Capillary Gas Adsorption Chromatography

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"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."

——Ivan Pavlov, Nobel Prize Winner, 1904

Contents

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Overview

The present state of gas–solid chromatography on open capillary columns is reviewed. The history of the method, its role in gas chromatography, procedures used to obtain the columns, fundamentals underlying chromatographic zone broadening, and applications of such columns are discussed.

1. Introduction

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

At present, gas chromatography is one of the major analytical methods in chemistry. Gas chromatographic methods are widely used in industry, agriculture, environmental control, medicine, and research.

Gas chromatography is of two types: gas–liquid[1–5] and gas–solid.[1–4,6,7] Although the latter is less popular, it is used in such important fields as isotope separation and volatile compound determination, where it exhibits certain advantages over its gas–liquid (gas–liquid–solid) counterpart.

Advantages and limitations of gas–solid chromatography are listed in Table I. It is evident that it is characterized by a number of advantages that overbalance its disadvantages. Note that some of the disadvantages, for example, chromatographic zone broadening, irreversible adsorption of the chromatographed compounds, or their catalytic conversions, can be ov-

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TABLE I. Advantages and Limitations of Gas-Solid Chromatography

advantages	limitations
1. high adsorbent stability over a wide temperature range and reduced detector background	1. chromatographic zone asymmetry as a result of nonlinear adsorption isotherm for a number of analyzed compounds
2. increased structural selectivity in the separation of geometric isomers (e.g., using molecular sieves or graphitized carbon black)	2. strong dependence of the retention on the sample size
3. high chemical selectivity when using complexing agent as an adsorbent (e.g., solid silver nitrate)	3. 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
4. enhanced adsorbent capacity permits separation of gases and volatile compounds at room temperature	4. more probable losses of the analyzed compound as a result of irreversible adsorption or catalytic conversions in the separation process
5. enhanced chemical stability of a number of adsorbents, ensuring the analysis of agressive compounds	5. limited number of commercially available adsorbents for gas-solid chromatography

TABLE II. 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 1000–5000 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 application of gas–liquid–solid chromatography is becoming wider due to the decrease of separation temperature

ercome by modification of the sorbent used. This modification can be effected by various techniques, most frequently by silanization (see, e.g., ref 3 and 6), by using small amounts of a stationary liquid phase (see, e.g., ref 3, 5, and 6), or by using heavy adsorbable carrier gases (see, e.g., ref 6–14). It is believed that the last technique offers the best promise, as it helps not only to modify the adsorbent but to perform a gradient elution by changing the concentration of a "heavy" adsorption-active component in the inert carrier gas as well.

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 II).

M. Golay, the founder of capillary chromatography, first proposed using open capillary columns with a sorbent layer on the inside 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 large thin layer of packing material in the remaining space on the periphery? The answer is why not indeed? I believe that such columns constitute nearly ideal columns for a wider range of analysis than present-day smooth tubular columns".[15]

As correctly stated by Ettre,[16] the idea of making a column with a porous sorbent layer on the inside 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 glasses by trimethylchlorosilane during capillary drawing

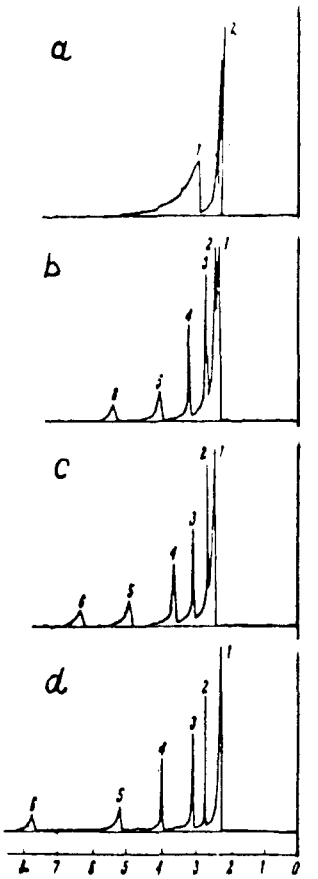

Figure 1. Chromatograms for vapor mixtures of organic compounds on open glass capillary columns whose inside surface is modified by various methods:[17] (1) acetone; (2) *n*-hexane; (3) benzene; (4) *n*-heptane; (5) *n*-octane. (a) Unmodified capillary column; (b) unmodified capillary column whose inside wall surfaces are coated with a silicone oil film; (c) capillary column modified with trimethylchlorosilane in the process of capillary drawing from a wide glass tube; (d) trimethylchlorosilane-modified capillary column whose inside wall surfaces are coated with a silicone oil film.

Kalmanovsky, Kiselev, and co-workers[17] made the following observations: "On nonmodified capillaries the separation was poor (see Figure 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 Figure 1b). The trimethylchlorosilane-modified capillary surfaces (Figure 1c) are distinguished by better separation characteristics as compared with those of the nonmodified

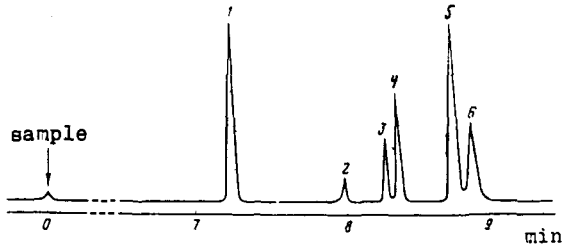

Figure 2. Separation chromatogram for hydrogen nuclear-spin isomers and isotopes on a capillary adsorption glass column.[19] Column length, 30 m; adsorbent, dry silica, 20 μm thick; separation temperature, 77.4 K; carrier gas, neon. (1) Helium; (2) paraprotium; (3) orthoprotium; (4) protium deuteride; (5) orthodeuterium; (6) paradeuterium.

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 a gas–solid variant of capillary chromatography".[17] Kalmanovsky and co-workers then noted that when the modified surface was coated with a silicone oil film, a better separation effect (Figure 1d) was obtained as compared with that in the case of the nonmodified capillary (Figure 1b). It should be noted that the modification was accomplished by the authors[17] in an unusual manner, i.e., in the process of drawing the capillary from a tube. The tube was preliminarily filled with liquid trimethylchlorosilane. The high temperature (ca. 700 °C) appears to lead to trimethylchlorosilane destruction and, as a result, formation of an adsorption layer on the glass surface of the capillary inside walls. The chromatograms shown in Figure 1 were obtained at 25 °C by chromatographic separation on capillary columns 15–20 m long and 0.3 mm across.

In 1961–1962 Mohnke and Saffert[18,19] obtained a silica layer on Jena glass capillaries after a prolonged (30 h) etching of the inside surface of the capillaries with aqueous ammonia solution at 170–180 °C. The thickness of the resultant silica layer was 10–20 μm. Note that their studies revealed a very important application of gas chromatography, viz., separation of gaseous isotopes and nuclear-spin isomers. Figure 2[19] 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.

A radically new method for preparing capillary adsorption columns, based on the application of an adsorbent layer on the inside capillary walls from a suspension, was proposed by Halasz and Horvath.[20,21] In such columns the production of the adsorbent layer is independent of the material of the inside column walls, its modification, etc. Figure 3[20] presents a chromatogram for a rapid separation of aromatic hydrocarbons on graphitized carbon black, a layer of which was applied on the inside copper capillary walls. Figure 4 shows a chromatogram for a rapid separation of freons on a capillary column with a boehmite (Al_2O_3) layer. The separation was performed by Kirkland[22] on a 75 m × 0.5 mm column.

Petitjean and Leftault,[24] Schwartz,[25] 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[26–30] as well as Ilkova and Mistryukov.[31]

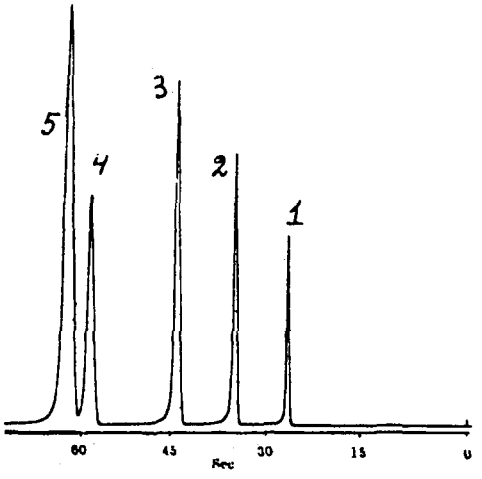

Figure 3. Separation chromatogram for aromatic hydrocarbons on an open capillary column with graphitized carbon black.[20] Column, silver-plated copper, 15 m × 0.25 mm; carbon black content, 5.4 mg/m; temperature, 245 °C; carrier gas, hydrogen. (1) Benzene; (2) toluene; (3) ethylbenzene; (4) *m*-xylene; (5) *o*- and *p*-xylenes.

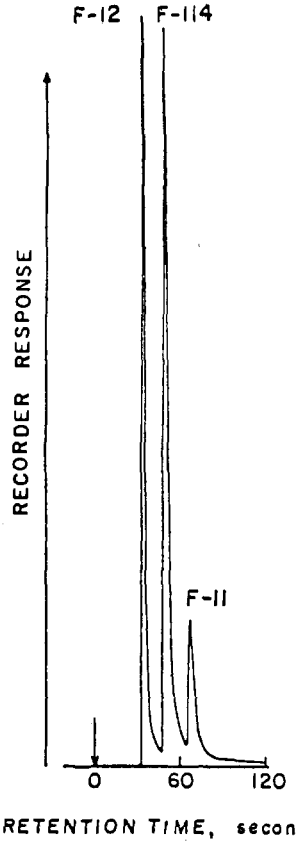

Figure 4. Separation chromatogram for some freons on an open capillary column with a boehmite (Al_2O_3) layer.[22] Column, 7.5 m × 0.5 mm; temperature, 22 °C.

An important contribution to the development of capillary chromatography using columns with inside walls coated with a porous layer, among which there are capillary columns with an adsorbent layer, was made by Ettre, Purcell, and co-workers.[32–34] Of special interest is their review[35] devoted to the theory, methods of manufacture, applications, and future of surface-coated open capillary columns.

Even the early works on capillary adsorption columns suggest, first, a remarkable resolving power of the me-

TABLE III. Proposed Classification of Open Capillary Columns

classification criterion	open tubular capillary column	
presence (or absence) of a porous adsorbent layer or solid support on the inside column walls presence (or absence) of a stationary liquid phase on the inside column walls	1. nonporous layer open tubular column (NONPLOT) (open capillary column with smooth (nonporous) inside wall surface) 1.1. adsorption (nonporous) wall open tubular column (AWOT) (open capillary adsorption columns with a nonporous wall surface) 1.2. wall-coated open tubular column (WCOT)	2. porous layer open tubular column (PLOT) (open capillary columns with a porous layer on the inside walls) 2.1. adsorption layer open tubular column (ALOT) (open capillary adsorption columns with a porous adsorbent layer on the inside walls) 2.2. support-coated open tubular column (SCOT)

thod, especially as regards isotope separation capabilities, and, second, its rapidity.

In the past few years interesting studies have been made, and applications of open capillary gas adsorption columns have been suggested by de Nijs and de Zeeuw.[36-38] Chrompack (The Netherlands) has arranged for commercial production of some types of these columns, using alumina, molecular sieves, and polymer adsorbents.[39-42]

A vital problem in gas chromatography seems to be classification of capillary columns. Some authors believe that the terms "open capillary columns with a porous layer on the inside wall surface" and "open capillary columns with a solid carrier layer on the inside walls" are badly confused. One reason for this situation is an insufficiently strict classification of capillary columns. We propose a more general classification based on the following criteria: (1) the presence (or absence) of a porous layer on the inside capillary column walls and (2) the presence (or absence) of a stationary liquid phase layer on the inside column walls (see Table III).

Nowadays only three of the six possible types of columns are used: open capillary columns with a nonporous wall surface coated with a stationary phase (wall-coated open tubular (WCOT)); open capillary columns with a porous layer on the inside walls (porous-layer open tubular (PLOT)); open capillary columns with a porous layer impregnated with a stationary-phase layer (support-coated open tubular (SCOT)).

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

In the chromatographic literature open capillary adsorption columns with a porous layer on their inside 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 nonporous (unextended) wall surface (AWOT).

The present review discusses open adsorption columns, i.e., AWOT and ALOT columns (see Table III), and compares their characteristics and analytical features.

2. On the Role of Open Capillary Adsorption Columns in Gas Chromatography

Open capillary columns for gas–liquid–solid chromatography (gas–liquid chromatography) are widely used in analytical practice (see, e.g., ref 43–49). The separation of compounds on these columns is mainly based on differences in the interactions of the molecules of the chromatographed compounds with a liquid stationary phase. However, gas–solid chromatography is equally expedient, and sometimes it is the only method possible for a number of problems.[50]

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*[6] Kiselev and Yashin wrote: "Significant progress has been attained in gas adsorption chromatography. The field of its uses has been materially extended to embrace now 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 adsorption/absorption chromatography, relying on the combined utilization of adsorption and dissolution (or near dissolution) processes. New potentialities are offered now by adsorption chromatography due to the use of enhanced pressures and strongly adsorbable carrier gases."

The remarkable features of gas–solid chromatography (GSC) have also been emphasized by Giddings:[51a] "One immediate advantage of GSC resides in the fact that a surface coated with any reasonable degree of uniformity will exhibit a C_k[51] value substantially smaller than C_l[51] 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 retentive mechanisms. The rigidly fixed forces of a solid surface contrast sharply with the fluid forces of a liquid phase." Obviously, gas–solid chromatography is characterized not only by certain advantages but also by a number of disadvantages as well. Its advantages and limitations are compared in Table I. It is evident that the odds are in favor of this method. This is confirmed by the practical applications of gas chromatography in which columns with such adsorbents as alumina, silica gel, graphitized carbon black, molecular sieves, organic polymers, etc. are widely used.[3,6]

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, open capillary columns are distinguished by a higher separating power. Thus the specific efficiency of capillary columns is 2000–4000 theoretical plates per meter whereas for packed columns this value is far

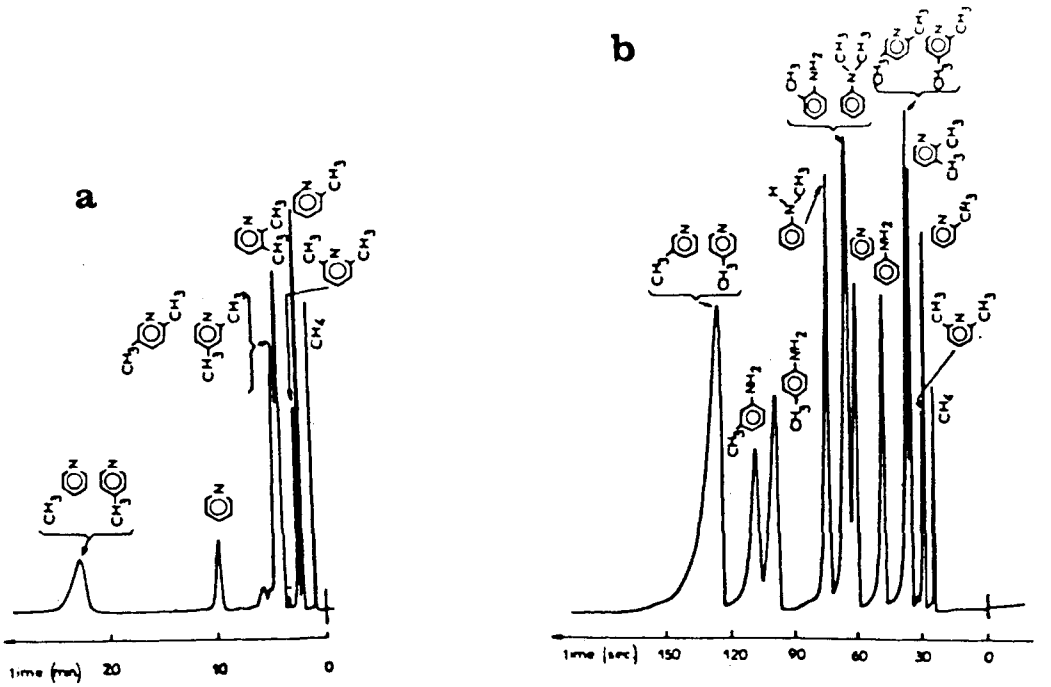

Figure 5. Separation chromatograms for nitrogen-containing compounds on a packed (a) and open capillary (b) column.[52] (a) Column, 4 m × 2 mm; sorbent, 5% cobalt phthalocyanine on Sterling MTG carbon black; temperature, 178 °C; elution order, methane, 2-picoline, 2,6-lutidine, 2,3-lutidine, 2,4-lutidine + 2,5-lutidine, pyridine, 3-picoline + 4-picoline. (b) 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.

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: 25 000–100 000 theoretical plates for capillary columns vs 1000–5000 theoretical plates for packed columns.

The separation selectivity of open 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.

The higher efficiency (and selectivity) allows one to use capillary columns to separate and identify 10–100 times as many compounds as in the case of traditional packed columns with a specified diameter (2–4 mm). Thus capillary chromatography greatly improves "the chemical sight" of the investigator.

Second, using open capillary columns extends somewhat the applications of gas–solid chromatography, which in turn permits one to separate 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.

Third, open capillary columns allow one to accelerate separation procedures. This is mainly explained by the simpler utilization of higher mass transfer and carrier gas rates.

Fourth, column miniaturization permits one to obtain improved temperature reproducibility in the process of separation. 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 of these advantages have had a stimulating effect on the development of gas–solid capillary chromatography over the past few years.

Franken and co-workers[52] separated nitrogen-containing compounds (see Figure 5) 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 analytical time (by a factor of ~12).

It should be pointed out that reducing the temperature to 137 °C permits a complete separation of 2,4- and 2,5-lutidine over 90 s. The data presented 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 the discrimination of the sample composition and improve separation characteristics. Therfore in the past few years chromatographers have given preference to wide capillary columns with a thick (a few micrometers) layer of immobilized stationary phase (see, e.g., ref 53 and 54).

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 unit length 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.

Table IV[53] compares 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.

TABLE IV. Characteristics of Two Types of Analytical Gas Chromatographic Columns: Packed and Wide Capillary (with a Thick Stationary Liquid Phase Layer) Variants[53]

column	length, m	inside diameter, mm	liquid-phase film thickness, μm	phase ratio	capacity factor	theor plates (N)
packed	2	2.26	5	26	8.3	4500
capillary	15	0.53	3	43	5.0	26000

It should be noted that the chromatogram in Figure 5, obtained over 150 s, describes the separation of compounds for which the capacity factors are comparable with those listed in Table IV (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 only natural that, as a rule, open capillary columns can be used without a splitter. The porous-layer capillary adsorption columns can be regarded as an efficient substitute for packed adsorption types. This property of such columns is discussed in more detail in the fourth section of this review.

The previous sections were devoted to open porous-layer capillary adsorption columns. However, as follows from the classification of the columns (see Table III), capillary gas chromatography includes one more type of adsorption column, viz., an open capillary type with a nonporous (unextended) inside wall surface. This type of column is distinguished by the following features: (1) a low sorption capacity, which can be described, for example, by the quantity $a_s = S/L$, where S is the total surface area of the inside column walls and L is the column length; (2) a high phase ratio $\beta_A = V_g/S$, where V_g is the gas-phase volume in the column and S is the total surface area of the inside column walls; (3) high rates of mass exchange between the gas phase and the inside column wall surface.

Such columns may be used only when samples are very small and the detectors used are very sensitive as larger samples bring about column overload, 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.

A low specific sorption capacity suggests that these columns can be used to advantage for separating high-boiling (nonvolatile) compounds. The small specific sorption capacity also allows one to reduce the separation temperature and hence to enlarge the number of compounds analyzed.

Scattered literature data as well as the results obtained by the present authors corroborate these considerations.

Figure 6 exemplifies this situation by a separation chromatogram obtained by the present authors for aromatic hydrocarbons with the use of a fused-silica column after its dehydration at 300 °C in a helium stream. The separation was effected under overload conditions and the toluene peak is asymmetric. Nevertheless, this experiment suggests that even the inside fused-silica capillary column walls can serve as an adsorbent capable of separating a fairly simple mixture.

Figure 7[55] presents a chromatogram for the 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 helium stream as eluent.

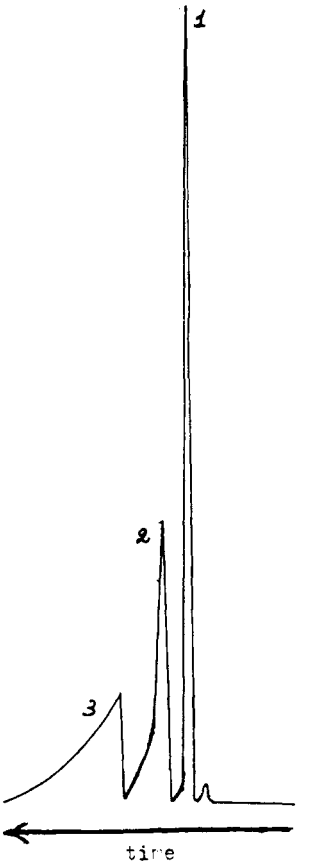

Figure 6. Separation chromatogram for hydrocarbons on a fused-silica capillary column: (1) methane; (2) benzene; (3) toluene. Column, 40 m × 0.19 mm; temperature, 50 °C; sample size, 10 ng/compound. The column surface was dehydrated at 300 °C in a helium stream.

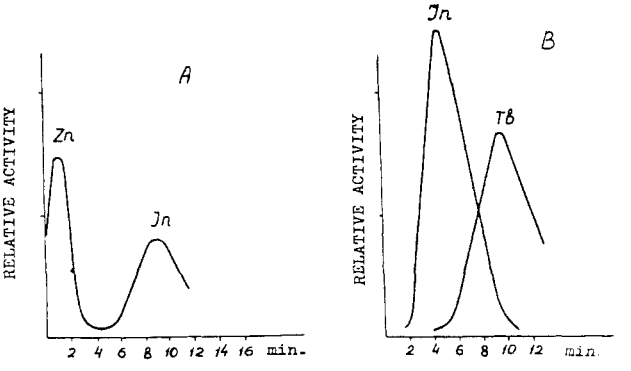

Figure 7. Separation chromatogram for nonvolatile chlorides on a glass column with the use of a helium/aluminum chloride vapor mixture as the carrier gas:[55] (A) separation of zinc and indium chlorides (temperature, 170 °C); (B) separation of indium and terbium chlorides (temperature, 200 °C). Column, 10 m × 1 mm; helium stream flow rate, 7.0 mL/min; aluminum chloride vapor pressure, ca. 150 mmHg.

Zvarova and Zvara[56,57] have demonstrated that at moderate temperatures (under 250 °C) lanthanide chloride, actinide chloride, and other chlorides can be separated by gas chromatography if use is made of a mixture of an inert gas and aluminum chloride vapors

TABLE V. Capacity Coefficient Dependence on Carrier Gas Nature

carrier gas	capacity factor		
	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

as 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. Excess aluminum chloride inhibits the dissociation of the unstable molecular complexes and dynamically modifies the column surface.[58] Despite the low efficiency of such a column, it was useful in separating for the first time 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.

We note an additional feature of gas adsorption chromatography, namely, the retention dependence on carrier gas nature. The transition from a light carrier gas to a heavy one leads to dynamic modification of the sorbent surface, to a decrease of distribution coefficients in the solid/gas system, and, consequently, to a decrease of retention time. Table V contains data on capacity coefficient dependence vs carrier gas nature, obtained by the present authors on a column with an Al_2O_3 layer (Chrompack, 50 m × 0.32 mm, 100 °C). As can be seen from Table V, the capacity coefficients of hydrocarbons in helium and nitrogen are practically the same, but in the case of carbon dioxide they are noticeably lower. Figure 8 shows chromatograms for some hydrocarbons separated on an Al_2O_3 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.

3. Fundamentals of Chromatographic Zone Broadening in Open Capillary Adsorption Columns

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

Interestingly, even in his early works Golay proposed[59,60] that to increase the column capacity ratio one should deposit a stationary liquid phase (SLP) layer not onto the smooth inside walls of the capillary columns but rather onto a porous layer of the solid carrier located on the capillary walls. In so doing, the SLP film thickness on the separate solid carrier particles remains equal to that in the case of a smooth capillary wall, but the amount of SLP per unit column length significantly increases due to the associated increase in the inside capillary surface. This 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 SLP volume in the column) and an increasing capacity factor k and, hence, in better separation.

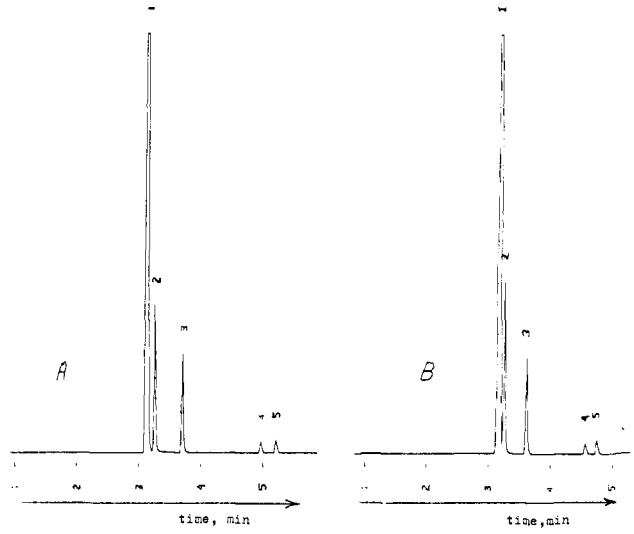

Figure 8. Chromatograms for some hydrocarbons separated on an Al_2O_3 capillary column using helium (A) and carbon dioxide (B) as carrier gases: (1) methane; (2) ethane; (3) propane; (4) isobutane; (5) *n*-butane. Fused-silica capillary column (Chrompack, The Netherlands), 50 m × 0.32 mm; adsorbent, Al_2O_3/KCl.

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

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

where H is the height equivalent to a theoretical plate (HETP), D_g is the diffusion coefficient of the chromatographed compound in the gas phase, 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 inside column walls.

As follows from eq 1, the magnitude of the last term, indicating the mass transfer resistance to the liquid phase, is inversely proportional to the F value. Thus the equation takes into account the fact that with increased porosity of the wall layer, the capillary column efficiency should grow (H decreases with F). In other words, the idea of a capillary column with a solid carrier porous layer had been exploited as early as at the stage of the derivation of this equation, as Ettre[16] pointed out. However, it should be noted that this equation, like other equations of Golay, relates to gas–liquid–solid (or gas–liquid) chromatography.

An equation describing the dependence of H on the linear carrier gas velocity for gas–solid chromatography was proposed by Giddings.[62,63] The first terms of Giddings' equation are virtually coincident with the first terms of Golay's equation. The main differences in Giddings' equation are in the fact that, first, it contains

TABLE VI. Coefficients of Mass Transfer Resistance for Open Tubular Capillary Columns

$$H = B/U + (C_g + C_s)U$$

type of capillary chromatography	analyzed compd	mass transfer coefficients (C), s: in the gas phase, helium	in the gas phase, nitrogen	in the stationary phase	C_g/C_s (He)	C_A/C_l
gas–solid (Al_2O_3)[37]	1,3-butadiene	1.3×10^{-4}	4.6×10^{-4}	$C_A = 1.8 \times 10^{-4}$	0.7	0.4
gas–liquid (dimethylsilicone)–solid[67]	tridecane	2.8×10^{-4}	10.6×10^{-4}	$C_l = 4.1 \times 10^{-4}$	0.7	

a term describing the mass transfer resistance in the adsorption layer on the inside capillary walls and, second, it includes the effect of the carrier gas pressure drop in the column on the broadening effect factor. Giddings's equation can be written as follows:

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

$$u_0 = L/(t_m f_2) \quad (3)$$

$$f_1 = \frac{9}{8}\frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)} \quad (4)$$

$$f_2 = \frac{3}{2}\frac{(P^2 - 1)}{(P^3 - 1)} \quad (5)$$

where $P = P_i/P_o$ (P_i and P_o 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 a HETP in the capillary column in a different form, assuming that the effect of pressure drop on the chromatographic zone broadening can be neglected, i.e., $f_2 \approx 1$ and $f_1/f_2 \approx 1$:

$$H = \frac{2D_g}{u} + \left[\frac{C_{gp}}{D_g} + C_A\right]u = \frac{2D_g}{u} + [C_g + C_A]u \quad (6)$$

or

$$H = \frac{2D_g}{u} + Cu \quad (7)$$

where

$$C_{gp} = \left[\frac{1 + 6k + 11k^2}{24(1 + k)^2}\right]r^2 \quad (8)$$

$$C_A = \frac{8}{a_k u_m}\frac{V_g}{S} f_n \left[\frac{k}{1 + k}\right]^2 \quad (9)$$

$$C_g = C_{gp}/D_g \quad (10a)$$

$$C = C_g + C_A \quad (10b)$$

To test the compliance of eq 7 with the experimental data, one can conveniently write it as follows:

$$Hu = 2D_g + Cu^2 \quad (11)$$

D_g values can be estimated by the Fuller equation[64] or by some other calculation method (see, for example, ref 65).

The C values for the chromatographed compounds, as found for the two carrier gases on the open capillary adsorption columns, make it possible to determine separately mass transfer resistance coefficients for the gas phase (C_g) and the adsorption layer (C_A). These methods were developed earlier by Perrett and Purnell for packed columns.[66]

de Nijs and de Zeeuw[37] estimated such coefficients for 1,3-butadiene in an open capillary adsorption (aluminum oxide) column. In so doing, they used Giddings' equation. The coefficients were found to be $C_g = C_{gp}/D_g$. The C value was also determined. With helium as the carrier gas, C_g(butadiene) = 1.3×10^{-4} s, whereas with nitrogen, C_g(butadiene) = 4.6×10^{-4} s. The same coefficient for the adsorption layer was found: $C_A = 1.8 \times 10^{-4}$ s. Thus, according to these authors, C_g and C_A represent quantities of the same order.

For comparison purposes we shall give similar coefficients for tridecane on an open fused-silica capillary column (24.7 m × 0.55 mm) with an SLP layer (dimethylsilicone CP-Si15-CB) on its inside walls at 150 °C. The resistance coefficients are as follows: in the liquid phase, $C_g = 4.1 \times 10^{-4}$ s; in the gas phase, C_g(tridecane, helium) = 2.8×10^{-4} s and C_g(tridecane, nitrogen) = 10.6×10^{-4} s. These data for gas–liquid capillary chromatography were obtained by Cramers and co-workers.[67] Note that the mass transfer resistance coefficients for the gas–solid and gas–liquid types of capillary chromatography are of the same order (see Table VI).

As an example the experimental dependence $Hu = f(u^2)$ is presented in Figure 9. These data were obtained by the present authors for a fused-silica column manufactured by Chrompack (Middelburg, The Netherlands) whose inside walls are coated with an adsorption layer composed of aluminum oxide and potassium chloride. When studying the dependence, one should consider the following factors.

First, note that the experimental data for the broadening of the hydrocarbon gases (methane, propane, and n-butane) in two carrier gases such as nitrogen and helium (Figure 9) are satisfactorily described by a linear equation in the Hu–u^2 coordinates; see eq 11.

Second, the diffusion coefficients for the analyzed gases, found in accordance with Giddings's equation and calculated by an equation proposed by Fuller and coworkers, compare well.

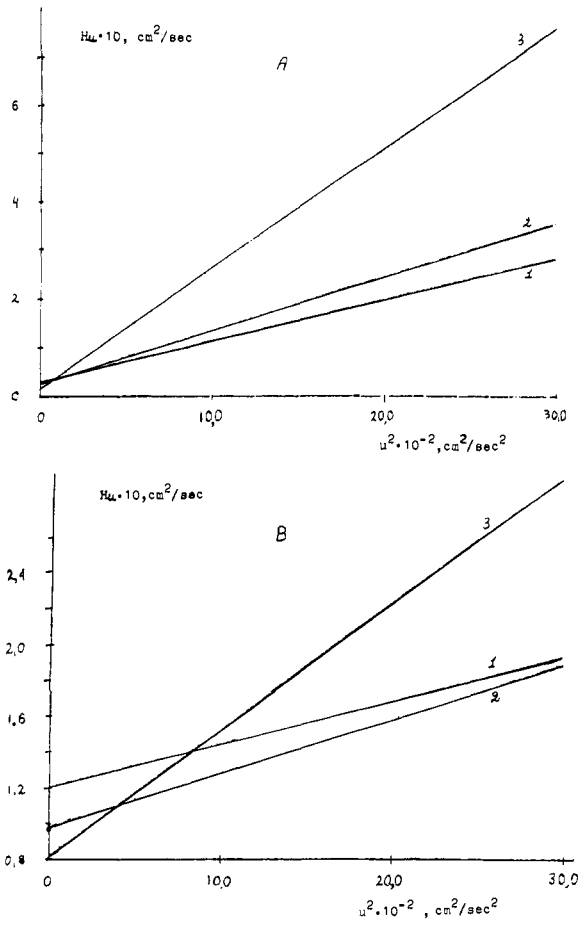

Figure 9. Dependence of Hu on u^2 for an open capillary adsorption column with an aluminum oxide layer on the inside capillary walls. Carrier gases: (A) nitrogen; (B) helium. (1) Methane; (2) propane; (3) butane. Fused-silica capillary column (Chrompack, The Netherlands), 50 m × 0.32 mm; adsorbent, aluminum oxide/potassium chloride mixture; column temperature, 100 °C; splitter, 1:50.

Thus the simplified form of Giddings' equation (eq 11) fits well the experimental data for open capillary adsorption columns 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.[64] Thus the diffusion coefficient for butane in helium as determined by the simplified Giddings equation was found to be 0.43 cm^2/s whereas that found by the calculation equation was 0.43 cm^2/s.

Note that earlier Goretti, Liberti, and Nota[26] reported on the agreement between the experimental data and eq 7 for open glass capillary columns having graphitized carbon black and found the values of the mass transfer coefficients. These values are listed in Table VI. It is from these data that the most important contribution to the broadening of the chromatographed compounds is made by a term describing transfer resistance (compare, for example, at carrier gas velocity 30 cm/s).

4. Dependence of Column Efficiency on Sample Size

One important characteristic of a column is the dependence of its efficiency (broadening of chromatographic zone) on sample size. This characteristic is

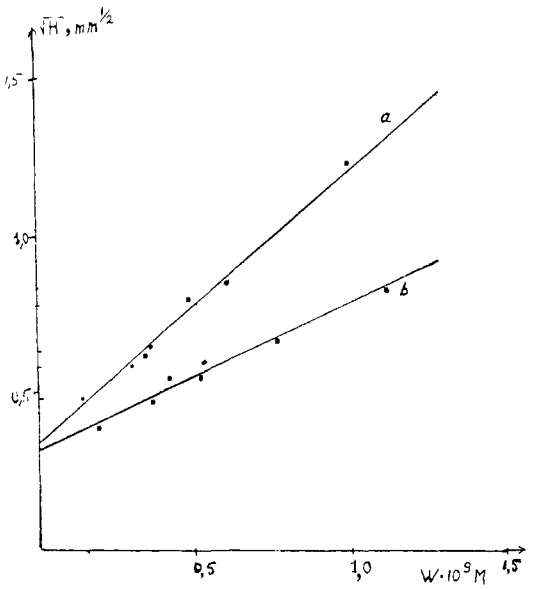

Figure 10. Dependence of H on sample size for n-butane on an open capillary adsorption column with an aluminum oxide layer on the inside walls; splitless (a) and split-type (b) sample injection technique. Fused-silica column (Chrompack, The Netherlands), 50 m × 0.32 mm with aluminum oxide; column temperature, 100 °C; detector, flame ionization type.

essential to the application of chromatographic data for physicochemical and analytical measurement. It is also important in considering the possibility of using a column without a splitter and in the application of the traditional method of sample injection for a capillary column. Thus a series of works is devoted to the discussion of the dependence of chromatographic zone broadening on sample size (see, e.g., ref 1, 3, and 68).

For quantitative evaluation of this dependence it is convenient to use a linear equation relating the height equivalent to a theoretical plate (HETP) or H values to sample size. Such a general equation has been proposed elsewhere.[69] At present, it appears to be in good agreement with the experimental data for open capillary columns with a stationary liquid phase layer (adsorbent) and for packed capillary columns.[70]

The dependence of column efficiency on sample size for an open capillary column with an aluminum oxide layer on its inside walls has been studied by the present authors. The initial experimental data were processed by the following equation:

$$H = H_0 + \lambda W \qquad (12)$$

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. Equation 12 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.

Figure 10 shows the H–W dependence according to eq 12 for the same 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 eq 12. When a splitter is used, the efficiency shows a marked increase (the H value decreases).

Interestingly, the H_0 value is virtually the same irrespective of sample injection technique (with or with-

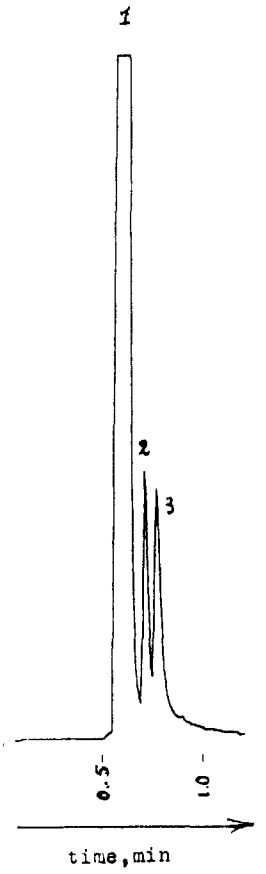

Figure 11. Splitless-mode separation of methane, isobutane, and *n*-butane on a glass capillary column coated with a SiO_2 layer. Sample volume, 0.5 mL.

out splitter). This characteristic is an additional test of eq 12.

The results obtained suggest that an open capillary column with an adsorption layer on the inside column walls can well be used in gas chromatography without a splitter although with a noticeable drop in efficiency. 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 immobilized liquid stationary phase layer (see, e.g., ref 53 and 54). At the same time, they are advantageous in that the rate of the mass exchange between the loose solid adsorption-active layer and the moving gas phase is higher than that of the immobilized stationary liquid phase thick layer.

Figure 11 shows an example of the separation of a methane–isobutane–*n*-butane mixture with injection (sample 0.5 mL) without a splitter on a glass capillary column with a silica layer. Analysis time is <1 min.

5. Preparation of Open Capillary Adsorption Columns

Methods for the preparation of open capillary adsorption columns differ in some respect from those used for making absorption columns with a stationary liquid phase layer.

The literature contains primarily the description of those adsorption capillary columns that are covered with a porous adsorbent layer. Columns of this type are distinguished by a high capacity and improved performance stability. Taking into account the kinetic broadening factors, it is desirable that the adsorbent layer on the inside column walls be homogeneous in terms of coverage and thickness, that this layer be mechanically fixed on the wall surface, and that the layer structure be fairly "loose" in order to provide for a high rate of mass exchange.

A classification of the available methods of adsorption capillary column preparation is presented in Figure 12.

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

Suspension Method

This method is based on the dispersion of a finished sorbent in a suitable liquid medium and filling the column with a suspension-type sorbent with subsequent removal of the volatile liquid. The method resembles very much that used for the application of a stationary liquid phase in the preparation of "classical" capillary columns. In both cases usage of either the dynamic or the static method is practical. The main difference consists in a heterogeneity (or microheterogeneity) of the system being introduced into the capillary during capillary adsorption column preparation. Here the suspension that is 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.[71-74] The rheological properties of the suspension undergo changes in the course of its application or column filling. Therefore the problem of preparing a sorbent layer that is homogeneous along the entire capillary length is com-

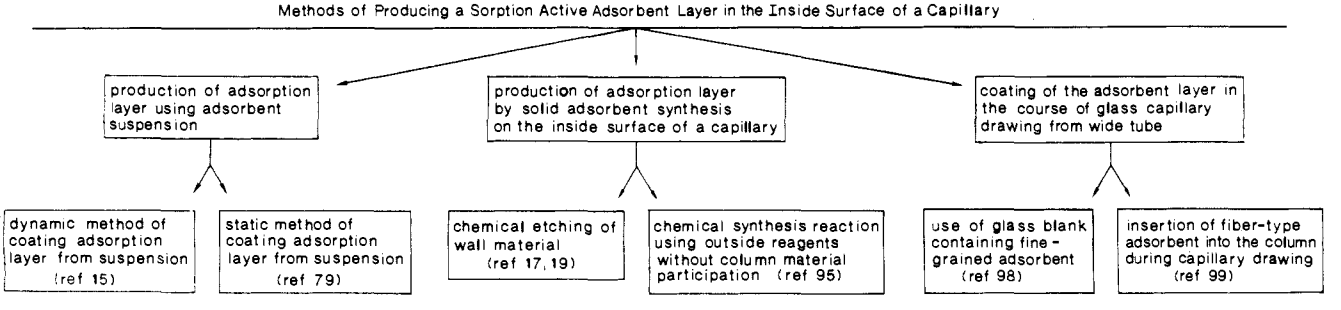

Figure 12. Classification of methods for the preparation of open adsorption columns.

plicated. Nevertheless, the suspension method of adsorption capillary column preparation was used even in the earliest works on capillary adsorption chromatography. Thus Schwartz and co-workers[25,75] applied a silica layer on the inside surfaces of polymeric, copper, and steel capillaries of length 4–400 m and inside diameter ~0.5 mm. The authors[25] ran into difficulties in using a suspension containing micron-size particles and therefore they decided in favor of true colloidal silica solutions. They used[25] 22% silica sol in a 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 suspension layer on its inner surface. Such a layer on the inside 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. The authors of ref 25 did not state whether the suspension stabilizer normally present in such systems remains on the silica particles after drying. Usually stabilizers are composed of surfactants that seem to modify the surface and hence affect 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 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[75-77] in their subsequent preparations of adsorption columns were led to use larger silica particles (ca. 4 μm) for preparation of adsorption columns.[25] 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. In the presence of *p*-toluenesulfonic acid it became covalently bonded to the silica surface to give a stable suspension in hydrophobic dispersion media. However, in this case one can also speak about the use 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 the separation of 13 isomers of C_5–C_7 hydrocarbons over 18 min. The efficiency as determined for 2,4-dimethylpentene was 550 theoretical plates per meter.[75-77]

Early in the 1960s the dynamic silica gel coating method was employed by Perkin-Elmer for the commercial preparation of copper capillary adsorption columns. These columns were ca. 400 m long × 0.5 mm i.d.[78] and were designed for the rapid analysis of light hydrocarbon gases.

Graphitized carbon black was also coated by a dynamic method.[20,79] The copper columns (15 m long × 0.25 mm i.d.) were coated with carbon black from suspension. The suspension was prepared by a rapid stirring of a mixture of 15 g of carbon black, 220 mL of trifluorotrichloroethane, and 30 mL of carbon tetrachloride. Thus a dispersion medium of this suspension has a density of ca. 1.5 g/cm^3. The high density of the dispersion medium allowed the production of a fairly stable suspension, which could be passed through the column without the risk of particle aggregation. Analysis of the data reported by the authors[20] indicates that after such a treatment the specific surface of the capillary column increased to 0.2–0.8 m^2, which permitted the separation of heptane isomers at 245 °C.

To enhance the graphite suspension stability it was also proposed that it should be treated with ultrasound.[80,81] A suspension composed of 0.25 g of Carbopack A, 5 mL of dichloromethane, and 20 mL of carbon tetrachloride was exposed to ultrasound at 20–24 kHz at an amplitude of 2 μm. The optimal exposure time was 40 min. The thus-obtained suspension was passed through the column in both directions at 0.6 mL/min. The capillary column was 10–15 m long × 0.4–0.5 mm i.d. and was made of glass.

A similarly prepared suspension based on graphitized carbon black Sterling MT was passed through the column at reduced outlet pressure. This was facilitated by the low density of the suspension, whose concentration did not exceed 1%.[81] However, this same property constitutes a disadvantage of the method as the amount of applied sorbent is insufficient for the effective realization of the adsorption variant. The layer obtained was used as a solid support for the stationary liquid phase.

Purcell[82] reported on the use of the dynamic method for the preparation of a column coated with molecular sieves 5A with particles sized around 20 μm. Later, columns with the same sieves applied by the same method became available from Chrompack.[42]

The most remarkable results with the use of the dynamic method were obtained with an aluminum oxide suspension.

The first attempt of this kind was undertaken by Kirkland,[22] 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 sol was passed through a column made of glass or stainless steel that was 10 m long with an inner diameter of ca. 0.25 or 0.5 mm. The column was ready for use after the suspension had been passed and the adsorption layer dried. The thus-prepared column was useful in separating a few freons with a moderate efficiency.

Further progress in the development of the dynamic method of Al_2O_3 application is associated with Schneider and co-workers.[83] They emphasize the following advantages of glass columns whose walls are coated with aluminum oxide: (1) the column walls have

a low (as compared with metal capillaries) adsorption activity (2) due to the presence of the negative charge on the glass capillary walls, the layers of the 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 quality of the finished column can be controlled by visual inspection; (4) glass columns of any dimensions can be prepared under laboratory conditions.

Let us exemplify this situation by considering the following method of column coating. A suspension is prepared by mixing 20 g of aluminum oxide, obtained by calcination of the hydroxide with particles not exceeding 2 μm, with 70 mL of a 5% colloidal Al_2O_3 solution (Beymal, manufactured by Du Pont), with addition of 0.3 mL of glacial acetic acid. This suspension is then treated in an ultrasound bath, filtered through sieves (300 mesh), and exposed for over 24 h. The thus-prepared suspension possesses thixotropic properties.

Using an aluminum oxide colloidal solution allows the preparation of a dispersion medium with an enhanced density and viscosity and thereby improved 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 suspension is applied by forcing it through the capillary at a rate of 4 mL/min. At this rate 0.6 mL of suspension will be sufficient to cover a 15-m length of the column. To prepare longer columns, the authors recommend 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 a nitrogen pressure of 0.3 MPa. A 65-m column 0.4 mm across can be dried in a week's time. After drying, the column is activated for 3 h at 300 °C. According to the authors,[83] the thus-obtained column contains ca. 6 mL of Al_2O_3 per meter of length. The amount of sorbent can be widely varied by changing the density of the suspension, 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% potassium chloride solution. After drying and heating, the column is ready for use.

The thus-obtained column possesses a fairly high efficiency. For example, for trimethyl-1-butyne (capacity factor 7.1) the column efficiency is 700 theoretical plates per meter. The total number of light hydrocarbons that were separated under isothermal conditions at 130 °C was over 50, with their partial concentrations in the gas mixture equal to ca. 1 ppb. Due to recent developments in the field of silica capillary columns, this procedure has been extended by de Nijs[37] to commercial production by Chrompack.[39-42] The dynamic method requires very concentrated suspensions as the column retains only that amount of sorbent that is contained in the thin film appearing after passing the suspension. Interestingly, in the use of a suspension prepared from spherical silica gel particles

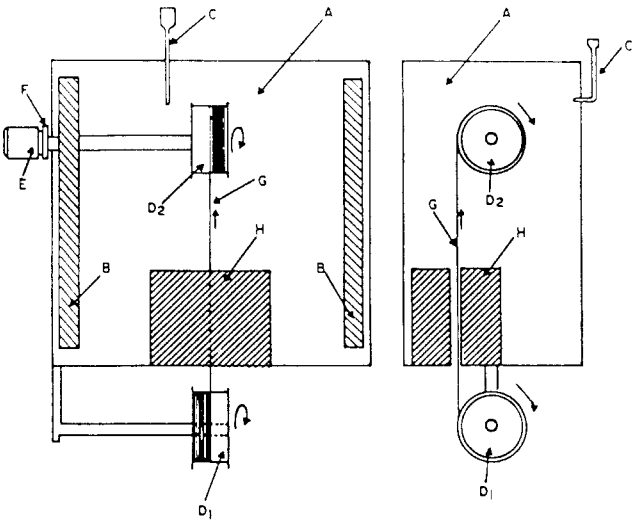

Figure 13. Device for adsorption capillary column preparation by the high-pressure static method: (A) air oven; (B) heater; (C) thermometer; (D_1 and D_2) reels; (E) electric motor; (F) connection; (G) capillary tube; (H) heated metallic block.

(5 μm) normally applied to HPLC, the inside capillary surface retains but a loose single layer of silica gel that covers no more than 50% of the capillary surface.

To increase the layer thickness, the static variant of the suspension method was attempted. For this purpose Horvath[79] designed a special device (see Figure 13). 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 block causes a fast evaporation of the liquid, and the high oven temperature prevents vapor condensation. Using such a device as modified by Mistrykov and co-workers[31] to accommodate glass capillary columns, Guiochon and co-workers[84] prepared a column with graphitized carbon black Sterling FTG. To do so, a 5% suspension of carbon black in dichloromethane was produced. With 0.05% squalane as the stabilizer, it was possible to retain the stability of the resultant suspension for 24 h. The method provided for the application of 10 mg/m of sorbent. A column 19 m long × 0.5 mm i.d. was useful in the separation of *o*-, *m*-, and *p*-xylenes at 165 °C. The layer thickness could be increased to 20 μm by using a high-pressure static method and a 20% carbon black suspension.[85]

The average thickness of the diatomite layer (Johns-Manville) produced by Ettre and co-workers with the aid of Horvath's device was 60 μm.[32] Since in this case a sorbent with 10-μm particles was used, it can be assumed that the authors were capable of producing a layer with a thickness equal to 6 times the particle diameter at one pass. Such a result is impractical 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 the disturbance of the suspension structure and formation of aggregated particles nonuniformly distributed over the column, with the result that the layer becomes inhomogeneous and the entire system's separating power lower. Moreover, the method is restricted to volatile dispersion

media only, characterized, as a rule, by low densities.

Preparation of the Adsorption Layer by Its Synthesis on the Inside Capillary Surface

Starting with the early attempts of adsorption capillary column production, the 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 removable from it. Moreover, the chemical reactions can be repeated in order to increase layer thickness.

Initially, researchers dealing with capillary columns attempted to obtain the sorbent by chemical conversions of the column material. This method has been widely applied to glass columns with the use of various etching and leaching techniques to obtain adsorption-active silica gel layers.

The first results of this kind were reported by Kiselev and co-workers[17,87] and Mohnke and Saffert.[18,19,86] Kiselev managed to separate C_1–C_4 hydrocarbons on a 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.

Mohnke and Saffert filled a capillary 80 m long (0.27 mm across) 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.

Alkaline etching of glass was also employed by Bruner and co-workers as well as other researchers.[29,88-90] 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.

The patent literature[91,92] describes the preparation of open capillary 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 which (external) was made of chemically stable glass and the other of which (internal) was made of sodium borosilicate glass. To obtain an adsorption layer of the 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 applied in gas chromatography (see, for example, ref 93).

Similar methods were proposed for the preparation of aluminum oxide (by treatment of aluminum capillaries in an oxygen stream)[24] and copper oxide (by treatment of copper capillaries with 40% HNO_3 and subsequent oxidation with dry O_2[94]).

Although the known methods of chemical treatment of capillary walls are readily realizable, they have the serious disadvantage that they are not universally applicable and are restricted as a rule to glass and metallic columns. Moreover, the composition and properties of the adsorption layer formed depend heavily on the composition of the column material, which may vary widely.

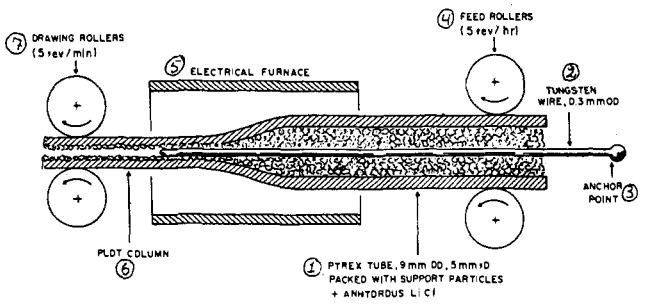

Figure 14. Device for adsorption capillary column preparation by the dynamic method: (1) Pyrex glass tube (9-mm o.d., 5-mm i.d.) filled with solid packing particles (solid carrier or adsorbent) and anhydrous lithium chloride particles; (2) tungsten wire (0.3-mm o.d.); (3) connection point for the tungsten wire; (4) feed rolls; (5) electric furnace; (6) finished column with an adsorbent layer on the inside walls; (7) drive rolls.

This disadvantage is nonexistent 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.[95] Although barium carbonate is not used as a pure adsorbent, it allows one to noticeably extend the surface. The method can be also used to advantage in a fused-silica capillary column.

Recently, a method for preparing a capillary column with a silica layer based on the hydrothermal treatment of silica sol inside the column has been proposed.[96] According to this method, the capillary is filled with silica sol to 80% of its volume, sealed, and heated to 180–210 °C over the several hours. Under such conditions small silica particles dissolve and then polymerize on the surface to form layer particles. Thus the inside surface silica layer is formed. The thickness of the adsorption layer depends on the sol concentration and the duration of process. Optimal sol concentration is 0.1–1.5%, and optimal duration of treatment is 5–11 h. Columns prepared by this method were applied to the high-speed analysis of light hydrocarbons.

Formation of the Adsorption Layer during Glass Capillary Drawing

The production of a glass capillary can be accomplished by inserting the finished sorbent into a capillary without need for its conversion to suspension. The capillary is drawn from a comparatively wide tube; therefore it can readily accommodate the sorbent prior to drawing.

Halasz and Heine[97] have used this method for 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 resultant 2-m column represented an intermediate variant of the packed and open capillary columns with a fairly high efficiency (3500 theoretical plates per meter) with respect to ethylene.

Later, the diameter of the wire was decreased to that of the inside channel, the wire passing through the softening (hot) zone and terminating in the capillary (Figure 14). Such a system allows one to rigidly specify the inside column opening size and hence the layer thickness. Thus Grant[98] obtained a column with a 100-μm layer, a 0.3-mm inside capillary diameter, and

a 0.1-mm tungsten wire. According to the author,[98] lithium chloride should be used as the binding layer. The height equivalent to a theoretical plate was 0.5 mm.

Since during the manufacture the sorbent suffers high temperatures (700–800 °C), the adsorbents should be composed of heat-resistant packings that withstand temperatures at least equivalent to the glass softening point. Therefore graphite was chosen as the only alternative to aluminum oxide. Goretti and co-workers[67,100] have thus made columns with a 50–100-μm layer and ca. 10-m capillary. The efficiency of the columns was ca. 1500 theoretical plates per meter with a fairly high permeability.

This method was modified by Liberti and co-workers.[99] They inserted into a tubular workpiece a 7.5-μm graphitized fiber which in the process of capillary drawing was played out from the reel and fed into the capillary to leave a 0.2–0.3-mm gap inside it. Therefore in this case the column can be regarded as an open one. The length of the finished columns varied between 1.5 and 10 m, with the inside diameter between 0.4 and 0.5 mm.

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 attaching of the adsorption layer particles to the capillary surface; (3) sufficient reproducibility; (4) application of a variety of adsorbents for making adsorption layers; (5) high rapidity 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: (1) the field of its application is restricted by thermostable sorbents (for example, polymeric sorbents cannot be used); (2) it is necessary to select the binding substance for producing the compact immobilized sorption layer individually for every kind of adsorbent and column material; (3) for adsorbents not stable at high temperature in air, it is necessary to draw the column media in an inert-gas atmosphere, which leads to complication of the apparatus.

The method of adsorption capillary column preparation by means of in situ synthesis of sorbents is applicable only to a limited number of adsorbents, but it allows the simultaneous solving of two problems: (1) forming of sorbent; (2) bonding of sorbent to the inside surface of the capillary.

In our view, the suspension method is the most universal method of gas adsorption capillary column preparation. The main unsolved problem is the bonding of the adsorbent to the inside walls of the capillary, and methods of bonding 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 an adsorption layer on its walls has not been solved yet, and this fact is holding back the wide application of adsorption capillary chromatography.

6. Applications of Open Capillary Adsorption Columns

In practical situations the chromatographer usually has to consider the following two column characteristics:

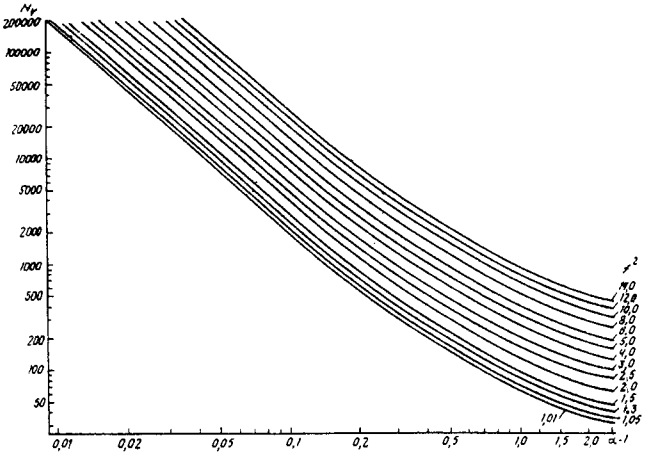

Figure 15. Graphic determination of the number of theoretical plates H required for the separation (R = 1.0) of a pair of compounds, depending on the sorbent selectivity α and f^2 parameter, whose values are controlled by the capacity factor k.[101]

its efficiency and selectivity of the sorbent used. Such an approach naturally holds for capillary adsorption columns as well.

For selection of feasible alternatives it would be desirable to construct a plot to rapidly determine the number of required theoretical plates and hence column length, provided the selectivity and capacity of the adsorbent used are known.

Figure 15[101] shows the dependence of the required plates (N) on the sorbent selectivity (α) for compounds distinguished by various capacity factors k_i. The role of the capacity factor in this plot is expressed by the function

$$f^2 = \left[\frac{k_i + 1}{k_i}\right]^2 = \left[1 + \frac{\beta}{K_{Di}}\right]^2 \qquad (13)$$

Here, each f^2 value has a definite dependence $N_r = 4(x)$ ($x = \alpha - 1$), K_{Di} is the coefficient of the compound distribution between the stationary solid and mobile gas phases, and β is the phase ratio (the ratio of the volume of the mobile phase to that of the stationary one).

We shall consider now the practical application of the plot in Figure 15. Suppose we have to find the required number of theoretical plates for a column with β = 40 for separating two components with α = 1.05 and K_{Di} = 100. For these two compounds f^2 = 2. From the point on the x axis corresponding $\alpha - 1$ = 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 intersection is equal to 16 000 theoretical plates. This is exactly the column efficiency sought that is necessary for the desired separation of these compounds.

Traditionally, volatile inorganic and organic compounds are mainly separated by gas–solid chromatography (see, e.g., ref 3, 6, and 7). Therefore gases with different isotopic composition can probably be conveniently separated by high-performance adsorption chromatography on open capillary columns at reduced temperatures. In 1962 the separation of nuclear-spin hydrogen isomers and isotopes appeared as the first brilliant analytic application of capillary adsorption chromatography. This was accomplished by Mohnke and Saffert.[19] The chromatogram showing the distinct separation of the components of this mixture was

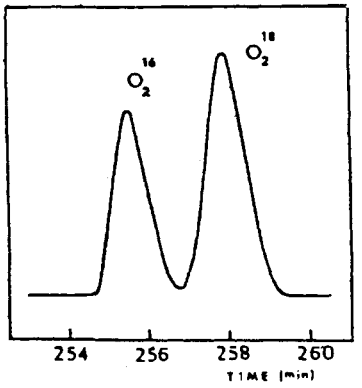

Figure 16. Chromatogram for the separation of an $^{16}O_2/^{18}O_2$ mixture[90] on a glass capillary adsorption column (175 m × 0.3 mm) at 77 K.

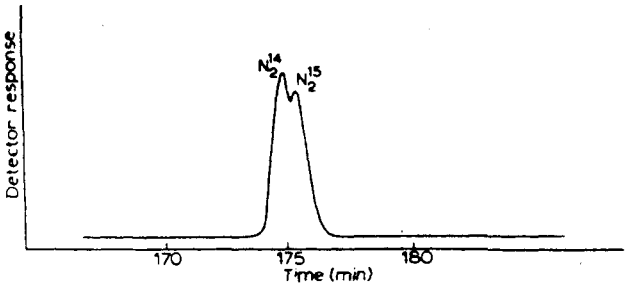

Figure 17. Chromatogram for nitrogen isotope separation.[81] Column, open capillary type with an adsorption layer on the inside walls (etching), 175 m × 0.2, mm; temperature, 77 K; carrier gas, helium/carbon monoxide (55:45) mixture.

presented in Figure 2. Further studies have revealed that nuclear protium and deuterium isomers can be separated faster if the column temperature is lowered to 47 K.[102]

Oxygen isotopes ($^{16}O_2$ and $^{18}O_2$) were separated by Bruner, Cartoni, and Liberti[90] on a capillary adsorption column (see Figure 16[90]). The adsorption layer on the inside glass column walls was generated by etching with 20% NaOH solution at 100 °C for a few hours. The isotopes were separated fairly well although it took a relatively long time (>4 h). The efficiency of the capillary column used was ca. 350 000 theoretical plates. A mixture of nitrogen (65%) and helium (35%) was used as the carrier gas.

$^{14}N_2$ and $^{15}N_2$ isotopes were separated by Cartoni and Possanzini[88] on an open glass capillary gas adsorption column whose inside walls were first etched to obtain an adsorption layer. A method for preparing such a column is described elsewhere.[89]

A separation chromatogram for nitrogen isotopes is presented in Figure 17. The experiment took about 3 h and still the separation was only partial. The result can be undoubtedly improved, e.g., by the optimization of separation parameters, an opinion shared by other authors.[103]

Note that nitrogen isotopes were separated at a very low separation factor (α = 1.006). A helium (55%)/carbon monoxide (45%) mixture was used as the carrier gas. The carbon monoxide served as a modifier of the silica adsorption layer surface on the column walls.

The separation of ^{20}Ne and ^{22}Ne isotopes is illustrated in Figure 18. This was done by Purer and co-workers[103] at a relatively low temperature, namely, 19 K. The HETP value for the glass column (82 m × 0.2, mm) was

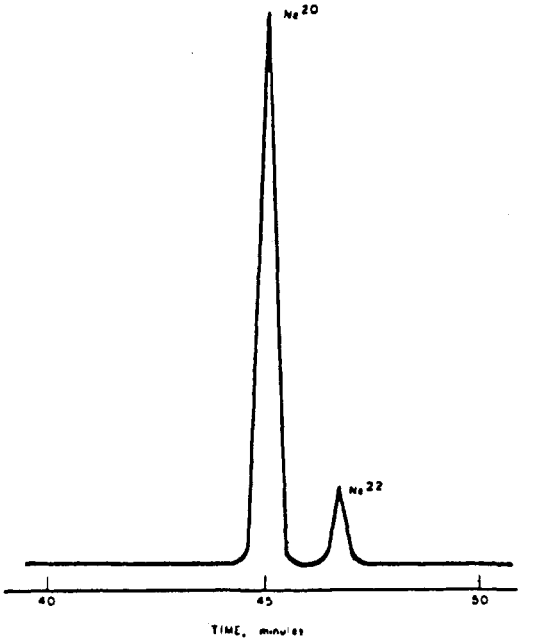

Figure 18. Chromatogram for neon isotope separation.[103] Column, capillary adsorption type, 82 m × 0.28 mm; temperature, 19 K; separation factor, 1.06.

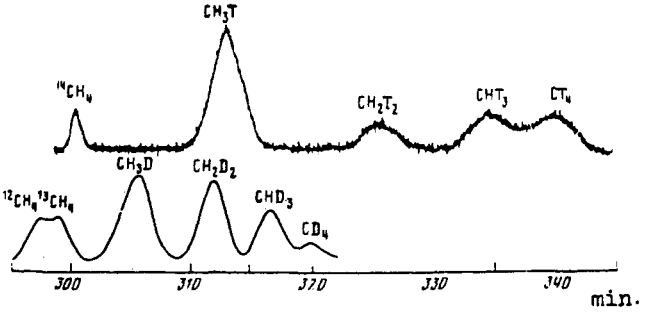

Figure 19. Chromatogram for the separation of deuterated and tritiated methanes.[28] Column, glass type, 47 m × 0.22 mm; temperature, 77 K.

0.8 mm at k = 0.8 and a separation factor of 1.06. A complete separation (R = 1.5) requires a column 45 m long.

To obtain an adsorption layer on the column walls, the initial capillary was etched with 10% sodium hydroxide solution for 6 h at 100 °C as proposed by Bruner and Cartoni.[29] It is also possible to separate a ^{21}Ne-containing mixture.[103]

Studies on hydrogen isotope separation[19] have had a stimulating effect on looking into the possibility of separating isotope-substituted molecules.

Figure 19 shows a chromatogram for separating methanes having different isotopic compositions.[28] Interestingly, along with the methanes that differ in hydrogen isotopic composition, it was possible to obtain a poor separation of those methanes that differ in carbon isotopic composition as well.

Thus the joke of some chromatographers that a chromatograph represents a simple and economic mass spectrometer seems to be a reasonable joke.

The separation of methanes was effected (see Figure 19) on an open glass capillary adsorption column containing a silica layer after etching with sodium hydroxide solution by the earlier described method.[29] The column used was rather efficient (70 000 theoretical plates) with symmetric methane peaks even at low

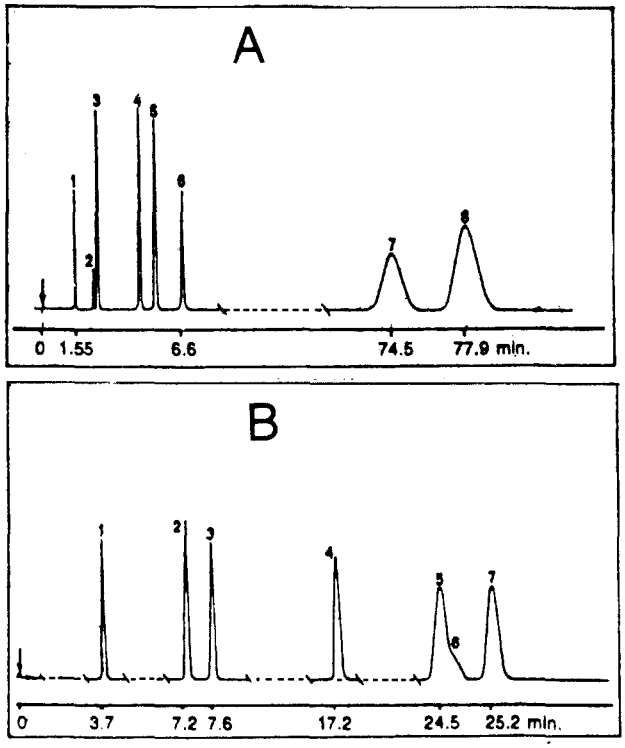

Figure 20. Chromatogram for the separation of deuterated ethanes (A) and deuterated methanes (B).[105] (A) Column, open fused-silica type, 25 m × 0.32 mm; adsorbent, molecular sieves 5A; temperature, 44.5 °C. (1) Helium; (2) argon; (3) oxygen; (4) nitrogen; (5) krypton; (6) methane; (7) hexadeuterioethane; (8) ethane. (B) Column, open fused-silica type, 75 m × 0.32 mm; adsorbent, molecular sieves 5A; temperature, 22.3 °C. (1) Helium; (2) argon; (3) oxygen; (4) nitrogen; (5) tetradeuteriomethane; (6) trideuteriomethane; (7) methane.

temperature. A mixture of helium (30%) and nitrogen (70%) was used as the carrier gas. A clear-cut separation of tritiated methanes, although in a much longer experiment, is described elsewhere.[104]

Isotope-substituted molecules, in our view, can be best separated with the aid of capillary adsorption columns using a layer of molecular sieves as the adsorbent. Figure 20[105] shows separation chromatograms for deuterated methanes and ethanes on an open capillary column with molecular sieves 5A. The separation of the deuterated ethanes (Figure 20A) was effected at an enhanced temperature (44.5 °C). The separation of the deuterated methanes was carried out at 22.3 °C (Figure 20B). Decreasing temperature and a variation in column length seem to give better separation results.

Analysis of the published data suggests that the separation of gaseous molecules of compounds having different isotopic composition is a promising area where good results can be achieved by capillary adsorption chromatography.

Some progress has also been attained in the separation of isotope-substituted liquid organic compounds. This is exemplified by Figure 21,[100] showing a chromatogram for separating benzene and benzene-d_6 as well as toluene and toluene-d_8. These compounds were separated on a capillary column with a graphitized carbon black layer.

Figure 22[26] gives separation chromatograms for oxygen- and nitrogen-containing compounds on an open capillary column with an adsorption graphitized carbon black layer 50–100 μm thick. The separation took about 10 min, which suggests the possibility of making finer

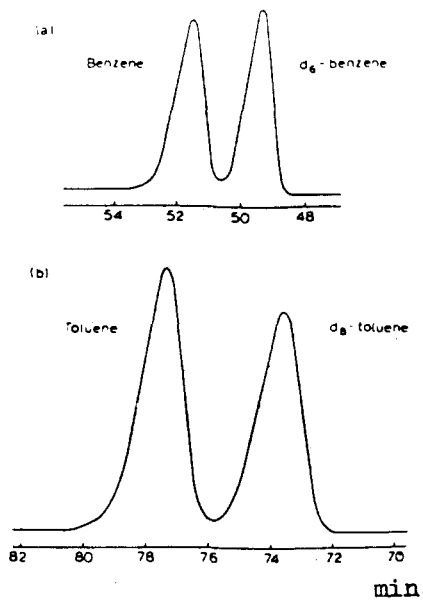

Figure 21. Chromatograms for the separation of (a) benzene/benzene-d_6 and (b) toluene/toluene-d_8 mixtures.[100] Column, 9.6 m × 0.15 mm; adsorbent, graphitized carbon black; temperature, 69.5 °C.

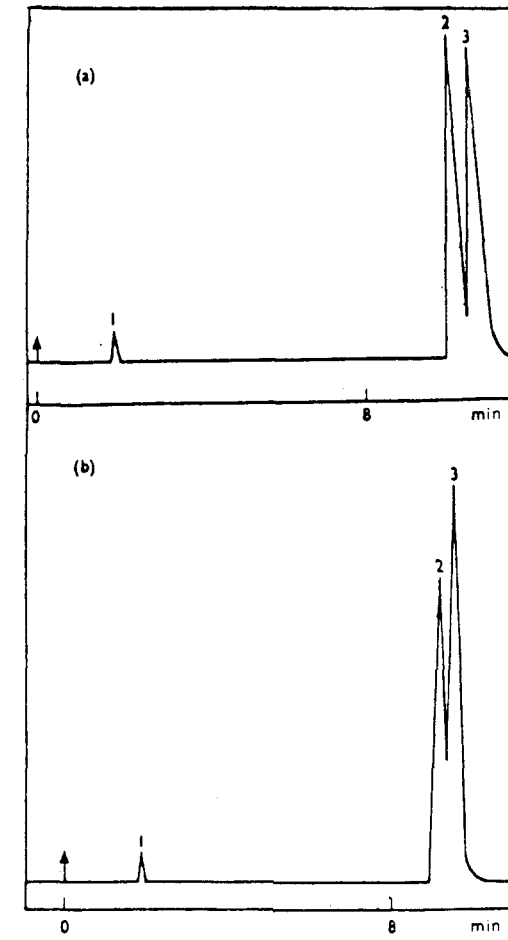

Figure 22. Chromatograms for the separation of acetone-d_6/acetone (a) and trideuterionitromethane/nitromethane (b) mixtures.[67] Column, 11 m × 0.2 mm; graphitized carbon black FT; temperature, 0 °C.

separations, e.g., for molecules differing by a few deuterium atoms.

Table VII[26] lists separation characteristics for a number of isotope-substituted organic molecules on open capillary columns with graphitized carbon black.

TABLE VII. Separation Data for Isotope-Substituted Compounds with the Use of Open Capillary Columns with Graphitized Carbon Black[26]

separated compd	type of graphitized carbon black	column length, m	sep temp, K	sep factor	capacity factor k	theor plates required for separation (R = 1.5)
CD_4/CH_4	FT	30.0	195.3	1.037	0.6	20000
C_2D_6/C_2H_6	FT	10.0	175.0	1.085	40.0	6000
C_2D_4/C_2H_4	FT	10.0	175.0	1.051	20.0	16700
C_6D_6/C_6H_6	FT	11.0	323.7	1.068	29.6	14600
C_6D_{12}/C_6H_{12}	FT	11.0	349.7	1.079	16.9	7500
C_7D_8/C_7H_8	MT	9.6	352.0	1.056	37.7	13500
C_5D_5N/C_5H_5N	MT	9.6	360.0	1.030	10.7	50000
$CDCl_3/CHCl_3$	FT	11.0	273.2	1.020	23.1	131900
CD_3NO_2/CH_3NO_2	FT	11.0	273.2	1.049	4.1	25500
CD_3COCD_3/CH_3COCH_3	FT	11.0	273.2	1.068	4.7	13100

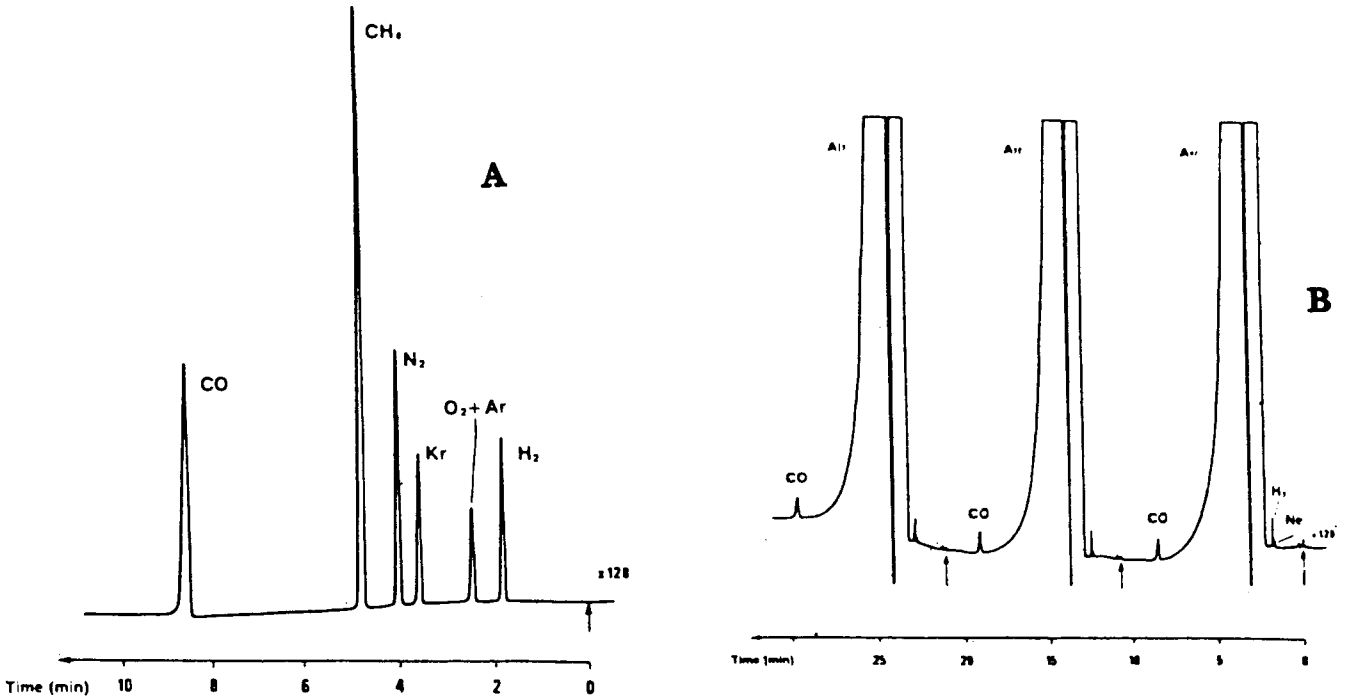

Figure 23. Chromatograms for the separation of a standard mixture of permanent gases in helium (A) and determination of carbon monoxide in air (B).[105] Column, 25 m × 0.32 mm; adsorbent, molecular sieves 5A; temperature, (A) 35 °C, (B) 80 °C.

The above examples point to the promise offered by capillary adsorption columns for separating isotope-substitued compounds. However, we believe that the best applications of these high-performance columns are in the area of routine analysis problems that at present are usually solved with the aid of packed columns whose efficiency is often insufficient.

Let us exemplify this situation by considering the separation of permanent gases on an open capillary column with molecular sieves. Such a column was apparently first described by de Zeeuw and de Nijs.[44] Using a similar column Verge[105] illustrated the possibility of its application to the solution of a variety of problems. In so doing, he used a high-sensitivity helium ionization detector. Figure 23[105] is concerned with the separation of a standard mixture of permanent gases in helium (A) and the determination of carbon monoxide in air (B). The carbon monoxide content is 2–3 ppm. Note that under these conditions at 35 °C one can observe a distinct separation of oxygen and argon (3 ppm).

Along with the determination of permanent gases, it is important in industrial situations to analyze the composition of hydrocarbon gases and light hydrocarbons. Compounds of this class are frequently separated by using aluminum oxide. Figure 24[83] shows the separation of light hydrocarbons on an open adsorption column with an aluminum oxide layer (adsorbent) (Figure 24A) as well as on a similar capillary column in which the layer is modified with squalane (Figure 24B). It is evident that such columns are distinguished by a fairly high efficiency and selectivity.

A very important contribution to the development of these columns was made by Chrompack (de Nijs and de Zeeuw).[36-38,106] Figure 25[104] presents separation chromatograms for hydrocarbon gases. The separation of the multicomponent gaseous hydrocarbon mixture on a Chrompack column is rather good.

Capillary adsorption columns are distinguished by a relatively high capacity and therefore can be used to advantage for impurity determination. Figure 26[108] shows a chromatogram for the determination of benzene and toluene in pure cyclohexane. The high column efficiency makes it possible to clearly separate the associated impurities and, hence, to enhance the reliability of this process.

Considering capillary columns with aluminum oxide, mention should be made of the possibility of performing

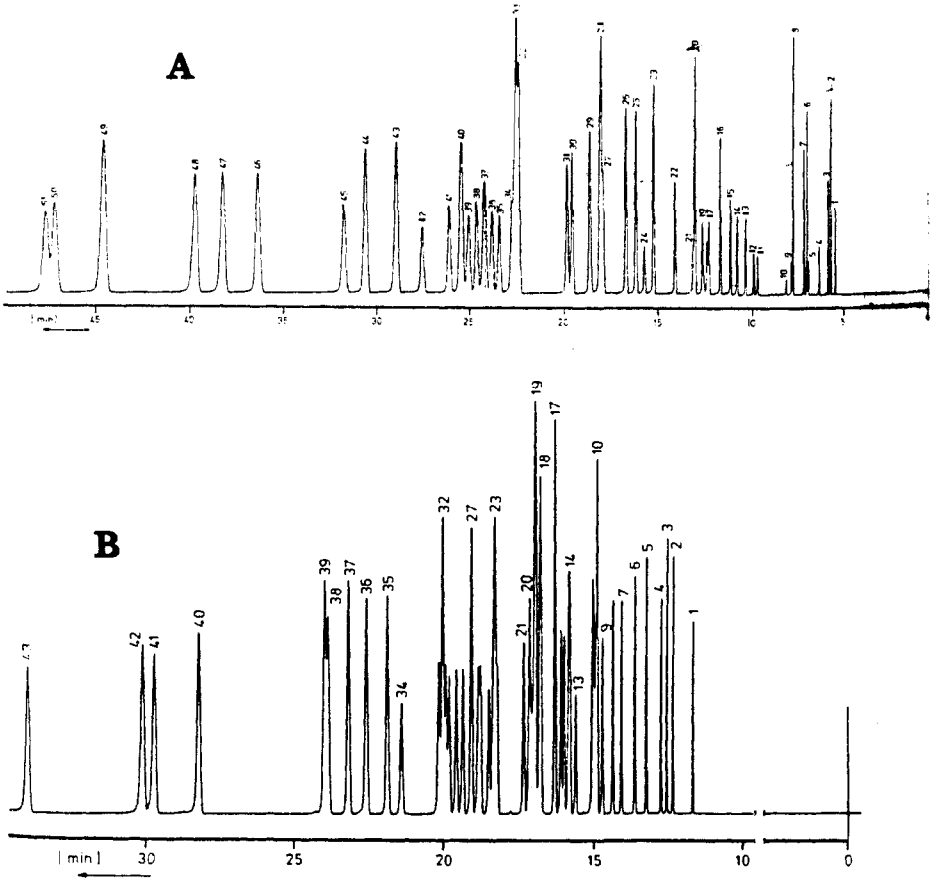

Figure 24. Chromatograms for the separation of light hydrocarbons on open capillary columns with an adsorption layer of aluminum oxide (A) and squalane-modified aluminum oxide (B).[83] (A) Column, 71 m × 0.40 mm; adsorbent, aluminum oxide (5.1 mg/m); temperature, 130 °C. (1) Methane; (2) ethane; (3) ethylene; (4) propane; (5) cyclopropane; (6) propylene; (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*-1,1-dimethylcyclopropane + 1,3-butadiene; (23) ethylcyclopropane; (24) trimethyl-1-butene; (25) cyclopentane; (26) *trans*-2-pentene; (27) 2-methyl-2-butene; (28) 1-pentene + methylenecyclobutane; (29) 2-methyl-1-butene; (30) *cis*-2-pentene; (31) trimethyl-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) trimethylpentane; (40) 1,2-pentadiene + 2,3-pentadiene; (41) vinylcyclopropane; (42) *n*-hexane; (43) *trans*-4-methyl-2-pentene + isopropylcyclopropane; (44) 2-methyl-1,3-butadiyne; (45) 1-methylcyclopentene; (46) 4-methyl-1-pentene; (47) *cis*-1,3-pentadiene; (48) *trans*-1,3-pentadiene; (49) trimethyl-1-butyne; (50) isopropylacetylene; (51) 2-pentyne. (B) Column, 129 m × 0.25 mm; adsorbent, aluminum oxide (0.6 mg/m); temperature, 100 °C. (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) triethylhexane; (9) *cis*-2,5-dimethyl-3-hexene; (10) 2,2,4-trimethylpentane + *trans*-2,2-dimethyl-3-hexene; (11) *trans*-2,5-dimethyl-3-hexane; (12) benzene + *n*-heptane; (13) 2,4,4-trimethyl-1-pentene; (14) 2,4,4-trimethyl-2-pentene + 2,2-dimethylhexene; (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-trimethyl-2-pentene; (22) trimethylheptane; (23) *cis*-4-methyl-3-ethyl-2-pentene + 3,4-dimethylhexane; (24) 3-ethyl-3-hexane; (25) 2-methyl-1-heptene; (26) 3-methyl-3-ethylpentane; (27) 2-methyl-3-ethyl-2-pentene + 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-vinylcyclohexane; (39) ethylcyclohexane; (40) ethylbenzene; (41) *p*-xylene; (42) *m*-xylene; (43) *o*-xylene.

rapid analysis of hydrocarbon gases for 100 s. This is especially essential in industrial applications. Figure 27[106] gives a separation chromatogram for C_1–C_4 hydrocarbons during this period. Despite the fact that the separation conditions were not optimal, the gases were separated fairly well.

Capillary adsorption columns are indispensable for sophisticated chromatographic systems for the rapid separation of mixtures whose components are characterized by a wide range of boiling points.

Multicomponent mixtures can be separated much better if care is taken in the selection of the appropriate sorbents whose selectivity should conform to the individual fractions (or even individual groups of compounds) in the mixture to be analyzed. Therefore gas chromatographic systems incorporating variable structures have long been used with packed columns, especially for industrial applications. Such systems allow one to automatically change the column connection order (in the on conditions), change the carrier gas flow direction in the specified system's points (or in the entire system), and have a given column connected to or disconnected from the system. All these factors permit improvement of the separation conditions for the individual groups of compounds, reduction of the analysis time, and enhancement of the column performance stability.

These ideas should be necessarily applied to capillary chromatography as well, and thereby significantly improve its real separating ability. Siemens (FRG) have

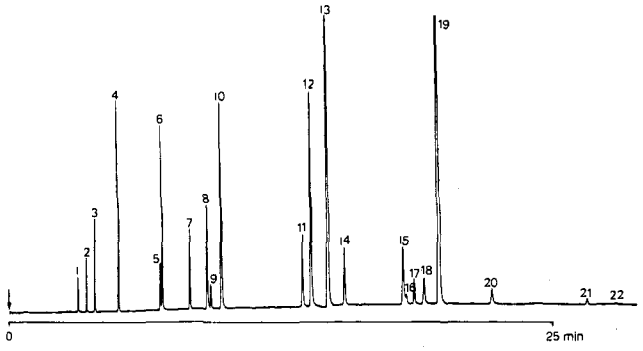

Figure 25. Chromatograms for the separation of hydrocarbon gases on an open capillary column with an aluminum oxide adsorption layer.[107] Column, fused-silica type, 50 m × 0.32 mm; adsorbent, aluminum oxide/potassium chloride; temperature, 70 °C with subsequent increase to 200 °C at a rate of 3 °C/min. (1) Methane; (2) ethane; (3) ethylene; (4) propane; (5) cyclopropane; (6) propylene; (7) acetylene; (8) isobutane; (9) propadiene; (10) *n*-butane; (11) *trans*-2-butene; (12) 1-butene; (13) isobutene; (14) *cis*-2-butene; (15) isopentane; (16) 1,2-butadiene; (17) methylacetylene; (18) *n*-pentane; (19) 1,3-butadiene; (20) 3-methyl-1-butene; (21) vinylacetylene; (22) ethylacetylene.

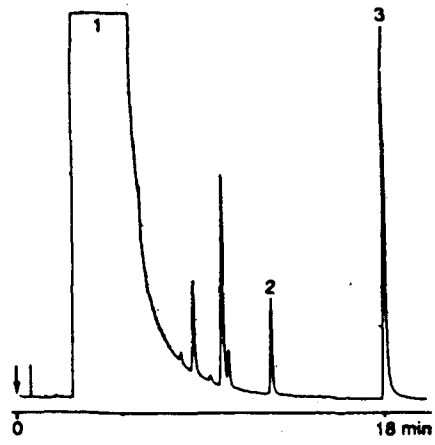

Figure 26. Chromatogram for the determination of aromatic hydrocarbons in cyclohexane on an open capillary column with an aluminum oxide layer.[108] Column, fused-silica type, 10 m × 0.53 mm; sorbent, aluminum oxide/potassium chloride; temperature, 80 °C with subsequent increase to 200 °C at a rate of 5 °C/min. (1) Cyclohexane; (2) benzene; (3) toluene.

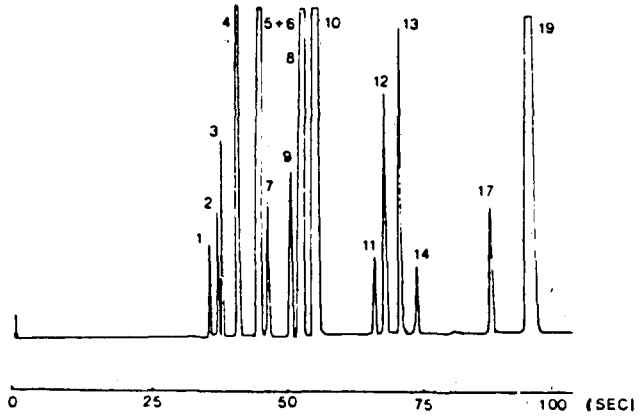

Figure 27. Chromatogram for the rapid analysis of C_1–C_4 hydrocarbons.[106] Column, fused-silica type, 50 m × 0.32 mm; sorbent, aluminum oxide; temperature, 130 °C. (1) Methane; (2) ethane; (3) ethylene; (4) propane; (5) cyclopropane; (6) propylene; (7) acetylene; (8) isobutane; (9) propadiene; (10) *n*-butane; (11) *trans*-2-butylene; (12) 1-butylene; (13) isobutylene; (14) *cis*-2-butylene; (15) isopentane; (16) 1,2-butadiene; (17) methylacetylene; (18) *n*-pentane; (19) 1,3-butadiene.

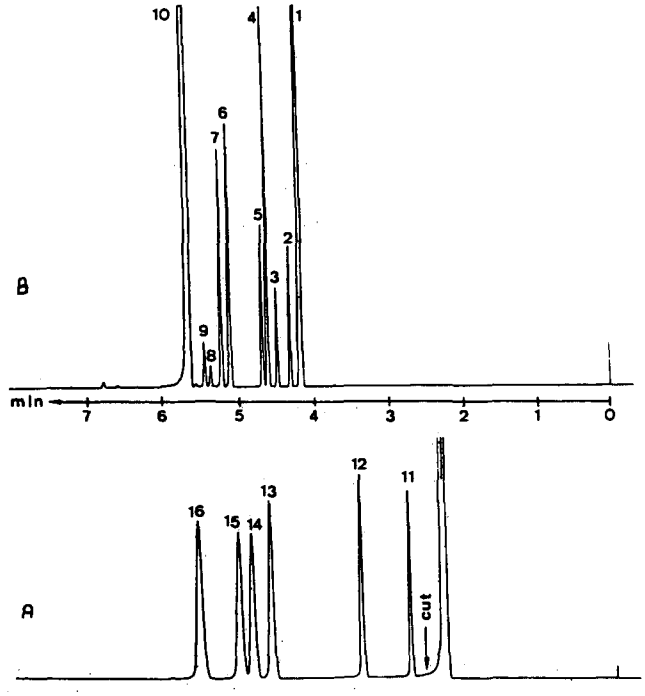

Figure 28. Application of multicolumn capillary gas chromatography to the separation of C_1–C_8 hydrocarbons (for explanations, see text).[109] (A) Chromatogram for the separation of C_1–C_8 hydrocarbons on the major open capillary column (24 m × 0.27 mm, bentone-34 impregnated with diisodecyl phthalate). (B) Chromatogram for the detailed separation of the C_1–C_5 hydrocarbons isolated in the first column (80 m × 0.4 mm, aluminum oxide).

developed a commercially available chromatograph (Sichromat) incorporating a flexible multicolumn system.

Figure 28[109] gives two chromatograms obtained on this device in the separation of C_1–C_8 hydrocarbons in *n*-pentane whose components differ sharply in boiling points and chromatographic characteristics. First, this complex mixture was separated at 75 °C on an open capillary column (24 m × 0.27 mm) with a modified bentone-34 clay applied on its inside walls and impregnated with diisodecyl phthalate. This principal column separates well benzene (11), toluene (12), ethylbenzene (13), *p*-xylene (14), *m*-xylene (15), and *o*-xylene (16) although C_1–C_5 light hydrocarbons are eluated faster from the column with a common peak.

For the rapid analysis of the light hydrocarbons, the first group of compounds with this peak is fed into the second open capillary column (80 m × 0.4 mm) whose inside walls are coated with a potassium chloride modified aluminum oxide. The separation temperature on this column is 115 °C. The following light hydrocarbons are separated: methane (1), propane (2), propylene (3), isobutane (4), *n*-butane (5), 1-butene, *trans*-2-butene, butadiene (6), and isobutene (7) as well as *cis*-2-butene (7). Note that both columns are operated simultaneously with a separation time on each of the columns not exceeding 6 min. The example cited demonstrates vividly the advantages of flexible multicolumn systems and the possibility of a radical improvement of the separating ability of capillary chromatography. Using such systems increases the bulk of the useful chromatographic information as a result of a single analysis.

The literature contains information on systems that, along with packed columns, use capillary adsorption

TABLE VIII. Reproducibility of the Retention Parameters and Compound Contents in the Analyzed Mixture for an Open Capillary Gas Adsorption Aluminum Oxide Containing Column Manufactured by Chrompack (The Netherlands)[a]

compd	retention time, min	SD,[b] %	concn %	concn SD,[b] %
CO_2	2.11	0.5	5.3	0.8
O_2	2.58	0.3	1.1	0.7
N_2	2.58	0.3	4.4	0.6
CH_4	5.54	0.15	5.0	0.8
CO	4.33	0.25	4.9	0.7
C_2H_6	6.91	0.15	2.2	0.6
C_2H_4	8.05	0.12	0.6	0.7
C_3H_8	9.05	0.10	2.1	0.8
C_3H_6	10.28	0.12	1.9	0.6
i-C_4H_{10}	11.73	0.10	0.4	0.8
n-C_4H_{10}	12.13	0.10	7.4	0.5
i-C_4H_8	13.05	0.10	6.7	0.5
C_4H_8	13.95	0.10	4.83	0.5
trans-2-butene	14.27	0.10	10.80	0.4
cis-2-butene	14.66	0.10	4.7	0.7
1,3-butadiene	16.28	0.09	38.8	0.8
i-C_2H_{12}	21.05	0.08	0.4	0.6
n-C_5H_{12}	22.18	0.08	1.0	0.8

[a] Reference 110. Statistical data obtained from 10 experiments (calculation made by the internal normalization method). [b] SD = standard deviation.

types as well (see, e.g., ref 110). Poy and Cobelli[110] have also provided experimental evidence (see Table VIII) that the reproducibility of the retention characteristics and results of determining component concentrations in the analyzed mixture while using a gas chromatograph fitted with an FID is fairly high. The data listed in Table VIII can be regarded as providing an experimental substantiation of the analytical and physicochemical applications of open capillary adsorption columns.

At present, adsorption chromatography relies, especially for polar compounds, on porous polymers used as the adsorbents.[111-113] Table IX[3] briefly summarizes the major field of uses of organic polymers in gas chromatography. The porous organic polymers used as adsorbents have some advantages, among which one can stress a high surface homogeneity with a controllable (within certain limits) porosity. Therefore, figuratively speaking, such polymers can be regarded as frozen organopolymeric phases.

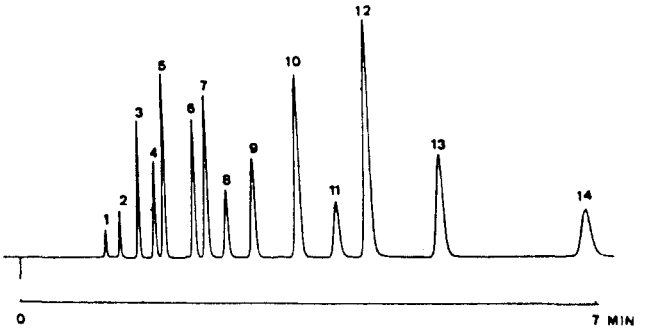

Figure 29. Chromatogram for the separation of C_1–C_4 alcohols in water.[38] Column, fused-silica type, 10 m × 0.3 mm; adsorbent, Poroplot (10 μm); temperature, 200 °C. (1) Methanol; (2) ethanol; (3) 2-propanol; (4) 1-propanol; (5) 2-methyl-2-propanol; (6) 2-butanol; (7) 2-methyl-1-propanol; (8) 1-butanol; (9) 2-ethyl-2-butanol; (10) 2-pentanol; (11) 3-methyl-1-butanol; (12) 1-pentanol; (13) 4-methyl-2-pentanol; (14) 2-ethyl-1-butanol.

Capillary columns with a surface layer on the inside polymer walls were first produced by Netherlands researchers.[38]

Figure 29[38] presents a separation chromatogram for alcohols in water. Good separation results were obtained for C_1–C_4 alcohols with the use of open capillary columns having an organic polymer. The same work reports on the separations using these columns in the case of formic and acetic acids, acetaldehyde and ethylene oxide, ammonia and water, etc.

Mention should be made of using a capillary column for separating organic natural adsorbents. Figure 30[114] shows the separation of naturally occurring organic acids on a natural polymer, i.e., cells of *Staphylococcus aureus*. The separation is quite suitable. The use of such adsorbents offers good promise. The above examples provide support for the practical application of capillary adsorption chromatography.

7. Conclusion

Application of gas adsorption capillary chromatography allows one to improve the main characteristics of chromatographic separation (efficiency, analysis rapidity, field of application, selectivity, etc.). The increased sorption capacity of gas adsorption capillary columns gives the possibility of using them in gas chromatography without splitting the carrier gas flow.

TABLE IX. Application of Organopolymeric Sorbent to the Separation of Organic Compounds[3]

porous polymer	recommended field of uses	nonrecommended field of uses
Chromosorb 101 Porapak P and PS	ethers, esters, ketones, aldehydes, alcohols, glycols, hydrocarbons, fatty acids	amines, anilines
Chromosorb 102 Porapak Q	light and permanent gases, hydrocarbons, alcohols, glycols, ketones, esters, nitriles, nitroalkanes	amines, anilines
Chromosorb 103	amines, amides, alcohols, aldehydes, ketones, hydrazines	acid compounds, glycols, nitriles, nitroalkanes
Chromosorb 104	nitriles, nitro compounds, sulfurous gases, nitrogen oxides, ammonium compounds, xylenols	amines, glycols
Chromosorb 105 Porapak N	aqueous mixtures of formaldehyde and acetylene in their separation from hydrocarbons and most gases	glycols, acids, amines
Chromosorb 106 Porapak Q	alcohols, C_2–C_5 carboxylic acids, alcohols, sulfurous gases	glycols, amines
Chromosorb 107 Porapak T	separation of formaldehyde from water, acetylene from low-molecular-weight hydrocarbons	glycols, amines
Chromosorb 108	gases, polar compounds such as water, aldehydes, alcohols, and glycols	
Porapak S	normal and branched alcohols, ketones, halogen hydrocarbons	acids, amines
Porapak R	esters, ethers, nitriles, nitro compounds	glycols, amines
Tenax-GC	high-boiling polar compounds, diols, phenols, methyl carboxylic ethers, amines, diamines, ethanolamines, amides, aldehydes, ketones	

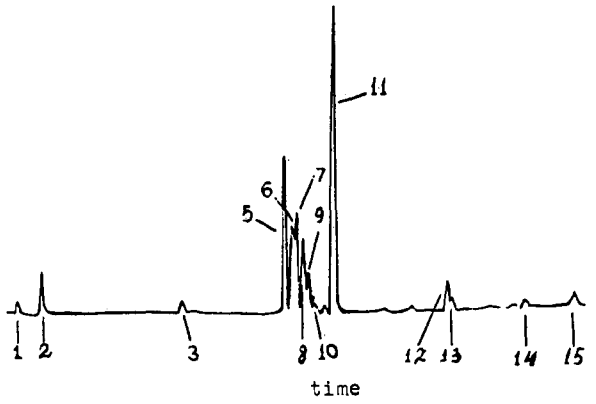

Figure 30. Chromatogram for the separation of unsaturated acids on an open capillary column with *Staphylococcus aureus* cell as the adsorbent:[114] (1) 14:1 tetradecenoic; (2) 14:0 myristic; (3) 15:0 pentadecanoic; (4) *c*-Δ^8-16:1 *cis*-hexadec-8-enoic; (5) *c*-Δ^9-16:1 *cis*-hexadec-9-enoic (palmitoleic); (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-12-enoic; (11) 16:0 palmitic; (12) 17:0 *cis*-methylenehexadecanoic; (13) *t*-Δ-17:0 *trans*-methylenehexadecanoic; (14) 18:1 octadecenoic; (15) 18:0 stearic.

The collective experience of investigators from different countries makes it possible to recommend the use of adsorption capillary columns for solving many important analytical problems.

It should prove worthwhile to pay attention to the development of such fields of gas adsorption capillary chromatography as the theory and optimization of separation conditions, reproducible methods of column production, application of sorbents of different selectivity, and increasing types of analyzed substances.

It is worthwhile to undertake a systematic study aimed at the development of gas adsorption capillary columns with nonporous (or slightly porous) surfaces.

It seems that some types of adsorption capillary columns will be useful in supercritical fluid chromatography.

Acknowledgment is made to Chrompack (The Netherlands) for capillary adsorption columns.

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