2

Stationary Phases

Vasile Matei, Iulian Comănescu and Anca-Florentina Borcea
Petroleum and Gas University of Ploieşti, Romania

1. Introduction

Gas chromatography is a physical method of separating and identifying mixtures, with application in chemical practice, scientific investigation, petroleum technology, environmental pollution control, the food industry, pharmacology, biology and medicine. Separation of the sample components takes place by adsorption by a solid or by dissolving in a non-volatile liquid, called the stationary phase. Separation takes place based on different partitions of the sample components between a stationary phase and mobile phase. The mobile phase, in gaseous state, must be insoluble in the stationary phase (solid or liquid), the mobile phase continuously circulating over the stationary phase. Separation and measurement of components in the sample are made in a device called a gas chromatograph. The "heart" of the device is the chromatography column. The chromatography column contains the stationary phase, solid or liquid, as packing material for packed columns, or on the walls of capillary columns. This method of analysis has undergone important developments in recent decades and contributed to the progress of important scientific and applied fields.

2. Requirements of stationary phases

The principle of gas chromatography (GC) is based on the capacity of the stationary phase to produce different separation times upon exiting a chromatographic column that contains, under one form or another, stationary phases for the various mixture components of the sample. Through GC analysis, the sample components are separated through the combined effect of the stationary and mobile phases. The mobile phase is generally a gas, such as H_2, He, N_2, AR etc. The stationary phase is fixed and can produce either adsorption or absorption. A thermodynamic equilibrium is established between the two phases; this is expressed through the theoretic plates. When the sample components are added between the two phases at equilibrium, a difference emerges that can be expressed as a function of the quantities of sample components.

Chromatography is a method of separating multicomponent mixtures. This method relies on differences in partitioning behaviour between a flowing mobile phase and a stationary phase in order to separate the components in a mixture and on different velocities of compounds in the mobile phase. The mobile phase is usually a permanent gas, such as hydrogen, helium, nitrogen, argon etc., as a constant flow with a certain pressure. The stationary phase may be a solid or a liquid that is immobilized or adsorbed in a solid. The

stationary phase may consist of particles (porous or solid), the walls of a tube (i.e. capillary) or a fibrous material.

Techniques by physical state of mobile and stationary phase:

Chromatography (C); Liquid chromatography (LC); Gas chromatography (GC); Paper chromatography (PC); Thin-layer chromatography (TLC) Column chromatography (CC) Gas-liquid chromatography (GLC); Gas-solid chromatography (GSC); Liquid-solid chromatography (LSC); Size-exclusion chromatography (SEC); Liquid-liquid chromatography (LLC); Ion exchange chromatography (IEC).

Components separated from the sample are placed in a chromatographic column, a tube in stainless steel, copper, aluminium or glass for packed chromatography, or quartz for capillary chromatography. The column contains the stationary phase as a granular porous solid. The columns are in the oven of the chromatograph, isotherm or temperature programmed. The mobile phase passes through the column at a constant flow, the flow values being correlated with the column type (packed, capillary). Thus, a primary classification could be gas-solid chromatography and gas-liquid-solid chromatography.

Capillary columns are used mostly, but not exclusively. They are the latest and best method, but they cannot replace totally the packed columns. The trends in column chromatography are:

1. Packed columns are still used in 20% of chromatographic analysis.
2. Packed columns are primarily for preparative applications, permanent gas analysis and sample preparation.
3. Packed columns will be used in the future because some applications demand packed columns not capillary columns.

Gas chromatography has several advantages as a physical method of separating gas mixtures, namely:

1. Resolution. The technique is applicable to systems containing components with very close boiling points. By choosing a suitable stationary phase or adsorbent, molecules with similar physical and chemical properties could be separated. Sample components could form in normal distillation, azeotropic mixtures.
2. Sensitivity. The properties of gas chromatographic systems are responsible for their widespread use. The detector based on thermal conductivity of the component can detect picograms of sample. The sensitivity is important considering that a chromatography test is less than 30 minutes. Analysis that typically occurs in about one hour or more can be reduced to the order of minutes due to the high diffusion rate in the gas phase and the phase to fast equilibrium between mobile and stationary phases.
3. Convenience. Operation in gas chromatography is a direct operation. It does not require highly qualified personnel to perform routine separation.
4. Costs. Compared with many other now affordable analytical tools, gas chromatography presents excellent cost value.
5. Versatility. GC is adaptable, from samples containing permanent gas up to liquids having high boiling points and volatile solids.
6. High Separation Power. If you use mobile phases with a low viscosity degree, very long columns will provide a strong separability

7. Assortment of Sensitive Detecting Systems. Detectors used in gas chromatography are relatively simple, with high sensitivity and fast responses given.
8. Ease of Recording Data. Output of the gas chromatograph detector can be conveniently connected to a potentiometer recorder, or integrating systems, computers that can store a large amount of information.
9. Automatization. Gas chromatographs can be used to automatically monitor various chemical processes that allow samples to be taken periodically and injected into the chromatographic columns to be separated and detected.

An ideal stationary phase is selective and has different adsorptivity for each sample component in order to ensure separation, as well as a wide array of operating temperatures. It has to be chemically stable and have a low vapour pressure at high operating temperatures. Some criteria for selecting an adequate stationary phase are:

- Is the stationary phase selective enough in separating the sample components so as to separate them one by one?
- Can there be an irreversible chemical reaction and can the mixture components be separated?
- Does the liquid phase have a vapour pressure low enough at operating temperature?
- Is it thermally stable?

For instance, we quote a separability criterion of sample components known as “component sympathy” for the fixed phase.

Thus, a light n-paraffin mixture with “sympathy” for non-polar stationary phase will separate on grounds of different boiling points; olefins, being polarisable, will show “sympathy” towards a polar stationary phase. The cis- and trans- components of an olefin mixture will separate on a stationary phase consisting of a complex of transitional metals, dissolved in an appropriate solvent, such as polyethylene glycol.

Identifying mixture components can be accomplished using chromatographic etalons – pure substances or known mixtures of components. In these cases, universal detectors may be used (FID, WCD). For unknown mixtures, mass spectrometry is recommended. For the universal detector WCD, only non-fuel components may be used, and for the FID, only fuel components that do not interact chemically with the stationary phase may be used.

The quantitative analysis of a given component is based upon evaluating the chromatographic peak, which is triangle-shaped when columns with filling are used; its surface is measured and divided by the total surface, in different percentages for different types of detectors.

For capillary columns with good resolution, the signal takes the shape of straight lines and calculating the composition of the mixture is done in the order of succession, dividing each individual line by the total number of lines and using an adequate calibration curve, drawn upon determinations of known compounds.

The results can be expressed as a percentage, g/L component in a known mixture, depending on the type of calibration or the calibration units.

Thermal stability is of great importance, since operating under severe circumstances can lead to short analysis intervals and incomplete use of the chromatographic column; for

instance, many stationary phases undergo degradation or decomposition at operating temperatures above 250^0 C, resulting in a lower operating life. On the other hand, certain components of unknown mixtures may reversibly or irreversibly poison the stationary phase components, deactivating it over time. In such cases, entry within the stationary phase can be accomplished using guarded columns that retain the poisonous components. It is vital that these components are known so as to prevent poisoning precious columns.

Before usage, the stationary phases placed into the GC columns must be conditioned and activated through streaming the mobile phase – the permanent gas.

Overall, stationary phases constitute a solvent with different selectivity for each component of the mixture in the analyzed sample.

2. Adsorption

Solid adsorbents as powdery material perform two functions in chromatography: the adsorbent itself (GS), in which case the separation takes place by adsorption, and support for stationary phase (non-volatile liquid), liquid stationary phase (GLS) coated on a granular material, in which case the separation takes place by absorption. Commonly, the size of the solid material used in chromatography is in the range of mesh (mesh - the number of openings per linear inch of a screen). Conversion between the Anglo Saxon and European expression (in mm) is presented in Table 1.

U.s. Mesh	Inches	Microns	Millimetres	U.s. Mesh	Inches	Microns	Millimetres
3	0.2650	6730	6.730	40	0.0165	400	0.400
4	0.1870	4760	4.760	45	0.0138	354	0.354
5	0.1570	4000	4.000	50	0.0117	297	0.297
6	0.1320	3360	3.360	60	0.0098	250	0.250
7	0.1110	2830	2.830	70	0.0083	210	0.210
8	0.0937	2380	2.380	80	0.0070	177	0.177
10	0.0787	2000	2.000	100	0.0059	149	0.149
12	0.0661	1680	1.680	120	0.0049	125	0.125
14	0.0555	1410	1.410	140	0.0041	105	0.105
16	0.0469	1190	1.190	170	0.0035	88	0.088
18	0.0394	1000	1.000	200	0.0029	74	0.074
20	0.0331	841	0.841	230	0.0024	63	0.063
25	0.0280	707	0.707	270	0.0021	53	0.053
30	0.0232	595	0.595	325	0.0017	44	0.044
35	0.0197	500	0.500	400	0.0015	37	0.037

Table 1. Mesh to millimetres conversion chart

Hereinafter we present the advantages of adsorption chromatography, which takes place at gas solid interaction, compared to GLS.

The advantages of gas chromatography gas-solid type from gas-liquid-solid can be summarized as follows: 1) stability of stationary phase on a wide range of temperatures; 2) a low detector noise limit; 3) lower values of HETP (height equivalent to a theoretical plate) than for gas-liquid chromatography (the adsorption-desorption process can be faster than the corresponding diffusion process in the liquid phase); 4) increased capacity of structural selectivity in separating geometrical isomers (e.g. using molecular sieves or graphitized carbon black); 5) high chemical selectivity when complexing agents are used as adsorbents; 6) high adsorption capacity allows the separation of gaseous or vapour compounds at room temperature; 7) increased chemical stability of adsorbents provides analysis of aggressive compounds; 8) important techniques have been developed in solids photochemistry and therefore there is better knowledge of adsorption; 9) numerous studies of heterogeneous catalysis were developed.

The limitations of this technique can be summarized as follows: 1) risk of asymmetric area due to the nonlinear adsorption isotherm of some analyzed compounds; 2) low reproducibility of chromatographic characteristics because adsorbents' properties are not as easily standardized as liquid substances; 3) more loss of the analyzed compounds as a result of irreversible adsorption or catalytic conversion of the separation process; 4) limited access to different commercial adsorbents for gas chromatography; 5) strong dependence of retention time of the sample size is common due to nonlinear adsorption, which combines the main advantage of gas-solid chromatography to the efficiency of capillary chromatography.

Adsorbents' selectivity is independent of the type of column used (packed or capillary column). Gas chromatography of adsorption has applications not only in the separation of gas mixtures with low boiling points, but also in the separation of hydrocarbon mixtures, as well as some organic compounds and some aromatic separation.

In the recent past there was a distinct tendency towards solid-gas chromatography. This can be attributed to two factors: first, new achievements in the field of adsorbents and second, using the improved logistics of gas chromatography (better trace analysis, more reproducible techniques for temperatures programming and high coupling techniques). Both solid and liquid stationary phases must have extraordinary properties, among which solid stationary phases are designed to solve many critical issues involved (Rotzsche, 1991). Adsorbents can be classified according to following criteria: chemical structure and geometric structure.

According to the chemical nature classification different interaction types of molecules' samples can take place. Kiselev & Yashin (1985) proposed grouping adsorbates into four groups (A-D), and in three groups (I-III) of adsorbents.

Adsorbents of type I have no functional groups or ions on the surface and thus they are not able to interact specifically with adsorbates. Interaction with all types of molecules A-D occurs non-specifically. Adsorbents are saturated hydrocarbons, graphite or rare gas crystals. The most important representatives of this type is graphitized carbon black (thermal graphitized carbon black) whose properties are close to ideal non-specific adsorbents. Similar to graphite are some inorganic compounds, such as graphite-like boron nitride (BN) or sulphides of metals (i.e. MoS) (Avgul et al., 1975).

Adsorbents of type II develop positive partial charge on the surface adsorbent. Besides these dispersion forces specific interactions develop leading to the orientation and localization of adsorbate molecules on centres having high charges. That concerns the salts having cations with positive charge with small ray, while negative charges are distributed in a relatively large volume (i.e. $BaSO_4$). Thus, the most significant representatives of this type are adsorbents with functional groups of protonated acids, such as hydroxylated silicagel, Lewis acids aprotic centres located on the surface. Molecules A type (saturated, rare gases) are non-specifically adsorbed and they are dispersion forces only. Molecules B, C and D can be adsorbed non-specifically. Type B includes molecules with electron density localized on some bonds or atoms: type II bonds of unsaturated or aromatic compounds, functional groups, atoms having electrons couple (ethers, ketones, tertiary amines, pyridines and nitriles), molecules with high quadrupole moments (N_2 molecules). Interactions between an adsorbent type II and an adsorbed type B develop between centres with electronic high-density (molecules in the sample) and positive charges of adsorbent (i.e. acidic proton of hydroxylated silica gel or a cation of Li, Na, Mg, Ca in acid zeolite or aprotic acids Lewis type on the surface). Type C molecules have a positive charge located on a metal atom and the excess of electron density is distributed on adjacent bonds (organometallic compounds). Type D are molecules containing peripheral functional groups (OH, NH, etc.) whose electronic density increase the density of some atoms (O, N) and reduce the density for other atoms (H). This group includes water, alcohols and primary and secondary amines. Specific interactions of type D adsorbates with Type II adsorbents involves the forces between the adsorbent centres with positive charges and the only couple of electrons of the atoms of O or N of the sample molecules.

Adsorbents type III. Adsorbents types III are specific having centres with high density centres on the surface. In this group are polymers as polyacrylonitrile, copolymers of vinylpyridine and divinylbenzene and polymers group with (C = O) and (–O–) on the surface. This group could include porous polymers based on styrene ethylvinylbenzene cross linked with divinylbenzene, varying by using different polymerization promoters and even non-specific dispersion forces. Adsorbents Type III includes crystalline surfaces formed by anions and chemically modified non-specific adsorbents covered with a monomolecular layer of adequate substance, creating negatively charged surface centres. Adsorbents type III interacts non-specific with adsorbates type A and specific with type B, C or D by forces from the negative charges of the adsorbent surface and from the positive charges of metallic atoms (C) or from functional groups (OH, NH) proton type (D) and dipole or induced dipole type (B).

Classification according to geometric structure

This classification concerns the possibilities to increase the surface. Increasing the surface meets a series of reserves, such as an increase in surface leads to increased dispersion with an increase in heterogeneity. Therefore, increasing contact points between particles will reduce the pore diameter with Knudsen diffusion disadvantage. Kiselev & Yashin (1985) have overcome these difficulties in the development of GCS. The adsorbents are geometrically classified as follows (Rotzsche, 1991).

Type 1 Non-porous adsorbents

Crystalline products with a smooth surface (sodium chloride, graphitized thermal carbon black, BN, MoS,). S_A in the range of 0.1 – 12 m^2/g.

Type 2 Uniformly porous adsorbents with wide pores. Silica gel with pore diameters between 10 and 200 nm (Porasil, Spherasil) and some other forms of silica gel chemical bonded (Durapak a.o.) and other polymers styrene divinylbenzene type with large pores (20 – 400 nm).

Type 3 includes adsorbents with a uniform pores system, but small pores. In this category should be mentioned molecular sieves (zeolites), carbon molecular sieves, porous glass and porous polymers. Pores diameter is around 10 nm.

Type 4 presents adsorbents with non-uniform pores. Among materials of this type there are activated carbon and alumina. Because of geometrical and chemical heterogeneity, having pores in the range 2-20 nm (mezopores) up to 200 nm, these adsorbents are not suitable for GCS. Classification is based on pores size. The difference between porous adsorbents and non-porous adsorbents consists in the free spaces form developed by the porous system. This system is quantitatively characterized by the following parameters (Rotzsche 1991):

- Specific surface area S_A (geometric size of the pore wall area/gram of adsorbent).
- Specific pore volume *V,* (total pore volume/gram of adsorbent).
- Mean pore diameter d_{So} (average diameter of 50% of the pores).
- Pore size distribution.

These parameters could be measured by gas chromatography and other methods, such are mercury porosimetry and reversed size exclusion chromatography. The ratio of pore diameters for porous adsorbents to the molecules diameters of the adsorbate is a significant parameter because the higher ratio is (the molecule diameters are smaller compared with pore diameters), the faster the adsorption equilibrium is reached. For a similar size of pore diameters and molecules diameters the adsorption rate depends equally on the pore shape and the adsorbate molecules' size. For narrow pores the adsorbed molecule on surface atoms of one pore could interact with other pore surface atoms and in this case the adsorbed molecules are trapped, and the transfer of molecules between adsorbent and mobile phase is stopped.

The most widely used chromatography supports are Kieselguhr (diatomaceous earth = light-coloured porous rock composed of the shells of diatoms) based, containing polysilicic acid in the hydrated amorphous silica form having a porous structure and containing varying amounts of metal oxides of Fe, Al, Mg, Ca, Na, K. These supports are known under different commercial terms, the most commonly used type being *Chromosorb*. They are found in several varieties, of which the most important are:

- *Chromosorb P* (pink) is reddish pink and has a surface area situated between 4 -6 m^2 / g. It has the advantage that it can be loaded with a large amount of liquid stationary phase (up to 25 30%) and has high mechanical strength. It is not sufficiently chemically inert and for this reason it is used mainly to separate non-polar substances.
- *Chromosorb W* (white) is white and has a smaller surface area than Chromosorb P, 1-2 m^2 / g. Therefore it can be loaded with a smaller amount of liquid stationary phase, up to 15%. It is chemically inert, but is friable, having a low mechanical strength. It has general usability, so it can be used to separate all classes of compounds, both polar and non-polar.
- *Chromosorb G* surface area is even smaller than Chromosorb W, of only 0.5 m^2 / g and can upload up to 5% stationary phase. But it has the advantage of combining the chemical inaction of type W with the mechanical strength of type P.

There are also supports of other types, but these are much less used. Such supports are based on synthetic polymers (i.e. Teflon), glass and others.

Next will be presented several examples of a few illustrative applications of some adsorbents (Poole, 2003) Table 2:

Stationary Phase		Maximum Temperature (°C)	Usual Applications
Alumina		200	Alkanes, alkenes, alkines, aromatic hydrocarbons - from C_1 to C_{10}
Silica gel		250	Hydrocarbons (C_1 – C_4), inorganic gases, volatile ethers, esther and ketone
Carbon		350	Inorganic gases, hydrocarbons (C_1-C_5)
Carbon molecular sieves		150	Oxygenated compounds (C_1- C_6)
Molecular sieves (5X and 13X)		350	Hydrogen, oxygen, nitrogen, methane, noble gases. Separation He/Ar and Ar/O_2. Hydrocarbons C_1 – C_3 on 3X, on 13X till C_{12} but no isomers. Cyclodextrine, halocarbons, permanent gases, hydrofluorocarbons, hydrocarbons C_1-C_{10}.
	Q	310	Hydrocarbons C_1-C_{10}, halocarbons C_1- C_2.
	S	250	Volatile organic solvents C_1 – C_6
	U	190	Nitrocompounds, nitrils, water, inorganic gases.

Table 2. Illustrative examples of some adsorbents and temperature values at which they are active

Table 3 briefly presents some gas chromatography main adsorbents’ characteristics (Grob & Barry, 2004).

Adsorbent	Polymeric material	Tmax, °C	Applications
HayeSep A	DVB-EGDMA	165	Permanent gases, including: hydrogen, nitrogen, oxygen, argon, CO, and NO at ambient temperature; can separate C2 hydrocarbons, hydrogen sulphide and water at elevated temperatures
HayeSep B	DVB-PEI	190	C1 and C2 amines; trace amounts of ammonia and water

Adsorbent	Polymeric material	Tmax, °C	Applications
HayeSep C	ACN-DVB	250	Analysis of polar gases (HCN, ammonia, hydrogen sulphide) and water
HayeSep D	High purity DVB	290	Separation of CO and carbon dioxide from room air at ambient temperature; elutes acetylene before other C2 hydrocarbons; analyses of water and hydrogen sulphide
Porapak N	DVB-EVB-	190	Separation of ammonia, carbon EGDMA dioxide, water, and separation of 165 acetylene from other C2 hydrocarbons
Porapak P	Styrene-DVB	250	Separation of a wide variety of alcohols, glycols, and carbonyl analytes
Porapak Q	EVB-DVB copolymer	250	Most widely used; separation of hydrocarbons, organic analytes in water and oxides of nitrogen
Porapak R	Vinyl pyrollidone (PM)	250	Separation of normal and branched alcohols
Porapak T	EGDMA (PM)	190	Highest-polarity Porapak; offers greatest water retention; determination of formaldehyde in water
Chromosorb 101	Styrene-DVB	275	Separation of fatty acids, alcohols, glycols, esters, ketones, aldehydes, ethers and hydrocarbons.
Chromosorb 102	Styrene-DVB	250	Separation of volatile organics and permanent gases; no peak tailing for water and alcohols
Chromosorb 103	Cross-linked PS	275	Separation of basic compounds, such as amines and ammonia; useful for separation of amides, hydrazines, alcohols, aldehydes and ketones
Chromosorb 104	ACN-DVB	250	Nitriles, nitroparaffins, hydrogen sulphide, ammonia, sulphur dioxide, carbon dioxide, chloride, vinyl chloride, trace water content in solvents
Chromosorb 105	Crosslinked polyaromatic	250	Separation of aqueous solutions of formaldehyde, separation of acetylene from lower hydrocarbons and various classes of organics with boiling points up to 200° C

Key: DVB—divinylbenzene; EGDMA—ethylene glycol dimethacrylate; PEI—polyethyleneimine; ACN—acrylonitrile; EVB—ethylvinylbenzene.

Table 3. Polymer type adsorbents

3. Types of stationary phase for adsorption

The conditions that liquid stationary phases have to meet are:

- To be a good solvent for the components of the sample, but the solubility of these components has to be differentiated;
- To be practically non-volatile at the temperature of the column (vapour pressure to be less than 0.1 mm Hg);
- Be chemically inert;
- Have a higher thermal stability.

The categories of the stationary liquid phase are:

- *Non-polar stationary phases*, which are compounds, such as hydrocarbons (paraffin) or silicone oils (polysiloxanes) without grafted polar groups. Examples of such stationary phases are: squalane ($C_{30}H_{62}$ hydrocarbon), silicone oils metylsilicon type (names OV 1, SE-30). These phases separate the analyzed compounds in order of increasing boiling points.
- *Polar stationary phases*, which contain a high proportion of polar groups, i.e. the average molecular weight polyethylene glycol (Carbowax 20M), silicone oils with cianopropil groups (OV 225 cianopropyl-methyl-phenyl silicone) diethylene glycol succinate (DEGS), nitrotereftalic ester of polyethylene glycol (FFAP) etc. They differentiate between the non-polar and polar compounds, retaining only those which are polar, and are used especially to separate polar compounds.
- *Intermediate polarity stationary phase*, containing polar groups in the lower concentration or polarizable groups grafted onto a non-polar support. Examples of such stationary phases are phenyl methyl silicone phase (OV 17), dinonyl phthalate, polyethylene glycols having high molecular weight. They are universal stationary phases, which can be used to analyze both polar and non-polar compounds.
- *Specific stationary phases*, which are used in certain cases. They contain compounds that interact only with certain components of the mixture to be analyzed, for example $AgNO_3$ dissolved in polyethylene glycol which forms adduct with olefins.
- *Chiral stationary phases*, containing chiral compounds interacting with only one optical isomer of a pair of enantiomers. Such phases are based on cyclodextrin or certain amino acids.
- Given the polarity of the stationary phase and possible interactions, organic compounds can be grouped in terms of chromatographic separation in the following five classes:
- *Class I* very polar compounds, able to give hydrogen bonds: water, glycerin, glycols, hydroxyacids, and amino acids. These compounds are difficult to separate by gas chromatography, due to high polarity. Excepting water, they derivatized before separation.
- *Class II* polar compounds, which have active hydrogen atoms: alcohols, carboxylic acids, phenols, primary and secondary amines, nitro and nitriles with a hydrogen atom in α position. These compounds are separated in polar stationary phases.
- *Class III* intermediate polarity compounds, without active hydrogen: ethers, esters, aldehydes, ketones, nitro and nitriles without hydrogen atom in α position. These compounds are separated on stationary phases of intermediate polarity.
- *Class IV* compounds with low polarity, but which have active hydrogen: aromatic hydrocarbons, alkenes, chloroform, methylene chloride, dichloroethane, trichloroethane

etc. These compounds are separated on stationary phases of intermediate polarity or non-polar.

- *Class V* non-polar compounds: alkanes, cycloalkanes. These compounds separate in non-polar stationary phases.

This classification is empirical and is only meant to facilitate choosing the most suitable stationary phase for chromatographic analysis. Many polymers contain mixtures of the above functional groups, as indicated in Table 4.

Name	Type	Structure	Density g/ml	Viscosity cP	Average Molecular Weight
OV-1	Dimethysiloxane gum	CH_3	0,975		> 10^4
OV-101	Dimethylsiloxane fluid	CH_3		1500	30000
OV-7	Phenylmethyl dimethyl Siloxane	80 %CH_3 20%C_6H_5	1.021	500	30000
OV-210	Trifluoropropyl methylsiloxane	50%$CH_2CH_2CF_3$ 50%CH_3	1.284	10.000	200000
OV-275	Dicyanoalkyl siloxane			20.000	5000

Table 4. Properties of some commercially available pol-siloxane phases

4. Kovats retention index

A universal approach (Kovats) solved the problems concerning the use, comparison and characterization of gas chromatography retention data. This reporting of retention data as retention time t_R is absolutely meaningless, because all chromatographic parameters and any experimental fluctuation affect the proper measurement of a retention time. Using relative retention data ($\alpha = t'_{R2}/t'_{R1}$) provided improvements, but the default of a universal standard usable for a wide range of temperatures for stationary phases of different polarity has discouraged its use. In the Kovats approach, to retention index I of an alkane is assigned a value equal to 100 times its number of carbon atoms. Therefore, for example, values I of n-octane, n-decane and n-dodecanese, are equal to 800, 1000, 1200, respectively, by definition, and are applicable to any columns, packed or capillary and to any mobile phase, independent of chromatographic condition, including column temperature. However, for any component, the chromatographic conditions, such as stationary phase, its concentration, support and column temperature for packed columns, must be specified. Since retention index is the preferred method of reporting retention data for capillary columns, stationary phase, film thickness and column temperature must also be specified for any component out of n-alkanes, otherwise I values are meaningless. A value I of a component can be determined by mixing a mixture of alkanes with the desired component and chromatography under specified conditions. A plot of the logarithmic adjusted retention time versus retention index is generated and a retention index of the solute considered is determined by extrapolation, as shown in the figure below for isoamyl acetate.

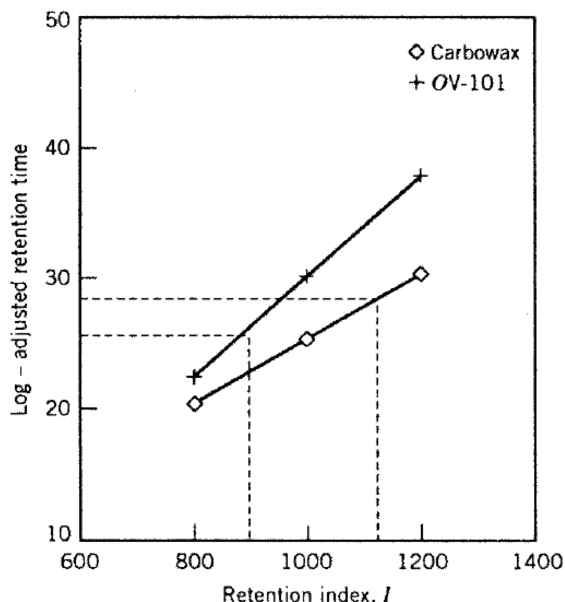


Fig. 1. Plot of logarithm-adjusted retention time versus Kovats retention index: isoamyl acetate at 120◦C (Grob & Barry, 2004).

Selectivity of stationary phases can be determined by comparing the values I of a solute on a non-polar phase, such as squalane OV 101 (I = 872) with corresponding I values of 1128 associated with more polar columns containing Carbowax 20M, for example. This difference of 256 units shows the superior retention of the Carbowax 20M column. Specifically, isoamyl acetate elutes between n-C11 and n-C12 on a Carbowax 20 M columns, but much faster on OV 101, where it elutes after n-octane. Retention indices in GC normalize instrumental variables, allowing retention data obtained by various systems to be compared. For example, isoamyl acetate with a retention index of 1128 will elute between C11 and C23 in the same chromatographic conditions. Retention indices are also very useful for comparing the relative elution order of the series of analytes on a specific column to a given temperature, and comparing the selective behaviour of two or more columns.

5. McReynolds classification of stationary phases

As shown, the most important criteria upon which stationary phases choice is made for a certain analysis is the polarity of the phase and of analyzed compounds. Numerical expression of this polarity, which would facilitate the choice, is not possible because there is no physical size that can be associated directly with the polarity (to some extent the dipole moment could be this size). For this reason, to express the stationary phase polarity they are using some reference compounds, which are arbitrarily chosen. Such a system was developed by Rohrschneider and later developed by McReynolds, based on the Kovats retention indices and using squalane as reference stationary phase, assigning it null polarity. A total of five reference compounds were selected: benzene, 1-butanol, 2-pentanona,

nitropropane and pyridine. Each of these compounds can be considered standard for certain classes of substances, which are similar in terms of chromatographic behaviour, as follows:

- *benzene* for unsaturated hydrocarbons and aromatic hydrocarbons;
- *1-butanol* for alcohols, phenols, carboxylic acids;
- *2-pentanona* for aldehydes, ketones, ethers, esters;
- *nitropropane* for nitroderivates and nitriles;
- *pyridine* for aromatic bases and heterocycles with nitrogen.

The steps to determinate the constants McReynolds for a particular stationary phase A, for packed columns, are as follows:

- each reference compound is analyzed on a column with 20% squalane as stationary phase, isothermal at 100 ˚ C and the corresponding retention indices are determinate;
- reference compounds are analyzed on a column containing 20% stationary phase A, under the same conditions and in such cases Kovats retention indices are established;
- McReynolds constants of the stationary phase A are calculated as follows:
- for benzene (denoted by x '): the difference between the retention index of benzene on stationary phase A and on squalane:

$$x' = I_R(phase\ A) - I_R(squalane) \qquad (1)$$

- for a butanol (denoted by y '): the difference between the retention index on phase butanol on stationary phase A and on squalane;
- The same applies for 2-pentanona (z'), nitropropane (u') and pyridine (s').

These McReynolds constants values were determined for a great number of common stationary phases and they are tabulated. Some values are also given in Table 5.

Name of the stationary phase	**X′**	**Y′**	**Z′**	**U′**	**S′**
Squalane $C_{30}H_{62}$	0	0	0	0	0
Methylsilicone OV-1	16	55	44	64	42
Methylsilicone SE-30	15	53	44	64	41
Methyl-phenyl-silicone (20% phenyl) OV-7	69	113	111	171	128
Methyl-phenyl-silicone (50%phenyl) OV-17	119	158	162	243	202
Cyanopropyl-methyl-phenyl-silicone OV-225	228	369	338	492	386
Carbowax 20M (Polyethylenglycol)	322	536	368	572	510
Nitroterephtalic ester of PEG (FFAP)	340	580	397	602	627
Diethyleneglycol succinate (DEGS)	496	746	590	837	835

Table 5. McReynolds constants values for some usual stationary phases

Currently there are hundreds of stationary phases used in gas chromatography and McReynolds constants allow selecting the one that promises the best separation of the components analyzed. Because obviously there are a number of stationary phases that have similar McReynolds constant values, they can be substituted in between without affecting separation. Thus, if there is a stationary phase recommended in the literature for separation, but is unavailable in a laboratory, it will be replaced with an equivalent.

There was an impulse of consolidating the number of stationary phases used in the mid-1970s. Leary et al. (1973) reported the application of the statistical technique *the nearest neighbour* for the 226 of the stationary phases of McReynolds study and suggested that a total of only 12 phases could replace the 226. Later it has been found that four phases, OV-101, OV-17, OV-225 and Carbowax 20M could provide GC analysis, satisfying 80% of a wide variety of organic compounds, and a list of six favourite stationary phases on which almost all gas-liquid chromatographic analysis could be performed: (1) dimethylpolysiloxane (OV-101, SE-30, SP-210); (2) 50% phenyl-polysiloxane (OV-17, SP-2250); (3) poly-ethylene-glycol of molecular weight> 4000 (Carbowax); (4) diethyleneglycol succinate (DEGS); (5) 3- ciano-propyl-polysiloxane (Silar-10 C, SP-2340) and (6) tri-fluor-propyl-polysiloxane (OV-210, SP-2401).

Another quality of McReynolds constants is guiding the selection of columns to separate compounds with different functional groups, such as ketones by alcohols, ethers by olefins and esters by nitriles. If the analyzer wants a column to elute an ester after an alcohol, the stationary phase should have a value Z' greater than the value Y'. Also, a stationary phase should have a value of Y′ greater than Z' in order to make ether elute before the alcohol.

6. Column type

Different chromatography types of column are presented by their diameters. Thus, there are three main types of column: packed columns, capillary columns and micro-packed columns.

Packed columns

The most used column materials are stainless steel, glass, quartz, nickel and polytetrafluorethylene (PTFE). Because of their good thermal conductivity and easy manipulation, stainless steel columns are widely applied. Glass columns are more inert. PTFE columns are used to separate mixtures of halogens and derivates. Classical packed columns′ inner diameters range from **1.5** mm to **6** mm. Very important for packed columns is the load; the load is directly proportional to the column cross-section and hence to the square of the inner diameter (Leibnitz & Struppe, 1984).

Capillary columns (open tubular columns)

The terminology used for capillary column includes names such as WCOT (well coated open tubular) which are capillary columns where the stationary phase is deposited directly onto the inner surface of the wall not including substances that could be considered support. SCOT (support coated open tubular) includes those capillaries that have deposited on the inner surface a finely divided support (NaCl, BaCO3, SiO2, etc.) in which stationary phase is submitted. PLOT (porous layer open tubular) columns contain capillaries with stationary phase deposited on a porous support consisting of a finely divided support for packed gas chromatography columns (Celite, Chromosorb, etc.). Porous material is deposited in the capillary tubes from the very first moment of column conditioning. Capillary columns BP, DP, SPB (bond phase) include capillary tubes that have stationary phase chemically immobilized on the surface of the capillary inner wall. When choosing a certain type of capillary column it is necessary to take into account the nature of the sample being analyzed, the equipment available and the effective separation. Capillary columns WCOT have better efficiency in separation than SCOT because the inner column diameter is smaller. SCOT columns can be considered as subgroups of PLOT columns, since all SCOT are PLOT columns, but not vice versa (Ciucanu, 1990). For capillary columns the inner diameter ranges from 0.10 to 0.20 mm.

Wall-coated open-tubular (WCOT) columns contain the stationary phase as a film deposited on the internal surface of the tube wall. The formation of a thin and uniform film along the total length of the column represents the key to capillary columns' efficiency.

Porous-Layer Open Tubular (PLOT)

To increase the sample capacity of capillary columns and decrease the film thickness, porous layers for the inside walls of the column tubing were used. The stationary phase amount is directly related to the efficiency of capillary columns and generates efficiency increasing due to porous layers.

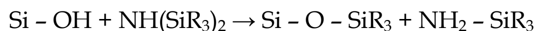
The method presented here used capillary columns of glass and quartz, the most used today. Glass capillaries are drawn from a device consisting of an electric furnace in which glass melts, two traction rollers which pull the column, a curved metallic tube for the spiral of the tube electrically heated at glass melting temperature. Capillary dimensions are set from the ratio of the two rolls' traction speed. Silica (quartz) tubes require temperatures of 1800-2000 ° C. After pulling, the capillary tube is covered with a polymer film in order to increase the tensile strength. Polyamide or polyimide polymers are used, which are stable up to temperatures of 350-400 ° C.

For the glass preparation, silica mixed with some metal oxides (Na_2O, CaO, MgO, B_2O_3, Al_2O_3 etc.) are used that break covalent bonds. In general, glass is chemically inert; however, because of impurities and the superficial structure, capillaries present catalytic activity and adsorption of the sample component. Metal oxides will act as Lewis acid. Molecules of analyzed compounds containing π electrons or non-participating electrons will react with Lewis acids. Adsorption and catalytic properties of glass and silica are due to silanol groups and siloxane bridges on the surface of the capillary tube. Also, water in the atmosphere adsorbs to the surface by hydrogen bonds. Heating the tube, water can be removed in order to form stable siloxane bridges. For a capillary tube to become a chromatographic column, the inner surface of the tube must be covered with a uniform and homogenous film of stationary phase.

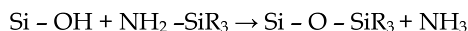
By silanization of silanol groups, the critical surface tension (one that is established between the solid surface and stationary phase) is significantly reduced, but has the same value for glass and quartz. Silanizated surfaces have a surface tension so small that only non-polar stationary phases (OV-101) can "wet" them. Polar stationary phases (Carbowax 20M) do not give uniform films. The basic elements of glass capillary tubes' chemistry are alkaline metal ions, silanol groups and siloxane bridges. These are active centres that catalyze at high temperatures the decomposition reactions of sample components as well as of the stationary phase. For these reasons these active centres have to be deactivated.

Capillary tube surface deactivation involves removing the metal ions and blocking out the silanol groups with no catalytic activity groups. Removal of metal ions of silica and glass capillary tubes is achieved by acid washing in a static or dynamic regime. An acidic wash causes not only metal removing, but also increases the number of silanol groups, by breaking the siloxane bonds on the surface of the tube. In the past, tubes' surface deactivation was with surfactants, but they have low thermal stability and are no longer used. Current methods use disilazane, cyclic siloxanes and polysiloxanes. In all cases siloxane groups turn into silicate esters. Methods to deactivate with silazane realize the blocking of silanol groups by reaction with hexamethyldisilazane, di-fenil-mehyl-disalazane, dibutiltetramethyldisilazane, dihexyltetramethyldisilazane etc.

Reaction for deactivation with disilazane is:



$$Si - OH + NH(SiR_3)_2 \rightarrow Si - O - SiR_3 + NH_2 - SiR_3$$



$$Si - OH + NH_2 - SiR_3 \rightarrow Si - O - SiR_3 + NH_3$$

Uniform films of stationary phase can be obtained when the adhesion forces between stationary phase and capillary column surface are greater than the stationary phase molecules. Cohesion forces are stronger with increased similarity between organosiloxanic groups and functional groups of stationary phase. Methyl groups have high thermal stability, are chemically inert and are used to deactivate capillary columns with non-polar stationary phase. Phenyl groups have lower thermal stability than methyl groups, but allow the deposition of medium polarity stationary phase. Cyanopropyl and trifluoropropyl groups are strong polar and it is difficult to bond on the glass by reaction with disilazane, because disilazane have a reduced thermal stability. Another method of blocking the activity of silanol groups is based on reaction with cyclosiloxanes. Deactivation with cyclosiloxanes allows bonding some functional groups similar to those of the stationary phase.

Another method for modifying the surface chemistry of glass and silica capillary tubes is based on the stationary phase, by blocking the surface active centres, as well as getting a very stable film of stationary phase. Carbowax 20M was the first stationary phase used to deactivate glass capillary tubes. This step is followed by a heating treatment.

Another method of decomposition of the stationary phase is to use radicalic initiators. The initiator used for immobilization of polyethylene glycol is dicumilperoxide. Another possibility of immobilization of Carbowax 20 M is based on the reaction between OH groups of polyethylene glycol with diisocyanate in the presence of dibutyltindilauril. A chemically inert and thermal stability capillary column improves also by immobilizing the stationary phase polysiloxanes type with terminal hydroxyl groups OH, such as OV-17-OH, OV-31-OH, OV-240-OH.

Changing the surface chemistry by immobilizing the stationary phase can be done with a large number of siloxane polymers. A simple method of immobilization is polymerization in a column of silicon monomers consisting in the formation of bonds Si–O–Si between siloxane polymers and the capillary column wall. Immobilization can be done in the presence of radicalic initiators. Immobilization of the stationary phase can be initiated also by gamma radiation at room temperature. Stationary phases without vinyl groups require a high dose of radiation. Immobilization in the presence of gamma radiation eliminates the danger of degradation of the stationary phase and allows very precise control of reaction.

Micro-Packed Columns

Due to their parameters concerning mass capacity, phase ratio, resolution and short analysis time, micro-packed columns are very attractive. They are micro pore tubes having inner diameters ranging from 0.3 - 1 mm and at lengths varying from 1 to 15 m, packed with particles 0.007-0.3 mm in diameter. Table 6 presents geometrical characteristics for packed columns and micro-packed columns.

	Irregular micro-packed column	**Classical packed columns**	**Regular micro-packed columns**
Tube i.d.(*d,*) [mm]	0.3-0.5	≥ 2	0.3-1.5
Particle size (*d,*) mm	0.05-0.15	0.12-0.30	0.04-0.3
d_p/d_c	0.04-0.10	0.07-0.25	0.25-0.5
sample capacity µg	5-20	>1000	1-10
h (mm)	0.4-1.2	>0.5	0.15-0.40
L ,m	1.8 (6 ft)	4.5 (15 ft)	4.5 (15 ft)
Preferred applications	Short columns permit high-speed analyses coupled techniques with MS.	Simple separation problems; trace analysis; coupled techniques with spectrometry	Multi-component analysis; high-resolution coupled technique with MS; trace analysis

Table 6. Geometrical characteristics for packed columns and micro-packed columns

Micro-packed columns are suitable for the analysis of multi-component mixtures and trace constituents, especially when coupling with mass spectrometry, thus allowing quickly analyses.

7. Operation column

Several parameters can be used to evaluate the operation of a column and to obtain information about a specific system. An ideal gas chromatographic column is considered to have high resolving power, high speed of operation and high capacity.

Column Efficiency

Two methods are available for expressing the efficiency of a column in terms of HETP (height equivalent to a theoretical plate): measurement of the peak width (1) at the baseline, $N=16(V_R/w_b)^2$ and the peak width at half the peak height (2), $N=5.54(VR/w_k)^2$, where N is the height equivalent to theoretical plate (HETP) and w has the significance from the graphic below (Figure 2).

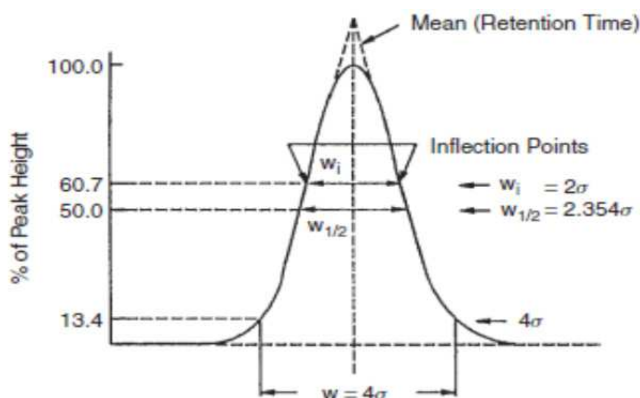


Fig. 2. Methods for expressing the efficiency of a column in terms of HETP

Effective Number of Theoretical Plates

Open-tubular columns generally have a larger number of theoretical plates. The *effective number of theoretical plates*, N_{eff}, characterizes open-tubular columns.

$$N_{eff}=16(V_R'/w_b)^2 \quad (2)$$

where V'_R the adjusted retention volume.

Separation Factor

The *separation factor* (S) describes the efficiency of open-tubular columns:

$$S= 16(V_R'/w_b)^2 =16(t'_R /w_b)^2 \quad (3)$$

where V'_R is the adjusted retention volume and t'_R is the adjusted retention time.

8. Preparation of columns

The most used technique for coating supports with high concentrations (>15%) of viscous phases is solvent evaporation. This technique leads to a uniform phase deposition. The steps to follow are presented below (Grob & Barry, 2004).

1. Prepare a solution of known concentration of liquid phase in the suitable solvent.
2. Add the desired amount of solid support in a known volume of the solution.
3. Transfer the mixture in a Büchner funnel, in order to remove the solvent excess.
4. Measure the volume of filtrate.
5. Dry the "wet" packing to remove residual solvent.
6. Calculate the mass of liquid phase retained on the support.

This technique allows obtaining a uniform coating of a support and minimizes the oxidation of the stationary phase during column.

9. The technology of capillary columns

The widespread use of fused silica for capillary columns is because it is inert compared to other glasses. In 1986 Jennings published a comparison of fused silica with other glasses, such as soda-lime, borosilicates and lead. Fused silica is formed by introducing pure silicon tetrachloride into a high-temperature flame followed by reaction with the water vapour generated in the combustion (Jennings, 1997). On the surface they have distinguished three types of silanol groups: adsorptive, strong, weak or none. The composition of some glass and silica are presented in Table 7.

Glass	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	B_2O_3	PbO	BaO
Soda-lime	68	3	15	-	6	4	2	-	2
Borosilicate (Pyrex 7740)	81	2	4	-	-	-	13	-	-
Potash soda-lead (Corning 120)	56	2	4	9	-	-	-	29	-
Fused silica	100								

Table 7. Composition of some glass and silica (Jennings, 1986)

10. Column performances

Column performances need to take into account van Deemter expression, carrier gas choice, effect of carrier gas viscosity on linear velocity and phase ratio. Column efficiency, the resolution and sample capacity of a capillary column depend on construction material of the column, the inner diameter and the film thickness of the stationary phase. The distribution coefficient K_D could be interpreted as a function of chromatographic parameters. For a given temperature column of a tandem solute-stationary phase, K_D is constant. In this situation, K_D represents the ratio between the concentration of solute in stationary phase and the concentration of solute in carrier gas:

$$K_D = k\beta = r/2d_f \quad (3)$$

where $\beta = r/2d_f$ is the phase ratio, r is the radius of the column and d_f is the film thickness of stationary phase.

11. Selecting stationary phases

Using packed columns for gas chromatography needs to have a "collection" of available columns packed with different stationary phases and variable lengths for different purposes. The non-volatile liquid phases for packed columns have a good selectivity, but the thermal stability as well as the difference of thickness of the film at elevated temperatures is low and this will affect the inertness of stationary phase and the efficiency of the column.

For the best choice of a stationary phase it is important to remember the motto "like dissolves like". A polar phase could lead to a lower column efficiency compared to a non-polar phase. The maximum temperature limits decrease, as well as the operation lifetime if operating temperature is high (Grob & Barry, 2004). The lower thermal stability of polar phases can be avoided using a thinner film of stationary phase and a shorter column for lower elution temperatures.

12. Installing, conditioning, exhausting and regeneration of chromatographic columns

On column installing it is important to select the proper ferrule, meaning that the inner diameter of the ferrule fits to the outer diameter of the column, in order to avoid loss of carrier gas. Table 8 presents the size of ferrules suitable to column size (inner diameter).

Ferrules inner diameter, mm	Columns inner diameter, mm
0.4	0.25
0.5	0.32
0.8	0.53

Table 8. Ferrules inner diameter compatible with columns inner diameter

In gas chromatograph the chromatography column is placed in the oven, after the injector and before the detector. Between the injector and the column a *retention gap* or *guard column* is often installed. Its length is 0.5-5.0 m and it is actually a deactivated fused-silica tube. In this retention gap the condensed solvent resides after injection, but it is removed by vaporization. The role of a guard column is to collect the non-volatile compounds and particulate matter from samples in order to avoid their penetration in the chromatography column and maintain the lifetime of the column.

Conditioning of chromatography columns is recommended for residual volatiles' removal. For capillary column conditioning there are three steps to follow:

1. Carrier gas flow has to be constant when column temperature is higher than room temperature.
2. The maximum temperature of the stationary phase or of the column must not be transcended because the chromatography column could be damaged.
3. For capillary column, in order to obtain a steady baseline, it is indicated only to purge carrier gas flow for 30 min at ambient temperature and then, with a rate around 4°C/min, elevate the temperature slightly over the maximum temperature limit and maintain for several hours. The first two procedures are also applicable for conditioning of a packed column.

When non-volatiles and particulate matter are accumulating on the inlet of the column or on the injector liner, the chromatography column is contaminated and it is no longer working to its full potential. This is reflected mostly in peak tailing and changes in the retention characteristics of the column. Column reactivation could be realized either by removing the inlet part of the column (1-2 meters) or by turning the column around and then applying step 3 for a longer time. The extreme solution is to remove the solvent.

13. Practical application of GC analysis for mixtures of hydrocarbons

One of the fields where GC is increasingly used is in the oil and gas industry, and specially the refinery sector. In refineries the GC is used not only for identifying the components from a mixture, and then concentration, but also as an integrate tool for loop control.

The gas mixture that you may find on a refinery is usually called "refinery gas", and is a mixture of various gas streams produced in refinery processes. It can be used as a fuel gas, a final product, or a feedstock for further processing. An exact and fast analysis of the components is essential for optimizing refinery processes and controlling product quality. Refinery gas stream composition is very complex, typically containing hydrocarbons, permanent gases and sulphur.

In this practical example of GC use in a refinery, the hydrocarbon mixture was an industrial C5 cut separated from a Fluidized Catalytic Cracking (FCC) plant. Table 9 (Comanescu & Filotti, 2010).

The gas chromatograph was a HP 5890 Series II apparatus, with a configuration and operating parameters similar to those for PONA analysis (ASTM D 6293-98). Commercially available standard (Agilent) for refinery gas analysis was employed for calibration of both hydrocarbons retention times and concentrations.

Component	Normal boiling point, °C	Raw refinery C5 cut (approx. average) % mass
C4 hydrocarbons	- - -	1.88
isopentan	27.85	45.76
1-pentene (α-amylene)	29.97	5.37
n-pentane	36.07	8.36
isoprene	34.07	0.25
2-pentene (β-amylene)	36.07 (trans) ; 36.94 (cis)	12.58
piperylenes	42.0 (trans) ; 44.0 (cis)	0.65
isoamylenes	31.16 (2-methyl-1-butene) ; 38.57 (2-methyl-2-butene) ; 20.1 (3-methyl -1-butene)	7.26 12.06 1.34
cyclopentene	44.24	2.33
C5+ hydrocarbons	- - -	2.16
Specific weight (d_{15}^{15})	- - -	6.652

Table 9. Composition of C5 fractions and boiling points of main C5 hydrocarbons

14. Analysis of natural products

Gas chromatography coupled with MS represents a fast and cheap method for the separation and identification of compounds from natural product mixtures. Alkylation of animal fats and vegetable oils for biofuel fabrication is one of the industrial processes that needs analysis of natural products, both for raw materials and for products (Christie, 1989).

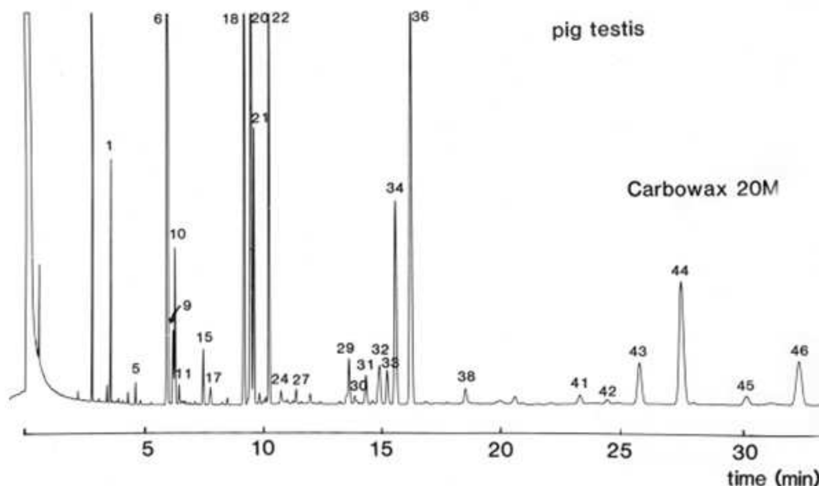


Fig. 3. Separation of the fatty acids (methyl esters) of pig testis on a fused silica column (25 m x 0.22 mm) coated with Carbowax 20M™ (Chrompak UK).

The separation of the methyl esters of the fatty acids of pig testis lipids on the Carbowax 20M™ column is illustrated in Figure 3. A gas chromatograph Carlo Erba Model 4130 split/splitless injection system was used. The carrier gas was hydrogen (1 ml/min), programme temperature was 165ºC for 3 min and then temperature was raised at a rate of 4ºC/min to 195ºC and maintained for 23 min.

The three 16:1 isomers are well separated and distinct from the C_{17} fatty acids. The C_{18} components are separated from a minor 19:1 fatty acid and C_{20} unsaturated constituents. The 20:3(n-3), which co-chromatographs with 20:4(n-6) are just separable on a slightly more polar Silar 5CP™ column. $C_{22,}$ important fatty acids are cleanly separated (Christie, 1989). Peaks can be identified in Table 10 (Christie, 1989).

Equivalent chain-lengths of the methyl ester derivatives of some fatty acids					
No	Fatty acid	Silicone	Carbowax	Silar 5CP	CP-Sil 84
1.	14.00	14.00	14.00	14.00	14.00
2	14-isobr	14.64	14.52	14.52	14.51
3	14-anteiso	14.71	14.68	14.68	14.70
4	14:1(n-5)	13.88	14.37	14.49	14.72
5	15:0	15.00	15.00	15.00	15.0
6	16:0	16.00	16.00	16.00	16.00
7	16-isobr	16.65	16.51	16.51	16.50
8	16-anteiso	16.73	16.68	16.68	16.69
9	16:1(n-9)	15.76	16.18	16.30	16.48
10	16:1(n-7)	15.83	16.25	16.38	16.60
11	16:1(n-5)	15.92	16.37	16.48	16.70
12	16:2(n-4)	15.83	16.78	16.98	17.47
13	16:3(n-3)	15.69	17.09	17.31	18.06
14	16:4(n-3)	15.64	17.62	17.77	18.82
15	17:0	17.00	17.00	17.00	17.00
16	17:1(n-9)	16.76	17.20	17.33	17.50
17	17:1(n-8)	16.75	17.19	17.33	17.51
18	18:0	18.00	18.00	18.00	18.00
19	18:1(n-11)	17.72	18.14	18.24	18.40
20	18:1(n-9)	17.73	18.16	18.30	18.47
21	18:1(n-7)	17.78	18.23	18.36	18.54
22	18:2(n-6)	17.65	18.58	18.80	19.20
23	18:2(n-4)	17.81	18.79	18.98	19.41
24	18:3(n-6)	17.49	18.85	19.30	19.72
25	18:3(n-3)	17.72	19.18	19.41	20.07
26	18:4(n-3)	17.55	19.45	19.68	20.59
27	19:1(n-8)	18.74	19.18	19.32	19.47
28	20:1(n-11)	19.67	20.08	20.22	20.35
29	20:1(n-9)	19.71	20.14	20.27	20.41
30	20:1(n-7)	19.77	20.22	20.36	20.50

Equivalent chain-lengths of the methyl ester derivatives of some fatty acids					
31	20:2(n-9)	19.51	20.38	20.58	20.92
32	20:2(n-6)	19.64	20.56	20.78	21.12
33	20:3(n-9)	19.24	20.66	20.92	21.43
34	20:3(n-6)	19.43	20.78	21.05	21.61
35	20:3(n-3)	19.71	20.95	21.22	21.97
36	20:4(n-6)	19.23	20.96	21.19	21.94
37	20:4(n-3)	19.47	21.37	21.64	22.45
38	20:5(n-3)	19.27	21.55	21.80	22.80
39	22:1(n-11)	21.61	22.04	22.16	22.30
40	22:1(n-9)	21.66	22.11	22.23	22.36
42	22:3(n-6)	21.40	22.71	22.99	23.47
43	22:4(n-6)	21.14	22.90	23.21	23.90
44	22:5(n-6)	20.99	23.15	23.35	24.19
45	22:5(n-3)	21.18	23.50	23.92	24.75
46	22:6(n-3)	21.04	23.74	24.07	25.07

*This document is part of the book "*Gas Chromatography and Lipids*" by William W. Christie and published in 1989 by P.J. Barnes & Associates (The Oily Press Ltd), who retain the copyright

Table 10. Equivalent chain-lengths of the methyl ester derivatives of some natural fatty acids*

15. Conclusions

1. Gas chromatography is an old and still current analytical method used in research and applied fields.
2. Separation of components in the sample is based on the difference of partition (adsorption or absorption) between a mobile phase in continuous motion, a permanent gas and a fixed phase called stationary phase, solid powder (separation by adsorption) or non-volatile liquid for separation by absorption.
3. Stationary phase is deposited in chromatography column, which is the heart of the gas chromatography apparatus.
4. Chromatography columns can be made of different materials: stainless steels, copper alloy, nickel, aluminium, plastics, glass, silica etc.
5. Chromatography columns can be packed, micro-packed, capillary, with differences in diameter, length, thickness of the packed-bed and, ultimately, with different column performance.
6. The materials most used for columns are glasses and silica, especially for capillary columns.
7. Using capillary columns have led to a considerable enlargement of the column length, shortening analysis time, increasing separation performance, the finding of stationary phases with improved performances both in terms of separability as well temperature resistance.
8. Efforts have increased to find the best stationary phase, allowing a good separation of geometric and optical isomers, for example polysiloxanes, and mixtures of different types and proportions with improved thermal resistance.

16. References

Avgul, N. N., Kiselev, A. V. & Poshkus, D. P. (1975). *Adsorbtsiya Gazovi Parovna Adnorodnikh Poverchnostyakh*, Khimiya, Moscow

Ciucanu, I. (1990). *Cromatografia de gaze cu coloane capilare*, Editura Academiei Romane, Bucharest

Christie, W. W. (1989). *Gas Chromatography and Lipids. A Practical Guide*, The Oily Press, Dundee, Scotland. URL: *www.lipidlibrary.aocs.org*

Comanescu, I. & Filotti, L. (2010). Vapour-liquid Equilibrium Data for C5 Saturated-Unsaturated Hydrocarbons Solutions with Solvents Monopropylene Glycol, Dipropylene Glycol or N-Methyl-2-Pyrrolidone, *Revista de Chimie* Vol.61: (10): 986-991

Grob, R. L. & Barry, E. F. (2004). *Modern Practice of Gas Chromatography*, Wiley-Interscience, New-York Jennings, W. G. (1986). *Comparisons of Fused Silica and Other Glasses Columns in Gas Chromatography*, Alfred Heuthig, Publishers, Heidelberg, Germany, 12-21

Jennings, W. G. (1997). *Analytical Gas Chromatography*, 2nd ed., Academic Press, San Diego, CA, 36-45

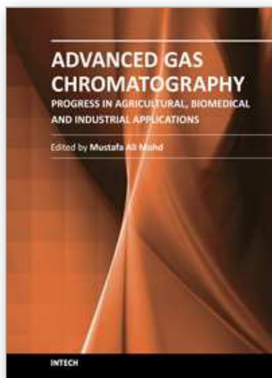
Kiselev, A. K. & Yashin, Ya. I. (1985). *Gas- and Flussigkeits-Adsorptionchromatographie*,VEB Deutscher Verlag der Wissenschaft, Berlin

Leary, J. J., Justice, J. B., Tsuge, S., Lowry, S. R. & Isenhour, T. L. (1973). Correlating gas chromatographic liquid phases by means of nearest neighbor technique: a proposed set of twelve preferred phases, *Journal of Chromatography Science* Vol.(11): 201-206

Leibnitz, E. & Struppe, H. G. (1984). Ed. *Handbuch der Gas-Chromatographie Vol. 2*, Akademische Verlagesellschaft Geest & Portig, Leipzig

Poole, C. F. (2003). *The Essence of Cromatography*, Elsevier, Amsterdam

Rotzsche, H. (1991). *Stationary Phases in Gas Chromatography*, Elsevier, Amsterdam



Advanced Gas Chromatography - Progress in Agricultural, Biomedical and Industrial Applications
Edited by Dr. Mustafa Ali Mohd

ISBN 978-953-51-0298-4
Hard cover, 460 pages
Publisher InTech
Published online 21, March, 2012
Published in print edition March, 2012

Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

Vasile Matei, Iulian Comănescu and Anca-Florentina Borcea (2012). Stationary Phases, Advanced Gas Chromatography - Progress in Agricultural, Biomedical and Industrial Applications, Dr. Mustafa Ali Mohd (Ed.), ISBN: 978-953-51-0298-4, InTech, Available from: http://www.intechopen.com/books/advanced-gas-chromatography-progress-in-agricultural-biomedical-and-industrial-applications/stationary-phases

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821