

Introduction

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1.1 HISTORY AND DEVELOPMENT OF CHROMATOGRAPHY

Many publications have discussed or detailed the history and development of chromatography (1–3). Rather than duplicate these writings, we present in Table 1.1 a chronological listing of events that we feel are the most relevant in the development of the present state of the field. Since the various types of chromatography (liquid, gas, paper, thin-layer, ion exchange, supercritical fluid, and electrophoresis) have many features in common, they must all be considered in development of the field. Although the topic of this text, gas chromatography (GC), probably has been the most widely investigated since the early 1970s, results of these studies have had a significant impact on the other types of chromatography, especially modern (high-performance) liquid chromatography (HPLC).

There will, of course, be those who believe that the list of names and events presented in Table 1.1 is incomplete. We simply wish to show a development of an ever-expanding field and to point out some of the important events that were responsible for the expansion. To attempt an account of contemporary leaders of the field could only result in disagreement with some workers, astonishment by others, and a very long listing that would be cumbersome to correlate.

TABLE 1.1 Development of the Field of Chromatography

Year (Reference)	Scientist(s)	Comments
1834 (4) 1834 (5)	Runge, F. F.	Used unglazed paper and/or pieces of cloth for spot testing dye mixtures and plant extracts
1850 (6) 1868 (7)	Runge, F. F. Goppelsroeder, F.	Separated salt solutions on paper Introduced paper strip (capillary analysis) analysis of dyes, hydrocarbons, milk, beer, colloids, drinking and mineral waters, plant and animal pigments
1878 (8)	Schönbein, C.	Developed paper strip analysis of liquid solutions
1897–1903 (9–11)	Day, D. T.	Developed ascending flow of crude petroleum samples through column packed with finely pulverized fuller's earth
1906–1907 (12–14)	Twsett, M.	Separated chloroplast pigment on CaCO ₃ solid phase and petroleum ether liquid phase
1931 (15)	Kuhn, R. et al.	Introduced liquid–solid chromatography for separating egg yolk xanthophylls
1940 (16)	Tiselius, A.	Earned Nobel Prize in 1948; developed adsorption analyses and electrophoresis
1940 (17)	Wilson, J. N.	Wrote first theoretical paper on chromatography; assumed complete equilibration and linear sorption isotherms; qualitatively defined diffusion, rate of adsorption, and isotherm nonlinearity
1941 (18)	Tiselius, A.	Developed liquid chromatography and pointed out frontal analysis, elution analysis, and displacement development
1941 (19)	Martin, A. J. P., and Synge, R. L. M.	Presented first model that could describe column efficiency; developed liquid–liquid chromatography; received Nobel Prize in 1952
1944 (20)	Consden, R., Gordon, A. H., and Martin, A. J. P.	Developed paper chromatography

TABLE 1.1 (Continued)

Year (Reference)	Scientist(s)	Comments
1946 (21)	Claesson, S.	Developed liquid–solid chromatography with frontal and displacement development analysis; coworker A. Tiselius
1949 (22)	Martin, A. J. P.	Contributed to relationship between retention and thermodynamic equilibrium constant
1951 (23)	Cremer, E.	Introduced gas–solid chromatography
1952 (24)	Phillips, C. S. G.	Developed liquid–liquid chromatography by frontal technique
1952 (25)	James, A. T., and Martin, A. J. P.	Introduced gas–liquid chromatography
1955 (26)	Glueckauf, E.	Derived first comprehensive equation for the relationship between HEPT and particle size, particle diffusion, and film diffusion ion exchange
1956 (27)	van Deemter, J. J., et al.	Developed rate theory by simplifying work of Lapidus and Amundson to Gaussian distribution function
1957 (28)	Golay, M.	Reported the development of open tubular columns
1965 (29)	Giddings, J. C.	Reviewed and extended early theories of chromatography

1.2 DEFINITIONS AND NOMENCLATURE

The definitions given in this section are a combination of those used widely and those recommended by the International Union of Pure and Applied Chemistry (IUPAC) (30). The recommended IUPAC symbol appears in parentheses if it differs from the widely used symbol.

Adjusted Retention Time t'_R . The solute total elution time minus the retention time for an unretained peak (holdup time):

$$t'_R = t_R - t_M$$

Adjusted Retention Volume V'_R . The solute total elution volume minus the retention volume for an unretained peak (holdup volume):

$$V'_R = V_R - V_M$$

Adsorbent. An active granular solid used as the column packing or a wall coating in gas–solid chromatography that retains sample components by adsorptive forces.

Adsorption Chromatography. This term is synonymous with gas–solid chromatography.

Adsorption Column. A column used in gas–solid chromatography, consisting of an active granular solid and a metal or glass column.

Air Peak. The air peak results from a sample component nonretained by the column. This peak can be used to measure the time necessary for the carrier gas to travel from the point of injection to the detector.

Absolute Temperature K. The temperature stated in terms of the Kelvin scale:

$$K = ^\circ C + 273.15^\circ$$

$$0^\circ C = 273.15 K$$

Analysis Time t_{ne} . The minimum time required for a separation:

$$t_{ne} = 16R_s^2 \frac{H}{\bar{u}} \left(\frac{\alpha}{\alpha - 1} \right)^2 \frac{(1 + k)^3}{k^2}$$

Area Normalization (Raw Area Normalization). The peak areas of each peak are summed; each peak area is then expressed as a percentage of the total:

$$A_1 + A_2 + A_3 + A_4 = \Sigma A; \quad \%A_1 = \frac{A_1}{\Sigma A}, \text{ etc.}$$

Area Normalization with Response Factor (ANRF). The area percentages are corrected for the detector characteristics by determining response factors. This requires preparation and analysis of standard mixtures.

Attenuator. An electrical component made up of a series of resistances that is used to reduce the input voltage to the recorder by a particular ratio.

Band. Synonymous with zone. This is the volume occupied by the sample component during passage and separation through the column.

Band Area. Synonymous with the peak area A : the area of peak on the chromatogram.

Baseline. The portion of a detector record resulting from only eluant or carrier gas emerging from the column.

Bed Volume. Synonymous with the volume of a packed column.

Bonded Phase. A stationary phase that is covalently bonded to the support particles or to the inside wall of the column tubing. The phase may be immobilized only by in situ polymerization (crosslinking) after coating.

Capacity Factor $k(D_m)$. See *Mass distribution ratio*. (In GSC, $V_A > V_L$; thus smaller β values and k values occur.) This is a measure of the ability of the column to retain a sample component:

$$k = \frac{t_R - t_M}{t_M}$$

Capillary Column. Synonymous with open tubular column (OTC). This column has small-diameter tubing (0.25–1.0 mm i.d.) in which the inner walls are used to support the stationary phase (liquid or solid).

Carrier Gas. Synonymous with mobile or moving phase. This is the phase that transports the sample through the column.

Chromatogram. A plot of the detector response (which uses effluent concentration or another quantity used to measure the sample component) versus effluent volume or time.

Chromatograph (Verb). A transitive verb meaning to separate sample components by chromatography.

Chromatograph (Noun). The specific instrument employed to carry out a chromatographic separation.

Chromatography. A physical method of separation of sample components in which these components distribute themselves between two phases, one stationary and the other mobile. The stationary phase may be a solid or a liquid supported on a solid.

Column. A metal, plastic, or glass tube packed or internally coated with the column material through which the sample components and mobile phase (carrier-gas) flow and in which the chromatographic separation takes place.

Column Bleed. The loss of liquid phase that coats the support or walls within the column.

Column Efficiency N . See *Theoretical plate number*.

Column Material. The material in the column used to effect the separation. An adsorbent is used in adsorption chromatography; in partition chromatography, the material is a stationary phase distributed over an inert support or coated on the inner walls of the column.

Column Oven. A thermostatted section of the chromatographic system containing the column, the temperature of which can be varied over a wide range.

Column Volume V_c . The total volume of column that contains the stationary phase. [The IUPAC recommends the column dimensions be given as the inner diameter (i.d.) and the height or length L of the column occupied by the stationary phase under the specific chromatographic conditions.] Dimensions should be given in meters, millimeters, feet, or centimeters.

Component. A compound in the sample mixture.

Concentration Distribution Ratio D_c . The ratio of the analytical concentration of a component in the stationary phase to its analytical concentration in the mobile phase:

$$D_c = \frac{\text{Amount component/mL stationary phase}}{\text{Amount component/mL mobile phase}} = \frac{C_S}{C_M}$$

Corrected Retention Time t_R^0 . The total retention time corrected for pressure gradient across the column:

$$t_R^0 = j t_R$$

Corrected Retention Volume V_R^0 . The total retention volume corrected for the pressure gradient across the column:

$$V_R^0 = jV_R$$

Cross-Sectional Area of Column. The cross-sectional area of the empty tube:

$$A_c = r_c^2 \pi = \frac{d_c^2}{4} \pi$$

Dead Time t_M . See *Holdup time*.

Dead Volume V_M . See *Holdup volume*. This is the volume between the injection point and the detection point, minus the column volume V_c . This is the volume needed to transport an unretained component through the column.

Derivatization. Components with active groups such as hydroxyl, amine, carboxyl, and olefin can be identified by a combination of chemical reactions and GC. For example, the sample can be shaken with bromine water and then chromatographed. Peaks due to olefinic compounds will have disappeared. Similarly, potassium borohydride reacts with carbonyl compounds to form the corresponding alcohols. Comparison of before and after chromatograms will show that one or more peaks have vanished whereas others have appeared somewhere else on the chromatogram. Compounds are often derivatized to make them more volatile or less polar (e.g., by silylation, acetylation, methylation) and consequently suitable for analysis by GC.

Detection. A process by which a chromatographic band is recognized.

Detector. A device that signals the presence of a component eluted from a chromatographic column.

Detector Linearity. The concentration range over which the detector response is linear. Over its linear range the response factor of a detector (peak area units per weight of sample) is constant. The linear range is characteristic of the detector.

Detector Minimum Detectable Level (MDL). The sample level, usually given in weight units, at which the signal-to-noise (S/N) ratio is 2.

Detector Response. The detector signal produced by the sample. It varies with the nature of the sample.

Detector Selectivity. A selective detector responds only to certain types of compound [FID, NPD, ECD, PID, etc. (see acronym definitions in Appendix B)]. The thermal conductivity detector is universal in response.

Detector Sensitivity. Detector sensitivity is the slope of the detector response for a number of sample sizes. A detector may be sensitive to either flow or mass.

Detector Volume. The volume of carrier gas (mobile phase) required to fill the detector at the operating temperature.

Differential Detector. This detector responds to the instantaneous difference in composition between the column effluent and the carrier gas (mobile phase).

Direct Injection. A term used for the introduction of samples directly onto open tubular columns (OTCs) through a flash vaporizer without splitting (should not be confused with on-column injection).

Discrimination Effect. This occurs with the split injection technique for capillary columns. It refers to a problem encountered in quantification with split injection onto capillary columns in which a nonrepresentative sample goes onto the capillary column as a result of the difference in rate of vaporization of the components in the mixture from the needle.

Displacement Chromatography. An elution procedure in which the eluant contains a compound more effectively retained than the components of the sample under examination.

Distribution Coefficient D_g . The amount of a component in a specified amount of stationary phase, or in an amount of stationary phase of specified surface area, divided by the analytical concentration in the mobile phase. The distribution coefficient in adsorption chromatography with adsorbents of unknown surface area is expressed as

$$D_g = \frac{\text{Amount component/g dry stationary phase}}{\text{Amount component/mL mobile phase}}$$

The distribution coefficient in adsorption chromatography with well-characterized adsorbent of known surface area is expressed as

$$D_s = \frac{\text{Amount component/m}^2 \text{ surface}}{\text{Amount component/mL mobile phase}}$$

The distribution coefficient when it is not practicable to determine the weight of the solid phase is expressed as

$$D_v = \frac{\text{Amount component stationary phase/mL bed volume}}{\text{Amount component/mL mobile phase}}$$

Distribution Constant $K(K_D)$. The ratio of the concentration of a sample component in a single definite form in the stationary phase to its concentration in the mobile phase. IUPAC recommends this term rather than the partition coefficient:

$$K = \frac{C_S}{C_G}$$

Efficiency of Column. This is usually measured by column theoretical plate number. It relates to peak sharpness or column performance.

Effective Theoretical Plate Number $N_{\text{eff}}(N)$. A number relating to column performance when resolution R_S is taken into account:

$$N_{\text{eff}} = \frac{16R_S^2}{(1 - \alpha)^2} = 16 \left(\frac{t'_R}{w} \right)^2$$

Effective plate number is related to theoretical plate number by

$$N_{\text{eff}} = N \left(\frac{k}{k+1} \right)^2$$

Electron-Capture Detector (ECD). A detector utilizing low-energy electrons (furnished by a tritium or ^{63}Ni source) that ionize the carrier gas (usually argon) and collect the free electrons produced. An electron-capturing solute will capture these electrons and cause a decrease in the detector current.

Eluant. The gas (mobile phase) used to effect a separation by elution.

Elution. The process of transporting a sample component through and out of the column by use of the carrier gas (mobile phase).

Elution Chromatography. A chromatographic separation in which an eluant is passed through a column during or after injection of a sample.

External Standardization Technique (EST). This method requires the preparation of calibration standards. The standard and the sample are run as separate injections at different times. The calibrating standard contains only the materials (components) to be analyzed. An accurately measured amount of this standard is injected. *Calculation steps for standard:* (1) for each peak to be calculated, calculate the amount of component injected from the volume injected and the known composition of the standard; then (2) divide the peak area by the corresponding component weight to obtain the absolute response factor (ARF):

$$\text{ARF} = \frac{A_1}{W_1}$$

Calculation Step for Sample. For each peak, divide the measured area by the absolute response factor to obtain the absolute amount of that component injected:

$$\frac{A_1}{\text{ARF}} = W_i$$

Filament Element. A fine tungsten or similar wire that is used as the variable-resistance sensing element in the thermal conductivity cell chamber.

Flame Ionization Detector (FID). This detector utilizes the increased current at a collector electrode obtained from the burning of a sample component from the column effluent in a hydrogen and airjet flame.

Flame Photometric Detector (FPD). A flame ionization detector (utilizing a hydrogen-rich flame) that is monitored by a photocell. It can be specific for halogen-, sulfur-, or phosphorous-containing compounds.

Flash Vaporizer. A device used in GC where the liquid sample is introduced into the carrier-gas stream with simultaneous evaporation and mixing with the carrier gas prior to entering the column.

Flow Controller. A device used to regulate flow of the mobile phase through the column.

Flow Programming. In this procedure the rate of flow of the mobile phase is systematically increased during a part or all of the separation of higher boiling components.

Flowrate F_c . The volumetric flowrate of the mobile phase, in milliliters per minute, is measured at the column temperature and outlet pressure:

$$F_c = \frac{\pi r^2 L}{t_M}$$

Frontal Chromatography. A type of chromatographic separation in which the sample is fed continuously onto the column.

Fronting. Asymmetry of a peak such that, relative to the baseline, the front of the peak is less sharp than the rear portion.

Gas Chromatograph. A collective noun for those chromatographic modules of equipment in which gas chromatographic separations can be realized.

Gas Chromatography (GC). A collective noun for those chromatographic methods in which the moving phase is a gas.

Gas-Liquid Chromatography (GLC). A chromatographic method in which the stationary phase is a liquid distributed on an inert support or coated on the column wall and the mobile phase is a gas. The separation occurs by the partitioning (differences in solubilities) of the sample components between the two phases.

Gas-Sampling Valve. A bypass injector permitting the introduction of a gaseous sample of a given volume into a gas chromatograph.

Gas-Solid Chromatography (GSC). A chromatographic method in which the stationary phase is an active granular solid (adsorbent). The separation is performed by selective adsorption on an active solid.

Heartcutting. This technique utilizes a precolumn (usually packed) and a capillary column. With this technique only the region of interest is transferred to the main column; all other materials are backflushed to the vent.

Height Equivalent to an Effective Plate H_{eff} . The number obtained by dividing the column length by the effective plate number:

$$H_{\text{eff}} = \frac{L}{N_{\text{eff}}}$$

Height Equivalent to a Theoretical Plate H . The number obtained by dividing the column length by the theoretical plate number:

$$H = \frac{L}{N} = \text{HETP}$$

$$= \frac{H}{d}$$

where d is the particle diameter in a packed column or the tube diameter in a capillary column.

Holdup Time t_M . The time necessary for the carrier gas to travel from the point of injection to the detector. This is characteristic of the instrument, the *mobile-phase* flowrate, and the column in use.

Holdup Volume V_M . The volume of mobile phase from the point of injection to the point of detection. In GC it is measured at the column outlet temperature and pressure and is a measure of the volume of carrier gas required to elute an unretained component (including injector and detector volumes):

$$V_M = t_M F_c$$

Initial and Final Temperatures T_1 and T_2 . This temperature range is used for a separation in temperature-programmed chromatography.

Injection Point t_0 . The starting point of the chromatogram, which corresponds to the point in time when the sample was introduced into the chromatographic system.

Injection Port. Consists of a closure column on one side and a septum inlet on the other through which the sample is introduced (through a syringe) into the system.

Injection Temperature. The temperature of the chromatographic system at the injection point.

Injector Volume. The volume of carrier gas (mobile phase) required to fill the injection port of the chromatograph.

Integral Detector. This detector is dependent on the total amount of a sample component passing through it.

Integrator. An electrical or mechanical device employed for a continuous summation of the detector output with respect to time. The result is a measure of the area of a chromatographic peak (band).

Internal Standard. A pure compound added to a sample in known concentration for the purpose of eliminating the need to measure the sample size in quantitative analysis and for correction of instrument variation.

Internal Standardization Technique (IST). A technique that combines the sample and standard into one injection. A calibration mixture is prepared containing known amounts of each component to be analyzed, plus an added compound that is not present in the analytical sample.

Calculation steps for calibration standard:

1. For each peak, divide the measured area by the amount of that component to obtain a response factor:

$$(\text{RF})_1 = \frac{A_1}{W_1}, \text{ etc.}$$

2. Divide each response factor by that of the internal standard to obtain relative response factors (RRF):

$$\text{RRF}_1 = \frac{(\text{RF})_1}{(\text{RF})_i}$$

Calculation steps for sample:

1. For each peak, divide the measured area by the proper relative response factor to obtain the corrected area:

$$(CA)_1 = \frac{A_1}{RRF_1}$$

2. Divide each corrected area by that of the internal standard to obtain the amount of each component relative to the internal standard:

$$(RW)_1 = \frac{(CA)_1}{(CA)_i}$$

3. Multiply each relative amount by the actual amount of the internal standard to obtain the actual amounts of each component:

$$(RW)_1 W_i = W_1$$

Interstitial Fraction ε_1 . The interstitial volume per unit of packed column:

$$\varepsilon_1 = \frac{V_1}{X}$$

Interstitial Velocity of Carrier Gas u . The linear velocity of the carrier gas inside a packed column calculated as the average over the entire cross section. Under idealized conditions it can be calculated as

$$u = F_c \varepsilon_1$$

Interstitial Volume $V_G(V_1)$. The volume occupied by the mobile phase (carrier gas) in a packed column. This volume does not include the volumes external to the packed section, that is, the volume of the sample injector and the volume of the detector. In GC it corresponds to the volume that would be occupied by the carrier gas at atmospheric pressure and zero flowrate in the packed section of the column.

Ionization Detector. A chromatographic detector in which the sample measurement is derived from the current produced by the ionization of sample molecules. This ionization may be induced by thermal, radioactive, or other excitation sources.

Isothermal Mode. A condition wherein the column oven is maintained at a constant temperature during the separation process.

Katharometer. This term is synonymous with the term *thermal conductivity cell*; it is sometimes spelled “catharometer.”

Linear Flowrate F_c . The volumetric flowrate of the carrier gas (mobile phase) measured at column outlet and corrected to column temperature; and F_a is volumetric flowrate measured at column outlet and ambient temperature:

$$F_c = F_a \left(\frac{T_c}{T_a} \right) \frac{P_a - P_w}{P_a}$$

where T_c is column temperature (K), T_a is ambient temperature (K), P_a is ambient pressure, and P_w is partial pressure of water at ambient temperature.

Linear Velocity u . The linear flowrate F_c , divided by the cross-sectional area of the column tubing available to the mobile phase:

$$u = \frac{F_c}{A_c} = \frac{F_c}{r_c^2 \pi} = \frac{L}{t_M}$$

where A_c is the cross-sectional area of the column tubing, r_c is the tubing radius, and π is a constant. The equation given above is applicable for capillary columns but not for packed columns; for packed columns, the equation becomes

$$u = \frac{F_c}{\epsilon_1 r_c^2 \pi}$$

Thus, one must account for the interstitial fraction of the packed column.

Liquid Phase. Synonymous with stationary phase or liquid substrate. It is a relatively nonvolatile liquid (at operating conditions) that is either sorbed on the solid support or coated on the walls of OTCs, where it acts as a solvent for the sample. The separation results from differences in solubility of the various sample components.

Liquid Substrate. Synonymous with stationary phase.

Marker. A reference component that is chromatographed with the sample to aid in the measurement of holdup time or volume for the identification of sample components.

Mass Distribution Ratio $k(D_m)$. The fraction $(1 - R)$ of a component in the stationary phase divided by the fraction R in the mobile phase. The IUPAC recommends this term in preference to capacity factor k :

$$k(D_m) = \frac{1 - R}{R} = \frac{K}{\beta} = \frac{C_L V_L}{C_G V_G} = K \left(\frac{V_L}{V_G} \right)$$

Mean Interstitial Velocity of Carrier Gas \bar{u} . The interstitial velocity of the carrier gas multiplied by the pressure-gradient correction factor:

$$\bar{u} = \frac{F_c j}{\epsilon_1}$$

Mobile Phase. Synonymous with carrier gas or gas phase.

Moving Phase. See *Mobile phase*.

Net Retention Volume V_N . The adjusted retention volume multiplied by the pressure gradient correction factor:

$$V_N = jV'_R$$

Nitrogen–Phosphorus Detector (NPD). This detector is selective for monitoring nitrogen or phosphorus.

On-column Injection. Refers to the method wherein the syringe needle is inserted directly into the column and the sample is deposited within the column walls rather than a flash evaporator. On-column injection differs from direct injection in that the sample is usually introduced directly onto the column without passing through a heated zone. The column temperature is usually reduced, although not as low as with splitless injections (“cool” on-column injections).

Open Tubular Column (OTC). Synonymous with capillary column.

Packed Column. A column packed with either a solid adsorbent or solid support coated with a liquid phase.

Packing Material. An active granular solid or stationary phase plus solid support that is in the column. The term “packing material” refers to the conditions existing when the chromatographic separation is started, whereas the term “stationary phase” refers to the conditions during the chromatographic separation.

Partition Chromatography. Synonymous with gas–liquid chromatography.

Partition Coefficient. Synonymous with the distribution constant.

Peak. The portion of a differential chromatogram recording the detector response or eluate concentration when a compound emerges from the column. If the separation is incomplete, two or more components may appear as one peak (unresolved peak).

Peak Area. Synonymous with band area. The area enclosed between the peak and peak base.

Peak Base. In differential chromatography, this is the baseline between the base extremities of the peak.

Peak Height h . The distance between the peak (band) maximum and the peak base, measured in a direction parallel to the detector response axis and perpendicular to the time axis.

Peak Maximum. The point of maximum detector response when a sample component elutes from the chromatographic column.

Peak Resolution R_S . The separation of two peaks in terms of their average peak widths:

$$R_S = \frac{2\Delta t_R}{w_a + w_b} = \frac{2\Delta t'_R}{w_a + w_b}$$

Peak Width w_b . The bar segment of the peak base intercepted by tangents to the inflection points on either side of the peak and projected on to the axis representing time or volume.

Peak Width at Half-Height w_h . The length of the line parallel to the peak base, which bisects the peak height and terminates at the intersections with the two limbs of the peak, projected onto the axis representing time or volume.

Performance Index (PI). This is used with open tubular columns; it is a number (in poise) that provides a relationship between elution time of a component and pressure drop. It is expressed as

$$PI = 30.7H^2 \left(\frac{u}{K} \right) \frac{1+k}{k + \frac{1}{16}}$$

Phase Ratio β . The ratio of the volume of the mobile phase to the stationary phase on a partition column:

$$\beta = \frac{V_I}{V_S} = \frac{V_G}{V_A} = \frac{V_0}{V_S}$$

Photoionization Detector (PID). A detector in which detector photons of suitable energy cause complete ionization of solutes in the inert mobile phase. Ultraviolet radiation is the most common source of these photons. Ionization of the solute produces an increase in current from the detector, and this is amplified and passed onto the recorder.

PLOT. An acronym for *porous-layer open tubular column*, which is an open tubular column with fine layers of some adsorbent deposited on the inside wall. This type of column has a larger surface area than does a wall-coated open tubular column (WCOT).

Polarity. Sample components are classified according to their polarity (measuring in a certain way the affinity of compounds for liquid phases), for example, nonpolar hydrocarbons; medium-polarity ethers, ketones, aldehydes; and polar alcohols, acids, and amines.

Potentiometric Recorder. A continuously recording device whose deflection is proportional to the voltage output of the chromatographic detector.

Precolumn Sampling (OTC). Synonymous to selective sampling with open tubular columns.

Pressure P. Pressure is measured in pounds per square inch at the entrance valve to the gas chromatograph [psi = pounds per square inch = lb/in.²; psia = pounds per square inch absolute = ata (atmosphere absolute); psig = pounds per square inch gauged, 1 psi = 0.069 bar].

Pressure Gradient Correction Coefficient j. This factor corrects for the compressibility of the mobile phase in a homogeneously filled column of uniform diameter:

$$j = \frac{3}{2} \left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right]$$

Programmed-Temperature Chromatography. A procedure in which the temperature of the column is changed systematically during a part or the whole of the separation.

Purged Splitless Injection. This term is given to a splitless injection (see *Splitless injection*) wherein the vent is open to allow the large volume of carrier gas to pass through the injector to remove any volatile materials that may be left on the column. Most splitless injections are purged splitless injections.

Pyrogram. The chromatogram resulting from sensing of the fragments of a pyrolyzed sample.

Pyrolysis. A technique by which nonvolatile samples are decomposed in the inlet system and the volatile products are separated on the chromatographic column.

Pyrolysis Gas Chromatography. A process that involves the induction of molecular fragmentation to a chromatographic sample by means of heat.

Pyrometer. An instrument for measuring temperature by the change in electrical current.

Qualitative Analysis. A method of chemical identification of sample components.

Quantitative Analysis. This involves the estimation or measurement of either the concentration or the absolute weight of one or more components of the sample.

Relative Retention $r_{a/b}$. The adjusted retention volume of a substance related to that of a reference compound obtained under identical conditions:

$$\begin{aligned} r_{a/b} &= \frac{(V_g)_a}{(V_g)_b} \\ &= \frac{(V_N)_a}{(V_N)_b} \\ &= \frac{(V'_R)_a}{(V'_R)_b} \\ &\neq \frac{(V_R)_a}{(V_R)_b} \end{aligned}$$

Required Plate Number n_{ne} . The number of plates necessary for the separation of two components based on resolution R_S of 1.5:

$$n_{ne} = 16R_S^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{1 + k}{k} \right)^2$$

Resolution R_S . Synonymous with peak resolution; it is an indication of the degree of separation between two peaks.

Retention Index I . A number relating the adjusted retention volume of a compound A to the adjusted retention volume of normal paraffins. Each n -paraffin is arbitrarily allotted, by definition, an index of 100 times its carbon number. The index number of component A is obtained by logarithmic interpolation:

$$I = 100N + 100 \frac{[\log V'_R(A) - \log(V'_R)(N)]}{[\log V'_R(n) - \log V'_R(N)]}$$

where N and n are the smaller and larger n -paraffin, respectively, that bracket substance A.

Retention Time (Absolute) t_R . The amount of time that elapsed from injection of the sample to the recording of the peak maximum of the component band (peak).

Retention Volume (Absolute) V_R . The product of the retention time of the sample component and the volumetric flowrate of the carrier gas (mobile phase). The IUPAC recommends that it be called *total retention volume* because it is a term used when the sample is injected into a flowing stream of the mobile phase. Thus it includes any volume contributed by the sample injector and the detector.

Sample. The gas or liquid mixture injected into the chromatographic system for separation and analysis.

Sample Injector. A device used for introducing liquid or gas samples into the chromatograph. The sample is introduced directly into the carrier-gas stream (e.g., by syringe) or into a chamber temporarily isolated from the system by valves that can be changed so as to instantaneously switch the gas stream through the chamber (gas sampling valve).

SCOT. An acronym for *support-coated open tubular column*. These are capillary columns in which the liquid substrate is on a solid support that coats the walls of the capillary column.

Selective Sampling. Refers to the transportation of a portion of a mixture onto the capillary column after it has passed through another chromatographic column, either packed or open tubular.

Separation. The time elapsed between elution of two successive components, measured on the chromatogram as the distance between the recorded bands.

Separation Efficiency N/L . A measure of the “goodness” of a column. It is usually given in terms of the number of theoretical plates per column length, that is, plates per meter for open tubular columns.

Separation Factor $\alpha_{a/b}$. The ratio of the distribution ratios or coefficients for substances A and B measured under identical conditions. By convention the separation factor is usually greater than unity:

$$\alpha_{a/b} = \frac{K_{D_a}}{K_{D_b}} = \frac{D_a}{D_b} = \frac{K_a}{K_b}$$

Separation Number (n_{sep} or SN). The possible number of peaks between two n -paraffin peaks resulting from components of consecutive carbon numbers:

$$n_{\text{sep}} = \frac{(t_{R_2} - t_{R_1})}{(w_h)_1 + (w_h)_2} - 1 = SN$$

See *Trennzahl number*.

Separation Temperature. The temperature of the chromatographic column.

Septum Bleed. Refers to the detector signal created by the vaporization of small quantities of volatile materials trapped in the septum. It is greatly reduced by allowing a small quantity of carrier gas to constantly sweep by the septum to vent.

Solid Support. The solid packing material on which the liquid phase is coated and that does not contribute to the separation process.

Solute. A synonymous term for components in a sample.

Solvent. Synonymous with liquid phase (stationary phase or substrate).

Solvent Effect (OTC). An effect noted in splitless injections for concentrating higher boilers at the head of the column so that the peak band will reflect the efficiency of the column and not the volume of the injection port liner. For this effect to occur, the oven temperature must be close to the boiling point of the major solvent component in the system so that it condenses at the head of the column and acts as a barrier for the solute.

Solvent Efficiency α . Synonymous with separation factor.

Solvent Venting (OTC). Refers to the elimination of the solvent or major ingredient in a mixture by heartcutting and flushing the solvent through the vent.

Span of the Recorder. The number of millivolts required to produce a change in the deflection of the recorder pen from 0 to 100% on the chart scale.

Specific Retention Volume V_g . The net retention volume per gram of stationary phase corrected to 0°C:

$$V_g = \frac{273 V_N}{T W_L} = \frac{j V'_R}{T W_L}$$

Specific Surface Area. The area of a solid granular adsorbent expressed as square meter per unit weight (gram) or square meter per milliliter.

Split Injection (OTC). The term given to the classical method of injecting samples into a capillary system wherein the sample is introduced into a flash vaporizer and the splitter reduces the amount of sample going onto the column by the use of restrictors so that the majority of the sample goes into the vent and not onto the capillary column. Typical split ratios are 100–1 and 200–1, where the lower number refers to the quantity going onto the column.

Splitless Injection (OTC). The term applied to a flash vaporization technique wherein the solvent is evaporated in the injection port and condenses on the head of the column. After a suitable time (usually 0.5 min), the splitter is opened and any of the remaining material in the flash vaporizer is vented. The solvent that will have condensed at the head of the column is then slowly vaporized through column temperature programming. Splitless injection is used to concentrate small quantities of solute in a large injection (2–3 μL) onto a capillary column. The solute should have a higher boiling point than the condensed solvent so that its relative retention time is at least 1.5 and its retention index is greater than 600.

Splitter. A fitting attached to the injection port or column exit to divert a portion of the flow. It is used on the inlet side to permit the introduction of very small samples to a capillary column and on the outlet side to permit introduction of a very small sample of the column effluent to the detector, to permit introduction of effluent to two detectors simultaneously or to collect part of a peak from a destructive detector.

Stationary Phase. Synonymous with liquid phase, distributed on a solid, in gas-liquid chromatography or the granular solid adsorbent in gas-solid chromatography. The liquid may be chemically bonded to the solid.

Stationary-Phase Fraction ϵ_S . The volume of the stationary phase per unit volume of the packed column:

$$\epsilon_S = \frac{V_S}{X}$$

Stationary-Phase Volume $V_L(V_S)$. The total volume of stationary-phase liquid on the support material in a particular column:

$$V_L = \frac{w_L}{\text{density}_L}$$

Surface Area. The area of a solid granular adsorbent A .

Tailing. In this condition the asymmetry of a peak is such that, relative to the baseline, the front is steeper than the rear.

Temperature Programming. In this procedure the temperature of the column is changed systematically during part or all of the separation process.

Theoretical Plate Number N . This number defines the efficiency of the column or sharpness of peaks:

$$\begin{aligned} N &= 16 \left(\frac{\text{peak retention time}}{\text{peak width}} \right)^2 \\ &= 16 \left(\frac{t_R}{w} \right)^2 \end{aligned}$$

Thermal Conductivity. A physical property of a substance, serving as an index of its ability to conduct heat from a warmer to a cooler surface.

Thermal Conductivity Detector (TCD). A chamber in which an electrically heated element will reflect changes in thermal conductivity within the chamber atmosphere. The measurement is possible because of the change in resistance of the element.

Thermistor Bead Element. A thermal conductivity detection device in which a small glass-coated semiconductor sphere is used as the variable resistive element in the cell chamber.

Trennzahl Number Tz . This term is comparable with separation number and is calculated from the resolution between two consecutive members of a homologous hydrocarbon series. It is usually considered as the number of peaks that could be placed between those two members of the series. It is used predominantly in capillary column work and is expressed as

$$Tz = \left[\frac{t_{R_2} - t_{R_1}}{(w_h)_1 + (w_h)_2} \right] - 1$$

True Adsorbent Volume V_A . The weight of the adsorbent packing is divided by the adsorbent density:

$$V_A = \frac{W_A}{D_A}$$

van Deemter Equation. This equation expresses the extent to which a component band spreads as it passes through the column in terms of physical constants and the velocity of the mobile phase:

$$\text{HEPT}(H) = A + \frac{B}{u} + Cu$$

where HEPT = height equivalent to a theoretical plate

u = linear velocity of carrier gas (mobile phase);

\bar{u} = average linear carrier-gas velocity

A = constant that accounts for the effects of “eddy” diffusion in the column

B = constant that accounts for the effect of molecular diffusion of the vapor in the direction of the column axis

C = constant proportional to the resistance of the column packing to mass transfer of solute through it

Velocity of Mobile Phase u . Synonymous with linear velocity.

WCOT. An acronym for *wall-coated open tubular column*. It is a capillary column in which the inside wall is coated with the stationary phase.

Weight of Stationary Liquid Phase W_L . The weight of liquid phase in the column.

WWCOT. A *whisker-wall-coated open tubular column*. It is a WCOT in which the walls have been etched before the stationary phase is deposited.

WWPLOT. An acronym for *whisker-wall porous-layer open tubular column*. It is a PLOT column in which the walls have been etched before deposition of the support.

WWSCOT. An acronym for *whisker-wall-support-coated open tubular column*. It is a SCOT column in which the walls have been etched before depositing of the support.

Zone. The position and spread of a solute within the column, the region in the chromatographic bed where one or more components of the sample are located. See *Band*.

1.3 SUGGESTED READING ON GAS CHROMATOGRAPHY

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1.4 COMMERCIAL INSTRUMENTATION

All leading instrument manufacturers produce and market gas chromatographs. In addition, many smaller speciality companies also manufacture and market GC units. Which instrument should be considered depends on the use to which they are to be utilized, and this ultimately establishes the criteria for purchase. GC units come in a variety of makes and models, from simple student instructional types (e.g., Gow-Mac Instrument Co.) up to deluxe multicolumn, interchangeable detector types (e.g., Agilent Technologies). We refer the reader to the "Lab Guide" issue of the *Journal of Analytical Chemistry* (**31**), *American Laboratory Journal* (**32**), and *LC/GC Journal* (**33**), rather than to one particular company, for a listing of the instrument manufacturers.

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