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Standard Practice for Packed Column Gas Chromatography[1]

This standard is issued under the fixed designation E260; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice is intended to serve as a general guide to the application of gas chromatography (GC) with packed columns for the separation and analysis of vaporizable or gaseous organic and inorganic mixtures and as a reference for the writing and reporting of GC methods.

NOTE 1—This practice excludes any form of gas chromatography associated with open tubular (capillary) columns.

1.2 *This standard does not purport to address all the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 8 and 9.1.3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E355 Practice for Gas Chromatography Terms and Relationships

E516 Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

E697 Practice for Use of Electron-Capture Detectors in Gas Chromatography

E840 Practice for Using Flame Photometric Detectors in Gas Chromatography

E1140 Practice for Testing Nitrogen/Phosphorus Thermionic Ionization Detectors for Use In Gas Chromatography

2.2 *CGA Publications:*[3]

CGA P-1 Safe Handling of Compressed Gases in Containers

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium

CGA P-12 Safe Handling of Cryogenic Liquids

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures

HB-3 Handbook of Compressed Gases

3. Terminology

3.1 Terms and relations are defined in Practice E355 and references therein.

4. Summary of Practice

4.1 A block diagram of the basic apparatus needed for a gas chromatographic system is as shown in Fig. 1. An inert, pressure or flow-controlled carrier gas flowing at a measured rate passes to the injection port or gas sample valve. A sample is introduced into the injection port, where it is vaporized, or if gaseous, into a gas sample valve, and then swept into and through the column by the carrier gas. Passage through the column separates the sample into its components. The effluent from the column passes to a detector where the response of sample components is measured as they emerge from the column. The detector electrical output is relative to the concentration of each resolved component and is transmitted to a recorder, or electronic data processing system, or both, to produce a record of the separation, or chromatogram, from which detailed analysis can be obtained. The detector effluent must be vented to a hood if the effluent contains toxic substances.

4.2 Gas chromatography is essentially a physical separation technique. The separation is obtained when the sample mixture in the vapor phase passes through a column containing a stationary phase possessing special adsorptive properties. The degree of separation depends upon the differences in the distribution of volatile compounds, organic or inorganic, between a gaseous mobile phase and a selected stationary phase that is contained in a tube or GC column. In gas-liquid chromatography (GLC), the stationary phase is a nonvolatile liquid or gum coated as a thin film on a finely-divided, inert support of a relatively large surface area, and the distribution is based on partition. The liquid phase should not react with, and should have different partition coefficients for, the various

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.19 on Separation Science.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, http://www.cganet.com.

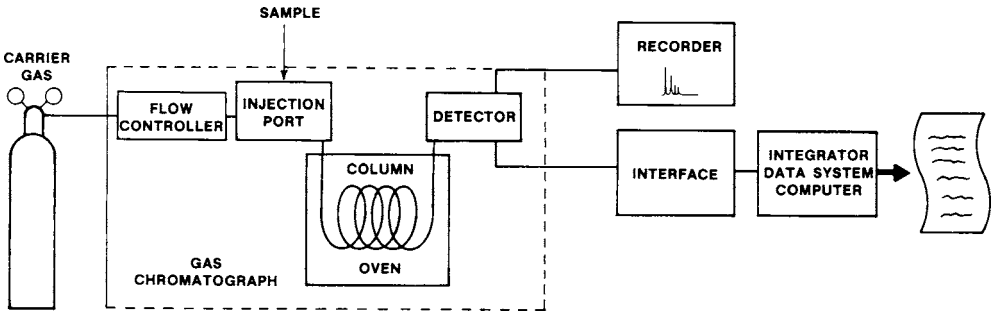


FIG. 1 Block Diagram of a Basic Gas Chromatographic System

components in the sample. In gas-solid chromatography (GSC), the stationary phase is a finely divided solid adsorbent (see 4.4).

4.2.1 After separation in the analytical column, the components are detected, and the detector signal is related to the concentration of the volatile components. Tentative identifications can be made by comparison with the retention times of known standards under the same conditions, either on a single column or preferably by injecting the sample onto two columns of different selectivity. Ancillary techniques, such as mass spectrometry or infrared spectrophotometry, are generally necessary for positive identification of components in samples.

4.2.2 Prior to performing a GC analysis, the following parameters must be considered:

4.2.2.1 Sample preparation.

4.2.2.2 Stationary phase and loading on support.

4.2.2.3 Column material required.

4.2.2.4 Solid support and mesh size.

4.2.2.5 Column length and diameter.

4.2.2.6 Instrument and detector type that will be needed.

4.2.2.7 Injector, column oven, and detector temperatures required for analysis.

4.2.2.8 Injection techniques, such as flash volatilization, on-column technique, purge and trap, pyrolysis, etc.

4.2.2.9 Carrier gas and flow rate.

4.2.2.10 Data handling and presentation.

4.3 In gas-liquid chromatography, the degree of separation possible between any two compounds (solutes), is determined by the ratio of their partition coefficients and the separation efficiency. The partition coefficient, K, is the ratio of the solute concentration in the liquid phase to the solute concentration in the vapor phase at equilibrium conditions. The partition coefficient is affected by temperature and the chemical nature of the solute (sample) and solvent (stationary phase).

4.4 Another mechanism for separation is gas-solid chromatography. With this technique there is no liquid phase, only a porous polymer, molecular sieve, or solid adsorbent. Partition is accomplished by distribution between the gas phase and the solid phase.

4.5 After the sample is resolved into individual components by the chromatographic column, the concentration or mass flow of each component in the carrier gas can be measured by an appropriate detector which sends an electrical signal to a recording potentiometer or other readout device. The curve obtained by plotting detector response against time is referred to as a chromatogram. For flame ionization and thermal conductivity detectors, either the peak areas or the peak heights are proportional to the concentration of the components in the sample within the linear range of the detector system. However, response fractors are not necessarily the same for all compounds, and linearity of detector response may depend on operating conditions. (Testing of detector performance is discussed in ASTM Standard Practices for the appropriate detector, see 2.1).

4.6 Components in a mixture may be tentatively identified by retention time. Ideally, each substance has a unique retention time in the chromatogram for a specific set of operating conditions. However, caution is required because the GC separation may be incomplete and a single peak may represent more than one compound. This is especially true of unknown mixtures and complex mixtures because of the very large number of possible compounds in existence and the finite number of peaks that a chromatograph might resolve. Additional characterization data may be provided by ancillary techniques, such as spectrometry.

5. Significance and Use

5.1 This practice describes a procedure for packed-column gas chromatography. It provides general comments, recommended techniques, and precautions. A recommended form for reporting GC methods is given in Section 14.

6. Apparatus

6.1 *Carrier Gas System*—Common carrier gases are helium and nitrogen. 7.6 provides more details on carrier gases. Means must be provided to measure and control the flow rate of the carrier gas. Any flow or pressure control and measurement combination may be used that will give an accurately known and reproducible flow rate over the desired range.

6.1.1 The main gas supply is regulated with a two-stage regulator which must have a stainless steel diaphragm. Rubber or plastic diaphragms permit oxygen or water to diffuse into the carrier gas. In addition, instruments will have a flow controller between the pressure regulator and column inlet to maintain a constant flow during temperature programming. Copper or stainless steel carrier gas lines, not plastic tubing, should be used to avoid diffusion of oxygen (air) into the carrier gas. When using the thermal conductivity detector, variations in the flow will change retention and response. The carrier gas line pressure must be higher than that required to maintain the

column flow at the upper temperature limit for the flow controller to operate properly. A pressure of 40 to 60 psi is usually sufficient.

6.2 *Column Temperature Control*—Precise column temperature control is mandatory if reproducible analyses are to be obtained. Temperature control must be within 0.1°C if retention times are to be compared with another instrument.

6.2.1 *Air Bath*—The thermostated forced-air bath is generally accepted as the best practical method of temperature regulation for most applications. Temperatures can be controlled by regulators or proportionally controlled heaters using a thermocouple or platinum-resistance thermometer as a sensing element. The advantage of a forced-air bath is the speed of temperature equilibration. Air bath ovens are readily adaptable to temperature programming and are capable of operating over a range of 35 to 450°C. This range can be extended down to – 100°C by using cryogenic equipment.

6.2.2 *Other Devices*—Liquid baths, drying ovens, incubators, or vapor jacket enclosures are less stable, less convenient means of providing a source of heat to maintain or raise the temperature of a chromatographic column. These devices are not recommended for precision chromatographic applications.

6.3 *The Injection Port*—The purpose of the injection port is to introduce the sample into the gas chromatographic column by instantaneous volatilization following injection into the gas chromatographic system. Two sample inlet types are in common use in gas chromatography: the flash vaporization and the on-column injection inlets.

6.3.1 The temperature of the flash vaporization inlet should be above the boiling points of the sample components and is limited by the amount of septum bleed generated and the temperature stability of sample components. It should be set at that temperature above which no improvement in peak shape occurs but should be determined by the nature of the sample and the volume injected, not by the temperature of the column. If the inlet temperature is too low, broad peak with a slowly rising front edge will result from slow vaporization of the sample. If the temperature is set far above what is necessary to produce fast vaporization, thermal decomposition of the sample, decreased septum life, and ghost peaks due to septum bleed may be observed. Generally, a good guideline is to maintain the inlet temperature 25 to 30°C higher than the highest boiling point of any sample component.

6.3.2 A glass liner placed inside the injection port will eliminate sample contact with hot metal inner walls of the inlet, which can catalyze thermal decompositions. Any debris left in the liner, especially from biological samples, can be a source of excessive sample adsorption. If a liner is used, the debris can easily be removed by replacing the liner. Deactivation of the glass liner by treatment with dimethyldichlorosilane may be necessary for some compounds.

6.3.3 With on-column injection technique, the sample is deposited in the liquid state directly on the column packing. The sample must be small enough to preclude flooding of the column, with possible detrimental effects to peak shape and column life. Ideally, the on-column inlet is a part of the column, so its temperature may be controlled as the column temperature is controlled. In practice, because an on-column inlet usually has a somewhat higher thermal mass than an equivalent sector of the rest of the column, the inlet must be heated somewhat above the maximum analysis temperature of the column oven. The criteria of good peak shape and quantitation should be used to determine the maximum required temperature for the inlet. One should consider the temperature limit of the column packing when heating the injection inlet and detector. With some samples, a nonheated injection port is adequate, especially with temperature-programmed operation.

6.3.4 *Injection Port Septum:*

6.3.4.1 The septum is a disc, usually made of silicone rubber, which seals one end of the injection port. It is important to change the septum frequently after two to three dozen injections, or preferably at the end of the working day. The best technique is to change the septum when the column is relatively cool (below 50°C) to avoid contact of stationary phase in a hot column with air (danger of oxidation). After the septum is changed, return the inlet temperature to that which was originally set. The inlet temperature should be the optimum for the particular analysis, as well as within the recommended operating temperature of the septum. If the septum is punctured too many times, it will leak air into the gas chromatographic system, even though it is under pressure. At high temperatures, above 150 to 200°C, air (oxygen) in the carrier gas from a septum leak will degrade the stationary phase. An excessive septum leak will also produce a change in carrier gas flow rate (a change in retention time) and loss of sample (irreproducible peak heights) due to outflow from the leak. When installing the septum, do not overtighten the retaining nut. The septa will swell at high temperature and extrude out of the injection port. A snug fit at room temperature is sufficient. It is important for septum life to make sure the injection needle is sharp with no bent tip. Fine emery cloth, or a fine sharpening stone, can be used to sharpen the point.

6.3.4.2 Ghost peaks may be observed in temperature programmed runs due to septum bleed. Septum bleed is due to the thermal decomposition, 300°C or higher, of the septum that produces primarily lower molecular weight cyclic dimethylsiloxanes. It contributes to baseline response and is frequently observed as evenly spaced peaks in a temperature programmed run in which no sample has been injected. This situation can be demonstrated by the disappearance of ghost peaks after placing aluminum foil (pre-cleaned with solvents such as methylene chloride or toluene) over the inner face of the septum or by turning off the injector temperature and making several blank runs. Septum bleed can be decreased by using either air- or water-cooled septum retaining nuts, by using a septum flush head, or by using special high-temperature septa which are available from a number of gas chromatographic supply houses.

6.4 *Detector Temperature Control*—The detector temperature should always be above that of the maximum operating analytical temperature, to prevent the possibility of condensation of sample components or stationary phase bleed in the detector and connecting line. Because there is usually some temperature gradient across a detector, the temperature should

be set at 30 to 50°C above the maximum analysis temperature to ensure that the entire detector is hot enough to prevent condensation. Usually, it is neither necessary nor desirable to use an excessively high temperature since this can result in reduced sensitivity, increased noise level, frequent need to clean the detector, and thermal decomposition of sample or stationary phase.

6.5 *Measurement of Temperature*—The choice of sensing elements used to measure temperature depends on the desired accuracy (control about a set point) and precision of the measurements. Instrument read-outs should be verified periodically. Some common temperature measurement devices are as follows:

6.5.1 *Standardized Mercury Thermometer:*

Range, °C	Accuracy, °C
0 to 100	±0.02
100 to 200	±0.05
200 to 400	±0.50

6.5.2 *Calibrated Platinum Resistance Thermometer:*

Range, °C	Accuracy, °C
−140 to 500	±0.01

6.5.3 Thermocouple (iron – constantan, or other).

6.6 *Analytical Column:*

6.6.1 The analytical column is a length of tubing (glass, metal, or plastic) that is filled with a packing material. It is discussed thoroughly in Section 7.

6.6.1.1 *Column Characteristics*—Specified by method.

6.6.1.2 *Carrier Gas*—Specified by method.

6.6.1.3 *Sample Size*—Variable within limits.

6.6.1.4 *Flow Rates of Carrier Gas and Detector Gases*—Variable within limits.

6.6.1.5 *Column Temperature*—Usually specified by method, and

6.6.1.6 *Physical or Chemical Characteristic of Compound Analyzed,* or both.

6.6.2 *Detector Characteristics*—Desirable detector characteristics should include the following:

6.6.2.1 Good stability (low noise level, minimum response to changes in temperature and flow rate).

6.6.2.2 Ruggedness and simplicity.

6.6.2.3 Sensitivity to the components for which analysis is desired. Use either a selective detector for materials of interest or one with a similar response for all components.

6.6.2.4 Linearity of response versus sample concentration. Wide linear range.

6.6.2.5 Rapid response to changes in column effluent composition (small internal volume or flow-through design, or both).

6.6.2.6 Detectors, which are nondestructive and do not contribute to band broadening may be used in series with other detectors.

6.7 *Types of Detectors*—The detector is located at the outlet end of the chromatographic column and both senses and measures the amount of components that have emerged from the column. The optimum detector should have high sensitivity, low noise level, a wide linearity of response, a response to all compounds of interest, and yet be insensitive to changes in flow and temperature. Selective detectors are characterized as having selective, or greatly enhanced response to certain components. Linearity is decreased for all detectors by column bleed. As many as forty detection systems have been reported, yet only about a dozen are commonly used. Table 1 shows some of the more commonly used detectors. Of these, the thermal conductivity, the flame ionization, the electron capture, the nitrogen-phosphorus, and the flame photometric detectors are the most popular. Nondestructive detectors should be vented to a hood to remove any toxic effluents from the workplace. The effluent from destructive detectors may also be toxic. Details on detectors can be found in the applicable methods in Practices E516, E594, E697, E840, and E1140.

6.8 *Programmed Temperature Operation*— The apparatus used in programmed temperature gas chromatography differs in some respects from that normally used for isothermal work. Basically, the column temperature is varied with time (program rate) to enhance speed of separations. The advantages of using programmed temperature operation include better resolution of lower boiling components because of lower starting temperature and greater sensitivity because of sharper peaks for the higher boiling components.

6.8.1 *Column Heater and Temperature Programmer*—It is of utmost importance that the column temperature program be reproducible, and that the difference between the set (desired) temperature and the true average column temperature be as small as possible. However, these requirements are difficult to achieve at high heating rates and with columns of large diameter. The mass of the column and its heater should be kept as small as possible. This will minimize thermal lag and will

TABLE 1 Applicability of Commonly Used Gas Chromatographic Detectors

Detector[A]	Applicability (Type of Compound)	Range of Minimal Detectable Amounts (grams)
Thermal Conductivity	All	10^{-6} to 10^{-7}
Flame Ionization	Organic	10^{-12}
Electron Capture	Halogenated and Oxygenated	10^{-12} to 10^{-15}
Flame Photometric	Sulfur, Phosphorus	10^{-11}
Alkali Flame	Nitrogen, Phosphorus	10^{-12} (even lower for phosphorus)

[A] Further information can be found in Practices E516, E594, and E697.

give proportionately small variations around the set temperature at any time. Proportional temperature controllers supply almost full power to the heater until the set point is very closely approached.

6.8.2 The recirculating air bath is the recommended method of heating in programmed temperature gas chromatography (PTGC). The obvious advantages are extremely rapid heating (and cooling after an analysis is completed) with very little temperature lag.

6.8.3 Liquid baths may be used for very low heating rates. They are commonly contained in taped Dewar flasks.

6.8.4 No matter what type of heating device is used, accurate control of the temperature program is necessary. This is usually accomplished by appropriate electronic systems that develop linear (or other) programming rates as desired.

6.8.5 Detectors for programmed temperature gas chromatography should be relatively insensitive to minor temperature and flow fluctuations and insensitive to stationary-phase bleed. These difficulties can be overcome by operating the detector at or near the upper temperature limit for the analysis and by using adequate flow controllers. If stationary-phase bleeding is excessive during PTGC runs, a second conditioning procedure (Section 9) might improve the situation. Alternately, a duplicate analysis column can be used on the reference side of the detector. By equalizing substrate bleed on both sides of the detector, the baseline drift can be substantially compensated. However, this technique does not improve column life and is detrimental to detector linearity. If at all possible, operate the column within its recommended temperature range.

6.8.6 When using the temperature programming technique, the resistance to carrier gas flow in the gas chromatographic column increases with increasing temperature. The flow controllers need a positive pressure of 10 psi to operate properly. By setting the second stage of the regulator to 40 to 60 psi, there will usually be sufficient excess pressure to maintain a constant gas flow through the column. Higher pressures might be required to maintain flow when using relatively long columns of 10 ft, or longer, or packings finer than 120 mesh.

7. Materials

7.1 *Stationary Phases*—The stationary phases (partitioning agents) that have been successfully used for specific separations are found most quickly by a literature search. Many phases are listed in ASTM publications AMD-25A and AMD-25A-51.[4] The most desirable stationary phases do not volatilize (bleed) significantly from the solid supports at temperatures required to elute the sample.

7.1.1 The polarity of the stationary phases is currently best characterized by McReynolds Constants.[5] The higher the McReynolds Constant, the more polar the phase. Rohrschneider constants can also be used to measure the polarity of stationary phases.[6]

7.1.2 The effects of using polar and nonpolar stationary phases are summarized as follows:

7.1.2.1 Nonpolar stationary phases separate compounds primarily by order of relative volatility or boiling point.

7.1.2.2 Polar stationary phases separate compounds by order of both relative volatility and relative polarity. With polar phases, nonpolar compounds will elute before polar compounds of the same boiling point.

7.1.2.3 Polarity alone is insufficient to describe the separation power of a column. One must consider the overall selectivity of a column towards a set of analytes. This selectivity is a summation of the effects of dispersive interactions, acid-base interactions and the dipole interactions offered by the various pendent groups in the stationary phase.

7.1.3 The stationary phases used in gas chromatographic columns have both minimum and maximum temperature limits. The chromatographer must be aware of the limits for the phase being used. Below the minimum temperature, the phase will behave as either a viscous liquid or a solid. Less efficient separation will be observed, and the chromatographic results will be exhibited as broader peaks in the gas chromatogram due to poor mass transfer of components in the stationary phase.

7.1.3.1 Above the maximum temperature limit, the phase will begin to bleed off the column at an accelerated rate, and the observed results will include a drifting baseline or excessive spiking on the baseline. Under these conditions, the liquid phase will decompose or volatilize, and thus be removed from the column. This situation will eventually lead to decreased retention times with broader peaks resulting in poorer resolution of very close peaks. Peak tailing will also be observed as the uncoated surface becomes exposed by removal of liquid phase, thus shortening column life. Bleeding also can expose bare support surface that can adsorb molecules being analyzed and reduce column efficiency. In extreme cases, phase bleeding will result in fouling the detector and connecting lines. The observed maximum temperature will depend upon many experimental variables, such as type of liquid phase column, conditioning, phase-loading level, column temperature, sensitivity setting of the detector, and purity of the carrier gas. In programmed temperature runs, the column can sometimes be operated for short periods about 25°C above maximum temperature. However, column bleed should be minimized for quantitative results since it decreases the linear range of all detectors.

7.2 *Active Solids:*

7.2.1 *Molecular Sieves*—The synthetic zeolite molecular sieve sorbents separate molecules by size and structural shape. Isomers with a more round shape, as branched versus straight chain molecules, diffuse in and out of the zeolite structure more easily than isomers with the long chain structures. Separations are affected by the differences in times required for molecules of different sizes to find their way into and out of the sieve-like structure of the adsorbent. Molecular sieves are most useful for separating H_2, O_2, N_2, CO, and CH_4. Carbon molecular sieves are also available, and can be used to separate O_2, N_2, CO, CO_2, H_2O, and C_1 to C_4 hydrocarbons.

7.2.2 *Porous Polymers:*

[4] *Gas Chromatographic Data Compilation* , ASTM, 1981.
[5] McReynolds, W.O., *Journal of Chromatography Science*, Vol 8, 1970, p. 685.
[6] Supina, W.R., and Rose, L.P., *Journal of Chromatography*, Vol 8, 1970, p. 214.

7.2.2.1 One type of porous polymer used in gas chromatography is available in the form of microporous cross-linked, polymer beads produced by copolymerizing styrene and divinylbenzene or more polar copolymers, or both. These materials are generally used as received without coating with any liquid phase. They provide symmetrical peaks for polar, hydrogen-bonding compounds such as water, alcohols, free acids, amines, ammonia, hydrogen sulfide, etc., and organic compounds up to molecular weights corresponding to about 170.

7.2.2.2 Another porous polymer is poly(2,6-diphenyl-*p*-phenylene oxide). This material is useful for the analysis of amines, alcohols, and hydrogen-bonding compounds. It is also used as an adsorbent for trapping trace organic compounds in water and air.

7.2.3 *Silica Gel, Alumina, and Carbon*— Among the active solid adsorbents are silica gel, alumina, and activated carbon. They are useful for low-boiling hydrocarbons.

7.2.4 Solid adsorbents modified by low concentrations of liquid phases may retain the advantageous properties of both. Some solid adsorbents can be modified by the addition of surface activating compounds such as wetting agents, silver nitrate, and the metal salts of fatty acids.

7.3 *Diatomaceous Earth Supports*—The most popular gas chromatographic supports are those prepared from diatomaceous earth, also called diatomaceous silica or kieselguhr. The two main types are white and pink in color. The white supports are recommended over the pink supports because of their more inert surface. The former are, however, very friable and must be handled very carefully when preparing packings and loading into gas chromatographic columns. Before using these supports, check the manufacturer's literature for comments on their use.

7.3.1 The white-colored supports are produced by calcination of diatomaceous earth with sodium carbonate as a flux. In this process, the diatomaceous earth fuses, due to formation of a sodium silicate glass. The product is white in color due to conversion of iron oxide into a colorless complex of sodium iron silicate. These white materials are used to prepare the more inert gas chromatographic supports. However, they are fragile and subject to abrasion from excessive handling in the course of sieving, packing, or shipping. Abrasion will produce finer particles, or fines, which will decrease column efficiency.

7.3.2 The pink-colored supports are prepared by crushing diatomaceous earth firebrick that has been calcined with a clay binder. The metal impurities remaining form complex oxides that contribute to the pink color of the support. These pink supports are denser than the white supports because of the greater destruction of the diatomite structure during calcination. They are harder and less friable than the white supports and are capable of holding larger amounts of liquid phase (up to 30 %) without becoming too sticky to flow freely. Their surface is generally more adsorptive than white supports. For this reason, they are not recommended for use in the gas chromatographic analysis of polar compounds. However, pink supports provide excellent efficiencies for the analysis of hydrocarbons and organic compounds of low polarity.

7.3.3 *Chemical Treatment of Diatomaceous Earth Supports*—Neither the pink nor the white materials give generally acceptable analysis of more polar compounds without further treatment. With these compounds, severe peak tailing is often observed, especially with the dense pink supports. This tailing is due to the presence of adsorptive and catalytic centers on all diatomaceous earth supports. The adsorptive sites are attributed to metal oxides (Fe, Al) and surface silanol groups, -SiOH, on the support surface. The latter are capable of forming hydrogen bonds with polar compounds.

7.3.3.1 Metal impurities are removed by washing with hydrochloric acid, which leaches out iron and aluminum and renders the surface both less adsorptive and less catalytically active. However, even with acid washing, the pink supports are still more adsorptive toward polar compounds than the white-type supports. Acid washing is sometimes followed by base washing, which seems to remove only minor amounts of metal impurities, but is a good pretreatment for supports that are to be used for the analysis of basic compounds.

7.3.3.2 Neither acid or base washing is effective in reducing peak tailing due to hydrogen bonding with the surface silanol groups, -SiOH. These groups are most effectively masked by treatment with dimethyldichlorosilane.

7.3.4 Acid-washed silanized grades of white diatomaceous earths are recommended as supports for nonpolar and medium polarity liquid phases. Because of the hydrophobic character of a silanized diatomaceous earth, even coating of the most polar liquid phases is difficult to achieve. Acid-washed, silanized grades of white diatomaceous earths are recommended as supports for the polar liquid phases, such as polyesters and silicones of high cyano-group content.

7.3.5 If the column is 6 ft (2 m), or less, use particle size of 100 to 120 mesh (125 to 149 μm) for highest efficiency under isothermal conditions. If the column is longer than 6 ft, use 80 to 100 mesh (149 to 177 μm) particles. If temperature programming is used, 80 to 100 mesh particles should be used to lessen resistance to carrier gas flow.

7.3.6 Further information concerning the liquid phase loading is given in 9.3.

7.4 *Halocarbon Supports*—The two types of halocarbon supports are those prepared from poly(tetrafluoroethylene) and poly(chlorotrifluoroethylene). These supports are relatively inert and are nonpolar. They eliminate peak tailing observed in the analysis of organic compounds capable of hydrogen bonding, such as water, alcohols, amines, etc. They are the preferred supports in the analysis of corrosive halogen compounds such as HF, BCl_3 , UF_6 , $COCl_2$, F_2 , and HCl.

7.4.1 Poly(tetrafluoroethylene) supports require special handling procedures. When used as received, they are soft and tend to form gums upon handling. They can also build up a static charge and spray out of the column during the packing operation. These problems can be virtually eliminated by cooling the support to 0°C before coating with liquid phase and by avoiding the use of glass vessels. Rinsing poly(tetrafluoroethylene) with methanol and drying before use is another way to eliminate the static-charge problem.

7.4.2 Supports prepared from poly(chlorotrifluoroethylene) are structurally harder and are much easier to handle and to pack into a column.

7.5 *Tubing Materials*—Tubing materials should be chosen on the basis of the following criteria:

7.5.1 They should be nonreactive with the stationary phase, sample solvent, and carrier gas.

7.5.2 They should possess physical properties to withstand temperature and pressure of operating conditions, and

7.5.3 They can be shaped to fit in the column oven of the chromatograph.

7.5.4 Satisfactory materials include glass, nickel, stainless steel, and glass-lined stainless steel. Glass is the material of choice, unless conditions prohibit its use. Nickel tubing is more inert than stainless steel in most applications. Less frequently used column materials are poly(tetrafluoroethylene), aluminum, and copper.

7.6 *Carrier Gas*—The use of an impure carrier gas will produce problems in gas chromatography. Trace water and oxygen can cause decomposition of the liquid phase coated on the support. The common carrier gases, helium and nitrogen, should contain less than 5 ppm water and less than 1 to 2 ppm oxygen by volume. An oxygen adsorption trap can be used to remove trace oxygen, while trace amounts of water and hydrocarbons with molecular weights higher than methane, can be trapped on a molecular sieve trap. Place the molecular sieve drier nearest the gas supply. Calcium sulfate has been used in drying tubes, but cannot dry carrier gas to the same level as molecular sieve.

7.6.1 For some applications, hydrogen may be the preferred carrier gas. However, additional safety precautions are required due to hydrogen's explosive nature.

7.6.2 Air (oxygen) can leak into the gas chromatographic system through loose fittings or a septum, that has been punctured too many times, even though the carrier gas is under a pressure of 40 to 60 psi. Keep all fittings on the gas delivery lines tight, and check them at periodic intervals. Change the septum in the injection port frequently. Plastic tubing should never be used for carrier gas, hydrogen fuel (for FID), or make-up gas lines due to the possibility of oxygen or moisture diffusing through the tubing wall.

7.6.3 Each cylinder of carrier gas has its own impurity level. Occasional tanks contain large amounts of impurities which might overcome a low-capacity oxygen adsorption trap and destroy a gas chromatographic column at high temperature. A new tank or a fresh oxygen adsorption unit, or both will improve this situation.

7.6.4 Always change the tank when the pressure is less than 200 psi. As the total pressure in the cylinder decreases, there is an increase in the partial pressure of the water and other impurities adsorbed on the inner walls of the gas cylinder. As a result, the last amounts of gas delivered from the gas cylinder contain high levels of impurities.

7.6.5 *Carrier Gas for Instruments with Thermal Conductivity Detectors*—A major factor in sensitivity is the difference in thermal conductivity of the compound being analyzed and the thermal conductivity of the carrier gas. Helium (thermal conductivity = 33.60 cal/cm-s-°C) is usually the carrier gas of choice.

7.6.6 *Carrier Gas for Instruments with Flame Ionization Detectors*—The most commonly used carrier gases are nitrogen or helium. A maximum impurity level of 0.05 volume % does not generally interfere with most applications. Hydrogen is less commonly used in the US but is more popular in Europe because of availability and relatively low cost.

NOTE 2—If hydrogen is used, special precautions must be taken due to its explosive nature, to ensure that the system is free from leaks and that the effluent is properly vented.

7.6.7 *Carrier Gas for Instruments with Electron-Capture Detectors*—Users should follow the manufacturers' recommendations for the choice of carrier gas. Some common ones are nitrogen or 95 % argon/5 % methane. When using a tritium source in the detector, do not use hydrogen as the carrier gas. Hydrogen will replace tritium in the source.

8. Hazards

8.1 *Gas Handling Safety*—The safe handling of compressed gases and cryogenic liquids for use in chromatography is the responsibility of every laboratory. The Compressed Gas Association, a member group of specialty and bulk gas suppliers, publishes the following guidlines to assist the laboratory chemist to establish a safe work environment: CGA P-1, CGA G-5.4, CGA P-9, CGA V-7, CGA P-12, and HB-3.

9. Preparation of Packed Gas Chromatographic Columns

9.1 *Preparation of the Tubing Material:*

9.1.1 Glass columns should be cleaned and deactivated, first by rinsing with 30 mL acetone and then 30 mL toluene. Next, fill the column with 10 volume % solution of dimethyldichlorosilane in toluene. Allow the solution to stand in the column for 30 min. Finally, rinse the column with anhydrous toluene and then anhydrous methanol to cap unreacted DMDCS CL groups. Dry the column by passing a stream of dry nitrogen through it. Cap both ends of the column until such time that it can be packed.

9.1.2 Metal columns should be cleaned thoroughly before packing by rinsing with methanol, acetone, and chloroform. The column should be dried by passing nitrogen or dry air through it. Do not blow house air through the column since this compressed air usually contains an oil aerosol from the pump.

NOTE 3—Most chromatographic supply houses provide metal tubing that has been washed with solvents and is ready for use.

9.1.3 An alternative procedure is recommended for nickel tubing and can be used to clean stainless steel tubing. Rinse the nickel tubing with ethyl acetate, methanol, and distilled water. Then fill the tube with 20 volume % nitric acid and let it stand for 10 min. (**Warning—**Work in a hood and wear safety equipment when using nitric acid.) Next, rinse the tube with distilled water to neutrality and then rinse with methanol and acetone. Finally, dry the column by blowing nitrogen or helium through it.

9.1.4 The column length is generally 3 to 6 ft (1 to 2 m). Shorter columns can be used to decrease the time of analysis or to separate high boiling compounds. Longer columns are used to improve resolution, but have longer analysis times. (Columns longer than 20 ft (6.1 m) require excessive pressures to maintain the proper carrier gas flow.) A compromise is usually made between analysis time and resolution. As a general rule,

an increase or decrease of column length by a factor of 3 to 4 is necessary to see a significant change in peak separation.

9.1.5 The diameter of the column can be ⅛ in. (3.2 mm) or ¼ in. (6.4 mm) outside diameter. The ⅛-in. column has less sample capacity, but greater efficiency, and is the most common type. Glass columns are generally 2 mm or 4 mm inside diameter. Some analysts have found that 3⁄16 in. (4.8 mm outside diameter) metal columns are the ideal combination between the capacity of ¼ in. (6.4 mm outside diameter) columns and the efficiency of ⅛ in. (3.2 mm) outside diameter columns.

9.2 *Choice of Diatomaceous Earth Support for Packed Columns*—See 7.3.

9.3 *Phase Loading on Diatomaceous Supports*—For preparative work and analysis of substances boiling below room temperature, use 15 wt % loadings for white-type supports and 30 wt % for pink-type supports. For general work, use loadings of the range of 3 to 15 wt %. For highest efficiency, shortest retention times, and the least amount of bleed during high-temperature operation, use 3 wt. % loadings. The lower phase loadings have lower sample capacity and elute components more rapidly and at lower temperatures. Always check the manufacturers' literature for suggested phase loadings for a particular support. For some applications (especially headspace analysis) loadings as low as 0.2 wt. % are used which result in very narrow peaks and short analysis times. High phase loadings tend to produce less reactive packings.

9.4 *Preparation of the Gas Chromatographic Packing*—The following procedures describe the coating of a solid support with stationary phase. The following four methods are commonly used to prepare gas chromatographic packings: *(a)* Filtration or Solution Coating Method, *(b)* Rotating Evaporator Method *(c)* Evaporative Method, and *(d)* Vacuum Evaporative Method. When preparing packings with loadings in the range of less than 5 wt %, the Filtration or Solution Coating Method is recommended. This method is preferred because it provides minimum handling of the friable white-type supports. For loadings of more than 5 wt. %, other methods can be used. The Rotating Evaporator Method is recommended, but should only be used if a rotating evaporator is available, which turns very slowly at 20 to 30 rev per min.

NOTE 4—A5 wt. % loading of stationary phase consists of 5 g stationary phase added to 95 g of support.

9.4.1 *Filtration or Solution Coating Method*—Prepare 100 mL of a solution of the desired phase in a vacuum filter flask. Use a suitable high boiling solvent (boiling point more than 60°C). The actual loading of the liquid phase on the support will depend upon both the viscosity of the phase solution and the density and mesh size of the support.

9.4.1.1 Add 20 g of support to the filter flask. Reduce the pressure in the filter flask for a few minutes with a water aspirator, then release the vacuum. Repeat this procedure for several cycles in order to remove air bubbles from the pores of the support particles. Be prepared to release the vacuum if the slurry foams excessively.

9.4.1.2 Allow the slurry to stand for several minutes. Pour the slurry into a coarse-frit sintered-glass filter funnel, and allow the solvent to drain freely until the support settles.

9.4.1.3 Apply vacuum cautiously and stop instantly when the solvent stops dripping. Dump the support into a flat borosilicate glass dish, and allow it to dry. Do not scrape the particles out of the funnel, since this might crush the particles. Do not resieve before use.

9.4.1.4 The actual phase loading will depend upon the viscosity of the phase solution and both the density and particle size of the support. For example, a 2 % solution of dimethyl silicone gum liquid phase will give a 3.8 wt % loading on white-type supports. A10 wt % solution of a less viscous liquid phase will give a 5.5 wt % loading on white-type supports and 7.5 wt % on pink-type supports. Loadings obtained with other phases on other supports are best determined by experimentation.

9.4.1.5 The best way to determine the percent loading is to extract it from the support by extraction in a Soxhlet apparatus and determine the weight loss. Alternatively, measure the volume of solution recovered and calculate the volume of solution held up by the support. Calculate the approximate percent loading on the support by assuming that the concentration of the solution does not change.

9.4.2 *Evaporative Method:*

9.4.2.1 Weigh out the desired amounts of support and phase. Use a larger amount than that required to account for attrition, spills, etc. Dissolve the liquid phase in a chemically inert, low-boiling solvent contained in a filtration flask (see Table 2). (Most catalogs of gas chromatography equipment suppliers contain lists of suitable solvents.)

9.4.2.2 Gradually add the support to the solution with gentle swirling or agitation but with no mechanical stirring. (Suggested solvents are given in Table 2.) The amount of solution should be just enough to wet the solid support and form a slurry with little excess solvent.

9.4.2.3 Evacuate the flask briefly several times to remove air bubbles from the pores of the support. Be prepared to release the vacuum if the slurry foams excessively.

9.4.2.4 Transfer the slurry to a large flat borosilicate glass dish, and slowly evaporate the solvent in a hood with no further handling. The dish must be of a size that the packing is spread on the bottom in a thin layer, no more than about ¼-in. thick. A borosilicate glass baking dish makes a suitable container.

9.4.2.5 The critical stage occurs when excess solvent has evaporated, but the bed is still quite damp with a slight excess of solvent. Break up the damp bed by gently raking it with a spatula. As the solvent evaporates from the surface of a static

TABLE 2 Solvent for Liquid Phases

Liquid Phase Type[A]	Solvent
Dimethyl Silicone	Toluene
Phenylmethyl Silicone	Ethyl Acetate
Cyanopropylphenyl Silicone	Methylene Chloride
Trifluoropropyl Silicone	Ethyl Acetate
Polyethylene Glycol	Methylene Chloride
Cyanopropyl Silicone	Methylene Chloride
Other Liquid Phases	Use solvent as recommended by supply house.

bed of support, it leaves a higher concentration of phase at the bed surface. Therefore, the bed must be broken up frequently during the final stages of solvent evaporation to prevent formation of an unevenly coated support.

9.4.2.6 Continue to air-dry the material in the hood until the last traces of solvent are gone. Avoid excessive handling of the particles to prevent formation of fines due to abrasion, especially in the case of the white-type supports.

9.4.3 *Rotating Evaporator Method*—Prepare the slurry of support and phase as described in 9.4.2.1 to 9.4.2.3, except in an indented, round-bottom flask. Connect the flask to a rotating evaporator. Rotate the flask very slowly (less than 20 to 30 revolutions per minute) and evaporate the solvent under reduced pressure (water aspirator). Very slow rotation is necessary to prevent the particles from abrading against each other. Use of a heat lamp increases the evaporation rate. This method is not recommended for fluorocarbon supports.

9.4.4 *Vacuum Evaporative Method*—Prepare a slurry of support and phase in a filtration flask of sufficient capacity. (Suitable solvents are given in Table 2.) Attach the flask to a vacuum source (water aspirator) and apply vacuum briefly. (Be prepared to release the vacuum if the slurry foams excessively.) Repeat this procedure several times in order to remove the air bubbles from the pores in the support.

9.4.4.1 Apply the vacuum for a longer period, and swirl the contents of the flask occasionally until all the solvent is almost evaporated. This is the critical stage.

9.4.4.2 Now shake the contents of the flask by gently bumping the flask on a wood or plastic board. This will break up the bed of packing. Do not allow the solvent to evaporate from the surface of the support bed. Otherwise, the solvent will evaporate and leave a higher concentration of phase at the bed surface.

9.4.4.3 Continue to apply vacuum until the packing is a freely flowing powder, then transfer it to a tray for air-drying in a hood.

9.4.5 *Fluidized Drying Technique*—This technique has been used to produce efficient, uniformly coated packings. During the drying stages of methods 9.4.1 to 9.4.4, when the packing has reached the consistency of a wet sand, add it to a fluidizer. Then dry the packing by passing a flow of inert, warmed gas (nitrogen or helium) through the bed of packing.

9.5 *Packing the Gas Chromatographic Column*—The purpose in packing a gas chromatographic column is to fill the column with packing as completely as possible, leaving no empty spaces. Two variations are noted in 9.5.3 and 9.5.4 (a pressure-fill procedure and a vacuum fill procedure).

9.5.1 It is preferable to coil the column before packing to prevent crushing of the support particles. Metal columns can be coiled after loading to meet equipment requirements. Bends in the packed region must never be made with radii less than those specified in 9.5.2, to avoid crushing the packing in the column.

9.5.2 Right-angle bends are often necessary to make connections to injection and detection systems, and must be made before packing the column since some tubing deformation will occur, which will crush some of the solid support. Bends for such purposes should be within 4 in. (10 cm) of the column ends. For coiled columns, minimum diameter mandrels should be as follows: for ⅛ in. (3.2 mm) OD column use a 1½-in. (38-mm) mandrel; for ¼ in. (6.4 mm) OD column use a 2-in. (51-mm) mandrel. These configurations do not preclude the use of U- or W-shaped columns. If a U- or W-shaped column is to be used, the minimum 180° bend diameter must be at least that given for the above mandrel sizes.

9.5.3 *Pressure Fill Procedure*—To each end of the column to be filled, fit a nut, a back ferrule, and a suitable front ferrule. Place a small plug of silanized glass wool into the detector end of the column, and cap the column by screwing in a metal cap with a 1/16-in. vent hole drilled into it. When analyzing trace acidic compounds, as organic acids and phenols, adsorption can be decreased by using phosphoric acid-treated glass wool to plug the column ends. Wear safety glasses when pressure-packing columns.

9.5.3.1 Attach the end of the empty column to an apparatus similar to that shown in Fig. 2. Add to the reservoir sufficient packing material to fill the column, plus about 30 %. Attach the upper end of the reservoir to a nitrogen supply line controlled

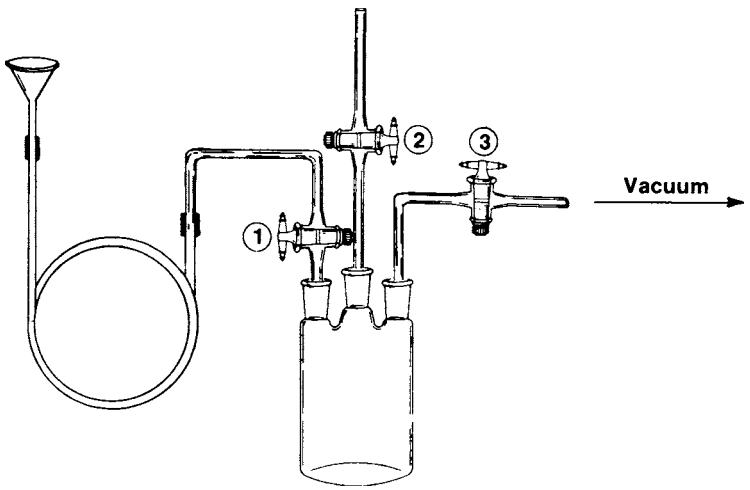


FIG. 2 Vacuum Fill Apparatus

to provide approximately 40 psi. Check that all connections are tightened, place a safety shield in front of the setup, and apply 40 psi to the system.

9.5.3.2 As the stationary phase starts to fill the column, gently tap the column with a wood rod (handle of spatula or screwdriver) or an electrical vibrator set at a very low vibration level. Continue tapping until the packing shows no voids and the level of packing in the reservoir remains constant.

9.5.3.3 Shut off the nitrogen supply and wait for the pressure to dissipate. Disconnect the column from the reservoir. Do not disconnect the column while it is under pressure. Have a clean beaker available to collect excess packing material that will fall from the opened reservoir. Tap out about ⅛ in. (3 mm) of column packing, and replace it with a silanized glass wool plug. Affix a metal column tag engraved with a description of the stationary phase, loading, support, and the assigned column number.

9.5.4 *Vacuum-Fill Procedure:*

9.5.4.1 Clamp the column so that the detector and injector ends point upward. Plug the detector end of the column with a ¼-in. plug of silanized glass wool. Use phosphoric-acid treated glass wool when analyzing for trace organic acids and phenols.

9.5.4.2 Attach a small funnel to the injection port end of the column. Attach the detector end of the column to a vacuum source, either a vacuum pump (preferably) or a water aspirator. (If a water aspirator is used, a 500-mL filter flask, or the device shown in Fig. 3, should be placed in the line between the pump and the column.) Do not turn on the vacuum yet.

9.5.4.3 Add 1 to 2 mL of packing to the funnel, and tap the column gently to settle the packing. A pencil or a wooden spatula handle can be used. Alternatively, the column can be stroked with a plastic saw. The use of an electric vibrator is not recommended. Excessive vibration will cause the particles to abrade against each other, producing fines and newly fractured surfaces that are not coated with stationary phase.

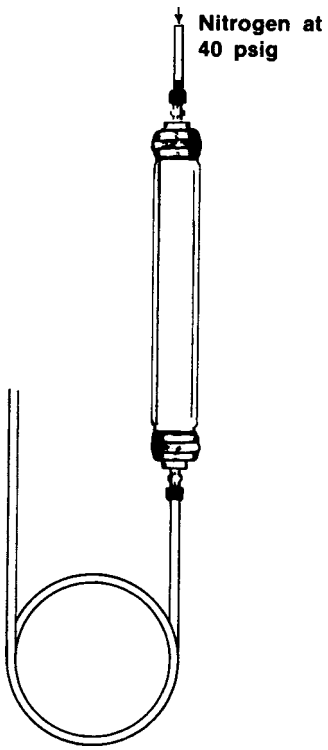


FIG. 3 Pressure Fill Apparatus

9.5.4.4 Turn on the vacuum source. Continue to add the packing in small increments with tapping until the column is full. Finally, apply pressure to the head of the column to pack it a little tighter. However, take care to make sure the pressure is equalized slowly, because packing will be blown out of the column if the pressure is released too suddenly.

9.5.4.5 Next, tap out enough packing to create a ⅛ in. (3 mm) void space at the injector port end of the column. Plug this end with a silanized glass wool plug. Do not pack the plug too tightly. This will either impede the carrier gas flow or crush the packing particles.

9.5.4.6 Higher efficiencies are always observed if the column is packed for on-column injection. In this technique, the column is packed so that there is space at the injection port end of the column, which is then placed inside the injection port. This void space should be of such a length that the injection needle just reaches, or slightly penetrates, only the glass wool plug, not the packing, when the column is installed. Thus the sample is injected almost directly onto the column.

9.6 *Conditioning of Packed GC Columns:*

9.6.1 The purpose of the conditioning process is to remove extraneous material (solvent and adsorbed material) from the column before analytical usage. Since the column is heated, the liquid phase also redistributes itself over the support surface to provide a more even coating.

9.6.2 Install the column into the gas chromatograph at the injection side only. Do not connect the column to the detector during the conditioning stage. Any column bleed might foul the detector and the connection lines between the column and detector. Turn on the normal analytical carrier gas flow and flush air out of the column at ambient temperature for 30 min.

9.6.3 Heat the column at a rate of 2°C/min to the conditioning temperature. The latter temperature should be at least 25°C higher than the analytical temperature but 25°C lower than the maximum operating temperature recommended for the liquid phase. Maintain this temperature overnight with carrier gas flow.

9.6.4 The next day cool the column and connect it to the detector. Detectors operated in very sensitive modes, particularly the electron capture detector, might require two or more days of conditioning at the higher temperatures before a satisfactory baseline is obtained. (Other sources for baseline drift and noise are impurities in the carrier gas, a dirty detector, air leaks in the gas-line fittings, insufficient carrier gas pressure, a much-punctured septum, chemical decomposition of the phase (due to presence of traces of acid or base on the support, in the phase, or on the inner column walls, and incorrect fuel gas ratios to the flame ionization detector.)

9.6.5 There is a special “no-flow” conditioning procedure which can be used with certain silicone phases, as methyl and methylphenyl silicones with or without low vinyl content. It has been reported to improve analysis for drug compounds. The procedure starts by conditioning the column for ½ h as described in 9.6.2. Turn off the carrier gas flow, cap the free end of the column with a metal cap, and heat at 310°C for 1.5

h with no carrier gas flow. Cool the column to 100°C. Uncap the oven, turn on the carrier gas flow, and continue the regular conditioning procedures listed in 7.6.3.

NOTE 5—This no flow conditioning procedure may damage or destroy non-silicone containing stationary phase or silicone containing functional groups other than phenyl or methyl.

9.6.6 Many of the liquid phases are commercial-grade material, and conditioning might require several days before the noise level is low enough to provide usable baselines at high sensitivity. The use of gas chromatographic-grade phases is recommended since they have been carefully purified and long periods of conditioning are usually not necessary.

10. Sample Injection Procedures

10.1 *Injection Technique*—Useful analyses are obtained only by injecting representative samples into the gas chromatograph. Since chromatographic samples are small, the best practices and procedures must be followed.

10.1.1 If elution is to be otherwise, the sample injection must be almost instantaneous in order to introduce the sample as a plug. Avoid unnecessary sample dilution and inadvertent trapping.

10.2 *Sample Size*—Sample sizes used for analysis with 2- to 5-mm ID packed columns are in the range of 0.1 to 10 µL multi-component liquids. Gas samples usually range from 10 µL to 2 mL.

10.2.1 There is frequently a reduction in retention times with sample size when the column is overloaded. Therefore, when identifying by comparison with a known sample, the same amount of each component must be used in an amount that does not overload the column. The sample size that overloads the column is that size which decreases the efficiency (Section 11) by 10 % compared to a smaller sample size. Sample overload is sometimes shown by peaks with sloping fronts and backs that are almost perpendicular to the baseline. (Another reason for this peak shape is insufficient vaporization of the sample. Either the injection port or the column temperatures, or both, are too low.)

10.3 *Sample Injection Devices*—Samples may be introduced by syringes, automatic sample injectors using syringes, or sample valves. (There are also devices that introduce capsules containing sample into the injection port.) For rigorous quantitative work, any sample introduction device should be flushed and filled at least three times with the sample immediately before use.

10.3.1 The most common method for liquids is the use of a syringe injection technique through a self-sealing septum. In the usual 10-µL syringe, there is approximately 0.8 µL of dead volume in the syringe needle. This volume is additional to the volume in the syringe barrel and can be measured by withdrawing the entire sample volume into the syringe barrel.

10.3.1.1 First, pump the sample back and forth vigorously in the syringe to wet the plunger and to remove air bubbles. Then withdraw the sample back into the syringe so that the entire volume can be read on the volume marks of the syringe barrel. When preparing the syringe for injection, never leave the sample solution in the needle. This technique will minimize sample boiling out of the needle when it is inserted into the hot injection port.

10.3.1.2 In an alternative procedure, called the solvent-flush technique, load the syringe in the following order: solvent, air, sample solution, and air, with only air remaining inside the needle. When the sample is injected, the solvent is the last to leave the syringe, and it rinses out sample residue in the needle.

10.3.1.3 Wipe the syringe needle off before injection. Insert the needle carefully through the GC septum, inject the sample at once, and withdraw the needle in one continuous motion.

10.3.1.4 Often the tip of the needle becomes bent, forming a fish hook that will tear the septum on subsequent injections. This can be detected by brushing the end of the needle gently over the end of a finger. A few strokes on a sharpening stone will remove the fish hook.

10.3.1.5 Syringes should be cleaned with a solvent that will remove all traces of contamination. Consult the manufacturer's literature for further information. Many chromatographic supply vendors sell suitable cleaning solutions and kits. Liquid sample valves, in both automated and manual versions, are also available.

10.3.1.6 Gas samples are most conveniently injected using gas-tight syringes. These devices are quite satisfactory for survey work because the sample size can easily be verified. However, the syringe needle is more likely to clog with pieces of septum material when gas samples are injected than when liquids are injected. If no chromatographic peaks are observed, test the syringe by injecting air into a liquid. If no bubbles are seen, unclog the needle with a wire or by filling the syringe without the needle and forcing solvent through the needle. However, repeatable results in gas analysis will only be obtained using gas sample valves that have a fixed sample loop. The latter valves can easily be automated.

10.3.1.7 A sealed, friable, or puncturable ampule containing a weighed amount of sample may be placed in the injection chamber. The ampule is physically broken to release the sample, which is then swept into the gas chromatographic column by the carrier gas.

10.4 *Sample Container*—Care must be taken in the design and construction of sample containers so that none of the components of interest are in any way changed or removed from the sample by reaction, diffusion, or adsorption. Stopcock grease and material desorbed from plastic cap liners are frequent sample contaminants.

11. Evaluation of Column Performance

11.1 Make a test mixture which contains a normal aliphatic hydrocarbon and the compound being analyzed, or one similar in structure. The aliphatic hydrocarbon peak should appear in the chromatogram near the second component in the test mixture. (Suggested aliphatic hydrocarbon mixtures are shown in Table 3.) The peaks of both components should be about the same size. The analytical conditions should be chosen so that both chromatographic peaks will appear about 4 to 6 times the retention time (distance) of the solvent peak. (If a selective detector is being used, choose a compound that will give a response to that detector.)

TABLE 3 n-Alkanes Used for Column Evaluation at 200°C

1 m 10 % Dimethyl silicone C_{18} , C_{20} , C_{22}
3 m 10 % Dimethyl silicone C_{14} , C_{16} , C_{18}
1 m 10 % Phenylmethyl silicone C_{20} , C_{22} , C_{24}
3 m 10 % Phenylmethyl silicone C_{16} , C_{18} , C_{20}
1 m 10 % Cyanopropyl silicone C_{24} , C_{26} , C_{28}
3 m 10 % Cyanopropyl silicone C_{20} , C_{22} , C_{24}
1 m 10 % Polyethylene glycol C_{24} , C_{26} , C_{28}
3 m 10 % Polyethylene glycol C_{18} , C_{20} , C_{22}

11.2 The different methods of determining column efficiency are shown in Eq 1-3. Figs. 4 and 5 show the measurements made on a chromatographic peak which are used to determine column efficiency.

$$N = 16\,(t_R/w_b)^2 \quad (1)$$

$$N = 5.54\,(t_R/w_h)^2 \quad (2)$$

$$H = L/N \quad (3)$$

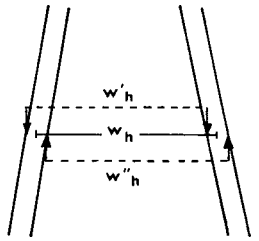
where:

N = number of theoretical plates,
t_R = retention time, or distance, measured in mm,
w_b = width of the peak at base, measured in mm, (Determined by extrapolating, as shown in Fig. 4 and Fig. 5.)
w_h = width of the peak at one-half the peak height, h, all measured in mm, (See Note 6.)
H = height equivalent to a theoretical plate, HETP, and
L = length of the column in millimetres, or in centimetres.

NOTE 6—The peak width may be measured to the nearest 0.1 mm by a magnifying loupe fitted with a scale graduated in 0.1 mm increments. The peak to be so measured should be at least 10 mm wide; this is arranged by choosing an adequately large chart speed.

11.3 Eq 1 is often used. However, it involves an extrapolation of the baseline, shown in Fig. 4 and Fig. 5, which can be in error. The use of Eq 2 is preferred because the term, w_h can be determined directly from the chromatogram without extrapolation. However, the width of the recorder pen line can be variable which can lead to difficulties in determining the true value of the peak width. Use a pen that writes with a sharp, thin line. The peak width should be measured from the leading edge of one line to the leading edge of the other line, as shown in Fig. 4. For accuracy, determine the peak width twice (see Fig. 4), and use the average value to calculate "*N*". To further minimize errors in determining the peak width, use a recorder chart speed that will give a minimum peak width of 4 to 5 cm. The peak height should be about 40 to 80% full-scale chart deflection. This can be achieved by either changing the detector sensitivity, or changing the sample size. However, be sure that the sample size does not exceed the capacity of the column.

(3b)



NOTE 1—Shows the procedure to measure the peak width, at w_h , to account for the thickness of the pen. Use the average of the two determinations, w'_h and w''_h , shown here.

FIG. 5 Procedure to Measure the Peak Width

11.4 The optimum efficiency occurs at the optimum carrier gas flow which can be determined by plotting the efficiency of the hydrocarbon peak versus carrier gas flow. General optimum values of the carrier gas flow rates are shown in Table 4, but should be determined for the particular column.

11.5 Calculate the efficiency of the second component. The results should be about the same for both components. If the efficiency of the second component is about 25 % lower than that of the hydrocarbon, the column might not be the best choice for analyzing the compound(s) of interest. A strong indication of nonsuitability is shown by comparatively greater tailing of the nonhydrocarbon component. Tailing can indicate strong interaction with the column packing (phase or support, or both), column tubing, or adsorption in the injection port or in lines leading from the column to the detector.

(3a)

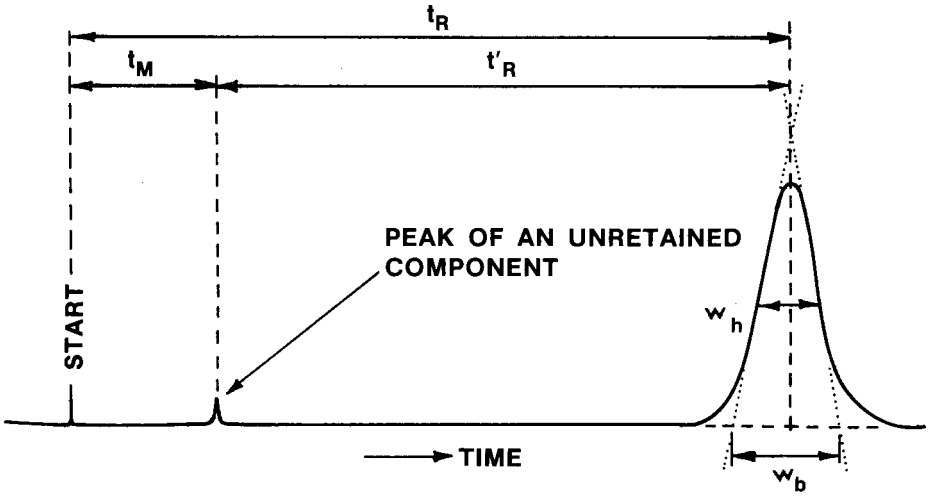


FIG. 4 Use of the Chromatogram to Calculate Column Efficiency

TABLE 4 General Optimum Values of Carrier Gas Flow Rates

Column Dimensions	General Optimum Carrier Gas Flow	
	Helium	Nitrogen
⅛ in. OD or 2 mm ID	30 mL/min	20 mL/min
¼ in. OD or 4 mm ID	60 mL/min	40 mL/min

11.6 Typical efficiencies are shown in Table 5. Not all gas chromatographic packings are capable of excellent efficiencies. For example, porous polymers, Teflon supports, and some liquid phases, such as trifluoropropyl silicone can give efficiencies less than 500 plates per foot.

12. Use of the Gas Chromatographic Packed Column

12.1 Certain precautions and preventive maintenance are necessary to obtain the best column performance. Some of these points have been made before and will be referred to in this section. Further precautions will also be discussed.

12.2 *Carrier Gas Purity*—Trace, or adventitious, oxygen and water in the carrier gas can produce degradation of liquid phases on the support. Purification of the carrier gas and necessary precautions are discussed in 7.6.

12.3 *The Injection Port*—The injection port is often a source of trouble. The temperature can be either too low or too high. See 6.3. Another problem is a leaking septum. See 6.3.4.

12.4 *Column Care:*

12.4.1 Never heat a gas chromatographic column with air in it. When any column is first placed in a gas chromatograph, flush any air (oxygen) out of it by flushing with carrier gas at normal flow rates for 15 to 30 min. at ambient temperatures. Then heat the column to the desired operating temperature. Always cool the column to room temperature before removing it from the gas chromatograph. If the column is to be used again, cap the ends with metal caps to prevent diffusion of air (oxygen) into the column during storage. Contact of the stationary phase with oxygen when hot or for prolonged periods of time at room temperature cause degradation of the stationary phase. This is particularly the case with polyglycols and polyester type phases and to a lesser extent cyanosilicones. Other phases are affected to a varying degree.

12.4.2 After long periods of use, column performance may degrade as shown by peak broadening, tailing, or gradual merging of adjacent peaks. Often the problem lies in the front end of the column. The injection port temperature might have been too high and destroyed the initial section of the liquid phase on the column packing. Residues or decomposition products might have built up on the glass wool plug. These problems can be remedied by repacking the first few inches of a glass column, or cutting off the first few inches of a metal column. Use fresh silanized glass wool to close the end of the column in both cases.

TABLE 5 Typical Efficiencies and Ratings of Gas Chromatographic Columns

Plates/ft	Plates/metre	HETP	Rating
500	1640	0.6 mm	Excellent
400–500	1300–1640	0.60–0.76 mm	Good
300–400	980–1300	0.76–1.0 mm	Fair
300	980	1.0	Poor

13. Methods of Qualitative Analysis

13.1 Identification of compounds by gas chromatography alone cannot be absolute, and the results must be considered with care. Elution of a compound is dependent upon carrier gas flow rate, column temperature, support size, amount and type of liquid phase, column dimensions, instrument dead volume, and column pressure drop. These parameters must be stable to obtain reproducible results. The recommended format for a gas chromatographic method is given in Section 15.

13.2 Tentative identification of a compound can be made by comparing its adjusted retention time against those of known standards using exactly the same chromatographic parameters.

13.2.1 The retention time is the time interval measured from the point of injection to maximum peak height of the sample. Adjusted retention time, t'_R, is derived by subtracting the time required for an unabsorbed gas, like air, or methane, t_M , to traverse the column (also called the gas holdup time) from the retention time, t_R .

NOTE 7—On some solid adsorbent columns, such as molecular sieves, there is no nonadsorbed component.

$$t'_R = t_R - t_M \tag{4}$$

13.2.2 Retention times are affected by all chromatographic parameters. As a result, direct comparison of retention times of the same components on different instruments or between laboratories should be done with caution. Use of relative retention time is an easy practical technique for providing elution data. The retention of a component is expressed relative to the retention of a known reference standard. The reference standard should possess structural or chemical similarity to the compounds being analyzed.

13.3 The retention of a given weight of compound is usually independent of its concentration if the compound does not overload the column producing skewed peaks. The retention of the compound is also independent of other substances present if there is no appreciable overlap with another compound. Substances that exhibit positive, or Langmuir-type, skewing (tailing) during elution will produce a decrease in retention as the concentration increases; while negative, or anti-Langmuir-type fronting will produce an increase in retention time with increased concentration.

13.3.1 The logarithm of the retention time of members of a homologous series run isothermally is usually a linear function of the number of carbon atoms of a molecule. Using this characteristic, two or three reference compounds can provide sufficient information to prepare a plot of the logarithm of the retention time versus carbon number, and they can identify other members of the series. Retention time, adjusted or not, is of little value in comparing the results from various instruments. The use of Kovats retention index, based on the relative retention of a compound to the retention of normal paraffins, provides a more reliable means of comparing the results obtained from different instruments (see Practice E355).

13.4 Absolute compound identification or characterization, must be made with ancillary techniques such as mass or infrared spectrometry, nuclear magnetic resonance, chemical analysis of the effluent, or spot tests for functional groups.

13.4.1 The samples for the analyses in 13.1-13.4 may be obtained by trapping components as they emerge from the chromatograph. A trap, glass capillary, or U-tube, is cooled with ice or dry ice, and placed in the effluent stream of the column. Several collections may be required to obtain a sufficiently large sample.

13.4.2 The collection of effluent is easiest with nondestructive detectors, see 6.7. In the case of destructive detectors, a split is made for the collection just before the detector.

13.4.3 Apparatus is also available so that the effluent from the gas chromatographic column can be analyzed directly by mass spectrometers or infrared spectrophotometers.

14. Methods of Quantitative Analysis

14.1 Gas chromatography can be used to determine quantitatively the composition of complex samples. There are several factors that must be considered before the sample is analyzed. The recommended format for gas chromatographic methods is given in Section 15.

14.1.1 *The Chemistry of the Sample*—The chemistry of the sample, if known, allows a chromatographer to select more accurately a column compatible with the sample and to anticipate potential interferences from reaction by-products.

14.1.2 *The Choice of a Detector*—A detector must be chosen with the needed selectivity and sensitivity. If components will be analyzed at low levels, an electrolytic conductivity electron capture, nitrogen phosphorus, microcoulometric, ionization, or flame photometric detector should be selected. The detector may be limited to these lower concentrations and not applicable to high concentrations.

14.1.3 *Initial Separation of Components*— Next, a column must be chosen that will resolve the components of interest in the sample within a reasonable amount of time. First, a rough separation should be achieved with known standards. Next, actual samples should be analyzed to determine if there are any interferences. A second column, or an ancillary technique (GC/mass spectrometry, GC/infrared spectrometry, etc., should be used to verify that additional components are not eluting with the component of interest. Each new sample adds the possibility of an interference eluting with the component of interest; therefore this should be checked often. If an interference is detected, the chromatographer must change the method to remove it. The several options for doing this are as follows:

14.1.3.1 Select a column stationary phase with a greater selectivity for either the interference or the component of interest.

14.1.3.2 Choose a different type of detector that would detect the component of interest but not the interference. Examples would be water not being detected by a flame-ionization detector, or hydrocarbons not detected by an electrolytic conductivity or electron capture detector.

14.1.3.3 Consider other types of chromatographic separation such as capillary gas chromatography for more efficient separation of volatile compounds, liquid chromatography for separation of non-volatile compounds, or another appropriate separation technique.

14.1.4 *Detector Sensitivity and Linearity*— Once the chromatographic separation has been optimized, the detector can be optimized and calibrated. Gas flows should be adjusted to the optimum levels to get peak sensitivity at the concentration range of the components of interest. The detector must also be clean and leak-tight. (See the manufacturer's manual for suggested procedures.)

14.1.4.1 The linearity of the detector over the desired concentration range of the component(s) of interest is determined using prepared standards. This step will determine what the response is to increasing amounts of component. The peak area or height should be plotted versus the concentration for about five concentrations near the expected sample concentration. There should be a linear correlation. Nonlinearity may be caused by reactivity, adsorptivity, thermal sensitivity, or excessive column bleed. If the latter is the cause, change to a more thermally stable column or one of different polarity. Column reactivity can be characterized by skewed, misshaped peaks. This can be corrected by installing a fresh column of the same type that does not have reactive sites. Test mixtures can be used to demonstrate nonreactivity. Other sources of adsorptivity or reactivity with the sample are the injection port, connecting lines to the detector, or glass wool. Each of these sources can be detected by carefully troubleshooting the system.

14.1.4.2 The detector performance should be checked periodically throughout the analysis. This can be done by injecting one of the linearity standards and comparing it to the linearity plot.

14.1.5 *Peak Area or Height Measurement*— Many types of peak area and height measurement techniques exist. The oldest methods for calculating the peak area are manual measurement with a ruler of the peak area using one of the following equations:

$$\text{peak area} = w_h \times h \tag{5}$$

where:

w_h = peak width at half height, and
h = peak height

or

$$\text{peak area} = \tfrac{1}{2}\, w_b \times h \tag{6}$$

where:

w_b = peak width at the base of the peak, and
h = peak height.

Another precise measurement defines the peak area as retention distance (in millimetres) times the peak height (also in millimetres). For peak height, this distance is simply measured from the baseline to the apex of the peak. However, these techniques now, for the most part, have been replaced by electronic integration, which is much faster. The proper use of these devices is crucial for accurate quantitative analysis. The instruction manual for the particular integrator should be

studied and understood thoroughly before attempting to use electronic integration for peak area or peak height measurement.

14.1.6 *Data Handling:*

14.1.6.1 All manufacturers supply an integral electrometer to allow the small electrical current changes to be coupled to recorders/integrators/computers. The preferred system will incorporate one of the newer integrators or computers that converts an electrical signal into clearly defined peak area counts in units such as microvolt-seconds. These data can then be readily used to calculate the linear range.

14.1.6.2 Another method uses peak height measurements. This method yields data that are very dependent on column performance and, therefore, not recommended.

14.1.6.3 Regardless of which method is used to calculate linear range, peak height is the only acceptable method for determining minimum detectability.

14.1.7 *Calibration*— It is essential to calibrate the measuring system to ensure that the nominal specifications are acceptable and particularly to verify the range over which the output of the device, whether peak area or peak height, is linear with respect to input signal. Failure to perform this calibration may introduce substantial errors into the results. Methods for calibration will vary for different manufacturers' devices but may include accurate constant voltage supplies or pulse generating equipment. The instruction manual should be studied and thoroughly understood before attempting to use electronic integration for peak area or peak height measurements.

14.2 *Types of Calculations:*

14.2.1 Each method of quantitative analysis has advantages and disadvantages. The four methods of quantitative analysis are as follows:

14.2.1.1 Internal standardization,

14.2.1.2 External standardization,

14.2.1.3 Normalization, and

14.2.1.4 Corrected area.

14.2.2 *Internal Standardization*—In this technique, a pure component (the internal standard) is added to a sample in a known amount. The peak area, or height, of all components of interest is compared to the peak area, or height, of the internal standard. These comparisons are referred to as response factors:

$$R_F = A_C/A_{IS} \times W_{IS}/W_C \quad (7)$$

where:

R_F = response factor,
A_C = peak area of component,
A_{IS} = peak area of internal standard,
W_{IS} = mass of internal standard, and
W_C = mass of component.

The amount of the component can be calculated from the weights of the sample and internal standard, the response factor, and the peak areas (or heights) as follows:

$$\%\ \text{Conc}_C = W_{IS}/W_S \times A_C/A_{IS} \times 1/R_F \times 100\,\% \quad (8)$$

where:

Conc_C = concentration of component in sample,
W_{IS} = mass internal standard,
W_S = mass sample,
A_C = peak area of component,
A_{IS} = peak area of internal standard, and
R_F = response factor.

This technique provides a correction for the relatively high variability of syringe injection and, therefore, yields a more precise method of analysis. Neither the quantity of solution injected, nor change in detector response, will alter the area ratio of the analyte and the internal standard. To achieve optimum performance, the internal standard must meet the following criteria.

14.2.2.1 The internal standard must elute in an area of the chromatogram that is free of sample components, or possible sample components.

14.2.2.2 The internal standard must not react with the sample or any of its components.

14.2.2.3 The internal standard and the sample must be homogeneous. A cosolvent may be used to produce a homogeneous mixture.

14.2.2.4 The internal standard must be easily and accurately added.

14.2.2.5 The internal standard must be pure.

14.2.2.6 The internal standard should elute near the component of interest.

14.2.2.7 The concentration of the internal standard, relative to that of the analyte, should be such that these two peaks are within 50 to 100 % of full scale deflection with the same electronic attenuation and sensitivity setting in order to allow manual measurements and calculations of parameters, if desired.

14.2.2.8 The most common use for the internal standard technique in chromatography is to correct for quantitative variations in the injection, particularly when using syringes. For this purpose, the internal standard need not be chemically related to the analyte, but must possess the criteria cited above and may be added in the final solution.

14.2.2.9 In certain applications, an internal standard with functional groups similar to the analyte may be desirable. For instance, those with a labile proton can be expected to exhibit similar adsorption isotherm behavior and to undergo similar physico-chemical transformations during such processes, as extraction from a complex matrix or derivatization, or both. Likewise, similar electronegative functional groups are likely to behave similarly towards an electron capture detector.

14.2.3 *External Standardization:*

14.2.3.1 This method compares peak areas or heights of components in a sample chromatogram to those in a standard solution injected separately. It is critical that accurate amounts of sample and standard be injected for the method to be valid. Generally, the solvent flush injection technique (see 10.3.1.2) or a sample valve of fixed volume is preferred.

14.2.3.2 The advantages of this method are as follows:

(1) Nondetected components do not bias the results.

(2) It can be used where several known components must be determined in a very complex sample.

(3) It can quantitate relatively reactive components.

(4) A single sample can be analyzed where maximum accuracy is not required.

(5) Nonlinearity has a minimal effect if the external standard is near the concentration of the sample.

14.2.3.3 The critical part of this method is the injection. The volume of sample in the injection syringe and standard must be accurately measured, allowing no bubbles in the slug of sample or standard solution. If the sample and standard have different densities, a correction must be made. Densities are easily determined by filling a 50-µL syringe to about 30 µL, wiping the needle, weighing it, expelling the sample, wiping the needle again, and reweighing it.

14.2.3.4 The peak areas or heights of the component in the sample and the standard compound are measured and the concentration calculated as follows:

$$\%\ \text{Conc}_C = A_C/A_{ES} \times W_{ES}/W_S \times \%\ \text{Conc}_{ES} \quad (9)$$

where:

Conc_C = concentration of component,
A_C = peak area of component in sample,
A_{ES} = peak area of external standard,
W_{ES} = mass of external standard injected,
W_S = mass of sample injected, and
Conc_{ES} = concentration of external standard in solution.

14.2.4 *Normalization*—This calculation assumes that every component elutes and that each has similar response factors. It is a fast procedure that requires no weighing. The sample is injected, and the peak areas or heights of all components are measured. The concentration of the component of interest is calculated as follows:

$$\%\ \text{Conc}_C = A_C/A_{ALL} \times 100 \quad (10)$$

where:

Conc_C = concentration of component of interest,
A_C = area of component, and
A_{ALL} = sum of areas of all components.

Severe errors result if the components have different response factors or do not all elute.

14.2.5 *Corrected Area*—This method corrects for differences in response but still assumes that all components elute and are observed by the detector. Response factors are used to correct for response differences as follows:

$$\%\ \text{Conc}_C = A_C/\left(A \times R_F\right)_{ALL} \times R_{F_C} \times 100\,\% \quad (11)$$

where:

Conc_C = concentration of component of interest,
A_C = peak area of component,
$(A \times R_F)_{\text{ALL}}$ = sum of peak areas times their respective response factors relative to a standard, and
R_{F_C} = response factor of component to the same standard.

15. Recommended Form for Writing Gas Chromatographic Methods

15.1 *General*—Not all of the steps outlined in this section may be needed to describe adequately a method. A number of variations in procedure format are shown in the publication, *ASTM Standards in Chromatography*.[7] Ideally, the procedure should be written so that it can be followed by a person with the equivalent of a high school-chemistry understanding or six to twelve months of practical laboratory experience. Critical steps should be identified along with any reasons that show why this step is necessary to achieve a successful analysis. Any involved procedures should be written in an Appendix so that the main points in the procedure can be read more easily.

15.2 *Recommended Form:*

15.2.1 *Title*—The title should be concise, but complete enough to identify the component(s) analyzed, the nature of the method (gas chromatography), the detector, and the materials to which it is applicable. Select words that easily lend themselves to indexing.

15.2.2 *Scope*—State as clearly as possible the range of application of method. In a separate paragraph, note interferring substances or any significant limitations of the method. This material could be placed in a later section (15.2.5), if an involved description is necessary.

15.2.3 *Pertinent Documents or References:*

15.2.3.1 *ASTM Standards.*

15.2.3.2 *Other Standard Methods*—Include any standard methods.

15.2.4 *Summary of the Method*—Describe the method in a general way, without going into details of the procedure. It may be appropriate to touch briefly on the following points: sample introduction technique, column dimensions and type of tubing material, nature of the packing material, mesh size of support or adsorbent, liquid phase loading (if a liquid phase was used), isothermal or programmed temperature and detector type (thermal conductivity, flame ionization, electron capture, etc.).

15.2.5 *Significance and Application*—Use this section for a more detailed discussion than can be fitted in the Scope.

15.2.6 *Definitions*—Include special definitions in this section. General chromatographic definitions are already available in Practice E355, to which reference can be made.

15.2.7 *Interferences*—Use this section for a more detailed discussion than can be fitted into the Scope.

15.2.8 *Special Comments*—Use this section to include a description of special requirements needed to achieve a successful analysis.

15.2.9 *Safety Precautions*—If the method involves hazards, insert a warning to this effect. Point out the nature of the hazards, and describe precautionary measures which must be taken. Refer to the latest OSHA regulations regarding all materials used in this procedure.

15.2.10 *Gas Chromatographic System*—List and describe the apparatus. Describe the essential features of the apparatus that are necessary to achieve the desired analysis. Avoid the use of trade names. Include schematic drawings or photographs if they are needed to clarify or supplement the text. The gas chromatographic conditions can be either summarized in a table, as in Table 6, or in the text as follows:

[7] *ASTM Standards on Chromatography*, ASTM, 1981.

TABLE 6 Summary of Gas Chromatographic Conditions

Column	Length, outside diameter, and internal diameter (or outside diameter and wall thickness); weight percent of specified stationary phase; specified solid support (mesh size and treatment; for example, acid-washed, silanized); approximate amount of total column packing in a given column length.
Temperatures:	
Sample inlet system	°C
Detector	°C
Column	
If isothermal	°C
If programmed	
Initial	°C (note any hold time at initial temperature)
Final	°C
Heating rate	°C/min
(State specific temperatures and times if isothermal operation and temperature programming are combined)	
Carrier gas	(specify)
Flow rate	cm^3/min^A
Detector	TCD, FID, ECD
Detector Sensitivity	Flame ionization detector—amps full scale deflection, AFS[B] Detector voltage or bridge current, if applicable.
Recorder characteristics	mV range, speed of full-scale deflection
Chart speed	cm (or in.)/min
Sample size	µL (or cm^3, if gas)

[A] Flow rate is best measured at the column or detector outlet, at the analytical temperature and flow rate.
[B] A flame ionization detector is assumed to be operated under optimum hydrogen and air flow rates, unless otherwise specified.

15.2.10.1 *Sample Injection Port*—Construction: stainless steel, glass liner, fitted for on-column injection with a glass or metal column, etc. Temperature at which used.

15.2.10.2 *Column Oven*—Isothermal or temperature programmed operation: give temperatures and programming rates required.

15.2.10.3 *Detector*—Type (flame ionization, thermal conductivity, etc.), temperature of operation, sensitivity required. Detector gases used and flow rates.

15.2.10.4 *Recorder*—Operating range (in millivolts), chart speed, time for full-scale deflection of pen.

15.2.10.5 *Integrator*—Note operating characteristics of integrator and parameters used.

15.2.11 *Preparation and Installation of the Chromatographic Column:*

15.2.11.1 *Tubing Material*—Note the type of material, as stainless steel, nickel, glass, or glass-lined tubing, as well as the dimensions (outer diameter and inner diameter, or wall thickness and length). Any pretreatment of the column material, solvent washing, or silanization should be mentioned.

15.2.11.2 *Partitioning Phase*—Solid adsorbent, if used (type and mesh size). Coated support if used (liquid phase, percent loading and coating procedure, support type and pretreatment, and mesh size). Note sources for special materials in footnotes. Provide preparation and purification method for materials not commercially available. In an Appendix, note other liquid phases that have been successfully used in this analysis.

15.2.11.3 *Column Preparation*—Describe the procedure used to pack the column. Note the amount of packing in the column.

15.2.11.4 *Column Installation*—Note if the column is set up for back-flushing, if a sample fraction is removed on a pre-column, or other special column arrangement.

15.2.11.5 *Column Conditioning*—Provide the column conditioning procedure.

15.2.11.6 *Column Evaluation*—Give the procedure for evaluating the column. Calculation of the resolution between two components in a standard mixture will often be sufficient. Provide some estimate of column life and signs of degrading column performance (loss of resolution, peak broadening, or tailing). Provide examples of good and bad chromatograms.

15.2.12 *General Apparatus*—Volumetric flasks and pipets, microsyringes for sample introduction, balance (capacity and sensitivity), heat lamps, hot plates, etc.

15.2.13 *Reagents and Materials:*

15.2.13.1 *Chemicals and Reagents*—Include derivatizing reagents. Note purity, or purification methods, if required.

15.2.13.2 *Calibration Standards*—Note purity required.

15.2.13.3 *Gas* (*or Gases*)—Carrier gas, fuel gases for flame ionization detector, special gas for electron capture detector, etc. Note purity required.

15.2.14 *Calibration*—Describe in detail the calibration procedure. State whether pure components or standard mixtures are used and the basis of measurement. Include equations and describe the preparation of any calibration charts. Show the calibration curve. If a trace method is described, provide a chromatogram of the lowest detectable amount. Lengthy procedures, such as the development of complex equations, or the preparation of standard mixtures, should be placed in a section of an Appendix.

15.2.15 *Procedure*—Include, in proper sequence, directions for carrying out the method. Refer to the pertinent parts of the calibration procedure in 15.2.14. Do not repeat these steps here. Possible subheadings are as follows:

15.2.15.1 *Final Conditioning and Adjustment of the Gas Chromatographic System*—This section is intended to include

adjustment and verification of the state of the chromatographic system before analytical use.

15.2.15.2 *Sampling*—Careful attention must be given to the sampling techniques since representative samples are essential to achieve successful analysis. Include special directions that may be required for taking samples, for preservation of samples, and for special treatment of samples prior to injection.

15.2.15.3 The remainder of the steps leading to the chromatogram.

15.2.15.4 *Typical Chromatogram*—Show, in a figure, a plot of the retention time (in minutes) versus the detector response. Label the known peaks (including the dead volume or unadsorbed gas peak) and indicate in parentheses the attenuation for each peak.

NOTE 8—When determining the retention time of the unadsorbed peak, the retention time of air is used for thermal conductivity detectors, methane for flame ionization detectors, and methylene chloride lead space vapors for ECDs.

15.2.15.5 *Retention Time Data*—Include a table listing retention times and relative retention times for all compounds of interest, for all recommended columns. Identify the unadsorbed peak and the reference material used for relative retention time calculations.

15.2.16 *Calculation*—State the reference point on which the calculations are based (for example, sample as received), the terms in which the results are finally obtained (weight, volume, or mole percent), and whether or not these values are normalized. Present the calculations in equation form, using letter symbols to designate variable values and numerical values of constants. Define the letter symbols in a legend immediately following the calculation equation.

15.2.17 *Report*—Show limits to be reported.

15.2.18 *Precision*—Limiting values for precision should be based on cooperative test results. Judgment as to the acceptability of results (95 % probability) should be based on the following criteria.

15.2.18.1 *Repeatability*—The following wording should be used: Duplicate results by the same operator should not be considered suspect unless they differ by more than the following amounts: (insert determined limits in tabular form).

15.2.18.2 *Reproducibility*—The following wording should be used: The result submitted by each of two laboratories should not be considered suspect unless the two results differ by more than the following amounts: (insert determined amounts in tabular form).

15.2.19 *Appendixes*—Supplementary information may be included in one or more Appendixes to the report. Examples of such information are: technique to improve column life, directions to clean the apparatus, leak check procedures, procedures to optimize column performance, development of equations used in the calculations, and precautions to avoid common causes of errors, etc.

16. Keywords

16.1 gas chromatography; GC; packed columns