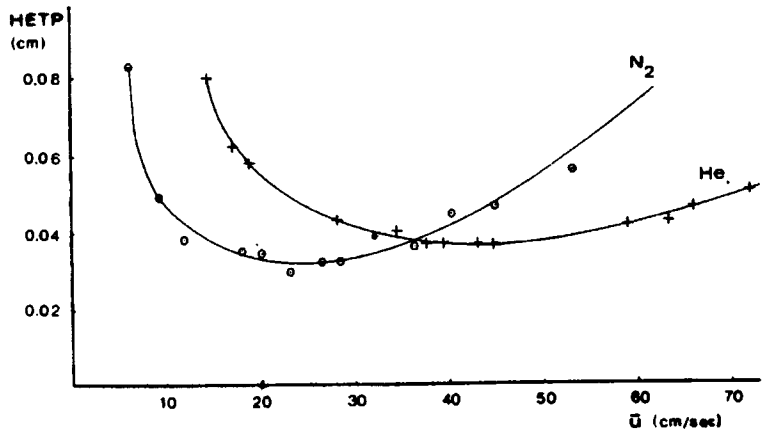

Fig. 7-1 Van Deemter plots for Al_2O_3/KCl fused silica column.

Al_2O_3/KCl, fused silica, column: 50 m × 0.32 mm Al_2O_3; Test component: 1,3-Butadiene; Temperature: 130 °C.

7.2 Release of Particles from the Column Wall upon Application

The adsorption type of capillary columns are generally manufactured by coating the inside of the capillary with a homogeneous layer of particles in the range of 0.1 – 1 micrometer diameter. These particles will generally stick to the column surface quite well as long as the layer is homogeneous and the carrier gas stream is stable. In practice it is often observed that particles elute from a ALOT column, due to pressure changes in the column upon injection of the sample.

Especially with valve switching techniques quite high pressure shocks are initiated which will lead to a distortion of the layer of particles especially in that part of the column which is connected with the valve switching device. The actual inlet pressure which is used to operate the column is also present between the particles. If there is a quick change of pressure above the particle layer, the pressure between the particles will cause a mini-explosion of the adsorbent layer which will generate individual particles which are transported with the carrier gas and may cause clogging or spikes in the detector.

7.2.1 Use of Pre-columns

To prevent this effect the pressure shock should be minimized. Therefore ALOT columns which are used with valve switching devices are coupled with a few meters of deactivated fused silica tubing. In most cases a 3 – 5 meter length will do. This capillary pre-column will act as a buffer for the pressure shocks which will result in reproducible analysis. Column coupling can be easily performed with the so-called "Quick-Seal" or "Press-Fit" type of column connectors. In the precolumn there will be some extra band broadening, but this can be neglected in practice.

7.2.2 Use of Particle Traps

Since a typical ALOT column contains over 100,000,000,000 particles with a diameter of 0.1 – 1 μm, there will always be some particles which will be released from the adsorption surface and find their way to the detector. The result will be a spike on the chromatogram which may cause problems in quantitative analysis. The amount of particles released depends on the type of adsorbent. Al_2O_3 and Molsieve adsorption surfaces are generally known to be very stable in normal applications. More critical are the

porous polymer coated ALOT columns. Due to the nature of the porous polymer and its physical behavior, the particles will elute more easy. For these types of ALOT columns it is recommended to use a "particle trap" which should be connected at the detector side of the column. The particle trap is a 1 – 2 meter fused silica capillary which is coated with a low viscosity stationary phase with a film thickness of 0.1 – 0.5 μm. The eluting particles will simply stick to the film of phase which has a gluing effect, preventing them from reaching the detector. The absolute retention of the particle trap capillary is a factor 100 – 250 lower then the retention of the adsorbent and can therefore be neglected. Methylsilicone phases like OV-101 or SE-30 will be ideal for particle traps.

7.3 Separation of Gases

The adsorbents are generally very suitable for separating gases due to their high retentivity and special selectivity.

7.3.1 Inert Gases

The inert gases can be very well separated on the molecular sieve type of adsorbent. Due to the pores in this material there is an enormous specific surface present, creating the highest possible retention. Typical molecular sieves have pore sizes of 3 – 5 Å diameter. Most widely used are molecular sieves of type 5A.

For separating permanent gases with capillary columns it is necessary to coat these columns with the thickest possible layer of particles. With suspension technology and special coating procedures it was possible to coat fused silica capillaries with 50 μm layers of molecular sieve particles. A typical separation obtained on a 0.53 mm (wide-bore) type of fused silica capillary is shown in Fig. 7-2. The oven temperature was 20 °C and a split injection was used. The analysis time was about two minutes, which already gives a very good separation between several permanent gases. The typically very difficult separation between argon and oxygen is almost baseline on a 10 meter wide bore capillary. These columns show typical plate numbers between 1000 and 1300 theoretical plates per meter (On CH_4, $k' = 4 - 5$). This particular analysis was performed with a flow rate of about 6 ml/min, allowing complete separation within 2 minutes.

On coating 0.32 mm fused silica capillary columns with molecular sieve adsorbents, the separation efficiency will be considerably higher than with 0.53 mm columns, as can be seen in Fig. 7-3. A 25 meter fused silica was coated with a 30 μm layer of molecular sieve, resulting not only in a baseline separation between argon/oxygen but also between helium/ Neon. A 0.32 mm i.d. capillary will provide at least 1500 – 2000 theoretical plates per meter (on CH_4, $k' = 4 - 5$).

The separation here was optimized by working under the optimal linear carrier gas velocity (40 cm/s) for hydrogen. It took about 6 minutes for methane ($k' = 4.5$) to elute at 30 °C. The 0.32 mm fused silica columns are operated at flow rates of maximally 2 ml/min which requires a thermal conductivity detector to be used with a cell volume of 10 μl or smaller. Such detectors are nowadays commercially available; however, the minimal flow rate for most detectors is about 4 – 5 ml/min which requires an extra carrier gas supply at the column outlet (make-up gas) of minimal

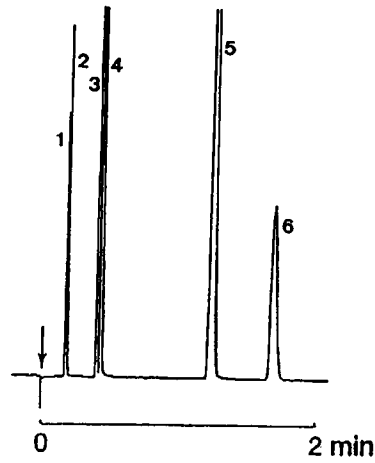

Fig. 7-2 Fast separation of permanent gases on 0.53 mm capillary column.

Column: 10 m × 0.53 mm, fused silica, Molsieve 5A, $D_f = 50$ μm; Oven: 20 °C; Carrier: H_2, 25 kPa , 6 ml/min; Injection: Splitter 1:60; Detection: μ-TCD; Peaks: 1 — helium; 2 — neon; 3 — argon; 4 — oxygen; 5 — nitrogen; 6 — methane.

2 ml/min which dilutes the column eluent. As the sensitivity of the detector is decreased in this way, a practical solution was found by the introduction of 0.53 mm internal diameter fused silica columns. These columns can be easily operated with flow rates up to 20 ml/min which also makes thermal conductivity detectors with much larger cell volumes applicable.

A typical application of a 0.53 mm fused silica ALOT Molsieve column is shown in Fig. 7-4. Laboratory air was injected on a 10 meter 0.53 mm Molsieve column which was operated at a flow rate of 10 ml hydrogen per minute. A 50 µl amount of air was injected directly onto the column with a direct injector using a tapered

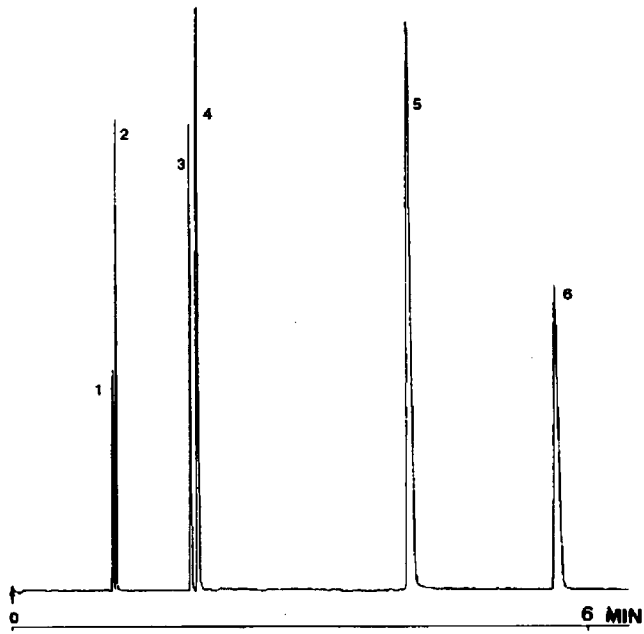

Fig. 7-3 Separation of permanent gases under optimal conditions on 0.32 mm capillary column.

Column: 50 m × 0.32 mm, fused silica, Molsieve 5A, D_f = 30 µm; Oven: 30 °C; Carrier: H_2, 80 kPa; Injection: Split, 1 : 100; Detection: µ-TCD; Peaks: 1 — helium; 2 — neon; 3 — argon; 4 — oxygen; 5 — nitrogen; 6 — methane.

injection port liner. Even with direct injection and the high flow rates used the separation between argon and oxygen is still acceptable. The nitrogen peak elutes within 50 s.

The wide bore (0.53 mm) Molsieve columns are ideal for applying the direct injection technique, making trace analysis of permanent gases in permanent gases possible. Fig. 7-5 shows the analysis of 100 ppm oxygen in pure nitrogen by using a Molsieve coated 0.53 mm fused silica capillary column operating at a flow rate of 35 ml/min. For this analysis a normal conductivity detector with a cell volume of 300 µl was used. Due to the high flow rate the detector cell volume is not critical. The analysis is completed within 30 s. Analysis time can be reduced even more by using shorter capillaries. The resolution power of the Molsieve coated capillary columns is very high so that only a 50 cm column was needed to obtain a

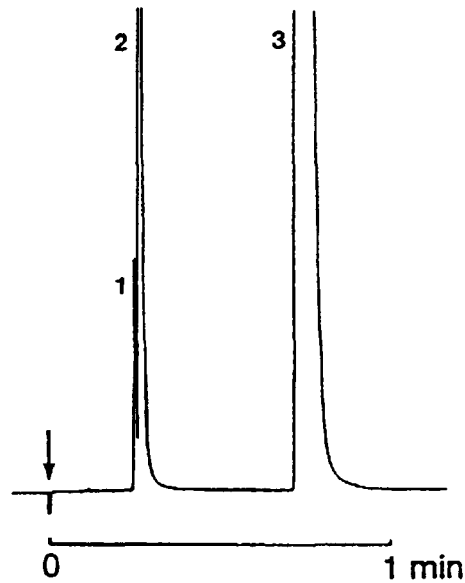

Fig. 7-4 Separation of laboratory air on 0.53 mm capillary with direct injection and high flow rate.

Column: 10 m × 0.53 mm, fused silica, Molsieve 5A, D_f = 50 µm; Oven: 25 °C; Carrier: H_2, 45 kPa; Injection: Direct, 50 µl; Detection: µ-TCD; Peaks: 1 — argon; 2 — oxygen; 3 — nitrogen.

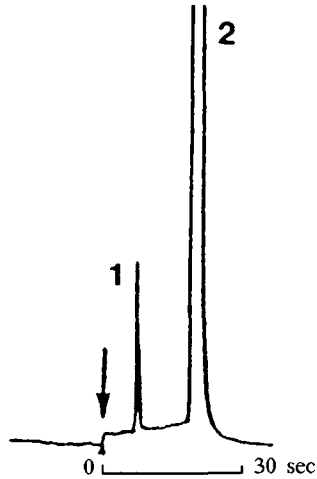

Fig. 7-5 100 ppm oxygen in nitrogen.

Column: 10 m x 0.53 mm, fused silica, Molsieve 5A, D_f = 50 μm; Oven: 25 °C; Carrier: H_2, 75 kPa; Injection: Direct, 30 μl; Detection: μ-TCD; Peaks: 1 — oxygen; 2 — nitrogen.

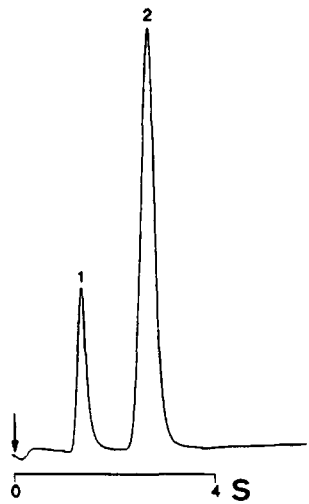

Fig. 7-6 Fast separation of oxygen and nitrogen.

Column: 0.5 m x 0.32 mm, fused silica, Molsieve 5A, D_f = 30 μm; Oven: 25 °C; Carrier: H_2, 10 kPa; Injection: Split, 1 : 50; Detection: μ-TCD; Peaks: 1 — oxygen; 2 — nitrogen.

resolution factor of 2.0 for nitrogen and oxygen. This type of separation is shown in Fig. 7-6. The analysis time has been reduced to about 4 s! The practical execution of such "high speed" applications is very difficult since the injection errors are very high.

With new technology of Micro Injectors (MI) and Thermal Conductivity Detectors (TCD) with cell volumes of 1 – 5 nanoliters (!), the use of very fast ALOT columns came within the reach of practical application.

Another unique application is shown in Fig. 7-7. Here a 100 ppb amount of methane could be determined by using a special type of detector, the helium Discharge Ionization Detector (DID). This type of detector, which is known to be very sensitive, made it possible to reach detection limits of ppb levels of permanent gases.

7.3.2 Carbon Monoxide

Carbon monoxide is a gas which is very difficult to analyze since it is a strong dipole and is very volatile. On porous polymer type adsorbents, carbon monoxide elutes very quickly and is difficult to quantify in the presence of inert gases. The molecular sieve type of adsorbent generates sufficient retention to separate carbon monoxide, as can be seen in Fig. 7-8.

The separation here was performed isothermally on a packed column at 70 °C. At this temperature it takes about 20 minutes for carbon monoxide to elute. On using a 0.53 mm capillary column the analysis temperature can be reduced to about 25 °C which results in an analysis time of only 3 minutes at the same column flow rate. The sample run on the 0.53 mm fused silica column was a 99.9 % carbon monoxide sample in which the inert gases were present as impurities (Fig. 7-9). Due to the fast analysis the peak broadening is reduced, which results in a high sensitivity. Under these conditions it is possible to analyze ppm levels of inert gases within a main stream of an inert gas. Practically the most critical step is the injection which has to be as fast as possible. However the high separation power of the Molsieve 5A capillary allows quite a large initial injection band, which practically means that the injection

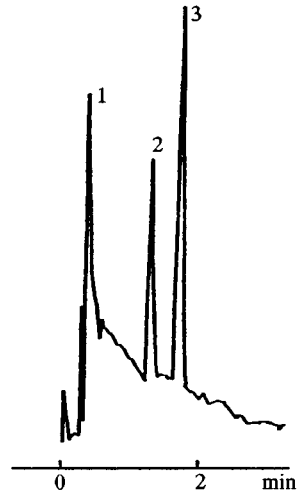

Fig. 7-7 Methane at the 100 ppb level.

Column: 25 m x 0.53 mm, fused silica, Molsieve 5A, D_f = 50 μm; Oven: 120 °C; Carrier: He, 27 ml/min; Injection: Direct valve injection, 2000 μl; Detection: DID (TRACOR); Peaks: 1 — oxygen; 2 — nitrogen; 3 — methane.

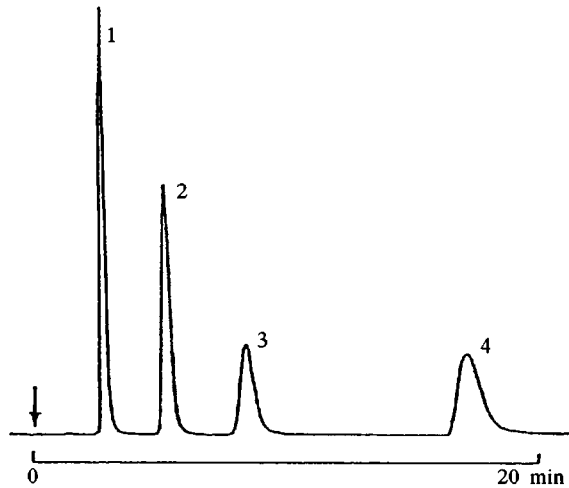

Fig. 7-8 Separation of permanent gases on packed column.

Column: 12 ft x 1/4" Molsieve 5A 60/80 Mesh; Oven: 70 °C; Carrier: He, 20 ml/min; Injection: Direct, 10 μl; Detection: TCD Sample: 5% in Helium; Peaks: 1 — oxygen; 2 — nitrogen; 3 — methane; 4 — carbon monoxide.

is not very critical. Sample volumes up to 1000 µl can be introduced by using injection valves.

7.3.3 Carbon Dioxide Carbon dioxide is a compound which is quite difficult to quantify. On liquid stationary phases CO_2 already shows some retention at temperatures of 30 °C, albeit only when very thick-film coated capillary columns are used. The separation between the air peak and CO_2 is possible only with very accurate control of the injection parameters. By using gas-solid chromatography the retention of CO_2 can easily be increased. Several materials show a very high retention towards CO_2, for instance aluminum oxide. CO_2 is adsorbed and will only elute at temperatures of 200 °C as a "shifted" baseline.

Molsieve 5A can be used; however, on this adsorbent too the CO_2 will not elute below 250 °C. The eluting peak will tail strongly and quantification is only possible above the 5%-level. By using the porous polymer type of adsorbents an acceptable retention behavior

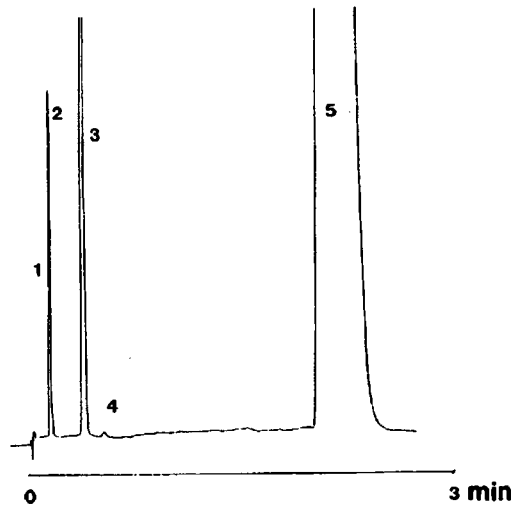

Fig. 7-9 Impurities in carbon monoxide.

Column: 10 m × 0.53 mm, fused silica, Molsieve 5A, D_f = 50 µm; Oven: 25 °C;
Carrier: H_2, 80 kPa, 20 ml/min; Injection: Direct, 25 µl;
Detection: TCD; Sample: 99.9 % Carbon monoxide;
Peaks: 1 — argon; 2 — oxygen; 3 — nitrogen; 4 — methane;
5 — carbon monoxide.

is obtained. Since these materials are based on styrene-divinylbenzene polymers, the characteristics are quite unique. Apart from having a unique selectivity, the porous polymer is not sensitive to moisture in the sample or the carrier gas, which results in reproducible retention times. A typical example of several inert gases including CO_2 separated on a porous polymer coated PoraPLOT U fused silica column is shown in Fig. 7-10. The carbon dioxide is very well separated from air, carbon monoxide and helium. With a capacity ratio of almost 1 at 25 °C, the CO_2 is very well resolved. Porous polymer type ALOT columns are widely used for analyzing polar/apolar volatile compounds, as will be discussed later. They are also often used in combination with a molecular sieve 5A type of ALOT column to make possible isothermal analysis of permanent gases including CO and CO_2.

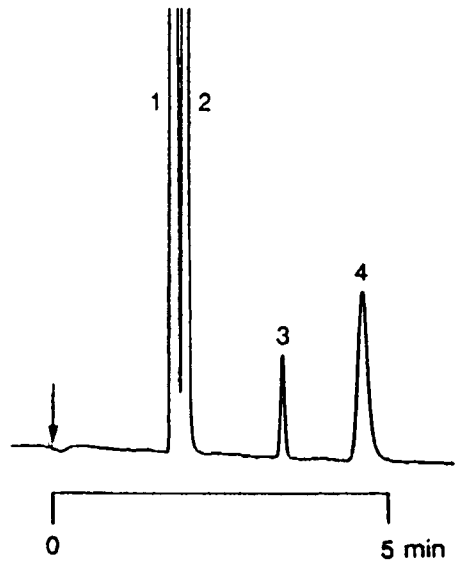

Fig. 7-10 Separation of permanent gases on porous polymer coated capillary

Column: 25 m × 0.53 mm, fused silica, PoraPLOT U, D_f = 20 μm; Oven: 25 °C; Carrier: H_2, 60 kPa; Injection: Split, 100 cc/min; Detection: μ-TCD; Sample: 1–10% of each component in inert gas; Peaks: 1 — helium; 2 — nitrogen + oxygen + carbon monoxide; 3 — carbon dioxide; 4 — ethane.

7.3.4 Carbon Monoxide, Carbon Dioxide and Air

A widely used application is the analysis of CO_2 and CO in air. Both components can be separated on a molecular sieve 5A type of ALOT column, but the CO_2 will elute at temperatures above 250 °C. Here a temperature program is absolutely necessary and CO_2 can only be quantified at levels of ca. 5 % or higher. On using a new carbon-type of adsorbent it was possible to tune the selectivity in such a way that CO and CO_2 were separated. Fig. 7-11 shows a separation of CO and CO_2 on a 25 m × 0.53 mm

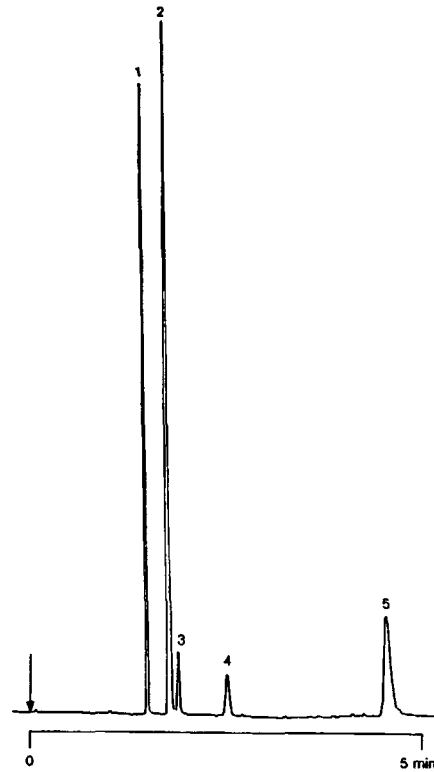

Fig. 7-11 Isothermal separation of CO and CO_2 in air.

Column: 25 m × 0.53 mm Fused silica CarboPLOT P7, D_f = 25 μm;
Oven: 100 °C; Carrier: H_2 , 20 kPa; Injection: Split, 100 ml/min;
Detection: μ-TCD; Sample conc.: 1–5% in air;
Peaks: 1 — helium; 2 — air; 3 — carbon monoxide; 4 — methane;
5 — carbon dioxide.

fused silica column coated with a 20 μm layer of CarboPLOT P7, a type of carbon with a very high specific surface. The oven was set at 100 °C isothermally allowing CO_2 to elute within 5 minutes. As can be seen from the chromatogram, CO is well separated from air while also CO_2 elutes with an acceptable peak shape within a reasonable time.

By decreasing the temperature to 40 °C it is possible to separate the air peak also into O_2 and N_2 (see Fig. 7-12). The CO_2 peak will not elute at temperatures of 40 °C. If CO and CO_2 have to be analyzed in the shortest possible time a temperature programmed analysis is necessary, as shown in Fig. 7-13. Total analysis time will be less than 4 minutes. With this type of adsorbent it is possible to separate air, CO, CH_4 and CO_2 on one column, without column switching. CO and CO_2 can be analyzed down to about the 500 ppm level in air.

7.3.5 Carbon Dioxide, C_1 – C_4 Hydrocarbons and Inert Gases

For the separation of hydrocarbons, permanent gases and CO_2 in one sample it is necessary to use a column switching system. With the ALOT columns available such a system is quite simple and can be built by most analytical chemists.

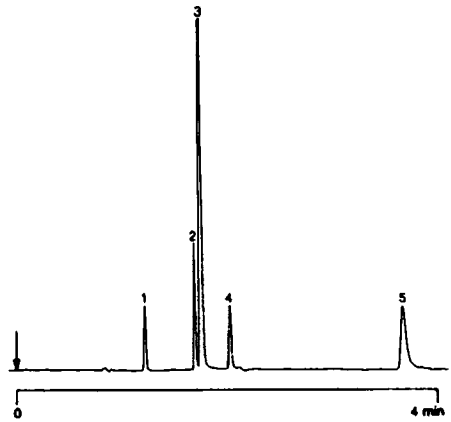

Fig. 7-12 Separation of O_2, N_2 and carbon monoxide.

Column: 25 m × 0.53 mm, fused silica, CarboPLOT P7, D_f = 25 μm; Oven: 40 °C; Carrier: H_2, 20 kPa; Injection: Split, 30 ml/min; Detection: μ-TCD; Sample conc.: 10–20%; Peaks: 1 — helium; 2 — oxygen; 3 — nitrogen; 4 — carbon monoxide; 5 — methane.

The basic column configuration is a precolumn which separates the C_{2+} hydrocarbons from the volatile fraction. In this application a 50 m x 0.32 mm fused silica coated with a polydimethylsiloxane was used. The film thickness was 5 µm. The volatiles elute as one peak from the first column and are injected directly onto a Molsieve 5A ALOT column using the six-port valve. Compounds like H_2, He, Ne, Ar, O_2, N_2, CH_4 and CO can be analyzed on the Molsieve 5A column. All hydrocarbons starting from C_2 will be separated on the first column. Since the maximum temperature of the methylsiloxane CP Sil 5 CB column

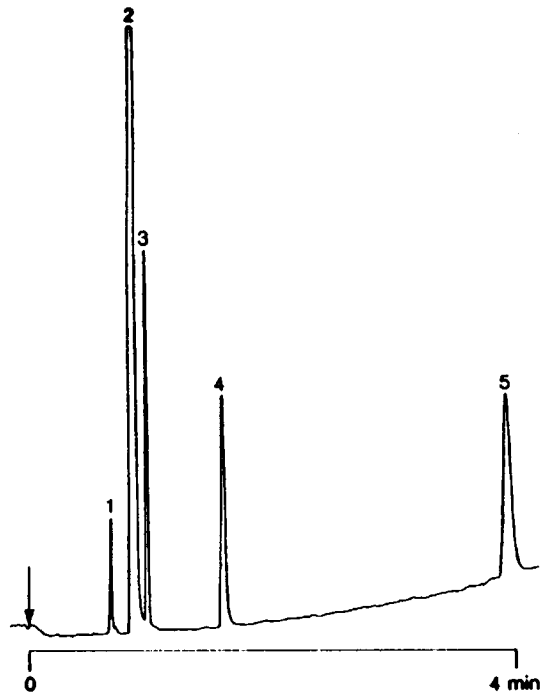

Fig. 7-13 Separation of CO and CO_2 in air.

Column: 25 m x 0.53 mm, fused silica, CarboPLOT P7, D_f = 25 µm;
Oven: 30 – 75 °C, 10 °C/min; Carrier: H_2, 20 kPa; Injection: Split, 100 ml/min;
Detection: µ-TCD; Sample conc.: 1% in air;
Peaks: 1 — helium; 2 — air; 3 — carbon monoxide; 4 — methane;
5 — carbon dioxide.

is at least 300 °C, it is possible to elute hydrocarbons up to C_{20}.

The valve configuration is shown in Fig. 7-14. The dimensions of the columns were adjusted in such a way that only one thermal conductivity detector was needed for this analysis. With a 10 meter Molsieve column the oxygen eluted just after the propane peak, and the nitrogen eluted between iso- and n-butane, see Fig. 7-15. By adjusting the length, internal diameter and pressure of the Molsieve column, the eluting inert gases can be positioned at any place in the chromatogram. With the same configuration it is therefore also possible to analyze several other inert gases and even CO.

The Molsieve type of adsorbent is ideal for separating most of the permanent gases although carbon dioxide is very strongly adsorbed. It is possible to elute CO_2 from Molsieve columns at temperatures above 250 °C and increased flow rates. By using such a strong temperature program the CO_2 can be quantified at "percent" levels. The peak shape is very poor which prevents quantitative work at lower levels. Also residual water will very often be present in the sample and

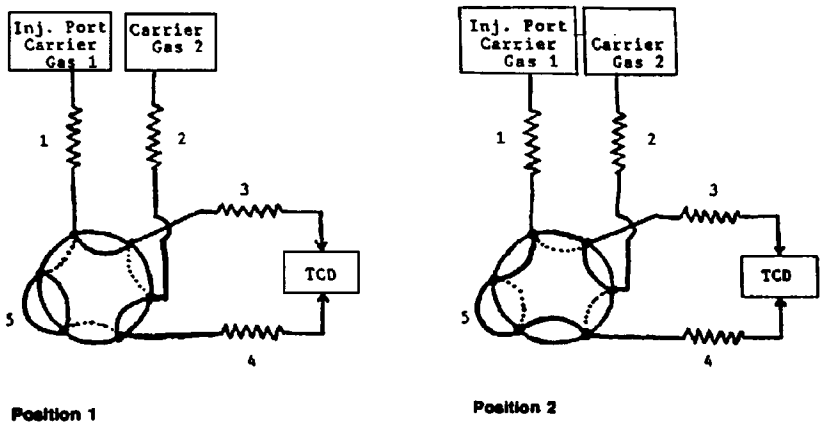

Fig. 7-14 Valve configuration for the separation of permanent gases with column switching.

will be absorbed by the molecular sieve, resulting in shifting retention times. It also leads to partial hydrolysis of the Molsieve zeolite, which will result in lower separation efficiency.

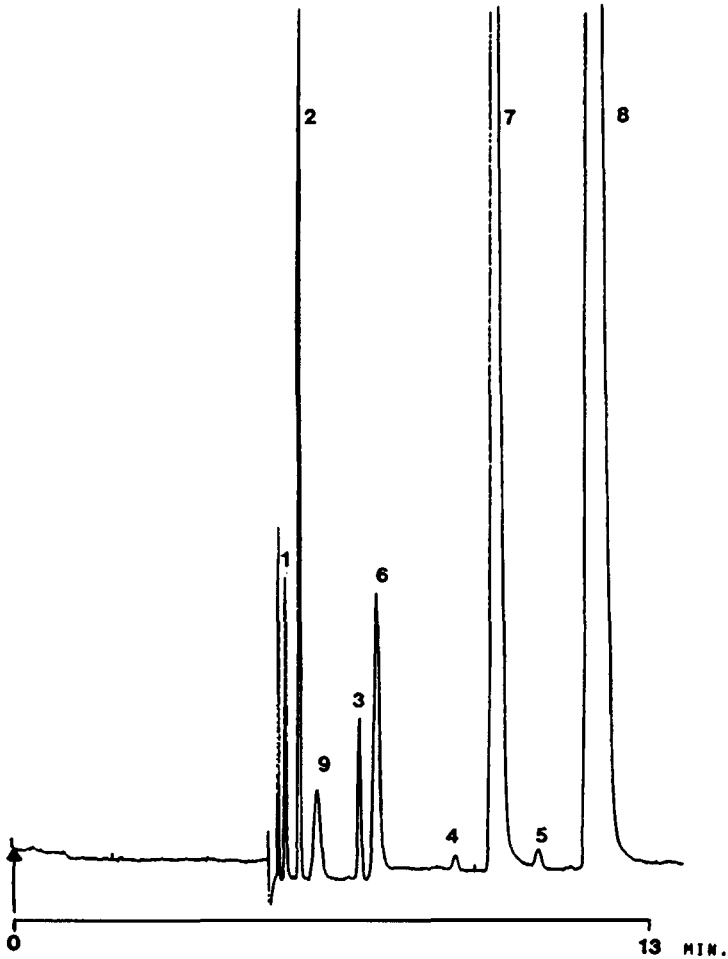

Fig. 7-15 Separation of permanent gases with column switching.

Columns: 50 m × 0.32 mm Dimethylpolysiloxane, D_f = 5 μm; 10 m × 0.32 mm Molsieve 5A, D_f = 30 μm; Oven: 25 °C; Carrier: H_2, 40 kPa at position 1; 31 kPa at position 2; Injection: Split: 10 ml/min; Detection: μ-TCD; Peaks: 1 — carbon dioxide; 2 — ethane; 3 — propane; 4 — isobutane; 5 — n-butane; 6 — oxygen; 7 — nitrogen; 8 — methane; 9 — helium.

Carbon dioxide can be analyzed very well by using porous polymer types of adsorbents. These materials have also been introduced coated in capillary columns. The porous polymer adsorbent has retention characteristics which are totally different from the Molsieve. Although it is not yet clear whether the retention of a porous polymer is caused by gas-solid or by a gas-liquid chromatographic process, the practical application of porous polymers has shown that they provide a high retention and that they are applicable for a wide range of compounds.

Fig. 7-16 shows the separation of a mixture of permanent gases separated on a porous polymer coated ALOT column. Here a 100% styrene-divinylbenzene porous polymer was used as the stationary phase. In Fig. 7-16A the split injection was used and in

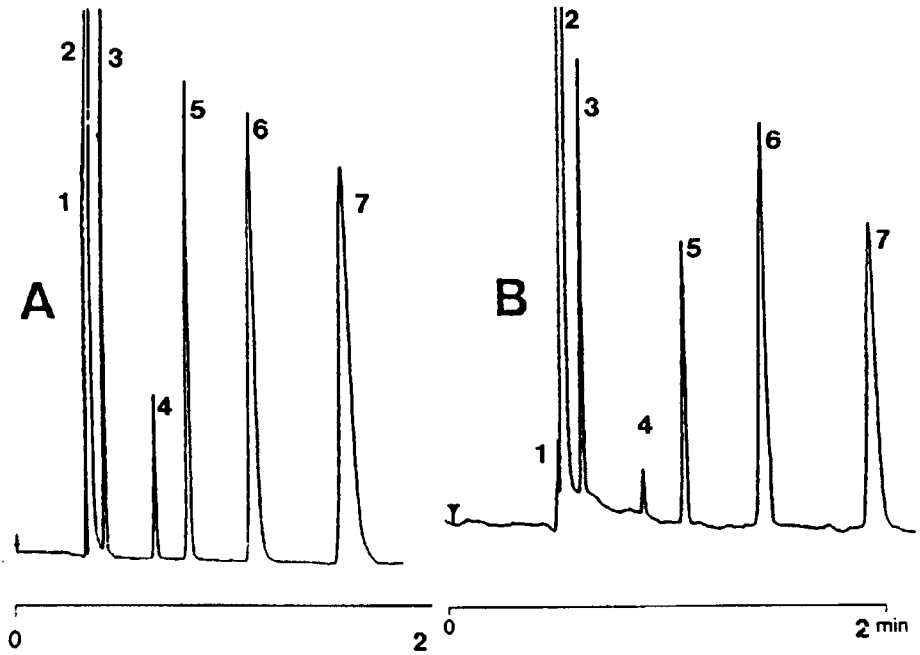

Fig. 7-16 Separation of permanent gases and $C_1 - C_2$ hydrocarbons.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 μm; Oven: 28 °C; Carrier: H_2, 40 kPa; Injection: A = Split; B = Direct; Detection: TCD; Peaks: 1 — helium; 2 — air + carbon monoxide; 3 — methane; 4 — carbon dioxide; 5 — nitrous oxide; 6 — ethylene; 7 — ethane.

Fig. 7-16B the direct injection technique was tested. As can be seen from the chromatograms, the CO_2 peak is very well separated from the inert gases and elutes as a symmetrical peak. CO_2 elutes with an approximate capacity ratio of 1. Also methane (peak 3) is baseline separated from the inert gases. However, the CO peak co-elutes with the air peak.

The application in Fig. 7-16 was performed on a 0.53 mm i.d. fused silica column. This is one of the most popular diameter columns because it is ideal for direct injection. Using the direct injection technique will always lead to loss some separation efficiency; how much is lost depends on the type of compound analyzed and the actual retention on the column. In Fig. 7-16 (A and B) the separation of peak 1 and 2 is significantly better with split injection. For separations of very volatile compounds with a capacity ratio smaller then 0.2 it is always recommended to use the split injection (of course, this is valid only for separation purposes).

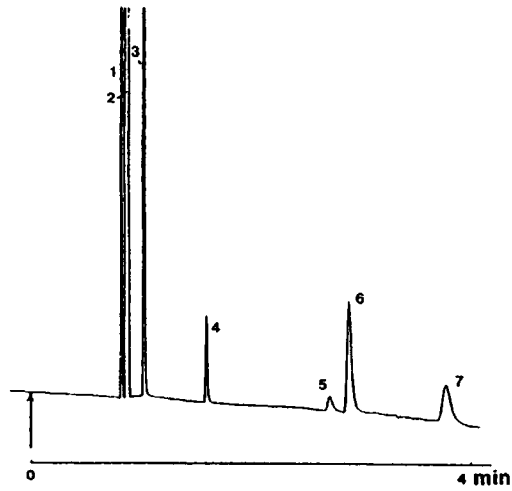

Fig. 7-17 Separation of permanent gases on high resolution ALOT porous polymer coated capillary column.

Column: 25 m x 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: 25 °C; Carrier: He, 70 kPa; Injection: Split; Detection: µ-TCD; Peaks: 1 — hydrogen; 2 — air; 3 — methane ;4 — carbon dioxide; 5 — ethylene; 6 — acetylene; 7 — ethane.

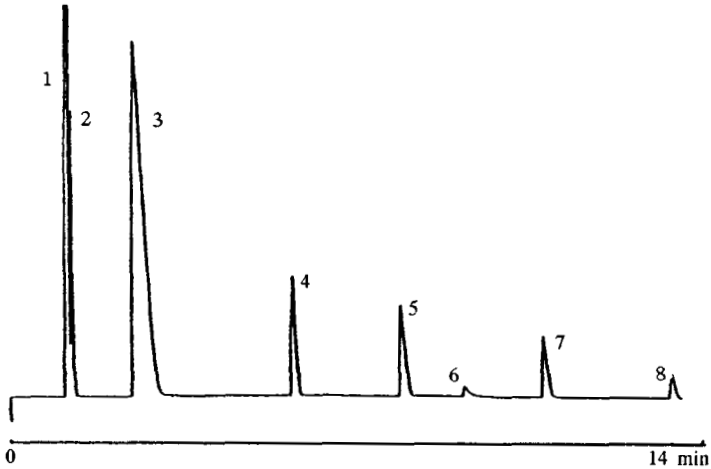

Fig. 7-18 Subambient separation of permanent gases.

Column: 10 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: –50 – 150 °C, 20 °/min; Carrier: H_2, 50 kPa; Injection: Split; Detection: µ-TCD; Peaks: 1 — nitrogen; 2 — oxygen; 3 — methane; 4 — carbon dioxide; 5 — ethane; 6 — water; 7 — propane; 8 — butane.

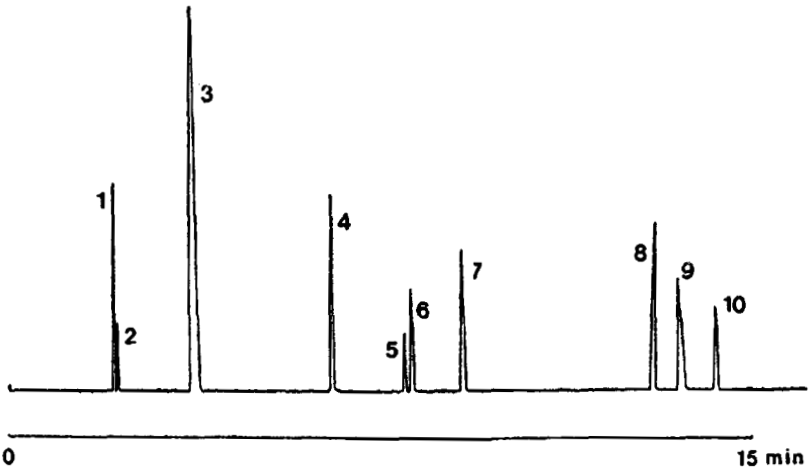

Fig. 7-19 Subambient separation of permanent gases.

Column: 25 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: –50 – 75 °C, 10 °/min; Carrier: H_2, 80 kPa; Injection: Split; Detection: µ-TCD; Peaks: 1 — nitrogen; 2 — oxygen; 3 — methane; 4 — carbon dioxide; 5 — ethylene; 6 — acetylene; 7 — ethane; 8 — propylene; 9 — propane; 10 — propyne (methylacetylene).

Typical critical separations on Molsieve and PoraPLOT Q capillary columns are:

On Molsieve 5A:
He/H_2; He/Ne; Ne/H_2; $H_2/D_2/T_2$/HD/HT/DT.

On PoraPLOT:
N_2/O_2; $He/N_2/O_2$; $H_2/N_2/O_2$; He/Ar; Ne/Ar; H_2/Ar; He/CO; H_2/CO; Ne/CO.

On using fused silica with a smaller internal diameter the separation efficiency increases considerably, especially if columns are operated under the optimal flow rate. Fig. 7-17 shows a separation of permanent gases, CO_2 and $C_1 - C_2$ hydrocarbons on a 25 meter, 0.32 mm fused silica capillary column. On using the split injection a baseline separation was obtained between hydrogen and air. Also the methane peak is already well separated from the air peak. The selectivity of the PoraPLOT Q porous polymer is also sufficient to separate ethylene and acetylene. There is still no separation between O_2 and N_2. On decreasing the analysis temperature to –50 °C, the air peak is starting to split-up on a 10 m column, see Fig. 7-18. On a 25 meter column it is possible to baseline separate the nitrogen and the oxygen, see Fig. 7-19. The elution order of the oxygen and nitrogen peak is reversed compared with Molsieve type separations. On Molsieve adsorbents the oxygen will elute first. On the porous polymer the nitrogen peak elutes first.

7.3.6 Sulfur Gases

Sulfur gases like H_2S, COS and SO_2 are very reactive and the only stationary phases which will elute these compounds with acceptable recovery are the porous polymers based on styrene-divinylbenzene. Although SO_2 is a compound which can react with a porous polymer it is possible to determine this compound down to low levels as shown in Fig. 5-20. Besides the SO_2 peak also the separation of COS and methyl sulfide is shown. Here a polar porous polymer PoraPLOT U was coated on fused silica giving a high resolution separation. PoraPLOT U is a porous polymer which is polymerized with divinylbenzene and also contains acrylic groups, giving it its high polarity. On

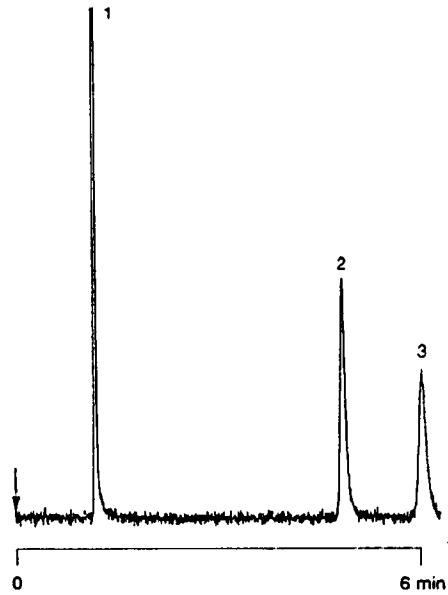

Fig. 7-20 Separation of sulfur gases.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT U, D_f = 20 µm; Oven: 50 °C;
Carrier: H_2, 40 kPa; Injection: Split, 100 ml/min;
Detection: FPD; Sample conc.: 50 – 100 ppm per compound;
Peaks: 1 — carbonyl sulfide; 2 — sulfur dioxide; 3 — methyl sulfide.

using the FPD and the porous polymers, these sulfur gases can be measured down to ppm levels.

Fig. 7-21 shows the separation of gases in a water sample. H_2S is very well separated from the other volatiles in the sample. The porous polymer also elutes the water peak as a very acceptable chromatographic peak due to its hydrophobic character.

7.4 Separation of $C_1 - C_5$ Hydrocarbons

The separation and quantitation of volatile hydrocarbons is one of the most important analyses in the petrochemical applications field. Depending on the type of hydrocarbons to be analyzed and the sample matrix a certain type of column is preferred. Generally hydrocarbons are easily quantified by gas chromatography. Since the hydrocarbon molecule does not contain a large dipole these compounds elute as symmetrical peaks from most GC columns. The chemi-

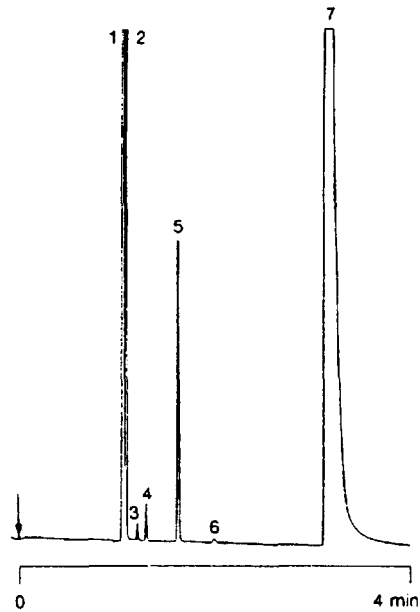

Fig. 7-21 Separation of gases in water.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT U, D_f = 20 µm; Oven: 100 °C; Carrier: H_2, 30 kPa; Injection: Split, 100 ml/min; Detection: µ-TCD; Sample conc.: Headspace, 0.1 – 10 %; Peaks: 1 — air + carbon monoxide; 2 — methane; 3 — carbon dioxide; 4 — ethane; 5 — hydrogen sulfide; 6 — propane; 7 — water.

cally bonded phases based on polydimethylsiloxanes will separate many hydrocarbons. However, in the range of $C_1 - C_4$ the bonded stationary phases do not provide the retention or the selectivity for adequate separations. Adsorbents like porous polymers and aluminum oxide show here their unique potential.

7.4.1 $C_1 - C_2$ Hydrocarbons

For the separation of methane, ethane, ethylene (ethene) and acetylene (ethyne) the most ideal adsorbent is aluminum oxide. This material has a very specific interaction with hydrocarbons which provides optimal selectivity especially for unsaturated hydrocarbons. As can be seen in Fig. 7-22 the Al_2O_3 ALOT column separates the C_2 hydrocarbons within 2 minutes with the highest possible resolution. Due to the high retention of Al_2O_3 the analysis temperatures can be relatively high. As this analysis was performed at

100 °C, the separation between ethane and ethylene can be improved even further by decreasing the analysis temperature.

Also porous polymers can be used for separation of light hydrocarbons. Although the selectivity of porous polymers for unsaturated hydrocarbons is not very high, the porous polymers offer specific advantages like:

1. Not sensitive to water in sample or carrier gas;
2. High retention for volatiles;
3. Elution of polar compounds.

Fig. 7-23 shows the separation of $C_1 - C_2$ hydrocarbons on a polar porous polymer coated capillary column. All compounds are baseline separated. The PoraPLOT U porous polymer with its high polarity will have the strongest interaction with unsaturated hydrocarbons. As a result acetylene elutes with the highest retention. By using the apolar porous polymer PoraPLOT Q, containing only styrene-divinylbenzene groups, the elution sequence is different, see Fig. 7-24. Acetylene (peak 4) elutes here together with ethane (peak 2) before ethylene (peak 3).

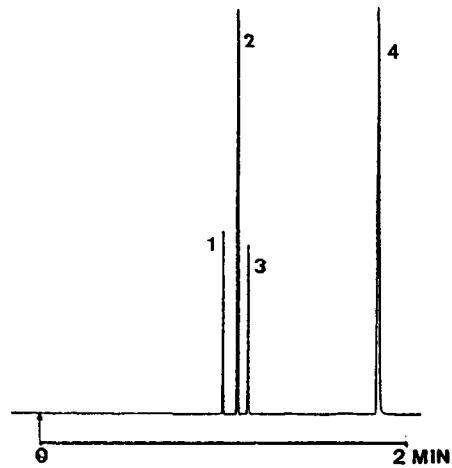

Fig. 7-22 Separation of $C_1 - C_2$ hydrocarbons.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/KCl, D_f = 5 µm; Oven: 100 °C; Carrier: H_2, 70 kPa; Injection: Split; Detection: FID; Sample conc.: 500 – 1000 ppm in N_2; Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — acetylene.

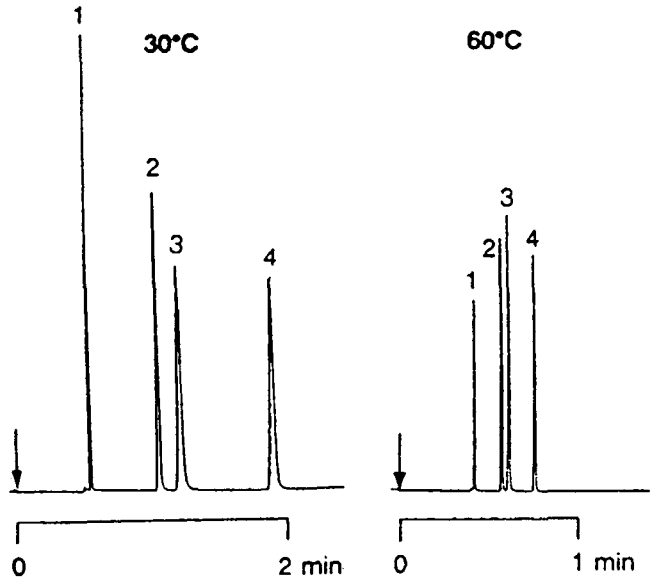

Fig. 7-23 Separation of $C_1 - C_2$ hydrocarbons on polar porous polymer ALOT column.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT U, D_f = 20 µm;
Oven: 30/60 °C; Carrier: H_2, 30 kPa; Injection: Split, 100 ml/min;
Detection: FID, 64×10^{-12} Afs; Sample conc.: 1 % in N_2;
Peaks: 1 — methane; 2 — ethylene; 3 — ethane; 4 — acetylene.

Compared with Fig. 7-22 it is clear that the selectivity of the Al_2O_3 adsorbent for C_2 hydrocarbons is much better.

7.4.2 $C_1 - C_4$ Hydrocarbons

As for the separation of $C_1 - C_2$ hydrocarbons, the most selective adsorbent to be used as stationary phase is aluminum oxide. With aluminum oxide it is possible to separate all $C_1 - C_4$ hydrocarbons with high resolution, see Fig. 7-25. The retention behavior of $C_1 - C_2$ hydrocarbons on aluminum oxide depends on the deactivation method used. Most widely used is deactivation with KCl which results in a relatively apolar Al_2O_3 surface. Also other deactivating salts can be used, altering the polarity of Al_2O_3 surfaces

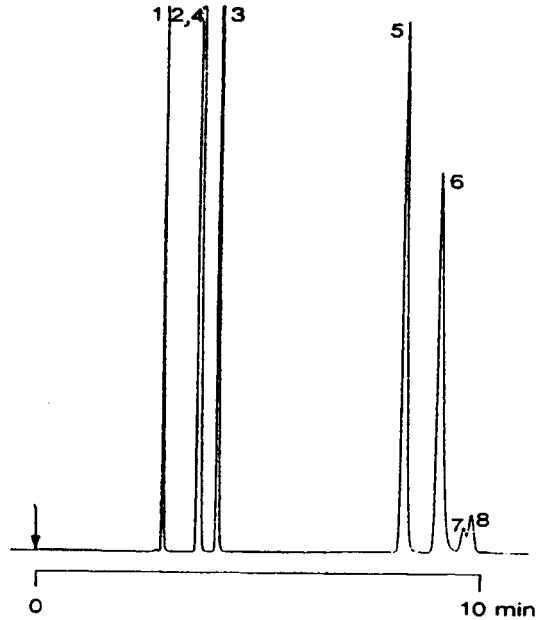

Fig. 7-24 Separation of $C_1 - C_2$ hydrocarbons on apolar porous polymer ALOT column.

Column: 25 m x 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 µm; Oven: 80 °C; Carrier: H_2, 30 kPa; Injection: Split, 100 ml/min; Detection: FID, 64 x 10^{-12} Afs; Sample conc.: 0.1 – 1 % in N_2;
Peaks: 1 — methane; 2 — ethylene; 3 — ethane; 4 — acetylene; 5 — propylene; 6 — propane; 7 — propadiene; 8 — methylacetylene.

completely. For instance, on using sodium sulfate the resulting column will have a higher polarity, which is best measured on the unsaturated hydrocarbon acetylene. A comparison between KCl and Na_2SO_4 deactivation is shown in Fig. 7-26. The sulfate ion is responsible for the higher polarity. Depending on the composition of the sample, one could choose the mode of deactivation for a certain selectivity.

If hydrocarbons are present in concentrations within approximately 3 decades, the Al_2O_3/KCl ALOT column is ideal. As shown in Fig. 7-27 in the separation of liquid pressure gas, all relevant hydrocarbons can be quantified within 4 minutes analysis time. More critical separations like the cyclopropane/propylene and *trans-*

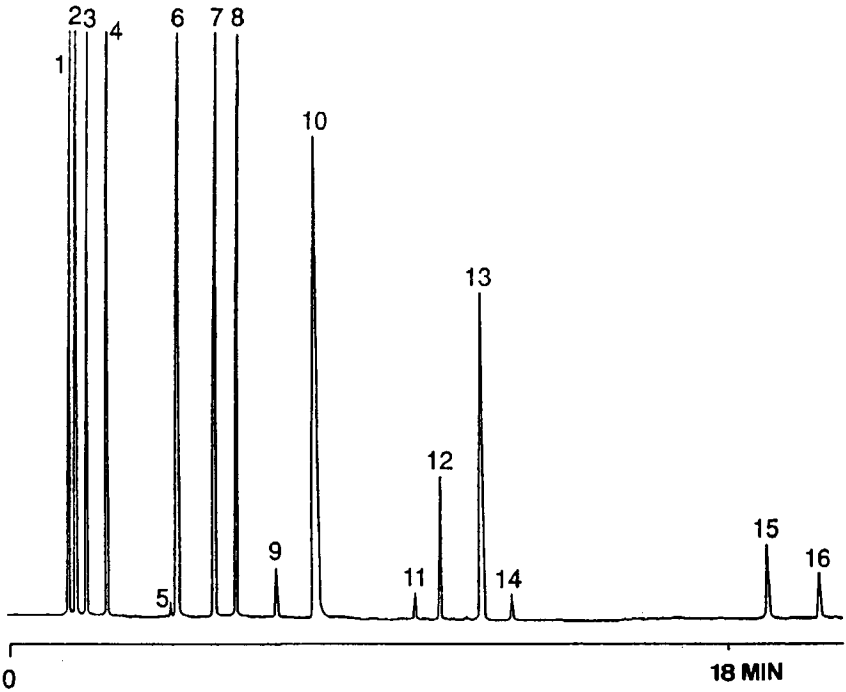

Fig. 7-25 Separation of $C_1 - C_4$ hydrocarbons on AL_2O_3 capillary ALOT column.

Column: 50 m x 0.32 mm, fused silica, Al_2O_3/Na_2SO_4, D_f = 5 µm; Oven: 70 °C – 200 °C, 3 °C/min; Carrier: H_2, 100 kPa; Injection: Split; Detection: FID; Sample conc.: 1 % in N_2; Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — propane; 5 — cyclopropane; 6 — propylene; 7 — isobutane; 8 — butane; 9 — propadiene; 10 — acetylene; 11 — *trans*-2-butylene; 12 — 1-butylene; 13 — isobutylene; 14 — *cis*-2-butylene; 15 — 1,3-butadiene; 16 — methylacetylene.

2-butylene/1-butylene the Al_2O_3/Na_2SO_4 is preferred. On the other hand, for the analysis of 1,3-butadiene the Al_2O_3/KCl adsorbent is preferred since the methylacetylene elutes before the 1,3-butadiene peak (see also Section 7.4.3).

A typical application for the Al_2O_3 ALOT columns is the environmental monitoring of hydrocarbons in the range of $C_2 - C_{10}$ as shown in Fig. 7-28. By using a temperature program up to 190 °C hydrocarbons up to C_8 will elute. The high retention of the aluminum oxide in combination with the selectivity makes the

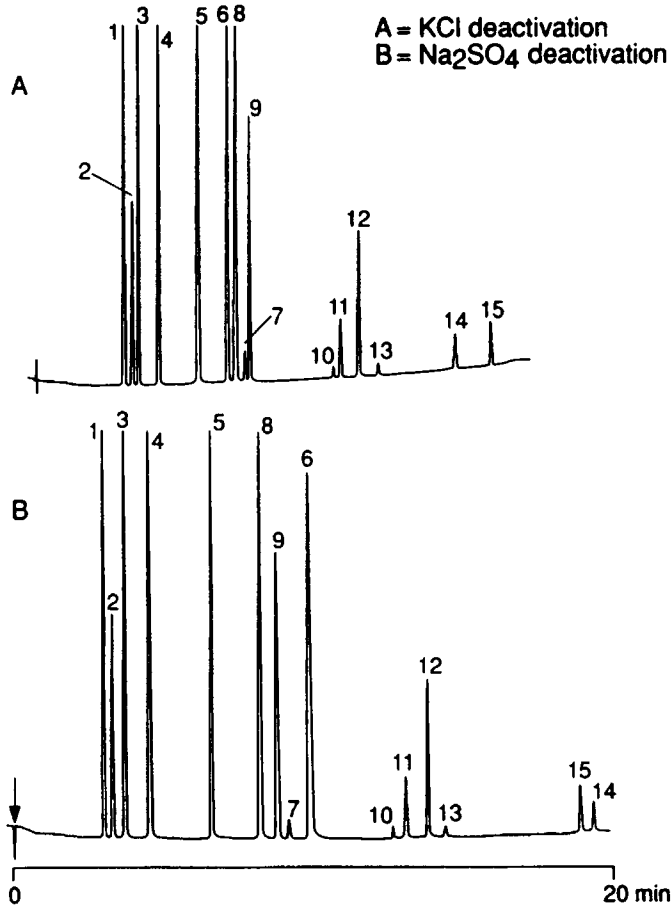

Fig. 7-26 Comparison of KCl and Na_2SO_4 deactivation of Al_2O_3 ALOT columns.

Columns: 50 m x 0.32 mm, fused silica, Al_2O_3, D_f = 5 μm;
Oven: 70 °C – 200 °C, 3 °/min; Carrier: H_2, 100 kPa;
Injection: Split; Detection: FID; Sample conc.: 1 % in N_2;
Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — propane;
5 — propylene; 6 — acetylene; 7 — propadiene; 8 — isobutane;
9 — butane; 10 — *trans*-2-butylene; 11 — 1-butylene; 12 — isobutylene;
13 — *cis*-2-butylene; 14 — methylacetylene; 15 — 1,3-butadiene.

separation of all important hydrocarbons possible. By combining the column with special sample-preconcentration techniques, environmental monitoring is performed down to sub-ppb levels (Ref. VOC-Air analyzer, Chrompack International).

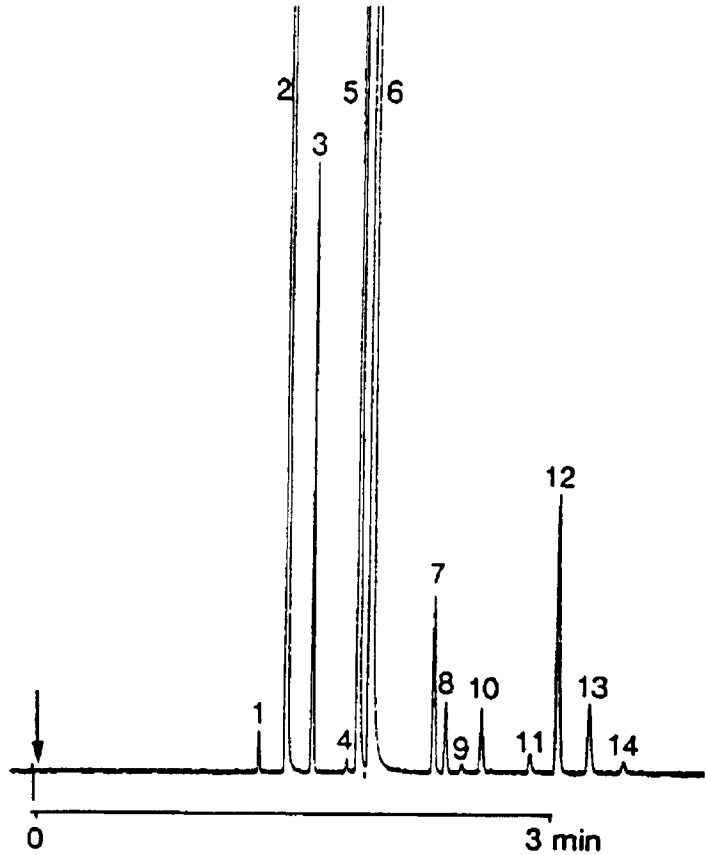

Fig. 7-27 Separation of $C_1 - C_4$ hydrocarbons in liquid pressure gas.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/KCl, D_f = 5 µm;
Oven: 130 °C; Carrier: H_2, 150 kPa; Injection: Split, 100 ml/min;
Detection: FID, 2×10^{-12} Afs; Sample conc: 1 – 30 % in N_2;
Peaks: 1 — ethane; 2 — propane; 3 — propylene; 4 — propadiene;
5 — isobutane; 6 — butane; 7 — *trans*-2-butylene; 8 — 1-butylene;
9 — isobutylene; 10 — *cis*-2-butylene; 11 — unknown; 12 — methylacetylene;
13 — 1,3-butadiene; 14 — unknown.

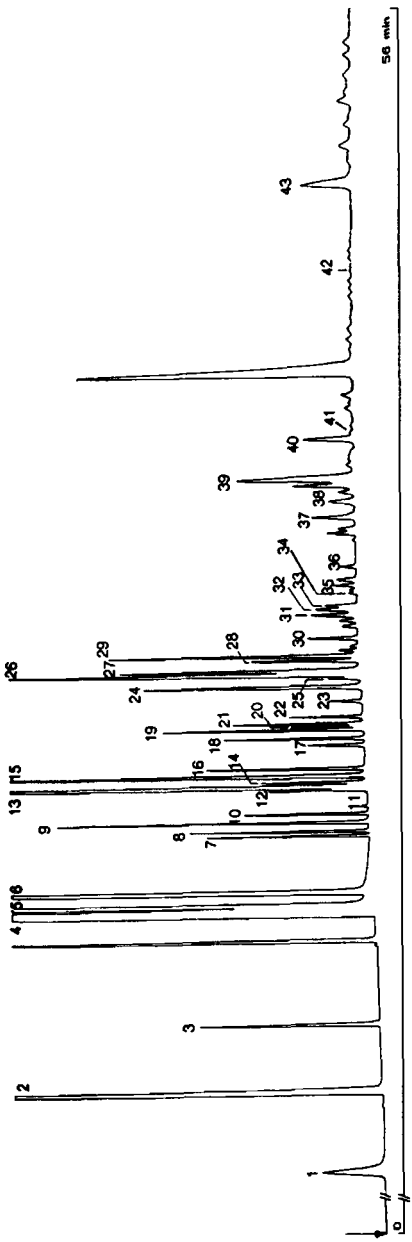

Fig. 7-28 Hydrocarbons in air, street level sample during evening rush hour.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/KCl, D_f = 5 μm; Oven: –20 °C (3 min) – 190 °C, 10C/min; Carrier: He, 100 kPa; Injection: splitless, 3 min, 2.0 ml; Detection: FID; Sample conc.: 740 PPB for ethylene; Courtesy: B.M. Hart, C.K. Laird, National Power Technology and Environmental Centre, Surrey, UK.
Peaks:
1 — ethane; 2 — ethylene;
3 — propane; 4 — propylene;
5 — isobutane; 6 — butane;
7 — *trans*-2-butylene;
8 — 1-butylene;
9 — 2-methylpropylene;
10 — *cis*-2-butylene;
11 — 2,2-dimethylpropane;
12 — cyclopentane;
13 — 2-methylbutane;
14 — methylacetylene;
15 — pentane; 16 — 1,3-butadiene;
17 — 3-methyl-1-butylene;
18 — *trans*-2-pentene;
19 — 2-methyl-2-butylene;
20 — 1-pentene;
21 — 2-methyl-1-butylene;
22 — *cis*-2-pentene; 23 — 2-butyne;
24 — 2,2-dimethylbutane;
25 — methylcyclopentane;
26 — 2,3-dimethylbutane;
27 — 2-methylpentane;
28 — 2-methyl-1,3-butadiene;
29 — hexane;
30 — 1-methyl-1-cyclopentane;
31 — *trans*-3-hexene;
32 — 4-methyl-1-pentene;
33 — *trans*-2-hexene;
34 — cyclohexene;
35 — 1-hexene; 36 — *cis*-2-hexene;
37 — 2,4-dimethylpentane;
38 — methylcyclohexane;
39 — 3-methylhexane;
40 — heptane; 41 — cycloheptane;
42 — cycloheptene;
43 — 2,2,4-trimethylpentane.

Separation of C_1–C_4 hydrocarbons can also be realized on porous polymer coated ALOT columns. Since the Al_2O_3 adsorbent is sensitive to water and also because polar impurities will accumulate, this material is not always the best choice. Depending on the possibility of reducing the content of water and/or polar impurities in the sample, the porous polymer ALOT column may be a suitable alternative. Although the selectivity for $C_1 - C_4$ hydrocarbons is totally different and far from ideal, there are a number of separations possible by using the porous polymer PoraPLOT Q coated ALOT columns of longer length. Fig. 7-29 shows the separation of the same mixture of hydrocarbons as in Fig. 7-26.

All $C_1 - C_3$ hydrocarbons are well separated and can be analyzed. The limited selectivity is best seen in the separation of the C_4 hydrocarbons. All C_4 hydro-

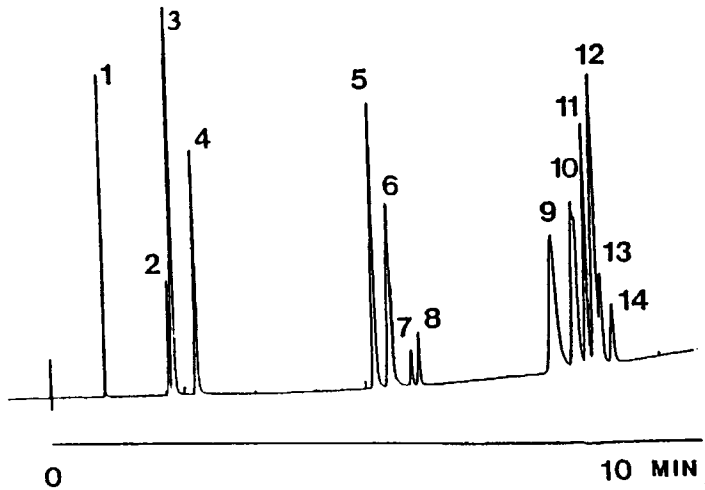

Fig. 7-29 Separation of $C_1 - C_4$ hydrocarbons on porous polymer ALOT column.

Column: 25 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: 30 °C – 150 °C, 10 °/min; Carrier: H_2, 70 kPa; Injection: Split; Detection: FID; Sample conc.: 1 – 5 % in N_2; Peaks: 1 — methane; 2 — ethylene; 3 — acetylene; 4 — ethane; 5 — propylene; 6 — propane; 7 — propadiene; 8 — methylacetylene; 9 — isobutane; 10 — 1,3-butadiene +1-butylene; 11 — isobutylene; 12 — butane; 13 — *cis*-2-butylene; 14 — *trans*-2-butylene.

carbons elute in a relatively small "time band" which results in poor separation. If present at equal concentrations the separation efficiency will be sufficient. If however one of the C_4 hydrocarbons is present at a high level the other peaks will be masked.

7.4.3 Hydrocarbon Impurity Analysis in Main Hydrocarbon Streams

To analyze $C_1 - C_4$ hydrocarbons at concentrations as low as 1 ppm the best adsorbent is aluminum oxide because of its unique selectivity. One of the most widely used applications is the analysis of butylene isomer streams. For the separation of butylenes the Al_2O_3 column with a sodium sulfate deactivation will provide the best selectivity. As can be seen in Fig. 7-30 the resolution between the four butylene isomers is very high. The most difficult butylene

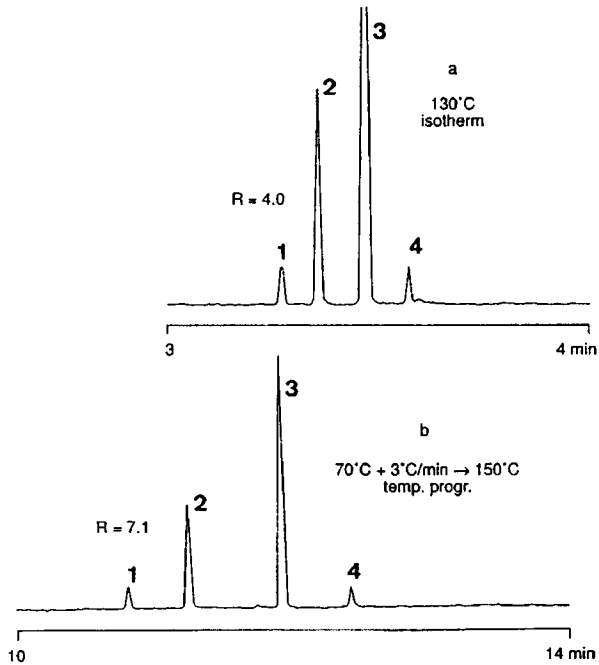

Fig. 7-30 Separation of butylene isomers (isothermal and temperature programmed separation).

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/Na_2SO_4 D_f = 5 µm; Oven: A: 130 °C isothermal; B: 70 °C – 150 °C, 3 °C/min; Carrier: H_2, 100 kPa; Injection: Split; Detection: FID; Sample conc.: 0.1 % in N_2; Peaks: 1 — *trans*-2-butylene; 2 — isobutylene; 3 — 1-butylene; 4 — *cis*-2-butylene.

isomers to separate are *trans*-2-butylene and 1-butylene. At 130 °C a resolution factor (Trennzahl) of 4.0 is realized, while under temperature programmed conditions the separation factor could be increased to even 7.1! Some analyses of pure 99% butylene streams are shown in Fig. 7-31 and Fig. 7-32. Even with the high levels of the pure component present, other hydrocarbons can be quantified down to ppm levels.

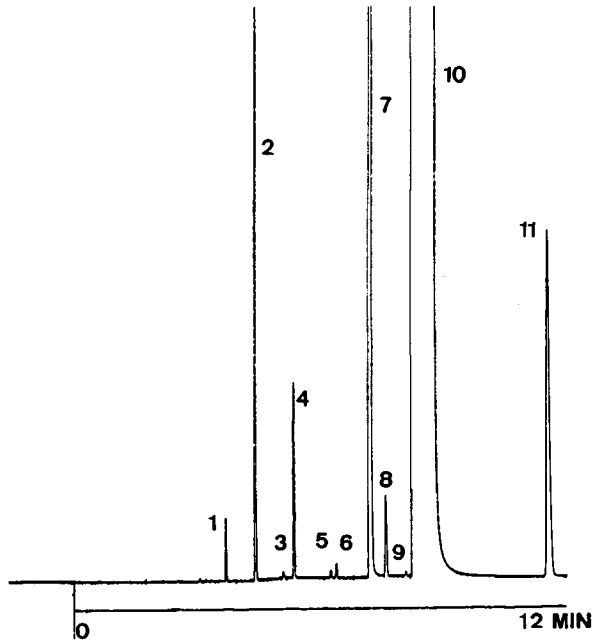

Fig. 7-31 Separation of impurities in pure *cis*-2-butylene.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/Na_2SO_4, D_f = 5 μm; Oven: 110 °C;
Carrier: N_2, 120 kPa; Injection: Split 1:10; Detection: FID;
Sample conc.: 5 – 100 ppm in *cis*-2-butylene;
Peaks: 1 — propane; 2 — propylene; 3 — isobutane; 4 — butane;
5 — unknown; 6 — unknown; 7 — *trans*-2-butylene; 8 — 1-butylene;
9 — isobutylene; 10 — *cis*-2-butylene; 11 — unknown.

Just as for the butylenes, aluminum oxide is also very selective for butadiene analysis. Fig. 7-33 shows the analysis of a 99% 1,2-butadiene sample. Also 1,3-butadiene analysis is very important and this com-

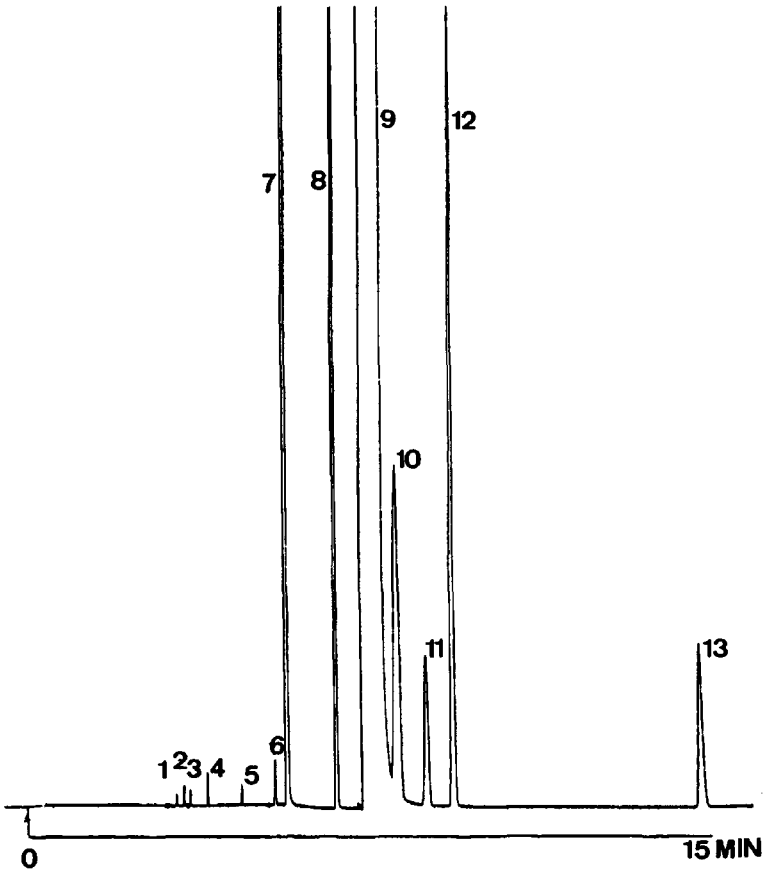

Fig. 7-32 Separation of impurities in pure *trans*-2-butylene.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/Na_2SO_4, D_f = 5 μm; Oven: 110 °C;
Carrier: N_2, 120 kPa; Injection: Split 1:10; Detection: FID;
Sample conc.: 5 – 100 ppm in *trans*-2-butylene;
Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — propane; 5 — propylene;
6 — isobutane; 7 — butane; 8 — unknown; 9 — *trans*-2-butylene;
10 — 1-butylene; 11 — isobutylene; 12 — *cis*-2-butylene.

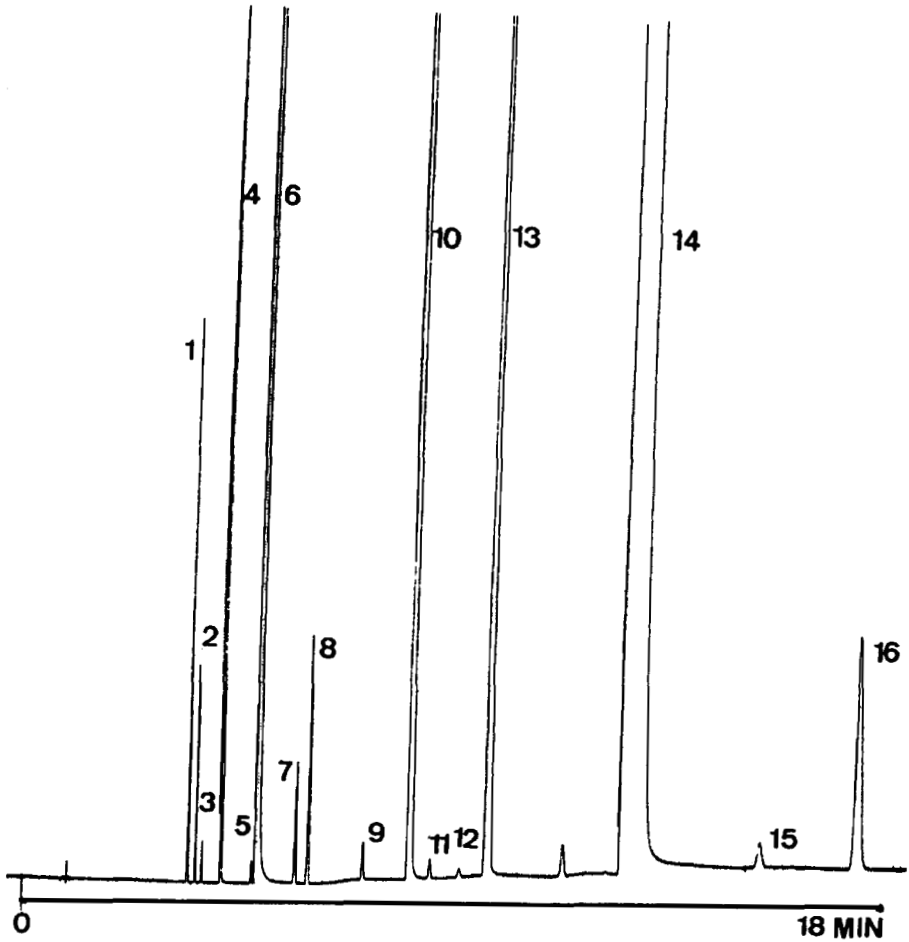

Fig. 7-33 Separation of impurities in 1,2-butadiene.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/Na_2SO_4, D_f = 5 μm; Oven: 110 °C;
Carrier: N_2, 120 kPa; Injection: Split, 1:10; Detection: FID;
Sample conc.: 1 – 100 ppm in 1,2-butadiene;
Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — propane;
5 — cyclopropane; 6 — propylene; 7 — isobutane; 8 — butane; 9 — unknown;
10 — *trans*-2-butylene; 11 — 1-butylene; 12 — isobutylene; 13 — *cis*-2-butylene;
14 — 1,2 — butadiene; 15 — 1,3-butadiene; 16 — unknown.

ponent is eluted as a single peak without interferences. The best separation is obtained on an Al_2O_3/KCl deactivated ALOT column as shown in Fig. 7-34 and 7-35. Two different types of 1,3-butadiene streams were analyzed. Often the methylacetylene has to be analyzed which is eluting in front of the 1,3-butadiene peak.

Also impurities in ethylene streams can be monitored very efficiently as shown in Fig. 7-36. In this particular industrial sample compounds up to acetylene had to be analyzed. The tailing on the main component is very typical for the type of column used and is a result of overloading the column. On reducing the amount of injected sample the tailing will disappear.

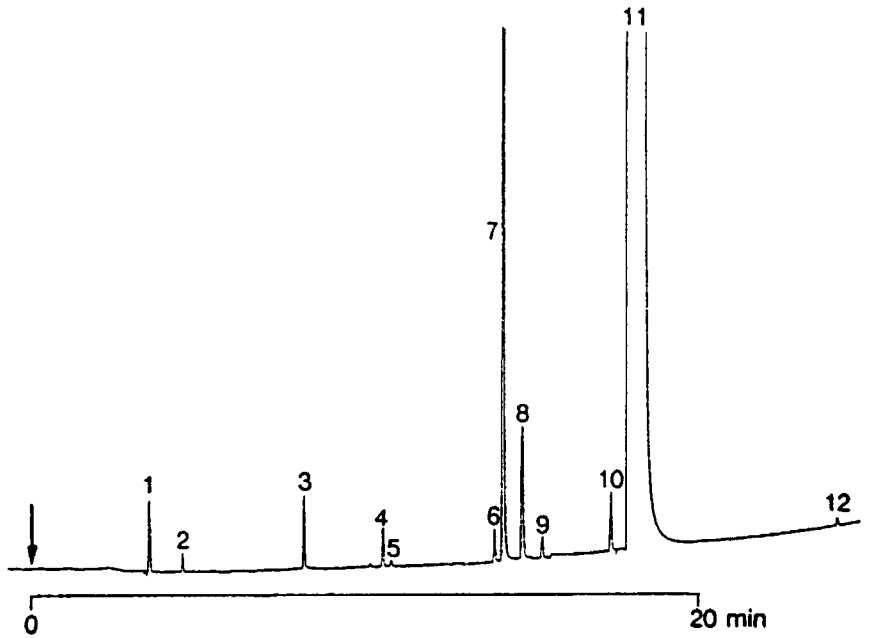

Fig. 7-34 Separation of impurities in 1,3-butadiene.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/KCl, D_f = 5 µm; Oven: 100 – 200°C, 6 °/min; Carrier: N_2, 140 kPa; Injection: Split, 1:20; Detection: FID; Sample conc.: 10 – 100 ppm in 1,3-butadiene; Peaks: 1 — methane; 2 — ethane; 3 — propane; 4 — propylene; 5 — isobutane; 6 — butane; 7 — *trans*-2-butylene; 8 — 1-butylene; 9 — isobutylene; 10 — *cis*-2-butylene; 11 — 1,3-butadiene.

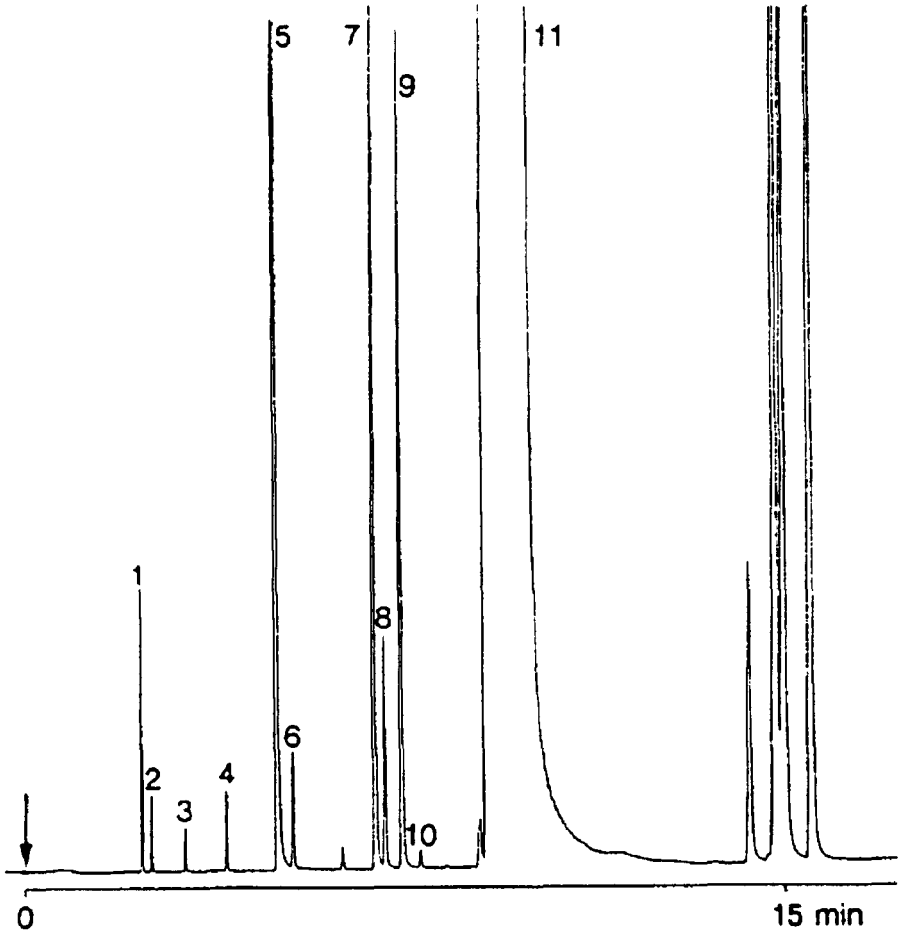

Fig. 7-35 Separation of impurities in 1,3-butadiene.

Column: See Fig. 7-34; Oven: 60 °C – 180 °C, 5 °/min;
Carrier: N_2, 85 kPa; Injection: Split, 1:15; Detection: FID;
Sample conc.: 25 – 250 ppm in 1,3-butadiene;
Peaks: 1 — methane; 2 — ethylene; 3 — propylene; 4 — propadiene;
5 — unknown; 6 — *trans*-2-butylene; 7 — 1-butylene; 8 — isobutylene;
9 — *cis*-2-butylene; 10 — methylacetylene; 11 — 1,3-butadiene; 12 — unknown.

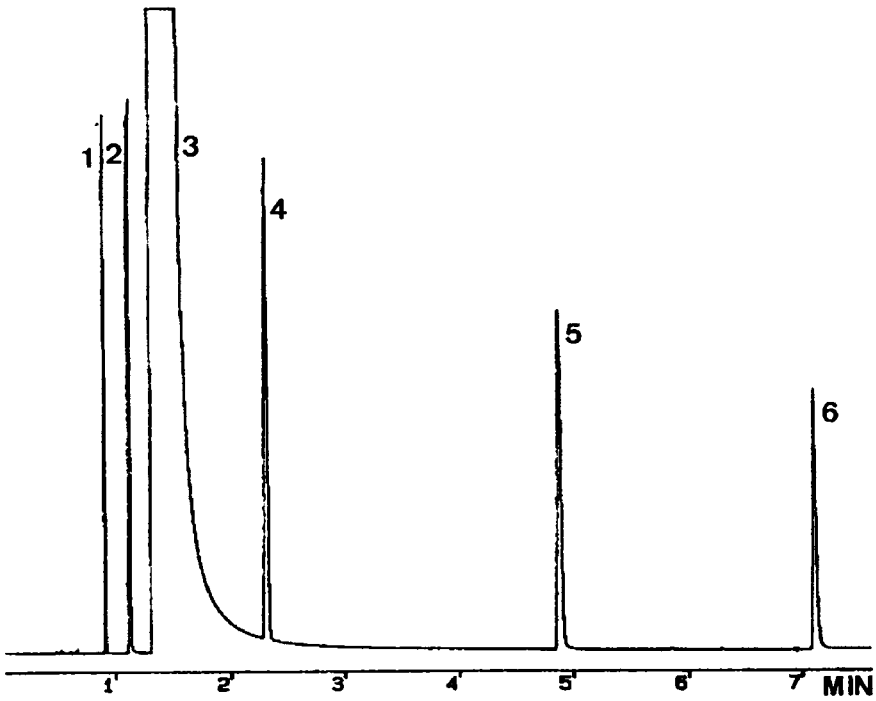

Fig. 7-36 Separation of impurities in ethylene.

Column: 50 m × 0.53 mm, fused silica, Al_2O_3/Na_2SO_4, D_f = μm;
Oven: 60 °C – 150 °C, 10 °/min;
Carrier: He ultrapure, 95 cm/s; Injection: Split, 1 ml; Detection: FID;
Sample Conc.: 99 % Ethylene stream; Courtesy: J. Luong, DOW Canada;
Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — propane; 5 — propylene;
6 — acetylene.

7.4.4 Hydrocarbons in the Presence of Water

One of the characteristics of aluminum oxide is its strong affinity for polar compounds. Water is a typical compound which is often present in samples and will be adsorbed on aluminum oxide. On introducing water the Al_2O_3 ALOT column will become more deactivated which will result in shorter retention times. In practical use this often presents a problem since integration parameters are set on certain retention times which should not have to be adapted after each analysis.

There are a number of solutions to overcome the water problem, of which several have been used in practice for a number of years.

1. The best solution would be to remove the water from the sample. This is possible but needs extra cleaning procedures which are time consuming and therefore not preferred.

2. A more practical method is to remove any water which is injected onto the column by using a temperature programmed analysis. Although water is adsorbed very strongly by the aluminum oxide, it will elute eventually at elevated temperatures. In practice, the Al_2O_3 ALOT column should be heated up to 200 °C for about 10 minutes to return it to its original state. Any water injected on Al_2O_3 columns will lead to a decrease of capacity. However, as this is a reversible process, water will not harm the Al_2O_3 coating at all.

3. If the water concentration in the sample is very low (in range of 1 – 3 ppm or lower), it is possible to run a series of samples isothermally. The Al_2O_3 column should be regenerated after a number of analyses. Often the Al_2O_3 column is conditioned during the night at 200 °C and used during the day for routine analysis at lower temperatures.

4. By separating the water from the hydrocarbon sample before it reaches the analytical Al_2O_3 ALOT column. A method which works quite well is to couple a 5 – 10 meter capillary coated with a polar phase with a high retention for hydroxyl group containing compounds. Such a phase is polyethylene glycol. Since it is possible to prepare chemically bonded thick films of polyethylene glycol on fused silica it is

also possible to do a pre-separation of water and $C_1 - C_5$ hydrocarbons. The water will be strongly retarded by the polyethylene glycol, while the $C_1 - C_5$ hydrocarbons will elute almost without retention. By using a simple 4-way valve the water can be sent to vent and analysis of $C_1 - C_5$ hydrocarbons can be done isothermally with reproducible retention times, independent of the moisture level.

5. As discussed in Section 7.4.2 it is also possible to use an ALOT column coated with a porous polymer which is non-sensitive to moisture. This will however only be effective for hydrocarbon analysis if there is sufficient resolution between the hydrocarbons of interest. As can be seen in Fig. 7-29 the selectivity of a porous polymer for C_4-isomers is not optimal at all.

7.5 Separation of Polar Volatiles

Polar volatile compounds containing polar functional groups (like alcohols, aldehydes, ketones, esters, mercaptans, sulfides, amines, nitriles) can be separated by using the porous polymer type of adsorbent in capillary adsorption chromatography. Materials like aluminum oxide and molecular sieves or carbosieves show too much interaction with the polar functional groups of these compounds which usually leads to strongly tailing peaks and high retention times even at high elution temperatures.

The separation of polar volatile compounds with application of adsorption materials in capillary columns is therefore somewhat restricted due to the limited number of adsorbents available. With the porous polymers several applications are possible, of which a few are shown in Fig. 7-38 – 7-55. The application is split up into three fields, in which there is a typical interest:

1. Hydrocarbons in combination with polar volatile compounds;

2. Halogenated volatile compounds;

3. Polar volatile compounds with different functional bonded groups (mostly solvents);

7.5.1 Hydrocarbons and Polar Volatiles with Different Functional Groups

Depending on the type of functional group present in the compounds to be analyzed the best adsorbent can be selected.

Vinyl chloride in $C_1 - C_4$ hydrocarbons

For most types of application the only choice will be the porous polymer type of adsorbent. However, there are a number of applications possible with aluminum oxide as adsorbent. A widely used application is shown in Fig. 7-37 which shows the separation of vinyl chloride in $C_1 - C_3$ hydrocarbons. In this analysis where it is very important to have the vinyl chloride quantified together with the volatile hydrocarbons, the aluminum oxide adsorbent will provide the selectivity to realize the separation. A practical problem which

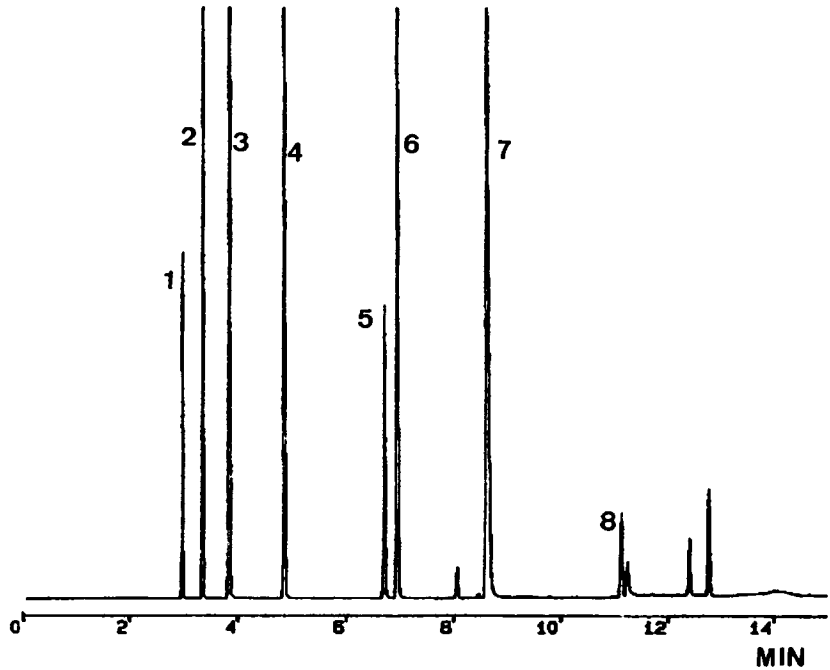

Fig. 7-37 Vinyl chloride in $C_1 - C_4$ hydrocarbons.

Column: 50 m × 0.32 mm, fused silica, Al_2O_3/Na_2SO_4, D_f = 5 μm; Oven: 70 °C (2 min) – 200 °C; 10°/min; Carrier: He, 80 kPa; Injection: Split; Detection: FID; Sample conc.: 100 ppm for hydrocarbons; 15 ppm for vinylchloride; Courtesy: J. Luong, Dow Canada.
Peaks: 1 — methane; 2 — ethane; 3 — ethylene; 4 — propane; 5 — cyclopropane; 6 — propylene; 7 — acetylene; 8 — vinyl chloride.

has been observed is that fresh aluminum oxide columns need some time to stabilize before giving reproducible quantitative data. This is not at all strange since aluminum oxide will act as a catalyst and may degrade several types of halogenated hydrocarbons. For this application the aluminum oxide is probably deactivated by the vinyl chloride degradation products; equilibrium is established after a number of analysis.

Methyl chloride in $C_1 - C_3$ hydrocarbons

Methyl chloride is a very volatile compound which can be analyzed ideally on a porous polymer type of ALOT columns. A typical separation of methyl chloride from $C_1 - C_3$ is shown in Fig. 7-38. In this application two porous polymer ALOT columns of different polarity were coupled. The apolar PoraPLOT Q porous polymer will not separate methyl

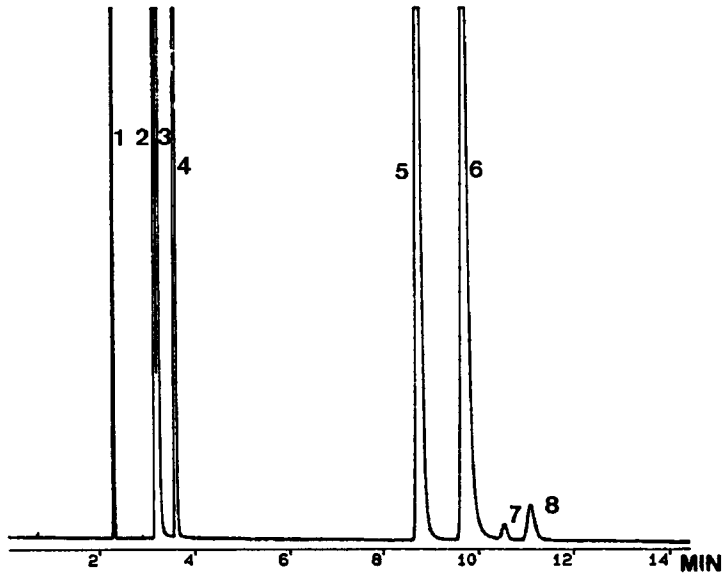

Fig. 7-38 Methyl chloride in $C_1 - C_3$ hydrocarbons.

Column: 3 m x 0.53 m, fused silica, PoraPLOT U coupled with 25 m x 0.53 mm F.s.PoraPLOT Q; Oven: 70 °C; Carrier: He,130 kPa; Injection: Split;
Detection: FID; Courtesy: J .Luong, Dow Canada.
Peaks: 1 — methane; 2 — ethane; 3 — acetylene; 4 — ethane; 5 — propylene; 6 — propane; 7 — methyl chloride; 8 — cyclopropane.

chloride from propane (see Fig. 7-39). The polar PoraPLOT U column will not separate the propane from the propylene. By coupling a short PoraPLOT U column before the PoraPLOT Q, the methyl chloride is baseline separated from propane.

Ethylene oxide, acetaldehyde and methanol in $C_1 - C_3$

The separation of ethylene oxide and acetaldehyde is shown in Fig. 7-39. The two compounds are well separated from the C_3-hydrocarbons and are just baseline separated. The eluting peaks are symmetrical which is a typical characteristic of porous polymer stationary phases. Ethylene oxide and acetaldehyde can be quantified if the concentrations of the compounds do not differ by more than a factor of 10. At higher concentrations there will be overlap due to

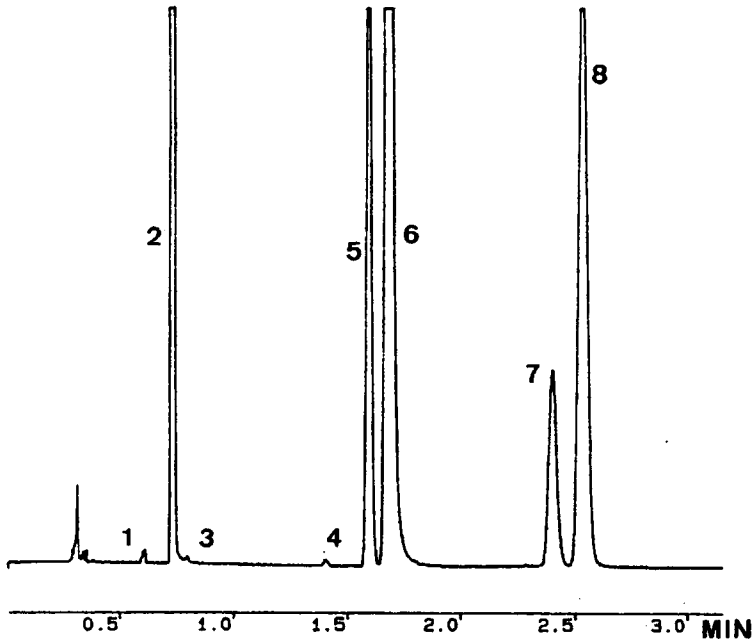

Fig. 7-39 Ethylene oxide and acetaldehyde in $C_1 - C_3$ hydrocarbons.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT Q; Oven: 90 °C; Carrier: He, 105 kPa; Injection: Split; Detection: FID;
Courtesy: J. Luong, Dow Canada.
Peaks: 1 — methane; 2 — ethylene/acetylene; 3 — ethane; 4 — propylene; 5 — propane + methyl chloride; 6 — cyclopropane; 7 — acetaldehyde; 8 — ethylene oxide.

overloading phenomena. Methanol elutes on the PoraPLOT Q just after propane and also elutes as a sharp peak, see Fig. 7-40.

$C_1 - C_4$ Nitriles and $C_1 - C_4$ Hydrocarbons

Nitriles can be analyzed very well on capillary columns coated with a low phase ratio of polymethylsiloxane. If there are also $C_1 - C_4$ hydrocarbons present the oven temperature should be lowered to provide sufficient capacity. If there are practical restrictions for reducing the oven temperature the porous polymer provides a good alternative since the analysis tem-

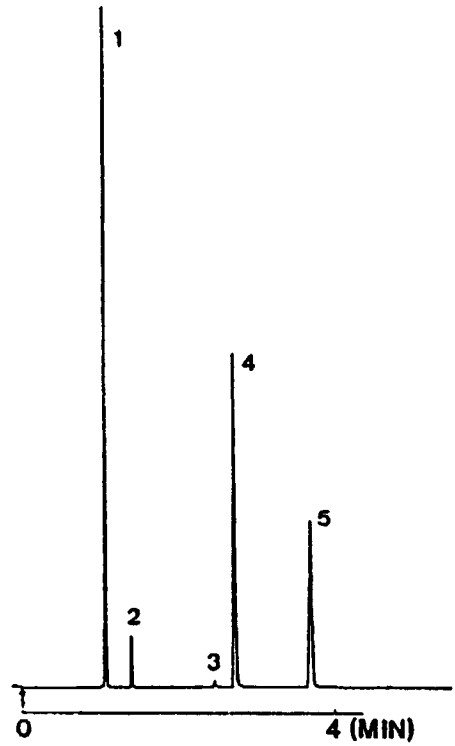

Fig. 7-40 Methanol and acetaldehyde in $C_1 - C_3$ hydrocarbons.

Column: 25 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: 100 °C;
Carrier: H_2, 70 kPa; Injection: Split; Detection: FID;
Peaks: 1 — methane; 2 — ethane; 3 — propane; 4 — methanol;
5 — acetaldehyde.

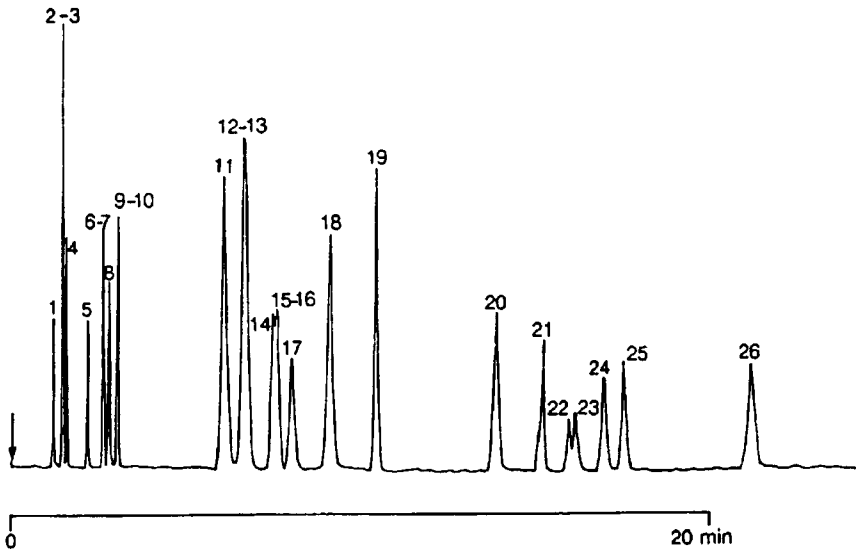

Fig. 7-41 Separation of $C_1 - C_4$ nitriles and $C_1 - C_4$ hydrocarbons.

Column: 10 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: 100 °C; Carrier: H_2, 2 ml/min; Injection: Split; Detection: FID; Sample: 1 – 3 ng per compound on the column; Courtesy: F. Raulin and L. Do, University Paris;
Peaks: 1 — methane; 2 — ethylene; 3 — acetylene; 4 — ethane;
5 — cyanogen; 6 — propylene; 7 — hcn; 8 — propane; 9 — allene;
10 — methylacetylene; 11 — isobutane; 12 — 1-butylene; 13 — isobutylene;
14 — butane; 15 — *trans*-2-butylene; 16 — ethylacetylene; 17 — *cis*-2-butylene;
18 — cyanoacetylene; 19 — acetonitrile; 20 — acrylonitrile; 21 — 1-pentene;
22 — pentane; 23 — 2-methyl-2-butylene; 24 — cyclopentane; 25 — propionitrile;
26 — methylacrylonitrile

perature can be about 40 – 60 °C higher while having the same capacity. Fig. 7-41 shows the separation of $C_1 - C_4$ nitriles and hydrocarbons isothermally at 100 °C. The carbonitriles all elute after the C_4 hydrocarbons with a comparable peak asymmetry.

Sulfur compounds

The porous polymer also provides good chromatography for sulfur(thio) substituted compounds. A series of sulfur compounds is shown in Fig. 7-42.

7.5.2 Halogenated Hydrocarbons

A typical group of compounds known for their volatility are the $C_1 - C_3$ halogenated hydrocarbons. Halogenated hydrocarbons are used on a large scale as solvents for a wide range of chemical products. They are also used for chemical reactions and as "driving

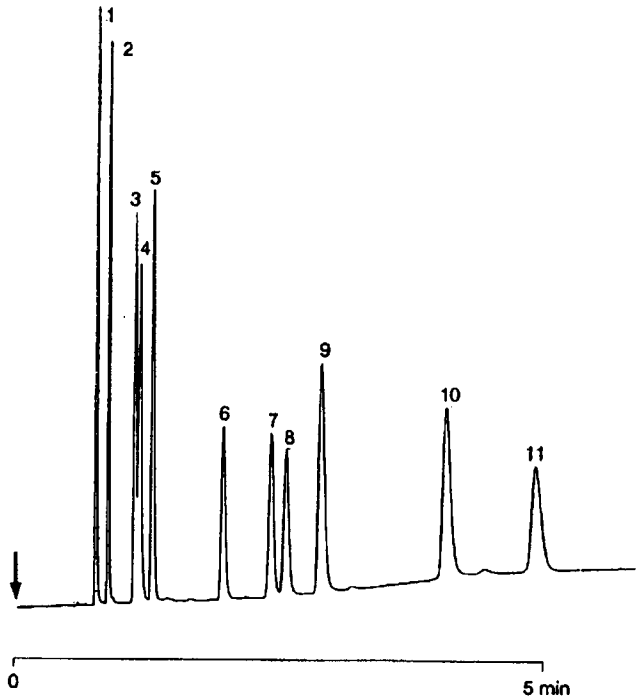

Fig. 7-42 Separation of sulfur compounds.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 μm; Oven: 210 °C – 250 °C, 15 °/min; Carrier: H_2,65 kPa; Injection: Direct; Detection: FID;
Peaks: 1 — 2-propanethiol; 2 — 1-propanethiol; 3 — 1-methyl-1-propanethiol; 4 — 2-methyl-1-propanethiol; 5 — 1-butanethiol; 6 — 1-pentanethiol; 7 — allyl sulfide; 8 — propyl sulfide; 9 — hexanethiol; 10 — heptanethiol; 11 — butyl sulfide.

gas" in pressure bottles. Due to their high volatility the $C_1 - C_3$ hydrocarbons are easily evaporated and released into the atmosphere. The carcinogenic action of many halogenated hydrocarbons has been recognized and they have to be used with special care.

Special methods have been developed by the EPA (Environmental Protection Agency, USA) to measure ppm/ppb levels of halogenated hydrocarbons in air, water and solids. A typical method widely used as standard method is the EPA 624 method which describes the analysis of 22 halogenated hydrocarbons in the range of $C_1 - C_6$ together with a number of aromatic hydrocarbons.

Another negative effect of halogenated hydrocarbons is the breakdown of the ozone layer which has been initiated by some halogenated hydrocarbons which are accumulating in the upper atmosphere. As a consequence the amount of UV radiation reaching earth is increasing, which increases the risks of cancer. These halogenated hydrocarbons, also known as "Freons" or CFC's (chloro-fluoro-carbons), have been widely used as refrigerant in refrigerators or as propellants, e.g., in hairsprays.

Much investment has been undertaken to find a suitable alternative, which will provide the same advantages but not the disadvantages. The use of multifluorinated hydrocarbons seemed to be one possibility; however, more research is necessary.

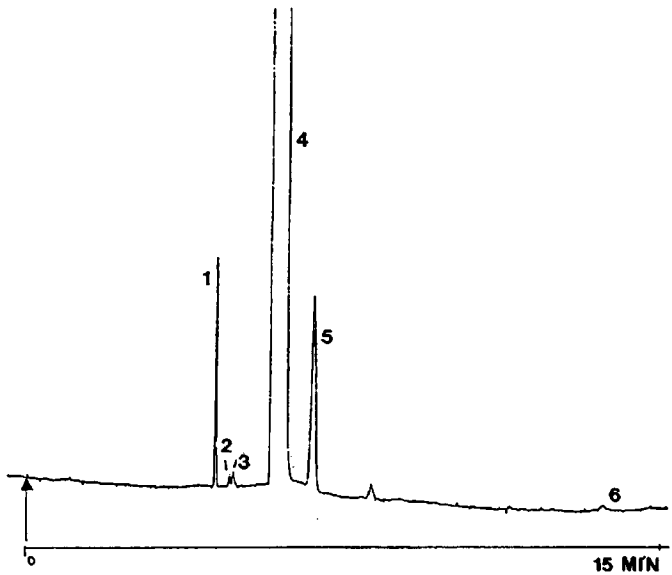

Fig. 7-43 Separation of Freons (chloro-fluoro-carbons) on methylsiloxane coated column.

Column: 50 m × 0.32 mm, fused silica, CP Sil 5 CB, D_f = 5 µm;
Oven: 30 °C – 100 °C, 10 °/min; Carrier: H_2, 70 kPa;
Injection: Split; Detection: FID; Peaks: 1 — CFC 23; 2 — CFC 32; 3 — CFC 143; 4 — CFC 22; 5 — CFC 12; 6 — CFC 21.

Separation of volatile halogenated compounds (CFC's)

For the general separation of volatile halogenated hydrocarbons a column should be used with a high retention. Since the halogenated hydrocarbons do not have a bonded group capable of hydrogen-bond formation, they can be analyzed on virtually any type of stationary phase giving symmetrical peaks. The most favored phases are the chemically bonded methylphenylsiloxanes with a film thickness of 1 – 3 μm.

For separation of CFC's the chemically bonded phases do not provide sufficient retention. Fig. 7-43 shows the separation of some CFC's on a 5 μm methylsiloxane coated capillary. The oven temperature was lowered to 30 °C to provide maximal capacity without cryogenic cooling.

Although there is resolution between the compounds in this mixture the typical peak broadening caused by the resistance to mass-transfer in the liquid phase is also seen. Fig. 7-44 shows the separation of a CFC mixture on a porous polymer ALOT column. This type of stationary phase offers the high retention which is required for separation of CFC's. Even by starting at a temperature of 100 °C the capacity factor for the PoraPLOT column is higher than with the 5 μm methylsiloxane started at 30 °C. For separating more volatile CFC's the "space" in the chromatogram of the porous polymer column is ideal. The tailing of peaks 4 and 12 in Fig. 7-44 is due to overloading. This phenomenon is typical for adsorption chromatography. On reducing the absolute amount of component injected the peak will become symmetrical.

Chloro-Fluoro-Carbons on aluminum oxide ALOT columns

Also aluminum oxide coated ALOT columns can be used for CFC separations. However, the behavior of aluminum oxide depends on the composition of the sample to be analyzed. As discussed previously for the separation of vinyl chloride (see Section 7.5.1), there are a number of halogenated hydrocarbons which can decompose on the active aluminum oxide surface. Depending on the type of degradation products formed, the aluminum oxide will be partly deactivated and retention behavior will be difficult to reproduce. Fig. 7-45 shown an analysis of Freon 12 and Freon 11 in a mixture of hydrocarbons. The

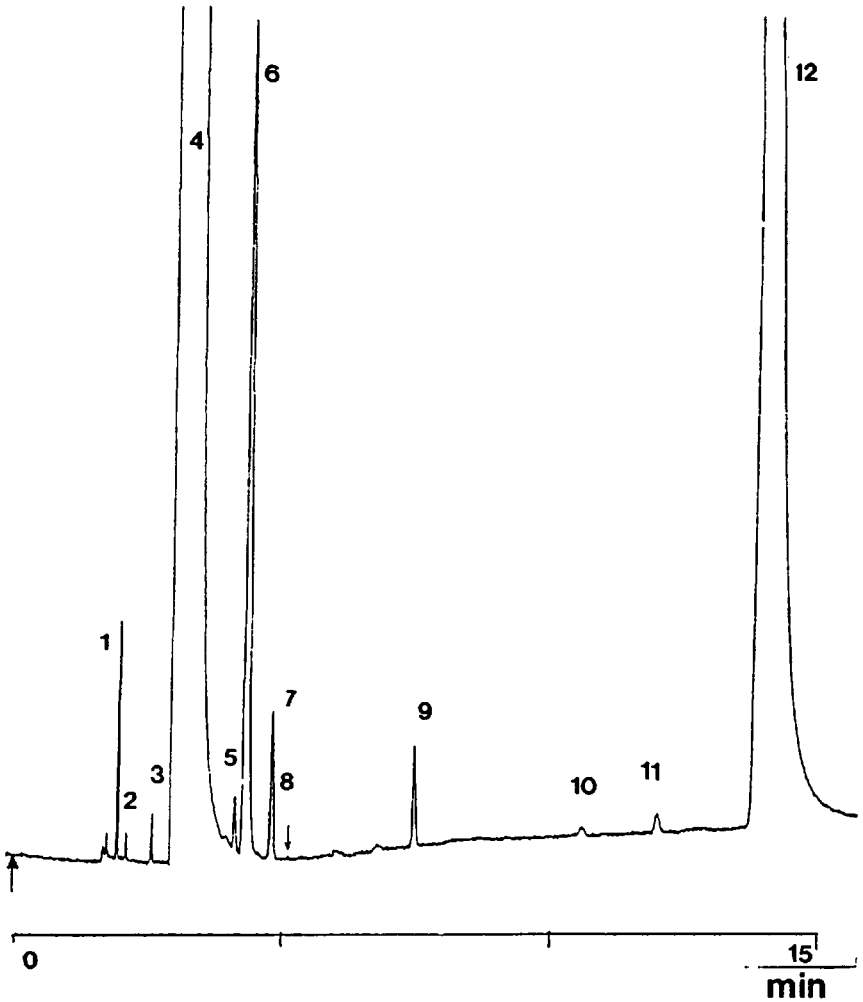

Fig. 7-44 Separation of halogenated hydrocarbons (chloro-fluoro-carbons).

Column: 25 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm;
Oven: 100 °C (3 min) – 150 °C, 10 °/min;
Carrier: H_2, 70 kPa; Injection: Split; Detection: FID;
Peaks: 1 — CFC 23; 2 — CFC 32; 3 — CFC 143a; 4 — CFC 22; 5 — CH_2Cl_2; 6 — CFC 12; 7 — CFC 31 unknown; 8 — CFC 142b; 9 — CFC 21; 10 — CFC 11; 11 — CF_3Cl_3; 12 — CFC 113.

separation is very good and analysis could be done down to ppm levels. (The distorted peak marked with "X" could be a CFC which is strongly adsorbed.) These results were also verified by other experiments which showed that aluminum oxide ALOT columns were well applicable for the analysis of fully halogenated hydrocarbons (T.Noy, J. Chromatogr. 393 (1987) 343).

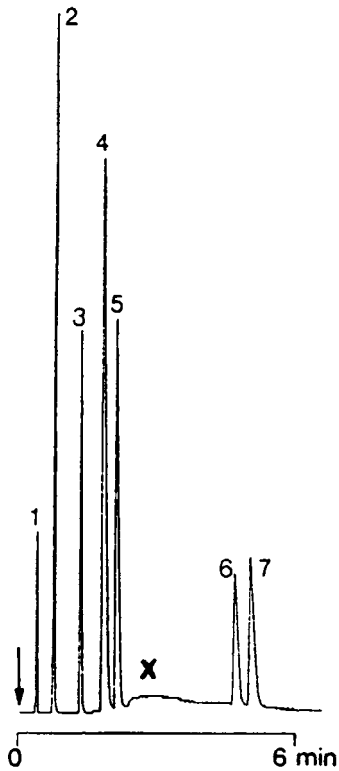

Fig. 7-45 Separation of halogenated hydrocarbons (chloro-fluoro-carbons).

Column: 50 m x 0.53 mm, fused silica, Al_2O_3/KCl, D_f = 10 μm;
Oven: 40 °C (1.5 min) – 75 °C, 10 °/min; Carrier: He, 6 ml/min;
Injection: Split; Detection: μ-TCD;
Peaks: 1 — air; 2 — propane; 3 — Freon 12 (CCl_2F_2); 4 — isobutane;
5 — butane; 6 — Freon 11 (CCl_3F); 7 — pentane.

As long as there were no C-H bonds in the CFC molecule, the eluting peak showed good recovery. With C-H bonds present the CFC was decomposed. The selectivity of aluminum oxide for CFC's is very high, as shown in Fig. 7-46. Due to the decomposition of the partly halogenated CFC's the quantitative analysis for these CFC's is very difficult.

Fig. 7-47 up to 7-49 shows the separation of several types of halogenated hydrocarbons on porous polymer coated ALOT columns.

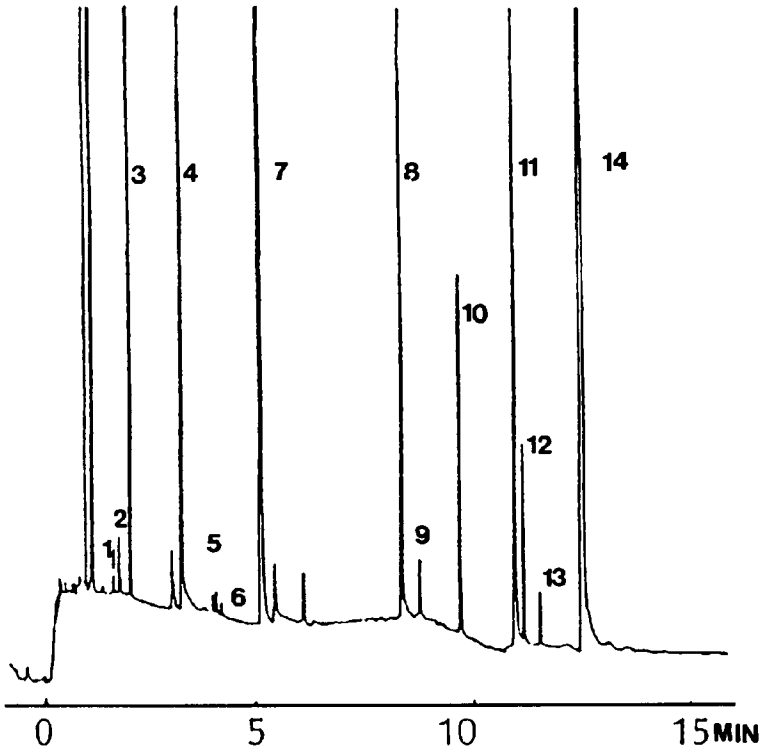

Fig. 7-46 Separation of chloro-fluoro-carbons on Al_2O_3/KCl ALOT column.

Column: 50 m x 0.32 mm, fused silica, Al_2O_3/KCl, D_f = 5 µm;
Oven: 80 °C – 200 °C, 10 °/min; Carrier: He, 80 kPa; Injector: Split;
Detector: ECD; Sample: 20 – 10.000 ppm;
Peaks: 1 — CF_3Br; 2 — C_2ClF_5; 3 — CCl_2F_2; 4 — CH_3Cl; 5/6 — $C_2Cl_2F_4$-isomers; 7 — CCl_3F; 8 — $C_2Cl_3F_3$; 9 — CH_2Cl_2; 10 — CCl_4; 11 — C_2HCl_3; 12 — $CHCl_3$; 13 — CH_3CCl_3; 14 — C_2Cl_4.

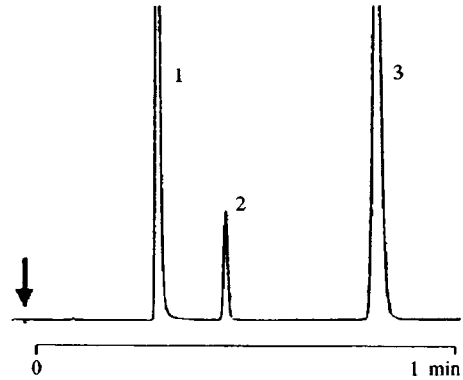

Fig. 7-47 Separation of very volatile chlorinated hydrocarbons.

Column: 25 m x 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 µm; Oven: 90 °C; Carrier: H_2, 10 ml/min; Injection: Direct, 10 µl headspace; Detection: FID; Sample conc.: 1 – 3%; Peaks: 1 — dichlorodifluoromethane; 2 — vinyl chloride; 3 — ethyl chloride.

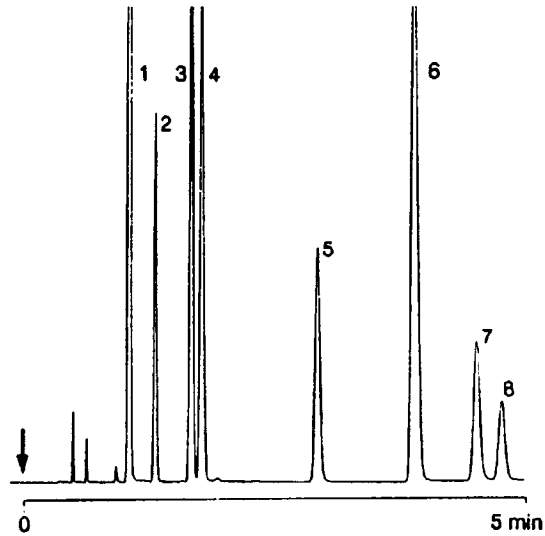

Fig. 7-48 Separation of chlorinated ethylenes.

Column: 25 m x 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 µm; Oven: 150 °C – 200 °C, 10 °C/min; Carrier: H_2, 10 ml/min; Injection: Direct, 10 µl headspace; Detection: FID; Sample conc.: 5 – 10%; Peaks: 1 — 1,1-dichloroethylene; 2 — *trans*-1,2-dichloroethylene; 3 — *cis*-1,2-dichloroethylene; 4 — 2-butanone; 5 — trichloroethylene; 6 — dimethyl disulfide; 7 — 4-methyl-2-pentanone; 8 — tetrachloroethylene;

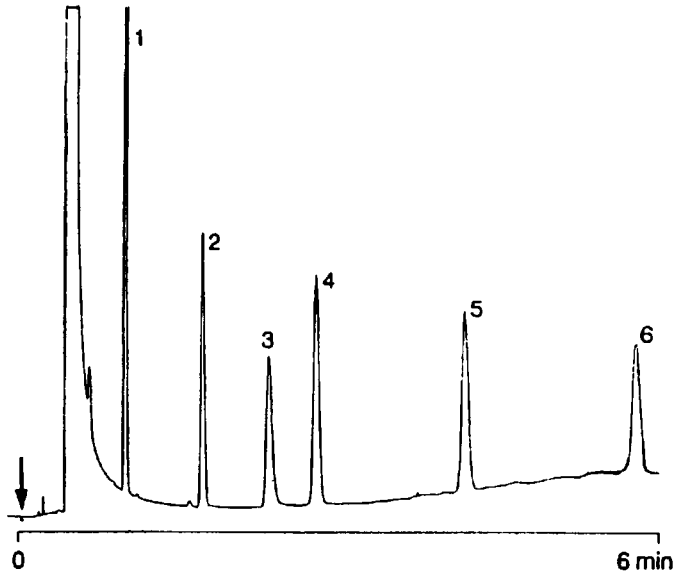

Fig. 7-49 Separation of halogenated methanes

Column: 25 m × 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 µm; Oven: 150 °C – 200 °C, 10 °/min; Carrier: H_2, 100 kPa; Injection: Direct, 100 µl Headspace; Detection: FID; Peaks: 1 — CH_2Cl_2; 2 — $CHCl_3$; 3 — CCl_4; 4 — $CHBrCl_2$; 5 — $CHBr_2Cl$; 6 — $CHBr_3$.

7.5.3 Solvents and Water

A wide application field for porous polymer type adsorbents has historically been the separation of solvents with packed columns. The porous polymers could be used for all types of solvents and by choosing the porous polymer with the right selectivity, most separations could be realized. On using the capillary ALOT column a high plate number is obtained so that only a few selectivities are sufficient to do most of the separations.

A typical characteristic of the porous polymer is its strong hydrophobic character. Due to this there is virtually no interaction with hydroxyl groups present in the compounds to be analyzed. As a result the retention volume of water will be very low. Fig. 7-50 shows the separation of water, methanol and ethanol on a porous polymer coated capillary. The water peak elutes almost without retention and with good symmetry

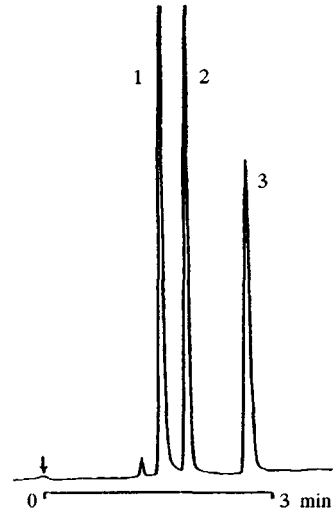

Fig. 7-50 Separation of water, methanol and ethanol.

Column: 10 m x 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: 175 °C;
Carrier: H_2, 50 kPa; Injection: Split; Detection: µ-TCD;
Peaks: 1 — water; 2 — methanol; 3 — ethanol.

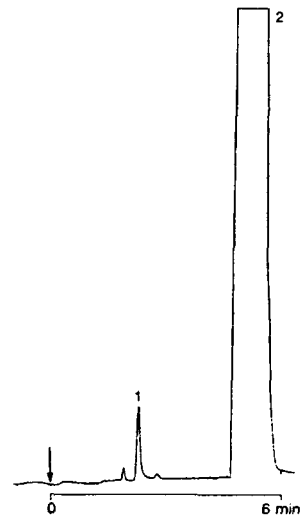

Fig. 7-51 Water in acetone.

Column: 10 m x 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 µm; Oven: 175 °C;
Carrier: H_2, 50 kPa; Injection: Split; Detection: µ-TCD;
Peaks: 1 — water (1000 ppm); 2 — acetone.

before the methanol peak. This particular separation was performed isothermally at 175 °C. This characteristic makes the porous polymer very suitable for analyzing water in different types of solvents. Since the small water peak will elute before the solvent it can be measured down to low levels. An example is shown in Fig. 7-51 were a sample of acetone is analyzed. The first eluting peak will correspond to approximately 1000 ppm water.

Although there is very little interaction between water and the porous polymer, the water peak will be retained at low temperatures. Fig. 7-52 shows the separation of natural gas at a temperature of 100 °C.

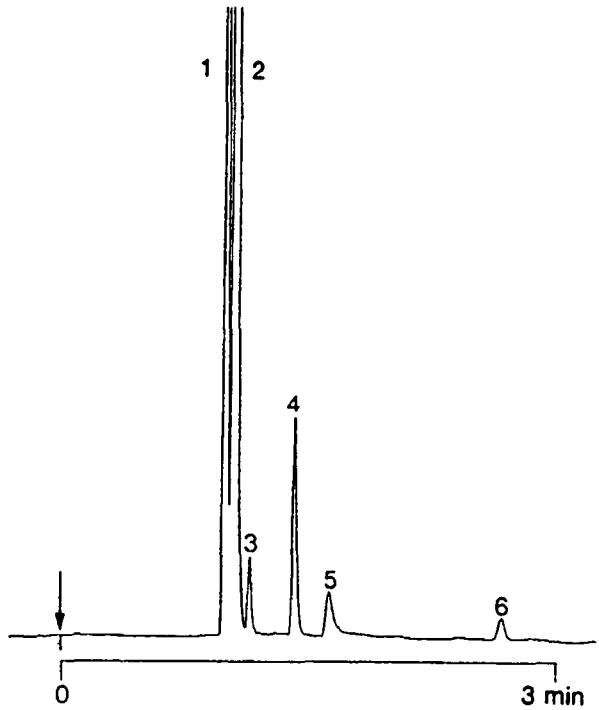

Fig. 7-52 Water in natural gas.

Column: 10 m × 0.32 mm, fused silica, PoraPLOT Q, D_f = 10 μm; Oven: 100 °C;
Carrier: H_2, 50 kPa; Injection: Split; Detection: μ-TCD;
Peaks: 1 — nitrogen; 2 — methane; 3 — carbon dioxide; 4 — ethane;
5 — water; 6 — propane.

Table 7-2
Solvents analysed on porous polymer ALOT columns.

Compound type	Number of carbon atoms	Compound type	Number of carbon atoms
Alcohols	1 – 8	Hydrocarbons	5 – 10
Aldehydes	1 – 5	Ketones	2 – 10
Aromatics	6 – 10	Nitriles	1 – 5
Esters	2 – 10	Thiols	2 – 7
Ethers	2 – 10	Chlorinated hydrocarbons	1 – 4
Fatty acids	1 – 5		

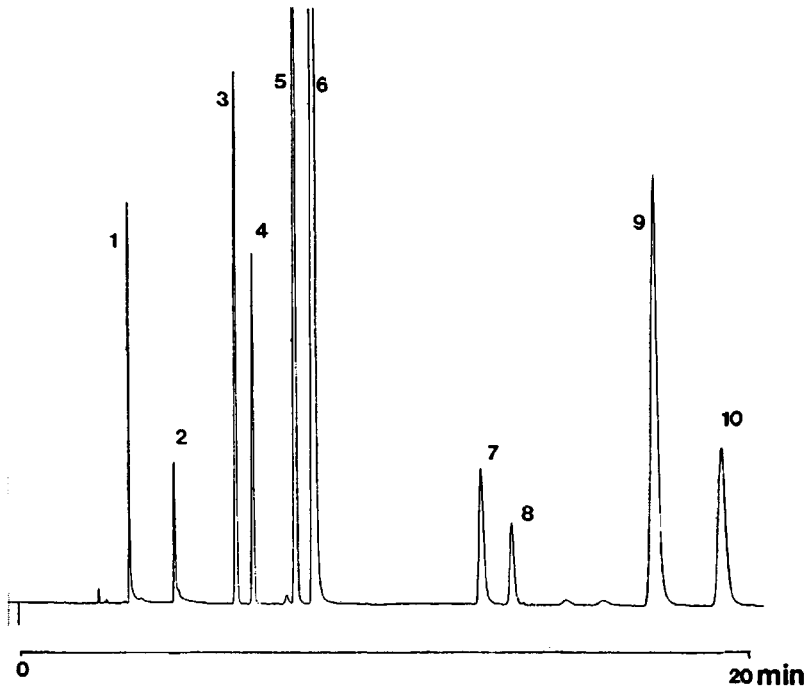

Fig. 7-53 Separation of solvents.

Column: 25 m x 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 µm; Oven: 150 °C;
Carrier: H_2, 60 kPa; Injection: Split; Detection: FID;
Peaks: 1 — methanol; 2 — ethanol; 3 — acetone; 4 — methylene chloride;
5 — diethyl ether; 6 — pentane; 7 — tetrahydrofuran; 8 — ethyl acetate;
9 — hexane; 10 — benzene.

The water peak (peak 5) elutes between ethane and propane with a capacity factor of about 0.8. Detection limits depend on the type and condition of the detector used. With the TCD it should be possible to measure water down to 10 – 20 ppm.

Figures 7-53 and 7-54 show typical separations of solvents with different polarities which are used in the analytical laboratory. The porous polymers can

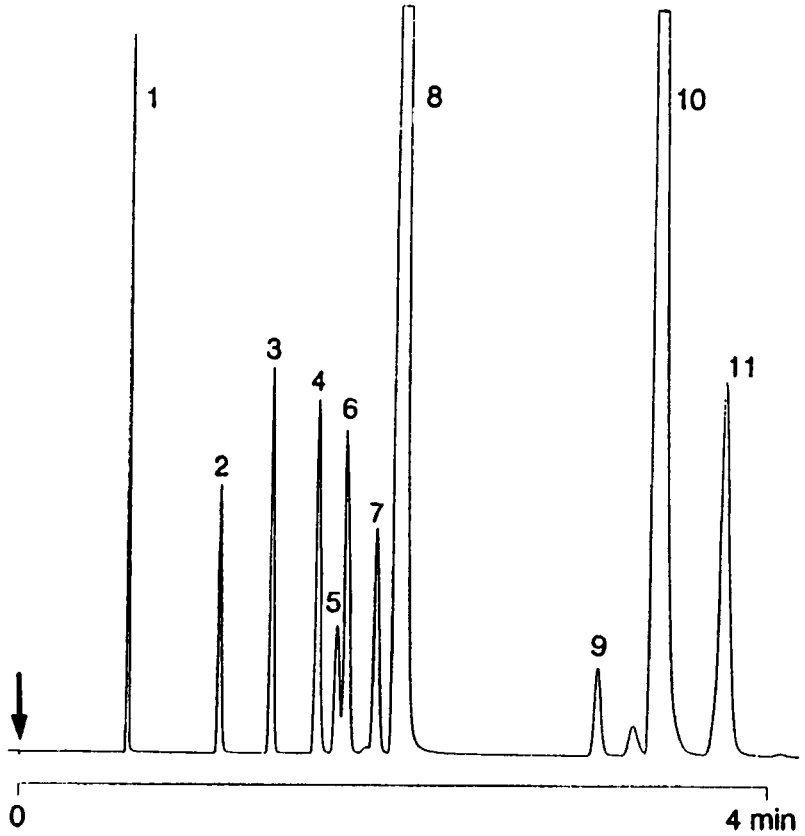

Fig. 7-54 Separation of solvents.

Column: 25 m × 0.53 mm, fused silica, PoraPLOT Q, D_f = 20 μm;
Oven: 100 °C – 200 °C, 10 °/min; Carrier: H_2, 100 kPa;
Injection: Direct, 10 μl headspace; Detection: FID;
Peaks: 1 — methanol; 2 — ethanol; 3 — acetonitrile; 4 — acetone;
5 — isopropanol; 6 — dichloromethane; 7 — methyl acetate; 8 — pentane;
9 — ethyl acetate; 10 — hexane; 11 — benzene.

be used for all types of solvents with different functional groups. As long as the molecule is volatile enough to be eluted from the porous polymer adsorbent, it can be analyzed. The maximum operating temperature of porous polymers is about 250 °C. Up to this temperature the wide range of solvents can be analyzed (see Table 7-2).

7.6 Separation of $C_1 - C_{12}$ Hydrocarbons

The separation of the $C_1 - C_{12}$ range of hydrocarbons is usually done on methylsiloxane liquid phases. There are a few specific separations which can only be realized by adsorption chromatography. Although adsorption chromatography is not ideal for the higher

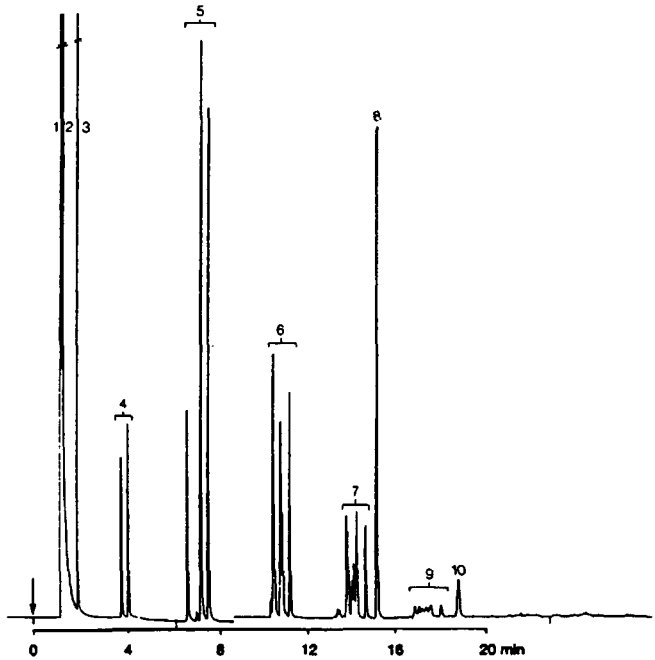

Fig. 7-55 Separation of $C_1 - C_8$ hydrocarbons in natural gas.

Column: 50 m × 0.53 mm, fused silica, Al_2O_3/KCl, D_f = 10 µm;
Oven: 30 °C – 200 °C, 10 °/min; Carrier: H_2, 50 kPa; Injection: Direct;
Detection: FID; Sample: Natural gas; Peaks: 1 — methane; 2 — ethane;
3 — propane; 4 — C_4-hydrocarbons; 5 — C_5-hydrocarbons;
6 — C_6-hydrocarbons; 7 — C_7-hydrocarbons; 8 — benzene;
9 — C_8-hydrocarbons; 10 — toluene.

boiling compounds there are some applications for aluminum oxide and molecular sieves.

7.6.1 $C_1 - C_{10}$ Hydrocarbons on an Aluminum Oxide ALOT Column

The aluminum oxide ALOT column is ideal for the separation of $C_1 - C_5$ hydrocarbons. The column's upper temperature is 200 °C which allows elution of hydrocarbons up to C_{10}. This is important, for instance, in natural gas analysis. Fig. 7-55 shows the analysis of natural gas on an aluminum oxide coated capillary. The benzene and toluene peaks (peak 8 and 10) are well separated from the other hydrocarbons. Very typical for the aluminum oxide ALOT column is the group-like elution of hydrocarbons of the same carbon number. All the (saturated) hydrocarbons seem to elute in quite a small window. In this analysis hydrocarbons elute up to C_8. In Fig. 7-56 a naphtha sample was analyzed which shows hydrocarbons up to C_9. The same type of elution pattern is also observed for the C_9 hydrocarbons.

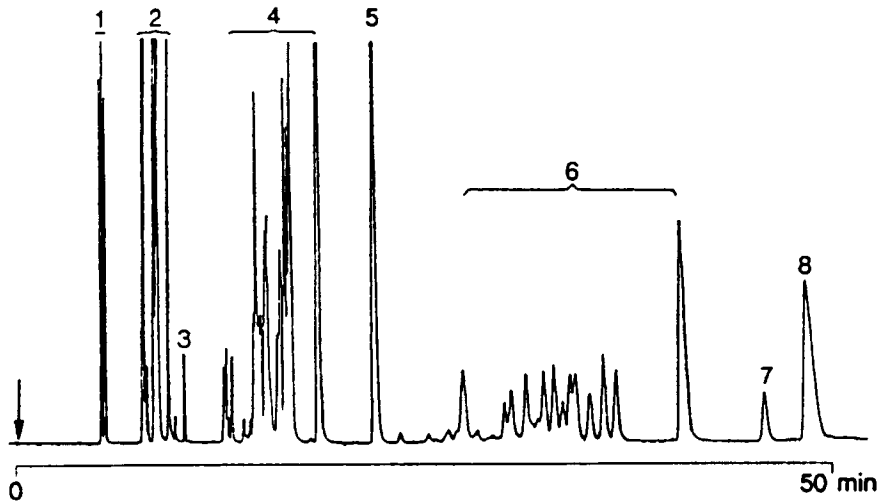

Fig. 7-56 Separation of $C_6 - C_9$ hydrocarbons in naphtha.

Column: 50 m x 0.32 mm, fused silica, Al_2O_3/KCl, D_f = 5 µm; Oven: 190 °C;
Carrier: He, 150 kPa; Injection: Split,; Detection: FID;
Peaks: 1 — C_6-hydrocarbons; 2 — C_7-hydrocabons; 3 — benzene;
4 — C_8-hydrocarbons; 5 — toluene; 6 — C_9-hydrocarbons;
7 — ethylbenzene; 8 — *m*- + *p*-xylene.

7.6.2 Naphthene/ Paraffin Separation on Molsieve 13X

Molsieve 13X is widely used in packed columns because of its specific separation characteristics in PNA analysis. The molecular "sieving" effect results in a very specific separation between naphthenic and aliphatic hydrocarbons of a certain carbon number, making a group-like separation and quantitation possible. This separation is usually done on a packed column with relatively low separation power. A direct comparison between a packed and a capillary Molsieve 13 X column is shown in Fig. 7-57. On both columns a sample of naphtha was analyzed using optimal conditions. The analysis on the capillary column was four times faster with a much higher resolution. Especially the separation efficiency of hydrocarbons of C_8 and higher is much better than on the packed column. The resolution on a 10 meter capillary ALOT column is high enough to resolve the fractions even into some of the individual isomers. Also the elution temperature was much lower due to the higher phase ratio in the capillary column. The elution temperature for n-undecane on the ALOT column was 380 °C while on the packed column a temperature of 470 °C was required.

As such a high resolution is not always required for PNA analysis the flow rate through the Molsieve 13X column can be increased by a factor of 4–8 which will reduce analysis time to about 7–8 minutes. Overloading phenomena will occur quite soon on this type of Molsieve 13X ALOT column due to the low capacity.

The average layer thickness of the column used for the application in Fig. 7-57 is about 0.2 μm.

On using split inlet systems the injection of small sample volumes will provide very good results; however, direct injection without splitting was not successful.

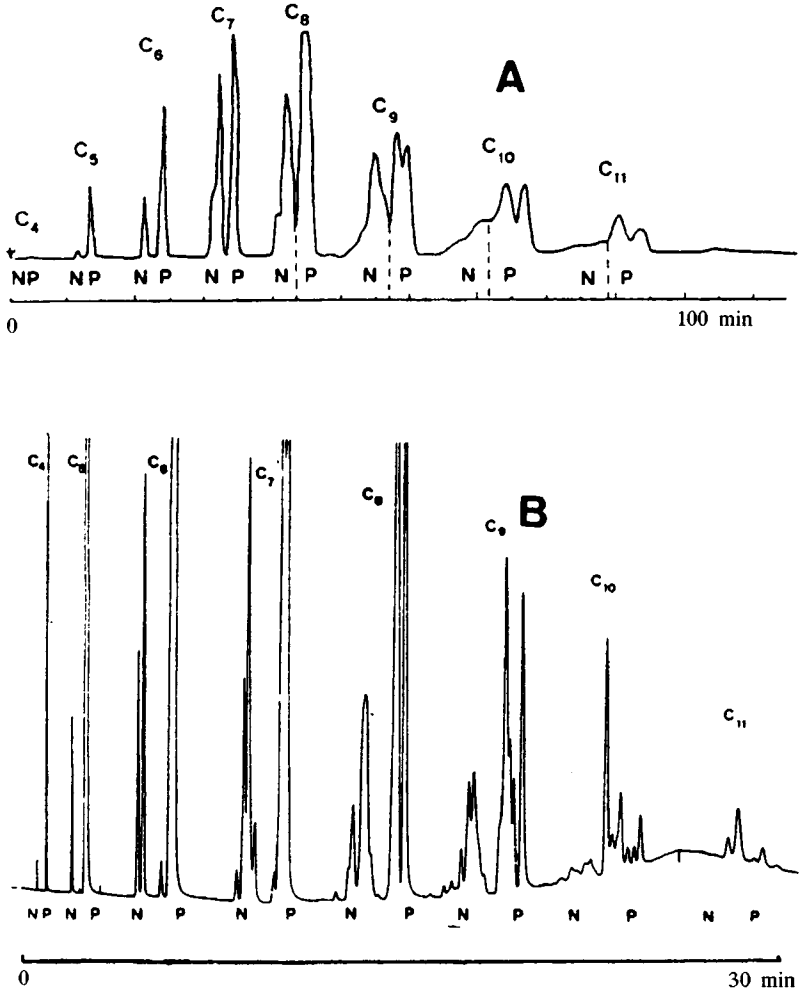

Fig. 7-57 $C_4 - C_{11}$ Naphthene/paraffin separation on Molsieve 13X ALOT column.

Column A: 5 m × 1/4" Molsieve 13X;
Oven: 150 °C – 500 °C, 4 °/min; Carrier: N_2, 300 kPa;

Column B: 10 m × 0.5 mm SS Molsieve 13X ALOT;
Oven: 150 °C – 380 °C, 10 °/min; Carrier: N_2, 12 kPa;

Injection: Split; Detection: FID.

Conclusion

Today, after traveling a long and thorny path, adsorption capillary chromatography has become a routine method in analytical practice. Although the development of this method has not yet finished, it would now appear possible to formulate some of the major results acieved in adsorption open tubular column development.

The application of gas adsorption capillary chromatography allows the analyst to improve some of the main characteristics of chromatographic separation (efficiency, selectivity, analysis speed, etc.).

The field of practical application of adsorption capillary columns is in a state of continuous development. These columns are utilized to great advantage in the gas, chemical and petrochemical industries, environmental analysis, etc.

The basic types of chromatographic adsorbents (alumina, molecular sieves, graphitized carbon black, organopolymeric adsorbents, etc.) can be used in adsorption capillary open tubular columns.

The theories of retention and efficiency (HETP) reflect the main features of adsorption capillary columns.

In the future it should prove worthwhile to pay more attention to the development of fields of gas adsorption capillary chromatography such as adsorption capillary columns in multidimensional gas chromatography, adsorption capillary columns with nonporous (or slightly porous) inner surfaces, theory of separation, optimization, application of modified

chromatographic methods, utilization of new selective adsorbents.

This book is devoted to adsorption capillary chromatography, a new method in routine analytical gas-solid chromatography. We should like to emphasize the important role of method in science and industry and to close this book by quoting Pavlov:

"Science moves in fits and starts, depending on the progress in methods of research. Every step forward in method takes us a step higher, affording a broader view of the horizon and of objects that were invisible before" (I.P. Pavlov, Nobel Prize Winner 1904).

Appendix

Since preparation of the manuscript of this book, various publications relating to capillary adsorption chromatography have appeared. The following selection is recommended to the reader:

1. De Vanssay, E., Capilla, P., Do, L., Sernberg, R., Raulin, F.: Gas Chromatography of Titan's Atmosphere. IV. Analysis of Permanent Gases in the Presence of Hydrocarbons and Nitriles with a Molsieve PLOT Capillary Column. J. Chromatogr., 1993, Vol. 639, pp. 255–259.
2. Sidisky, L.M., Robillard, M.V.: Carbon Layer Open Tubular Columns. J. HRC, 1993, Vol. 16, pp. 116–119.
3. Bruner, F., Crescentini, G., Mangani, F.: Graphitized Carbon Black. A Unique Adsorbent for Gas Chromatography and Related Techniques. Chromatographia, 1990, Vol. 30, pp. 565–572.
4. Konyukova, S.V., Maksimov, V.N., Zenkevich, I.G.: Identification of Fluoroorganic Compounds from Gas Chromatographic Retention Indices. Zh.prikl. khimii, 1994, No.1, pp.135–137 (in Russian).
5. Castello, G.,Vezzani, S., Moretti, P.: The Selectivity and Polarity of Carbon Layer Open Tubular Capillary Columns Modified with a Polar Liquid Phase. J. HRC, 1994, Vol. 17, pp. 31–36.
6. Menaidenko, S.A., Belyakova, L.D., Larionov, O.G., Alishoev, V.R., Berezkin, V.G.: Chromatographic Properties of Barium Sulfate Layer Open Tubular Capillary Columns Modified with Different Polymers, Zh. Fiz. khimii, 1993, Vol. 67, pp. 2033–2037 (in Russian).
7. Alishoev, V.R., Berezkin, V.G., Malyukova, I.V.: Gas Adsorption Chromatography on Open-Tubular Capillary Columns with Aluminum Oxide, Zavodsk. laboratoriya, 1994, Vol. 60, pp. 6–7 (in Russian).
8. Berezkin, V.G., Malyukova, I.V., Alishoev, V.R.: Dependence of Retention of Organic Compounds on Carrier Gas Pressure in Capillary Adsorption Chromatography, J. Chromatogr. A 1995, Vol. 699, pp. 155–159.

9. Berezkin, V.G., Malyukova, I.V., Alishoev, V.R., De Zeeuw, J.: Influence of the Carrier Gas on Retention Capillary Gas–Solid Chromatography, J. HRC, 1996, Vol. 19, pp. 272–276.

10. De Zeeuw, J.: Analysis of Natural Gas Using a Porous-Polymer-Coated Capillary Column and Temperature Programming, LC-GC International, 1994, Vol. 4, No. 12, pp. 36–38.

11. De Zeeuw, J., Buyten, J., Peene, J., Mohnke, M., LC-GC International, 1994, Vol. 7, No. 11, pp. 644–651.

12. Majors R.E. LC-GC International. New Chromatography Columns and Accessories at the 1995 Pittsburgh Conference, Part II, LC-GC Int., 1995, Vol. 8. No. 6, pp. 312–323.

13. Bruner, F., Attarann Rezai, M., Laattanzi, L.: New GC Quartz-Lined Aluminium Capillary Columns Coated with Graphitized Carbon Black Modified by Liquid Phase, Chromatographia, 1995, Vol. 41, pp. 403–406.

14. Peltonen, K., Vaaranrinta, R.: Sampling and Analysis of 1,3-Butadiene in Air by Gas Chromatography on a Porous-Layer Open-Tubular Fused-Silica Column J. Chromatogr., A, 1995, Vol. 710, pp. 237–241.

15. De Zeeuw, J., Luong, J.: Separation of Low ppm Levels of Fixed Gases and Impurities in Hydrogen Feed Stocks using Metal Capillary PLOT Columns and Valve Switching Techniques. In: Book of Abstracts presented at Pittcon '96 March 3–8, 1996. McCormick Place, Chicago, Illinois, 152p.

16. De Zeeuw, J., Reinkofer, R., van Zee, H.: Increased Temperature Stability for Styrene-Divinylbenzene Porous Polymer Coated PLOT Columns. Ibid. 406 P.

17. De Zeeuw, J., Luong, J.: The Design and Optimization of a Bench Top Fixed Gas Analyzer using Metal Capillary Column Technology. Ibid. 413p.

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