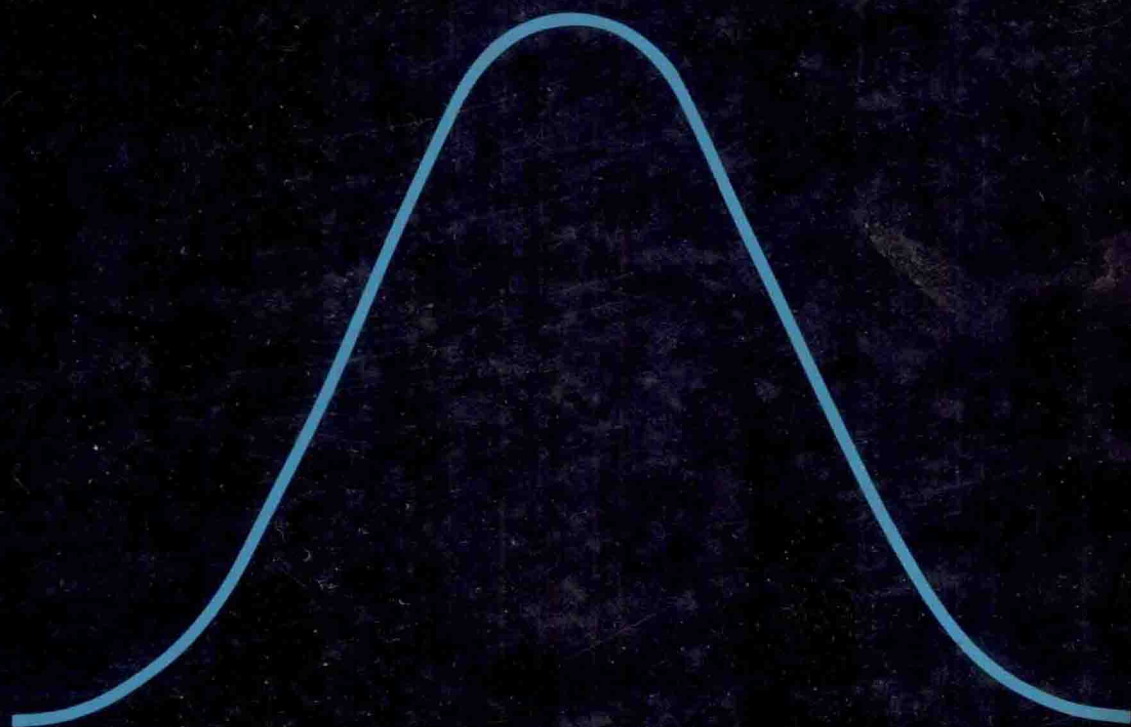


Introduction to Analytical Gas Chromatography

History, Principles, and Practice



John A. Perry

Introduction to ANALYTICAL GAS CHROMATOGRAPHY

History, Principles, and Practice

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PREFACE

On the invitation of Dr. Jay Curtice, now Chairman of the Department of Chemistry of Roosevelt University, in the spring of 1964 I began teaching a 16-week graduate-level evening credit course in gas chromatography. Since then it has been presented at least once each year.

Responding to my questionnaires, students in the course have described themselves as full-time working chemists. Ranging in age from 21 to over 70 years, they have an average age of perhaps 28. Usually, they have earned at least a bachelor's degree, have not had experience in gas chromatography, and have registered only for this course.

This book was written for people such as these, to provide them with orientation and insight in language they find clear and comprehensible. For perspective, a topic is often presented against its history. Throughout, reasons and principles are stressed.

The book is selective in choice of topic and depth of treatment. For each topic, once it has been chosen, the relevant technical background is furnished. The topic is then developed in a way that is understandable to readers usually thoroughly ill at ease with mathematics and electrical circuitry. In discussions, for instance, names always accompany symbols. Derivations can be read.

Because the treatment is cumulative, the book should be read from front to back. However, the chapters on qualitative and quantitative analysis (Chaps. 13 and 14) can be understood without first reading the chapter on derivatization.

I acknowledge the friendly and effective assistance of Miss Anne O'Donnell and of Dr. Peter Klein in the treatment of gas chromatography-mass spectrometry. Mr. E. M. Bens reviewed the chapter on supports, helped clarify and strengthen the section on the preferred diatomaceous earth, and furnished additional valuable (and beautiful) photographs. Dr. Mathieu H. J. van Rijswijk reviewed the chapter on quantitative analysis and commented generously and constructively on my treatment of his high-precision algorithm. I thank both of these experts for their help.

I thank Miss Bernadine Palka, who has read the complete text several times, suggested many improvements, caught innumerable errors. The book is the better for her.

I am deeply grateful for the manifold cooperation of the Regis Chemical Company of Morton Grove, Illinois. And my gratitude to my wife, Inger, is boundless.

John A. Perry

NOTATION

For each symbol, the location of its definition or first appearance follows its explanation.

- a 1. Constant expressing fraction of corrected retention volume that may be used as the maximum acceptable sample volume (pages 9, 28):

$$V_{\max} = a \frac{V_M^{\circ} + K V_L}{\sqrt{n}} = a \frac{V_R^{\circ}}{\sqrt{n}}$$

2. Constant in equation for vapor pressure p° (Chap. 11 only). P. 224, Eq. 11.3.
- A The eddy diffusion term of the Jones-van Deemter equation. P. 6.
- ADC Analog-to-digital converter. P. 362.
- A_{\min} The minimum detectable peak area as a function of digital noise. P. 377, Eq. 14.10.
- b Constant in equation for vapor pressure p° . P. 224, Eq. 11.3.
- B The axial molecular diffusion term of the van Deemter equation. P. 7.
- c Constant in equation for vapor pressure p° (Chap. 11 only). P. 224, Eq. 11.3.
- c_L Constant in the C_L term of the Jones-van Deemter equation. P. 86, Eq. 6.30.
- c_2 Constant in the C_2 term of the Jones-van Deemter equation. P. 92, Eq. 6.63.
- $c_1 \dots c_{12}$ Constants.
- C The overall term that expresses resistance to mass transfer in the Jones-van Deemter equation. P. 8.
- C_{gas} This symbol, cited on p. 232 in a quotation, has the meaning of our C_G .
- C_{liq} This symbol, cited on p. 232, in a quotation has the meaning of our C_{LP} .
- C_{\max} The weight-per-volume concentration in the mobile phase of solute at the peak apex (page 346, Eq. 14.1):

$$C_{\max} = \frac{\sqrt{n}}{V_R^{\circ}} w_I \sqrt{2\pi}$$

C_t	The solute concentration at time t following injection at concentration C_0 into an insufficiently hot injection port that produces exponential rather than plug sample introduction. P. 199. Eq. (10.16).
C_D	The maximum solute weight-per-volume concentration in the mobile phase that does not exceed the linear dynamic range of the detector. P. 346.
C_G	The term of the Jones-van Deemter equation that expresses resistance to mass transfer in the gas phase. P. 91. Eq. (6.54).
C_L	The weight-per-volume concentration of solute in the liquid stationary phase. P. 20. P. 21, Eq. (2.8).
C_{LP}	The term of the Jones-van Deemter equation that expresses resistance to mass transfer in the liquid stationary phase. P. 88, Eq. (6.40).
C_M	The weight-per-volume concentration of solute in the gas mobile phase. P. 21, Eq. (2.8).
C_0	Initial sample concentration on sample injection. P. 199, Eq. (10.16).
C_2	The term of the Jones-van Deemter equation that expresses resistance to mass transfer due to velocity distribution in the mobile phase. P. 92, Eq. (6.64).
C_3	The term of the Jones-van Deemter equation that expresses interaction of the nominally independent C_G and C_2 terms. Not a very important term.
d	Internal diameter of an open tubular column. P. 214.
d_f	The thickness of the annular coating of the stationary phase in a wall-coated open tubular column. P. 190, Eq. (10.15).
d_p	Particle diameter. P. 6
d_p^*	The particle diameter as used in the reduced plate-height equation. In the case of gas-liquid chromatography, d_p^* refers to the pore size of the inert support rather than to the inert support particle diameter. P. 111, Eq. (7.13).
d_C	The internal diameter of a column. P. 9.
d_G	The effective thickness of the gas phase; the shortest distance through the carrier gas from one surface of the stationary phase to another. P. 89, Eq. (6.45).
d_L	The effective thickness of the liquid stationary phase. P. 8.
db	Decibels. A decibel is equal to 10 times the base-10 logarithm of a power or rejection ratio. For example, 60 db implies a ratio of one million.
D	Diffusivity; dimensions: (distance) ² /time. Defined p. 199, Eq. (10.18). The diffusivity is identically the diffusivity coefficient; see p. 78, Eq. (6.1).
D	Detectability: the smallest quantity that will cause a detector response equal to twice the noise level. P. 143.
D_m	The diffusivity of the mobile phase, as used in the equation for reduced plate height. P. 111, Eq. (7.15).
D_G	The diffusivity of the carrier gas. P. 84, Eq. (6.21).
D_L	The diffusivity of the liquid stationary phase. P. 8.
e	The base of the natural logarithms. First used, p. 171.
e_b	Bucking voltage. This is the voltage that is developed by a potentiometric recorder within itself to equal the signal being measured, so that the difference ($e_b - e_i$) approaches zero as the recorder approaches balance. P. 352.
e_i	The voltage of a source of potential. P. 151.

- $e_{i\text{-span}}$ An electric potential just sufficient to cause a full-scale pen deflection of a potentiometric recorder. P. 354.
- e_o The voltage delivered by a voltage divider.
- e_r A reference voltage within a potentiometric recorder in terms of which an incoming voltage is measured. P. 352.
- E Electron affinity, pertaining to electron capture. P. 171.
- E_d Dispersion interaction energy. P. 57.
- E_i Dipole-induced dipole interaction energy. P. 57.
- E^* The concentration of an electron-capturing species in an electron capture detector. P. 171.
- F Flow rate of column effluent; p. 145. Gas flow rate entering mixing chamber; p. 199, Eq. (10.17). And gas flow rate, p. 240.
- F_a Flow rate of added gas in flame ionization detector, p. 145 (see also V_e , effective detector volume, p. 145).
- F_c The temperature-corrected carrier gas flow rate, measured at the column exit pressure and corrected to column temperature. P. 18.
- h The height equivalent to a theoretical plate: $h = L/n$. Longer symbol: HETP. P. 5, Fig. 1.5.
- h The reduced plate height. P. 111, Eq. (7.13).
- H The height equivalent to an effective theoretical plate: $H = L/N$. Longer symbol: HEETP. P. 213.
- ΔH_s Differential heat of vaporization of solute from infinitely dilute solution. P. 225. Eq. (11.7).
- ΔH_v Heat of vaporization of the pure organic liquid. P. 224, Eq. (11.4).
- Hz Hertz: one cycle per second.
- i Current of electricity.
- I Kovats Retention Index. P. 60. Eq. (5.1).
- I_b The standing current of an electron capture detector. P. 165.
- I_e The current observed in an electron capture detector while an electron-capturing species is in the detector. P. 171.
- $I_{PT(i)}$ Kovats Retention Index of substance i from programmed temperature data. P. 246, Eq. (11.30).
- I_X Ionization energy for species X . P. 57.
- ΔI Kovats Retention Index difference. P. 60.
- j Pressure gradient correction factor. P. 19.
- k Capacity factor: $k = K/\beta = p/q = t'_R/t_M$. Also called partition ratio or, less frequently, the mass distribution ratio. P. 22. Eq. (2.10).
- k_B Boltzman constant. P. 56.
- k_{TC} Coefficient of thermal conductivity. P. 149, Table 9.1.
- Δk_{TC} Thermal conductivity coefficient difference. P. 149, Table 9.1.
- K Partition coefficient: $K = C_L/C_M = (w_L/V_L)/(w_M/V_M) = (w_L/w_M)(V_M/V_L) = k\beta$. Also called distribution coefficient. Pages 21, 22.
- K_a Adsorption partition coefficient. P. 59.

- K_H Henry's Law constant. P. 225, Eq. (11.7).
- K^* Coefficient of electron capture. P. 171.
- ℓ A distance, the travel through which causes a given type of peak spreading during molecular "random walking." P. 83. Eq. (6.14).
- L Column length. See Fig. 1.5, p. 5.
- m
1. Constant.
 2. In the filtration method of packing preparation, the ratio m of solution volume retained on the support to the weight of the support: $V_S = mW_S$. P. 182; see also p. 183, Eq. (10.3).
- M Subscript; refers to mobile phase. P. 20.
- n
1. Number of theoretical plates: $n = 16 (t_R/w_b)^2$. P. 4.
 2. Number of carbons in an homologous series (Chap. 11 only). P. 224, Eq. (11.1).
 3. In the filtration method of packing preparation, the ratio n of solution volume V_S retained on the support to the total volume V_T of the solution (Chap. 10 only). P. 182, Eq. (10.4).
- n Number of opportunities for causing broadening. Chap. 6 only. See, for instance, p. 83, Eq. (6.15).
- n_1, n_2 Numbers of interdiffusing molecules in derivation of Einstein's Law of Diffusion. (Chap. 6). P. 79. Eq. (6.2).
- N
1. Number of theoretical effective plates: $N = 16 (t'_R/w_b)^2 = n/[k/(1+k)]^2$. P. 41, Eqs. (4.9), (4.12).
 2. Net number of molecules crossing area 0 in derivation of Einstein's Law of Diffusion (Chap. 6 only). P. 79. Eq. (6.2).
- N_C Effective carbon number: the number of carbons a n -paraffin would have to have to yield the same response from a flame ionization detector as a given molecular species. For n -heptane, $N_C = 7.00$. P. 161.
- \cdot The designation and magnitude of an area, in the derivation of Einstein's Law of Diffusion. P. 78. Eq. (6.1).
- p
1. The weight fraction of solute in the stationary phase. P. 22. Eq. (2.11).
 2. Partial pressure (Chap. 11 only). Pages 226, 227.
- p° Standard vapor pressure for a given molecular species. P. 224. Eq. (11.3).
- Δp_{ne} Pressure drop necessary for a separation. P. 214. Eq. (10.28).
- P_1, P_2 Equivalent grams of stationary phase on supports 1 and 2, in equivalent loading. P. 129. Eq. (8.1).
- P_i Carrier gas pressure at the inlet of a column. P. 19.
- P_o Carrier gas pressure at the outlet of a column. P. 19.
- PP Performance parameter: $PP = \Delta p_{ne} t_{ne}$. P. 214. Eq. (10.28).
- q The weight fraction of solute in the mobile phase. P. 22. Eq. (2.11).
- r
1. Electrical resistance. P. 151.
 2. Internal radius of column (Chap. 10 only), P. 190. Eq. (10.14).
 3. Heating rate in programmed temperature gas chromatography (Chap. 11 only). P. 240.
 4. Effective distance of molecular separation (Chap. 5 only). P. 57.

- R Gas constant. P. 224. Eq. (11.4).
- R_s Resolution. P. 41. Eq. (4.13).
- $$R_s = \frac{\sqrt{N}}{4} \frac{\alpha - 1}{\alpha}$$
- R_I Intrinsic resolution. P. 245. Eq. (11.29).
- R_{IT} Isothermal intrinsic resolution. P. 244. Eq. (11.27).
- R_L Linear dynamic range of a detector. P. 347.
- [R] The time-dependent resolution of Struppe. P. 215. Eq. (10.33).
- S The sensitivity of a detector in grams per second. P. 143.
- SF The Glueckauf separation factor. P. 42; see Fig. 4.2.
- t 1. The time for a molecule of diffusivity D to diffuse distance Δ : $D = \Delta^2/2t$. Eq. (6.4), p. 79.
2. The time interval after sample injection (Chap. 10 only). P. 199, Eq. (10.16).
- t_e The time at which a peak is found to end. P. 377, Eq. (14.11).
- t_s The time at which a peak is found to start. P. 377, Eq. (14.11).
- t_{ne} The minimal time necessary for a separation. P. 214, Eq. (10.28).
- t_G The time spent by a solute molecule in the gas phase while passing through a column. P. 84. Eq. (6.23).
- t_L The time spent by a solute molecule in the liquid stationary phase while passing through a column. P. 86. Eq. (6.31).
- t_M The gas holdup time: The elapsed time from sample injection to peak apex of an unretained solute. P. 17.
- t_M^o The time from sample injection to peak apex of an unretained solute, corrected for pressure gradient: $t_M^o = j t_M$.
- t_N The net retention time: $t_N = t_R^o - t_M^o$.
- t_R The time from sample injection to peak apex; the unadjusted, uncorrected, observed retention time. P. 4.
- t_R' The adjusted retention time: $t_R' = t_R - t_M$. P. 24.
- t_R^o The corrected retention time: $t_R^o = j t_R$.
- T Absolute temperature. P. 171.
- T_a In Eq. (14.6), p. 348, the isothermal temperature for elution, following sample injection at a lower temperature T_0 .
- T_b Boiling point. See Trouton's rule. P. 228, Eq. (11.18).
- T_0 1. In programmed temperature gas chromatography, the *initial temperature*. This is the column temperature at the beginning of a temperature program and may be the column temperature on sample injection. P. 240. Eq. (11.23)
2. In Eq. (14.6), p. 348, the injection temperature of a cold column or pre-column, as used in enhancement of trace detection.
- T_r In programmed temperature gas chromatography, the *retention temperature*. This is the column temperature at which a solute is eluted during a temperature program. P. 240. Eq. (11.23).
- T' In programmed temperature gas chromatography, the *significant temperature*, at which a programmed temperature process is equivalent to an isothermal. P. 241.

- u 1. Carrier gas velocity, measured. P. 87. Eq. (6.34).
 2. Dipole moment (Chap. 5 only). P. 57.
 \bar{u} Average carrier gas velocity. P. 4.
 \bar{u}_o Optimum carrier gas velocity. P. 5, Fig. 1.5.
 u_{opt} Optimum carrier gas velocity. P. 98. Eq. (7.3).
 u_L The velocity of a peak apex along a column. P. 86. Eq. (6.33).
 u_S The velocity of a peak apex with respect to the carrier gas. P. 90. Eq. (6.50).
 v In the equation for reduced plate height, the reduced velocity:
 $v = d_p^* u / D_m$. P. 111. Eq. (7.14).
 V 1. Retention volume. P. 240.
 2. Mixing chamber volume (Chap. 10 only). P. 199. Eq. (10.17).
 3. Effective volume of a flame ionization detector *without* added gas (Chap. 9 only). P. 145.
 V_a The isothermal retention volume for elution temperature T_a . P. 348. Eq. (14.6).
 V_e The effective internal volume of a detector. P. 145.
 V_{eff} The effective internal volume of a detector (same meaning as V_e). P. 203. Eq. (10.21).
 V_g The specific retention volume. P. 224. Eq. (11.2).
 V_{max} That volume of a sample that will not cause any more than 10% peak broadening with respect to any smaller volume of it. $V_{max} = a V_R^o / \sqrt{n}$, but the "constant" a is determined by experiment, namely, by injecting successively smaller samples until resolution no longer improves with further decrease in sample size. P. 9.
 V_r The isothermal retention volume for elution temperature T_r (see Eq. (14.6)). The elution temperature is usually an arbitrarily chosen temperature for isothermal elution from a column used as a cold trap; the elution temperature is thus to be distinguished from the retention temperature, which is associated with a temperature program. P. 243.
 V_F The filtrate volume ($V_T - V_S$) of solution from filtration impregnation. P. 184. Eq. (10.12).
 V_L Volume of stationary phase in the column. P. 9. See also p. 24, Eq. (2.21).
 V_M The retention volume for air, uncorrected for gas compressibility. It is used in determining V_R' . P. 19. Eq. (2.2).
 V_M^o The column dead volume: $V_M^o = j V_M$. P. 20. Eq. (2.4).
 V_N The net retention volume, adjusted for column gas volume and corrected for gas compressibility: $V_N = V_R^o - V_M^o$. It is the net retention volume that is directly and linearly related to the stationary phase volume V_L by the partition coefficient K : $V_N = K V_L$. P. 20. Eq. (2.6).
 V_R The unadjusted, uncorrected, retention volume. $V_R = F_o t_R$. P. 19. Eq. (2.1).
 V_R' The adjusted retention volume, uncorrected for gas compressibility: $V_R' = V_R - V_M$. P. 20. Eq. (2.5).
 V_R^o The corrected retention volume. P. 19. Eq. (2.3).
 V_S In filtration impregnation, the volume of solution that is retained on the support. P. 182. On p. 184, Eq. (10.12).
 V_T In filtration impregnation, the total volume of solution used. P. 184, Eq. (10.12).

V_{T_r}	Retention volume measured isothermally at retention temperature. P. 244.
V_0	The isothermal retention volume corresponding to a column temperature T_0 on sample injection. P. 243. See also Eq. (14.6), p. 348.
w	Weight.
w_b	Peak width at base, where the base is defined as the distance between the intercepts of the peak tangents with the interpolated baseline. P. 4.
w_f	The width of a digital matched filter. P. 375.
w_p	The peak width detected as part of the van Rijswick algorithm. P. 377.
w_L	The weight of stationary phase in a column. P. 24, Eq. (2.21).
w_P	In filtration impregnation, the weight of the packing. P. 182. Eq. (10.1).
w_S	In filtration impregnation, the weight of the support. P. 182. Eq. (10.1).
$w_{T,L}$	In filtration impregnation, the total weight of stationary phase to be used. P. 183. Eq. (10.11).
w_D	The maximum weight of a given solute that may be injected without exceeding the linear dynamic range of the detector. P. 346, Eq. (14.2). P. 347, Eq. (14.3).
w_L	Weight of solute dissolved in the stationary phase: $k = w_L/w_M$. P. 22, Eq. (2.9).
w_M	Weight of solute in the mobile phase: $k = w_L/w_M$. P. 22, Eq. 2.9.
w_S	The minimum detectable weight of a trace component. P. 347. Eq. (14.4).
x	In filtration impregnation, the weight fraction of stationary phase in a packing. P. 183, Eq. (10.2).
z	Carbon number of a n-paraffin, in connection with the Kovats Retention Index. P. 60. Eq. (5.1).
Z^*	The temperature-independent factor in the equation describing the temperature dependence of the electron capture coefficient. P. 171.
α	Relative retention. $\alpha = t'_{R2}/t'_{R1} = K_2/K_1 = k_2/k_1$. P. 24. Eq. (2.19).
α_p	Polarizability. P. 57.
β	Phase ratio, also called column characteristic. $\beta = V_M/V_L$. P. 22. Eq. (2.12).
γ	Tortuosity factor. P. 84. Eq. (6.23).
δ	Solubility parameter. P. 70.
λ	Packing irregularity factor. P. 83. Eq. (6.16).
ρ_L	Density of stationary phase (in bulk). P. 24. Eq. (2.21).
σ	Standard deviation, the square root of the variance. P. 80.
σ_T^2	1. The total variance, which is the sum of the variances arising from independent causes. P. 80. Eqs. (6.5) and (6.6). 2. The plate height contribution from the effective internal volume of a detector (Eq. (10.21) only). P. 203.
τ	Response time, p. 199, Eq. (10.16). This is identically the time constant used in Eq. (10.20), p. 199; and is also the effective time interval in Eq. (10.21), p. 203. The concept is the same in each case.
τ_D	The time constant for concentration decrease at the entrance to a mixing chamber. P. 199, Eq. (10.18).
τ_G	The typical time required for a solute molecule to diffuse through the mobile phase to a gas-liquid interface. P. 88. Eq. (6.42).

τ_L	The typical time required for a solute molecule to diffuse through the stationary phase to a gas-liquid interface. P. 86. Eq. (6.30).
τ_M	The time constant for concentration decrease at the exit of a mixing chamber. P. 199. Eq. (10.17).
τ_2	The time during which unit peak spreading due to velocity distribution takes place. P. 91. Eq. (6.56).
Δ	<ol style="list-style-type: none">1. The distance diffused in time t according to Einstein's Law of Diffusion: $D = \Delta^2/2t$. P. 79. Eq. 6.4. See also p. 78.2. Sampling interval (Chap. 14 only). P. 377, Eq. (14.7); p. 377, Eq. (14.8); and p. 377, Eq. (14.10).
Δp	Pressure required to produce a desired carrier gas flow. P. 180.

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GAS CHROMATOGRAPHY: A SIMPLE DESCRIPTION

The word "chromatography," formed from the Greek "chroma" meaning "color," and "graphein" meaning "to write," was coined by Tswett [1, 2] around 1900 to describe his process of separating mixtures of plant pigments. He washed the pigments down a column of adsorbent powder, thus separating them into colored (chroma) bands (graphein) on the powder. Such a separation of the components of a mixture for qualitative or quantitative analysis, or for isolation and recovery of the components, is the desired end of any type of chromatography.

In gas chromatography (Fig. 1.1), the mixture (solute) to be separated is vaporized and swept over a relatively large adsorbent or adsorbent surface inside a long narrow tube, or *column*. The sweeping is done by a steady stream of inert "carrier" gas, which serves only to move the solute vapors along the column. The different components are moved along the column at different rates and, under proper circumstances, become separated. The analyst arranges matters so that the separation is complete within a minimum time and can then be detected and recorded.

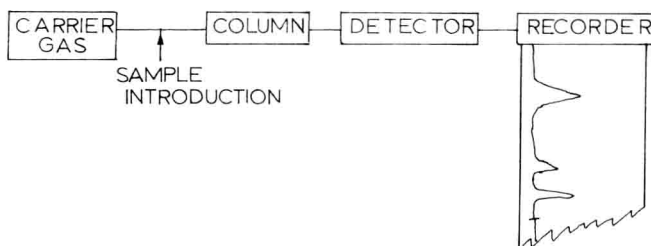


FIGURE 1.1 The gas chromatograph usually consists of a regulated supply of carrier gas, a means for sample introduction, a column for separating the components of the sample, a detector for detecting and signaling the components as they emerge in sequence from the column, and a recorder for measuring and recording the signal from the detector.