

**GAS CHROMATOGRAPHY***Lial W. Brewer***INTRODUCTION**

Chromatography is a collective term for separations of mixtures based on the partition of substances between two immiscible heterogeneous phases, one of which is a stationary or fixed phase with a large surface area, and the other a moving or mobile phase which flows over the first phase. Gas chromatography is the most recent branch of chromatography and includes all the chromatographic processes in which the substance to be analyzed occurs in the gaseous or vapor state or can be converted into such a state.

**Development**

Although the first records of gas chromatography go back hundreds of years,<sup>1</sup> its true history began during World War II when a large industrial chemical company instituted a crash program for its development.<sup>2</sup> The first published work appeared in the early 1950's based on the successful experiments by James and Martin,<sup>3</sup> following an earlier suggestion made by Martin and Synge in 1941.<sup>4</sup> In the years between 1952 and 1956 the early apparatus and initial methods of application were developed. In 1956 the first commercial instruments appeared on the market, and since that time there has been a spectacularly rapid and widespread development in theory, techniques and applications of gas chromatography. Today, it is one of the most widely applied and versatile analytical tools available in basic and applied research and in quality control.

**Applications**

The success of gas chromatography is due to its simplicity of operation, high separation power and speed. The technique is capable of separating and measuring nanogram amounts of substances. In general, gas chromatography is suitable for analysis of substances with vapor pressures of at least 10 millimeters of mercury at the temperature of the column. Because the gas chromatograph separates, detects, qualifies and quantitates the individual components of a volatilized sample in a single step, it is an indispensable tool in every branch of chemistry. The wide choice of column packings, detectors and temperature controls allows versatile applications not only to the field of chemistry but also biology, medicine, industrial research and control, environmental health and scientific studies of the structure of chemical compounds, chemical reactions, partition coefficients, heats of solution and many others.

Specific separations and measurements accomplished by the use of gas chromatography in the medical-biochemical field include saturated and unsaturated fatty acids in low concentration, posi-

tional and configurational isomers of unsaturated fatty acids, straight-chain and branched-chain fatty acids, sterols and steroids, alkaloids, amino acids, urinary aromatic acids, bile acids, vitamins, blood gases, and toxic trace components in air, water, food and pesticides.

Recent developments in the field of toxicology enable the fractionation and determination of such substances as steroids, lipids, barbiturates, drugs and blood alcohol.<sup>5</sup> The limited size of samples available and the low concentration of substances present in the field of toxicology make it a valuable tool for the complete characterization and analysis of mixtures of toxic substances. The progressive development of pyrolysis has led to the separation and identification of polymers and non-volatile substances. Advances have also been made in the miniaturization of gas chromatographic equipment. For example, a very small gas chromatograph-mass spectrometer was sent on one of the moon shots to separate and identify atmospheric components automatically. The aerospace<sup>6</sup> and nuclear submarine fields<sup>7</sup> have also used gas chromatographs to check air quality in working and sleeping environments for personnel. Gas chromatography has been used recently in the remote sampling and analysis of tunnel atmosphere after nuclear testing at the Nevada Test Site.<sup>8</sup>

In the field of industrial hygiene the chromatograph has been used to identify and quantitate solvent exposures by the analysis of breath samples. When toxic organic substances have either no recognized biological metabolite or one whose excretion cannot be correlated with atmospheric concentrations of the initial substance, it is difficult to evaluate the effects of exposures; however, breath analysis by a gas chromatographic procedure may be developed for certain organic solvents found to be expired after exposure at predictable rates. In addition, many industrial hygiene departments operate product identification programs which require the complete analysis of proprietary products. Additives to many commercial products can appreciably increase the toxic properties of less hazardous materials. An example is the addition of carbon tetrachloride to typewriter cleaner, which normally contains only trichloroethylene. Another example is the addition of benzene to gasoline for an increased performance efficiency. Before the development of gas chromatography tedious procedures involving fractional distillation and determination of physical constants were required for detection of such additives.

The analysis of solvents for changes in formulations is performed frequently in the industrial hygiene laboratory. The regular product may be analyzed and comparative chromatograms prepared for other batches at specific times to check for any alteration of the product. Furthermore, many solvents of unknown composition (trade name given without compositional information or, in other cases, a lost label or marking) can be analyzed for complete identification and determination of components. In-plant air samples containing solvent vapors can be chromatographed, avoiding the tedious chemical separation methods. Chlorinated hydrocarbons, for example, can be readily assayed in mixtures and each component identified whereas only total chlorinated hydrocarbons can be determined chemically. This is extremely important since each compound has a different Threshold Limit Value and tolerance level.

There is almost no type of vaporous compound whose analysis by gas chromatographic methods has not been described in the literature. A partial list of pertinent references is included at the end of this chapter.

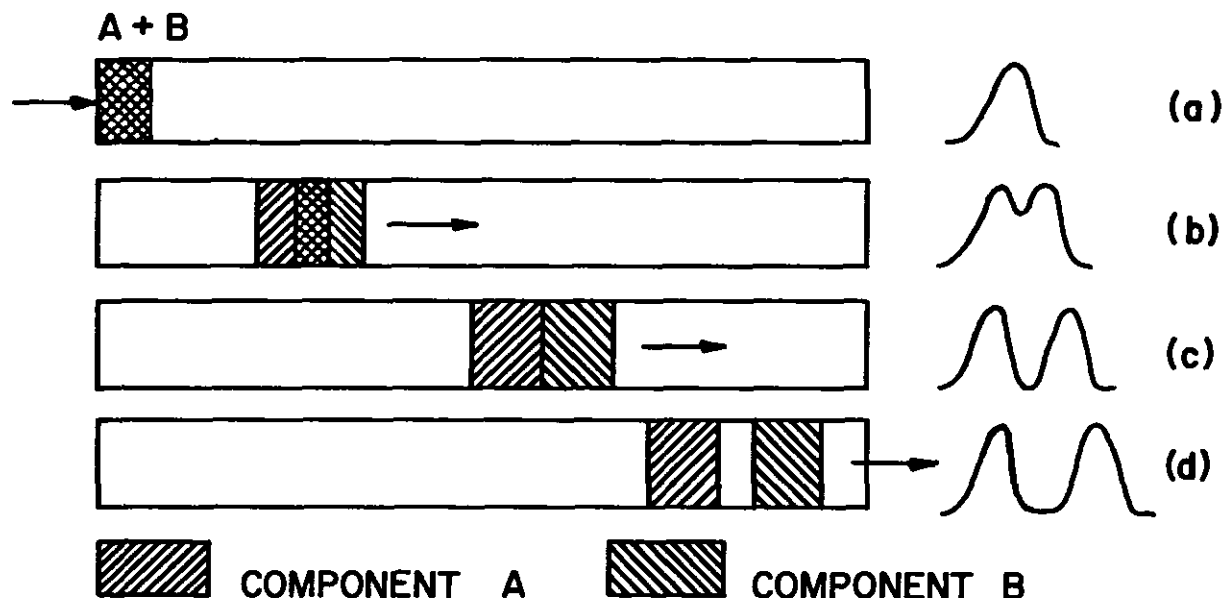
### THEORETICAL ASPECTS OF GAS CHROMATOGRAPHY

#### Principle

Gas chromatography can be compared analytically to fractional distillation; however, it is a much more efficient type of separation technique. A good distillation column may have 100-200 theoretical plates, whereas a chromatographic column may separate components with 1000 to 500,000 theoretical plates. Basically, gas chromatography consists of the partition of compounds

between two phases. One phase is a fixed or stationary phase. This phase may be either a solid, as in adsorption chromatography, or a liquid held by a solid, as in partition chromatography. The second phase is mobile and is generally referred to as the moving phase. This phase may be a gas, liquid, vapor, or volatile solid. There are two principles of separation based on the previously noted difference in the nature of the stationary phase: (1) gas-solid chromatography (GSC) in which the moving phase is a gas and the stationary phase is an active solid such as alumina, charcoal, silica gel, molecular sieves, or the newer plastic granules (e.g., Poropak<sup>®</sup>); (2) gas-liquid chromatography (GLC) in which the moving phase is a gas and the stationary phase is a liquid distributed on an inert solid support. GLC is used for the separation of a variety of compounds, generally organics, while GSC is used for the separation of gases.

The principle of operation involves the introduction of small amounts of a gaseous or liquid sample solution containing nanogram amounts of analytically desired gaseous or vaporizable components which are carried under controlled temperature conditions by an inert carrier gas into a column containing the stationary phase. Phase equilibria occur between the sample components, the mobile phase and the stationary phase; the components are separated, due to differences in absorption, solubility and chemical bonding, into distinct bands (or zones) of molecules. These fractions move through the column at different rates and emerge as separated components, as shown in Figure 21-1. The carrier gas emerging from the column passes through a detector which produces a signal proportional to the quantity



Szepesy L: Gas Chromatography. Chemical Rubber Company Press, 1970, p. 14.

Figure 21-1. Separation of Components Into Bands of Molecules Which Move Through Column at Different Rates.

of each component. The detector response is amplified and shown on the recorder as a peak. The chromatogram that is obtained is a plot of time versus the intensity of a series of peaks representing the eluted components in the carrier stream. The length of time required for each of the peaks to appear on the chart is the retention time and is characteristic for each of the substances present under a given set of chromatographic conditions. The retention time, therefore, identifies the substance, and the area of the peak is a quantitative measurement which is proportional to the amount of each fraction present.

A proper selection of injection port, column, and detector temperatures, column materials, and the detector determines the effectiveness of the chromatographic separations of the components of each type of sample.

#### Basic Design

There are many commercial models of gas chromatographs available today, with considerable variation in design and arrangement of components. The latest trend in design is the modular concept, consisting of a simple addition of component parts with different functions. Starting with the basic unit, the performance of the apparatus can be expanded by addition of other units, depending on the type of analysis to be done. Gas chromatography may also be combined with other chromatographic, spectrometric and chemical methods of analysis by collecting the separated components from the gas chromatograph and incorporating other equipment into the system, either directly or indirectly. The recent coupling of computers with gas chromatographs allows completely automatic operation along with the storage and processing of data for estimation of the concentrations of the sample components.

The basic design of the apparatus consists of: (1) carrier gas system, (2) sample injector, (3) column, (4) thermostat, (5) detector and (6) recorder. Figures 21-2 and 21-3 show schematic

diagrams, respectively, of single and dual column assemblies, respectively. A general discussion of the components, with a brief explanation of the parameters pertinent to different applications of gas chromatography, is presented for the selection of proper instrumentation.

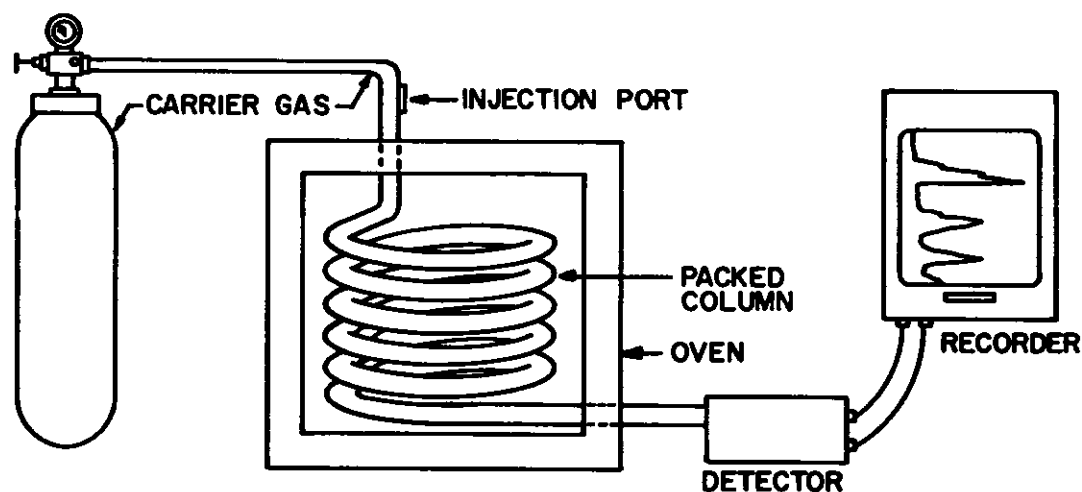
### COMPONENTS OF THE GAS CHROMATOGRAPH

#### Carrier Gas System

The carrier gas is the mobile phase used to transport the sample through the column at a selected steady rate. To ensure constant and reproducible conditions, the system is composed of a gas cylinder, pressure and/or flow control, manometer, flow meter and pre-heater.

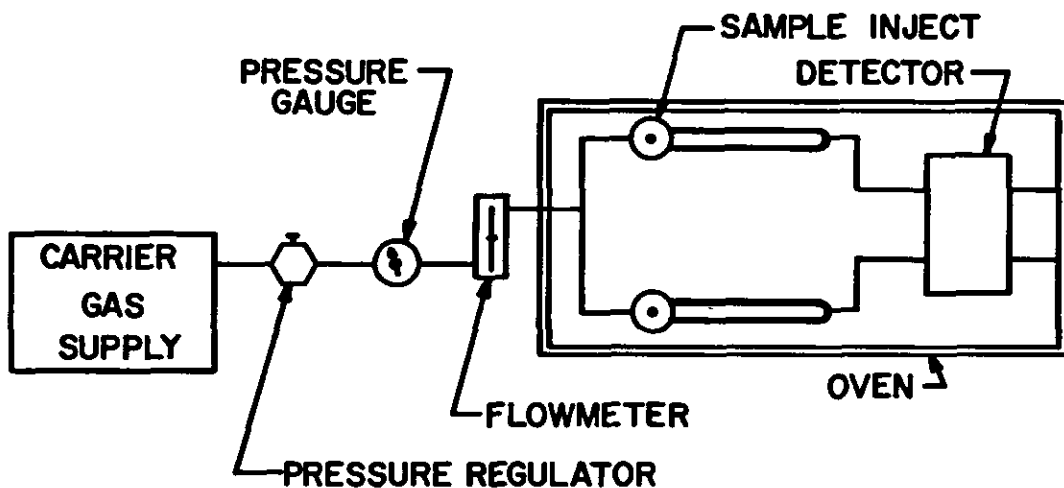
In principle, any gas which does not interfere either with the stationary phase or the components of the sample would be a suitable carrier. However, the properties of the carrier gas affect the separations in the column as well as the detection of the emerging components. The gases generally used are: helium, argon, hydrogen and nitrogen. Other gases may also be used. In selecting a carrier gas, detection is the primary factor to be considered since separation can be improved by some means other than changing the carrier gas.

Since hydrogen is so reactive and flammable, helium is the ideal carrier for use with thermal conductivity detectors. Nitrogen, though readily available, is not too useful for these detectors since its thermal conductivity does not differ too greatly from that of many sample components. The thermal detector measures the difference between the heat conductivity of the pure carrier gas and that containing the components of the sample. The greater the difference between the two heat conductivities the greater will be the observed signal. The thermal conductivity of gases is inversely proportional to the square root of their molecular weight and consequently hydrogen and helium are the most suitable carrier gases for



Instruments, Inc.: What Is Gas Chromatography. Tulsa, Oklahoma.

Figure 21-2. Single Column.



Prepared by Sandia Laboratories draftsmen.

Figure 21-3. Dual Column.

thermal conductivity detection.

The most commonly used types of carrier gases and their use with various detectors are as follows:

*Air and Oxygen* may be used in certain cases as carrier gas with the flame ionization and thermal detectors. However, their use is limited by the possibility of reactions with the stationary phase or the components of the sample.

*Argon* is the most generally used gas with radiation detectors such as Beta ionization, and with flame ionization detectors, with limited use in thermal detectors.

*Carbon Dioxide* is used with flame ionization and gas density balance detectors, with limited use with the thermal detector.

*Carbon Monoxide* is used with the flame ionization detector.

*Helium* is used with the thermal conductivity, thermionic emission, flame ionization and cross section detectors.

*Hydrogen* is used with the gas density and thermal conductivity detectors. It is used as a fuel with the flame ionization detector. To avoid the possibilities of impure hydrogen, the use of hydrogen produced from the electrolysis of water is often more suitable for the operation of flame ionization detectors.

*Neon* is used with radiation detectors.

*Nitrogen* is used with radiation, flame ionization and gas density detectors. It has limited use with the thermal conductivity detector.

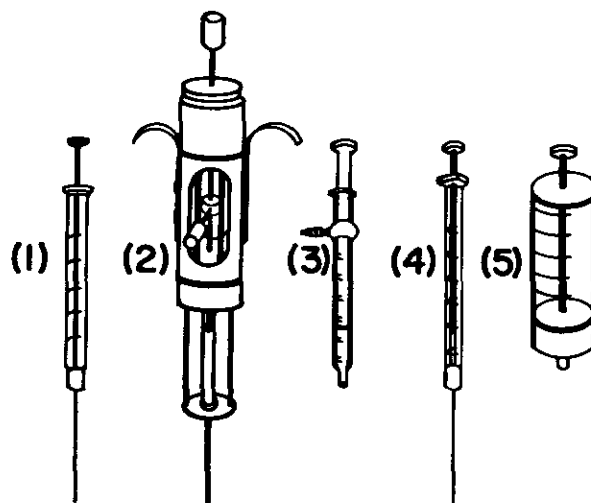
*SF<sub>6</sub>* is used when detecting permanent gases using a density balance detector.

A constant flowrate is important to eliminate the effect of changes in column resistance. Heating of the gas before it enters the sample injector is necessary in the case of some detectors and advisable in other detection methods and is accomplished by means of a pre-heater.

#### Sample Injection System

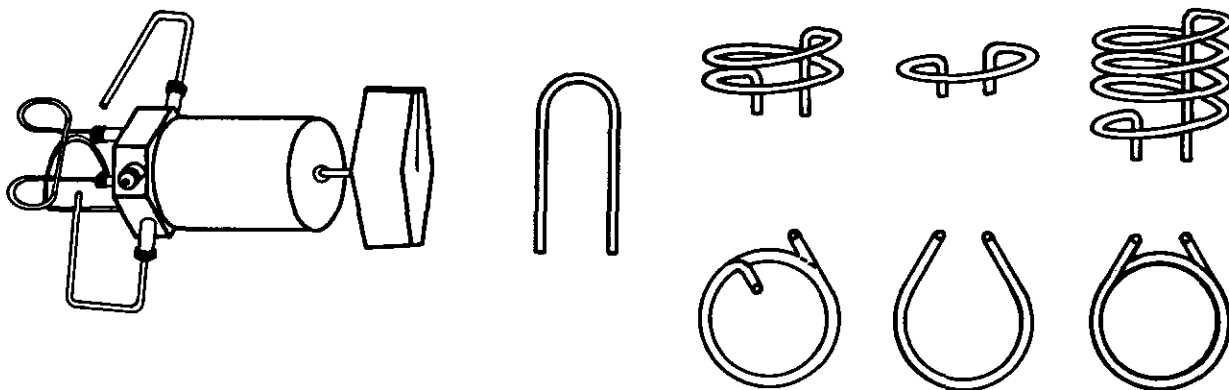
The sample injector, located ahead of the

column, is designed to allow the introduction of a sample rapidly and in a reproducible manner into the column. It is essential that representative samples of the material to be analyzed be introduced. Since such samples must be small in quantity, a careful manipulative technique must be employed with the method of injection. It is highly desirable that the sample injection be almost instantaneous to convert the sample into a composite plug of gas which is pushed through the column by the carrier gas. This is accomplished by the enclosure of the injection port in a metal



Syringes #1, 3, 4 and 5: Hamilton Syringe Catalog. Syringe #2: Beckman Syringe Instruction Sheet.

Figure 21-4. Syringes Used in Gas Chromatography (1) Hamilton 10 ul. liquid syringe, (2) Beckman variable volume liquid micro-syringe, (3) purge type gas syringe, (4) standard Hamilton gas syringe and (5) large volume transfer and dilution syringe.



Beckman Instruments, Inc.: Bulletin #756A. Fullerton, California.

Figure 21-5. Gas Sampling Valve (Beckman).

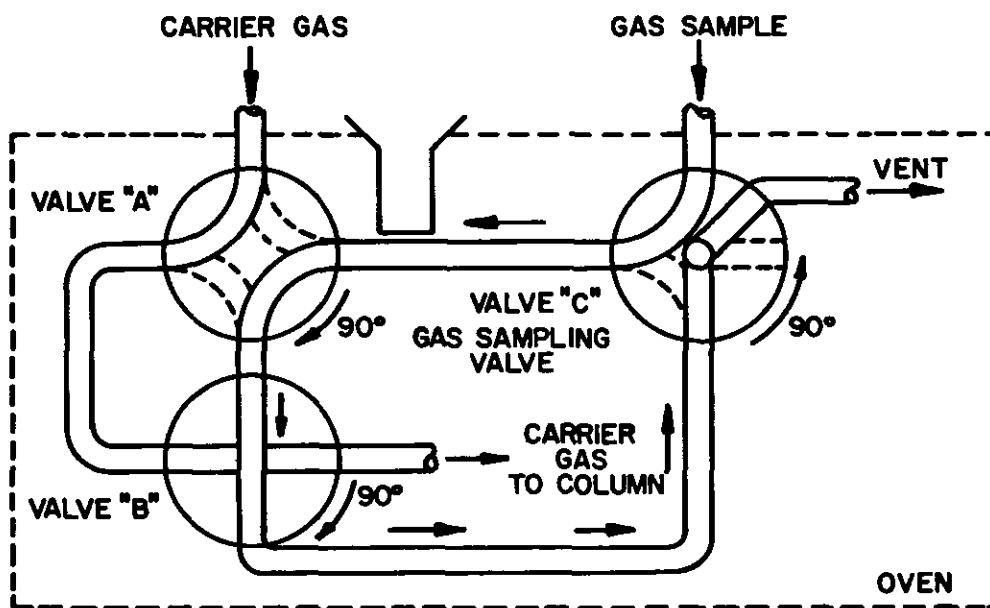
block which is heated independently to a temperature approximately 50 to 100 degrees above the column temperature. The solvent and sample are, therefore, flash evaporated when injected, without changing the gas flow or the thermal conditions of the column. The quantity of liquid sample ranges from 1 to 10 microliters and gas samples vary from 0.05 to 50 milliliters.

Most samples are introduced by means of a small, calibrated syringe or a microsyringe, such as the Hamilton syringe. These syringes are made for delivering either liquids or gases. Liquid syringes are available in sizes of 1 microliter to 500 microliters. Gas tight syringes are available in sizes of 50 microliters to 2500 microliters. For calibration with larger volumes of gases, plastic syringes are available in sizes from 0.5 to 1.5

liters. Figure 21-4 shows several types of syringes used in gas chromatography.

Samples may also be introduced to the column using a gas sampling valve, illustrated in Figure 21-5. The gas sample may be introduced to the gas sampling loop under pressure or by drawing the sample into the loop using a small vacuum pump or a two-way squeeze bulb. The gas sample can also be delivered to the loop from a pressure container, such as a plastic or rubber bag or a large syringe. The only requirement is that sufficient sample be available to thoroughly purge the sample loop, as shown in Figure 21-6.

A third method of injection is by the use of a sealed ampoule which is broken inside a chamber, which replaces the gas sampling valve, so that the sample is swept into the column.



Instruments, Inc.: What Is Gas Chromatography. Tulsa, Oklahoma.

Figure 21-6. Gas Sampling.

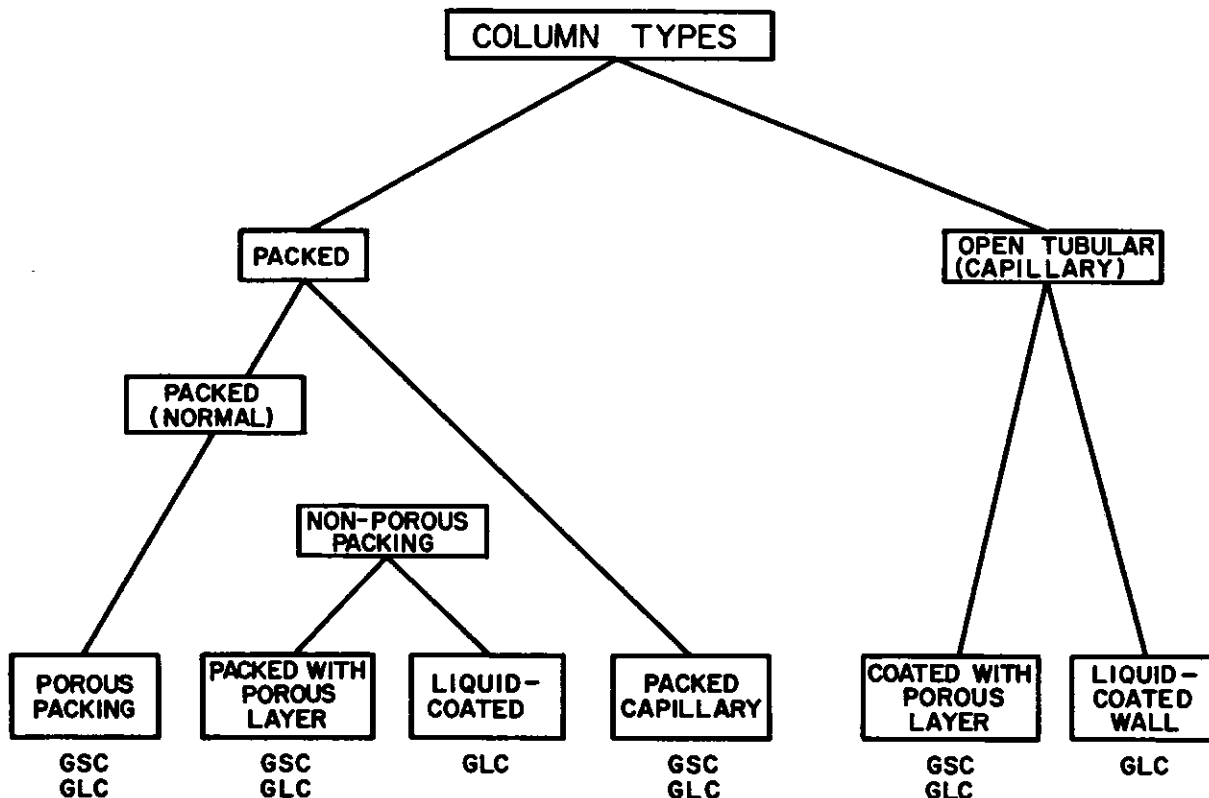
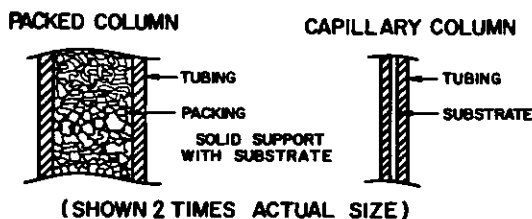
Other types of samplers include pyrolysis systems and solid samplers.

**The Column**

The column is the "heart" of the chromatograph. Provided that the equipment is good and operating conditions are suitably chosen, the analysis will be as good as the performance of the column selected because it is here that separation of the sample components is effected. Because of the wide variation in packing materials and liquids used as stationary phases, the long life, and the ease of changing columns in the instrument, it is possible for the analyst to select the best packing and column length for each particular sample type. Several columns with different types of packings can be built into the same apparatus and can be operated in series or parallel with each other.

Columns are rigid containers made of stainless steel, copper, aluminum or glass. There are two basic types of columns — the packed column and the capillary or open tubular column (Golay). The *packed column* consists of a length of tubing 1-6 millimeters I.D. and usually 0.5 to 6 meters in length, which is normally coiled or looped to be accommodated in the space provided in the instrument. This tubing is packed with a finely divided inert solid support, which is coated with a thin layer of a nonvolatile liquid, referred to as the liquid phase. The *capillary column* is an empty tube, the inner walls of which serve as the support or adsorbent. This type of column has an I.D. of 0.1-1.0 millimeter and usually is 30-100 meters in length.

The basic difference between gas-liquid and gas-solid chromatography is in the column pack-



Instruments, Inc.: What Is Gas Chromatography. Tulsa, Oklahoma.

Figure 21-7 & 8. Types of Columns and their Operation. Various Size Sample Tubes (usually 1 to 10 ml volume).

ing. In gas-liquid chromatography the column is packed with a solid material made up of particles on which is deposited a known volume of non-volatile liquid constituting the liquid phase. In gas-solid chromatography the packing is generally an active solid (adsorbent) which separates the sample components by differences in their adsorption characteristics. Figures 21-7 and 21-8 illustrate the two types of columns and their types of applications. The following factors influence the efficiency of a column:

**Column Length** — the efficiency is directly proportional to the length; however, analysis time is also increased with length due to flow resistance. Therefore, the column length is selected by references to the degree of separation and the analysis time required.

**Column Diameter** — the performance of the column increases with decreasing column diameter. Columns with 2-4 millimeter I.D. give optimal separation.

**Nature of Solid Support** — the material should be inert and porous, provide a large surface area, and be heat stable.

**Granule Size of Support** — the column efficiency is dependent on the particle size. The solid support phase is graded on the basis of the mesh size through which it will pass. The column diameter generally determines the proper mesh size as follows:

6-millimeter diameter column — 60/80 mesh  
3-millimeter diameter column — 80/100 mesh

**Quantity of Liquid Phase** — the concentration is adjusted in accordance with the mesh size. The optimum range is 10-15% by weight.

**Type of Liquid Phase** — the principal characteristics to be considered are polarity, volatility, low viscosity and thermostability.

**Temperature Control** — it is essential for the temperature to be maintained thermostatically at a point suitable for separating the components of the sample. The control can either be isothermal or programmed such that the temperature is accurately reproduced for samples and standards.

### Solid Supports

The purpose of the solid support is to provide a large surface area for holding a thin film of liquid phase. The main requirements for adequate support material are: chemical inertness and stability, large surface area, relatively low pressure drop and mechanical strength. Such material may be organic or inorganic but must be of a known and standard size. The most commonly used materials consist of diatomaceous earth processed or modified in various ways. Since diatomaceous earth supports are not completely inert, they are often treated chemically to inactivate them. An example of diatomaceous earth supports are the Chromosorbs (Johns-Manville Corp.)

**Chromosorb P** — calcinated diatomaceous earth processed from firebrick (C-22).

**Chromosorb W** — flux-calcinated diatomite prepared from Celite Filter Aids.

**Chromosorb G** — developed especially for gas chromatographic analysis.

The various Chromosorbs are available in different

qualities, such as non-acid washed, acid washed, silanized with hexamethyldisilane, and acid washed and silanized with dimethyldichlorosilane.

Besides the various diatomaceous earth supports, porous polymer beads, Teflon and glass beads are used. The Poropak<sup>R</sup> resins are examples of porous polymer beads which have partition properties of a highly extended liquid surface without the problems of support polarity or liquid phase volatility which hamper gas-liquid chromatography. The general properties and applications of some types of Poropak<sup>®</sup> resins are as follows:

**Poropak N** — an intermediate polarity packing useful in separating formaldehyde from aqueous solution. Stable to 250 degrees C.

**Poropak P** — has the lowest polarity of all types and has the ability to separate systems of intermediate polarity. Usable up to 300 degrees C.

**Poropak P-S** — is similar to type P; however, the labile sites have been deactivated by silanization to improve peak shape and the efficiency of separation with aldehydes and glycols.

**Poropak Q** — separates hydrocarbons by vapor pressure and is usable up to 300 degrees C.

**Poropak Q-S** — is similar to type Q; however, labile sites are deactivated by silanization, and as a result highly polar materials such as organic acids may be analyzed in aqueous solution and show no tailing.

**Poropak R** — is suitable for the separation of water from highly reactive inorganics such as chlorine and hydrochloric acid.

**Poropak S** — is suitable for the separation of normal from branched alcohols and is stable up to 250 degrees C.

**Poropak T** — has the highest polarity of all the Poropak<sup>R</sup> resins and is stable up to 250 degrees C.

Poropak<sup>R</sup> resins may be used for the separation of most gases and compounds in the moderate boiling range (up to 200°C.). High boiling aromatic and cyclic materials are strongly retained by Poropak<sup>R</sup> and are very difficult to elute. When strongly polar materials, such as acids or aldehydes, are to be analyzed silane treated supports should be used. All Poropak<sup>R</sup> resin columns require a pre-treatment before use. The column should be purged with gas while heating to rid the resin of residual preparation chemicals.

### Liquid Phase

The liquid phase of the column packing is that chemical which actually is responsible for the separation of the various compounds in the mixture in gas-liquid chromatography and must be capable of dissolving the components and releasing them, preferentially by the difference in their volatility, from the solution. The liquid used will be chosen to effect separation of the compounds to be analyzed. In general, the choice of liquid phase is based on the polarities of the substance to be separated and of the liquid phase. The higher the polarity of the liquid the more it will retain polar components compared to non-polar

substances with the same boiling point. The liquid phase should be non-volatile, thermostable, and have low viscosity. Its boiling point should be approximately 250 to 300 degrees C. which will be higher than the optimal temperature at which the analysis is performed. The column coatings which are non-polar liquids are: squalane, silicone

oil, esters of high molecular weight alcohols, dibasic acids and Apiezon L. The polar compounds are: polyethylene glycol, polyesters, ethers, carbohydrate esters, and derivatives of ethylenediamines. Table 21-1 lists some of the common liquid phases with their properties and applications.\*

Table 21-1  
Some Common Liquid Phases

Solvents: Acetone = A; Benzene = B; Chloroform = C; Methanol = M; Toluene = T; Water = W.

Polarity: non-polar = -; fairly polar = +; strongly polar = ++.

Liquid phase	Solvent	Maximum temperature, °C	Polarity	Applications
Tri-isobutylene	A	30	+	Saturated and unsaturated C <sub>1</sub> -C <sub>8</sub> hydrocarbons
Dimethylsulpholane	M	50	++	Saturated and unsaturated C <sub>1</sub> -C <sub>8</sub> hydrocarbons
n-Hexadecane (n-cetane)	B	50	-	C <sub>1</sub> -C <sub>8</sub> hydrocarbons, halogen derivatives
β, β-Oxy-dipropionitrile	M	70	++	C <sub>1</sub> -C <sub>7</sub> paraffins, olefins, cyclo-paraffins, aromatics, alcohols, ketones, esters
Paraffin oil	T	100	-	Hydrocarbons, chlorine compounds, sulphides
Carbowax 400 (polyethylene glycol)	M	120	++	C <sub>1</sub> -C <sub>8</sub> alcohols, ethers, ketones, amines
Tricresyl phosphate (tritoyl phosphate)	C	125	++	Aromatics, halogen derivatives, oxygen compounds
Carbowax 600	M	140	++	Oxygen compounds, halogen derivatives, nitrogen compounds
Squalane	T	150	-	Hydrocarbons, halogen derivatives, sulphides
(hexamethyltetracosane)				
Dinonyl phthalate*	A	150	+	Hydrocarbons, halogen derivatives, oxygen compounds
Carbowax 1500*	M	150	++	Aromatics, oxygen compounds, halogen derivatives, nitrogen compounds, sulphur compounds
Carbowax 6000	M	200	++	Aromatics, oxygen compounds, halogen derivatives, nitrogen compounds, sulphur compounds
Carbowax 20 M*	M	200	++	As above, plus polyfunctional alcohols
Ucon LB (polypropylene glycol)	M	200	+	Aromatics, alcohols, ketones, essential oils, amines
Ucon HB (polynikylene glycol)	M	200	+	As above
Silicone oil DC 550*	A	200	-	Esters, aldehydes, hydrocarbons, boranes
Benton 34	T	200	++	Aromatics
Polyesters of succinic acid (e.g. LAC 296)	C	200-240	+	} Esters of fatty acids, ethers, essential oils, and amino-acid esters
Polyesters of adipic acid (e.g. Resoflex)	C	200-240	+	
Silicone elastomer, XE 6A XE 60 (cyano)	A	250	+	Phenols, aromatics, terpenes, steroids
Apiezon M	T	275	-	Higher alcohols, fatty acid esters, essential oils
Apiezon L*	T	300	-	Higher oxygen compounds, fatty acids, nitrogen compounds, steroids, metal organic compounds
Silicone elastomer, SE 30 (dimethyl)	T	300	-	Alkaloids, steroids, nitriles, hydrocarbons, inorganic and metal organic compounds
Silicone elastomer, SE 52 (methyl-phenyl)	T	300	+	Alkaloids, steroids, carbohydrates
Silicone grease (vacuum)	T	350	-	Fatty acid esters, halogen compounds, inorganic compounds
Poly-phenyl tar	T	400	-	Polycyclic aromatics
Inorganic salts and salt cutectics (e.g. LiCl)	W	400-500	-	Inorganic and metal organic compounds, metal halides

\* According to the survey of the Data Sub-Committee of the Gas Chromatography Discussion Group the most widely used liquid phases. "Gas Chromatography," Butterworth & Co. Ltd., London, England; Muszaki Konyvkiado, Budapest.



To some degree the detector used must also be considered when selecting a column. For example, if a thermal conductivity detector is used, and the sample contains water (which the detector senses), Teflon would be a better support since it suppresses the tailing of the water peak which would otherwise obscure some peaks. On the other hand, the flame ionization detector does not respond to water and therefore the problem of tailing does not occur. When the electron capture detector is used, a liquid phase with low bleeding rate is very important. In such systems, DC-200 silicone oil with high viscosity is recommended.

#### Adsorbents

In gas-solid chromatography various adsorbents are used as column packings. With the growth of gas-liquid chromatography, the use of adsorbents and their applications are:

*Silica Gel* — used in the analysis of inorganic gases and light hydrocarbons.

*Molecular Sieves* — used for the separation of permanent gases such as hydrogen, oxygen, nitrogen, carbon monoxide, methane and ethane. Carbon dioxide and higher hydrocarbons are adsorbed irreversibly on molecular sieves at low temperatures.

*Activated Charcoal* — used for the separation of air, carbon monoxide, methane, carbon dioxide, acetylene, ethylene, ethane, propylene and propane.

*Chromosorb* — used for the separation of nitrogen, hydrocarbons, acid gases and basic gases.

*Poropak Q* — can be used to separate such widely different materials in the gas phase as air, carbon dioxide, sulfur dioxide, nitrous oxide, nitric oxide, hydrogen sulfide, hydrogen cyanide, carbon oxysulfide, hydrogen chloride, chlorine and ammonia.

*Poropak N* — used to separate acetylene from ethylene and ethane.

The regeneration time and temperature for adsorbents is as follows:

Alumina, silica gel and activated charcoal — 30 minutes at 100°C.

Molecular sieves — 30 minutes at 300°C.

Poropak N and T — 30 minutes at 180°C.

Poropak Q, R, S, Q-S — 30 minutes at 230°C.

Chromosorb — 30 minutes at 140°C.

#### Detectors

Detectors must sense continually, rapidly and with high sensitivity the components which appear in the carrier gas as it emerges from the column, by means of changes in a physical or chemical property of the effluent gas stream. The corresponding electrical response is amplified and fed to a recorder. One of the chief factors in the wide-spread application of gas chromatography is the availability of a great variety of highly efficient detectors.

The essential quality of a detector is determined by the following factors: (1) sensitivity, (2) signal-to-noise ratio, (3) drift, (4) linearity, (5) independence of extraneous variables, (6) ease of calibration, (7) speed of response, (8) chemical inertness, and (9) range of application.

There are basically eight types of detectors: *Thermal Conductivity* (katharometer) — measures change in heat capacity.

*Gas Density* — measures change in density.

*Flame Ionization* — measures difference in flame ionization due to combustion of the sample.

*Beta-Ray Ionization* — measures current flow between two electrodes caused by ionization of the gas by a radioactive source.

*Photo-Ionization* — measures current flow between two electrodes caused by ionization of the gas by ultraviolet radiation.

*Glow-Discharge* — measures the voltage change between two electrodes caused by the change in discharge by different gas compositions.

*Flame Temperature* — measures change in temperature caused by difference in gas composition in the flame.

*Dielectric Constant* — measures the change in the dielectric constant caused by difference in composition of gas between plates of a capacitor.

A summary of the common commercial detectors is presented in Table 21-2. A description of several detectors is as follows:

*Thermal Conductivity Detector* — the most widely used detector. Uses either a hot wire or thermistor as the sensing element. The resistance changes due to sample components, and the detector measures the thermal con-

Table 21-2  
Summary of the Common Commercial Detectors

Name	Type	Analyzable Materials	Maximum Sens. GMS/Sec.
Thermal Conductivity (Katharometer)	Measures Changes in Heat Capacity	All	10 <sup>-7</sup>
Ion Cross Section	Beta-Ray Ionization	All	10 <sup>-7</sup>
Argon Diode	Beta-Ray Ionization	Most Organics	10 <sup>-13</sup>
Electron Affinity	Beta-Ray Ionization	Electron Absorbing Materials Only	10 <sup>-14</sup>
Flame Ionization	Ionization In Hydrogen Flame	All Organics	10 <sup>-12</sup>
Thermionic Emission	Hot Filament Ionization	All	10 <sup>-10</sup>

ductivity of the sample stream as opposed to the reference stream of the pure carrier gas. The response is approximately proportional to the concentration of sample component in the detector. This type of detector is a non-destructive detection system. Examples of thermal conductivity are shown in Table 21-3.

Table 21-3  
Examples of Thermal Conductivity

Gas	Relative Conductivity at 100°C (Air = 1)
Hydrogen	6.94
Helium	5.54
Methane	1.72
Ethane	1.09
Oxygen	1.032
Air	1.000
Nitrogen	.998
Carbon Monoxide	.924
Methyl Alcohol	.727
Carbon Dioxide	.690
Acetone	.557
Carbon Tetrachloride	.288

**Ionization Gage Detector** — uses a heated filament to ionize substances having ionization potentials less than that of helium. Only a small fraction of the effluent passes through the gage. The ionization current produced in the cell is a measure of the concentration of the sample component.

**Flame Ionization Detector** — uses hydrogen/air or hydrogen/oxygen flame. This flame ionizes the organic sample material and the ions are collected by an electrode which is positive in relation to the flame. This electrical potential causes a current flow which is an instantaneous measurement of the component concentration. This detector has a high sensitivity, about 500-2000 times that of the thermal detector. It also has a fast response time, a very small effective cell volume and a high signal-to-noise ratio.

**Beta Argon Ionization Detector** — a radioactive source ionizes the effluent from the column causing an ion current to flow from the collision of metastable argon ions with the sample molecules. This current is a measure of concentration. The sensitivity is much higher than that of the thermal conductivity detector for all components except light gases with ionization potentials above 11.7 electron volts. Minimum detectability of components is in the general range of  $10^{-9}$  grams per sec. This gage is less sensitive than the flame ionization gauge.

**Electrolytic Conductivity Detector** — used for the detection of halogen, sulfur and nitrogen containing organic compounds. Its principal use is for the detection of residues of chlorinated hydrocarbon type pesticides and nitro-

gen containing pesticides such as carbamates and triazines. The Coulson<sup>10</sup> electrolytic conductivity detector is probably the simplest to operate and easiest to maintain of all the element selective detectors. Yet it has good selectivity and sensitivity. The system consists of a prolyzer, a gas-liquid contactor, a gas-liquid separator, and a simple pair of platinum electrodes in a d.c. bridge circuit. The prolyzer converts the organically bound halogen, sulfur, or nitrogen to oxidized or reduced substances that form electrolytes when dissolved in water. These electrolytes are detected by the change they produce in the conductivity of water in the detector cell. Conductivity is measured between the two platinum electrodes of the cell by means of a simple d.c. bridge and recorded continuously on a one-millivolt strip-chart recorder.

**Semiconductor Thin Film Detector** — a detector for gaseous components, based on the fact that the adsorption and desorption of gases causes changes in electrical conductivity of semiconductors. At high temperatures (near 400°C) the adsorption and successive desorption processes on the surface of semiconductors take place very rapidly and may indicate a marked change in electrical conductivity by the use of thin film semiconductors. This property of thin film is applicable to the detection of gaseous components. An example of this type detector is the P-N junction.

**P-N Junction Detector** — this semiconductor thin film detector has the advantage over the original type of thin film detector in that the sensitive element is readily available and does not have to be specially prepared. The element is a reversed biased semiconductor diode. These diodes are affected by ambient gases.

**Glow-Discharge Detector** — the composition of the gas chromatographic effluent is measured by the change in voltage across a gaseous discharge.

**Radio-Frequency Discharge Detector** — the collisions between sample components and r-f excited rare gas atoms causes changes in light emission. Low vapor concentrations are measured by changes in this light emission when the solute molecules are ionized.

**Micro Cross-Section Detector** — a concentration of ion pairs is produced when the effluent stream is subjected to ionization radiation. The number of ion pairs is proportional to the cross-section area available for ionization in each sample. As solute concentration increases, more ion pairs are formed; thus greater current is passed.

**Helium Beta Ionization Detector** — a simple and ultra sensitive gas chromatographic detection device which was developed for the analysis of permanent gases. The detector consists of two electrodes closely spaced (approximately 1 mm) either in a concentric or parallel geometry. The internal detector volume is 150 microliters. A tritium impregnated

foil serves as one electrode. A constant potential is applied to one electrode while the other electrode lead is connected to an electrometer capable of measuring small ( $10^{-11}$  amps) changes in current. Helium passing from a chromatographic column is excited to the metastable state (energy level = 19.8 eV). All permanent gases except neon are ionized in turn and produce a positive increase in the detector current. Neon shows a negative peak. Sensitivity as low as 10 ppb is demonstrated with chromatograms for hydrogen, oxygen, argon, nitrogen, carbon monoxide and carbon dioxide. Linear response is shown over a range of 10,000.

**Electron Capture Ionization Detector** — this detector utilizes an ion chamber containing a gas with free electrons at an applied potential just great enough to collect completely the free electrons generated by a radioactive source. Molecules from the sample (which have an affinity for the free electrons) will capture the free electrons and become negative ions. The detector current decreases in the presence of the electron capturing molecules. Other types of detectors include the Gas Density Balance, Alkali Flame Ionization, and Alpha Ionization as well as mass spectrometers and automatic titrators.

### Temperature Control

For precise and reproducible gas chromatographic analysis there must be temperature control of (1) the injection system, (2) the column, (3) detector and (4) fraction collector, if used. The injection system must be heated to a point that will volatilize the sample instantaneously and keep it in the vapor state until it reaches the column, which is also heated to assure that the sample components remain in the gaseous state for the passage through the separation column. The detector likewise must be heated to keep the sample components in the vapor phase. The temperature of each component part of the gas chromatograph must be precisely controlled and reproducible so that constant sample retention times may be attained.

If a fraction collector is used, its temperature must also be high enough to keep the components gaseous until collected in a cold trap.

Each instrumental component can have a separate control system or the temperature of the assembly may be controlled by a single system. In the single control system the injector, column, detector and fraction collector are all located in a constant temperature oven. When the component parts have separate controls, each can be set at an optimal value. Generally, the single temperature control is for isothermal operating conditions.

If the sample components have a very wide boiling range, programmed temperature control is most valuable. In the programmed mode, the injector, detector and collector are set at a constant temperature and the column temperature is varied at a known and constant rate. This shortens the analysis time considerably when dealing with the widely separated boiling point components. The programmed temperature control must be very reproducible or the results can be confusing. As the control must be regulated very closely, these systems are costly. A comparison of chromatograms prepared using constant and programmed column temperatures is shown in Figure 21-9.

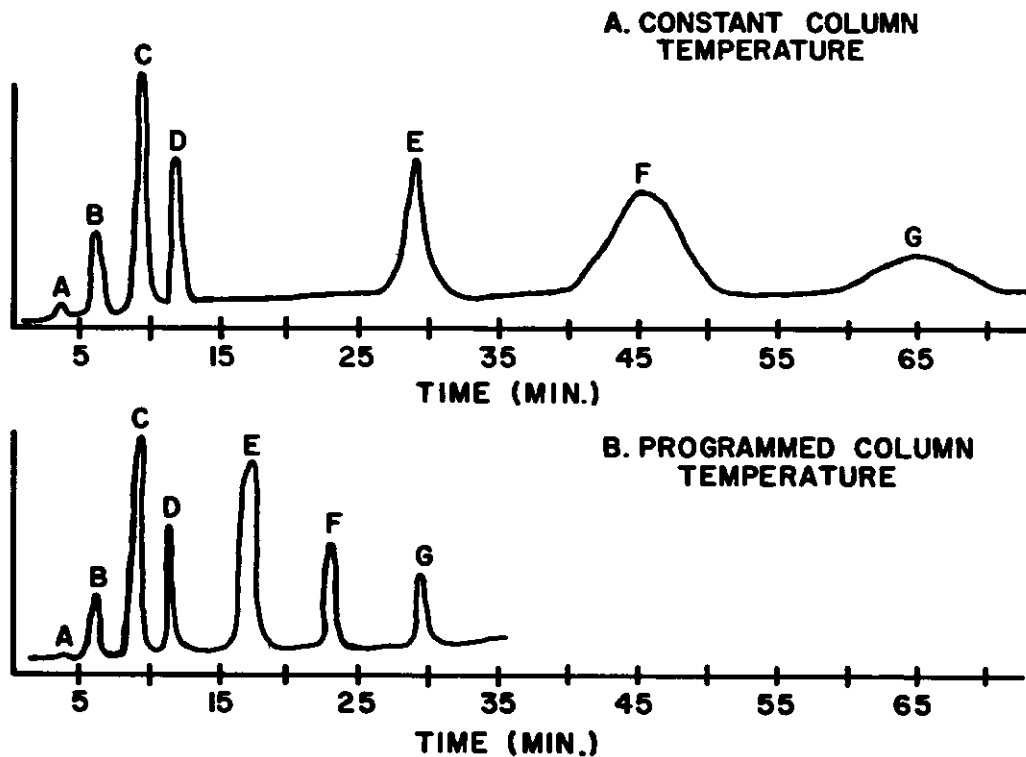
### Recording Devices

The response of the detector is plotted as a chromatogram by the millivolt recorder. The chromatogram is a plot of detector response versus time. With only carrier gas flowing through the detector, the recorder is adjusted to read zero. This zero reading is referred to as the base line. Each separated component evokes a response by the detector which registers a peak on the chromatogram. The chromatogram will give two different kinds of information: (1) identification by retention time, the time it takes for the peak to appear after injection of the sample, and (2) quantitative estimation of a component of the sample, which can be obtained by comparing the area of the peak with that produced by a standard sample of the same component substance at a known concentration.

There are two types of strip chart recorders in use — the galvanometric and potentiometric. Galvanometric recorders are inexpensive but require an amplifier. Potentiometric recorders are more expensive but do not always require an amplifier.

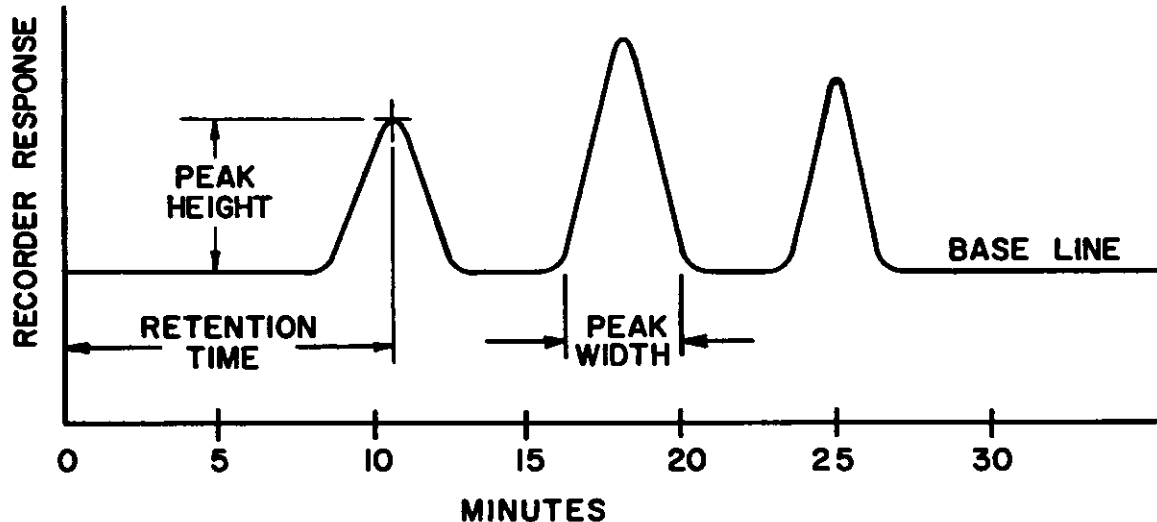
Figure 21-10 is a diagrammatic example of a typical chromatogram indicating the several measurements of interest.

Digital readout may be employed by using one of several types of printing integrators, which merely print out numbers corresponding to the area under the chromatographic curve. There are several types of integrators: mechanical, electromechanical and electronic. The most generally used is the mechanical or disc integrator, which measures mechanically the height of the curve. The electromechanical integrator converts the voltage change from the detector signal to a digital signal directly. The electronic integrator is similar to the electromechanical unit but uses a voltage totaling circuit instead of a direct signal.



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Figure 21-9. A Comparison of Chromatograms Prepared Using Constant and Programmed Column Temperatures.



Prepared by Sandia Laboratories draftsmen.

Figure 21-10. Diagrammatic Example of a Typical Chromatogram.

Other readout systems may be used as ancillary equipment, such as mass spectrometers, attached directly through concentrators to the chromatograph, or flow type infrared or ultraviolet spectrophotometers.

#### Collection Systems

The system for collecting chromatographed sample components can be very simple or quite elaborate. The simplest system is that of collecting the vapor on a cold plate at the detector outlet. This technique can be used with salt plates for infrared spectral analysis. The vapor may also be collected in miniature condensers cooled with ice, dry ice-acetone or other cryogenic systems. The vapor may be kept in this stage, passed through heated tubes to gas analysis systems such as infrared gas analysis cells, or introduced into mass spectrometer sampling systems through a helium separator.

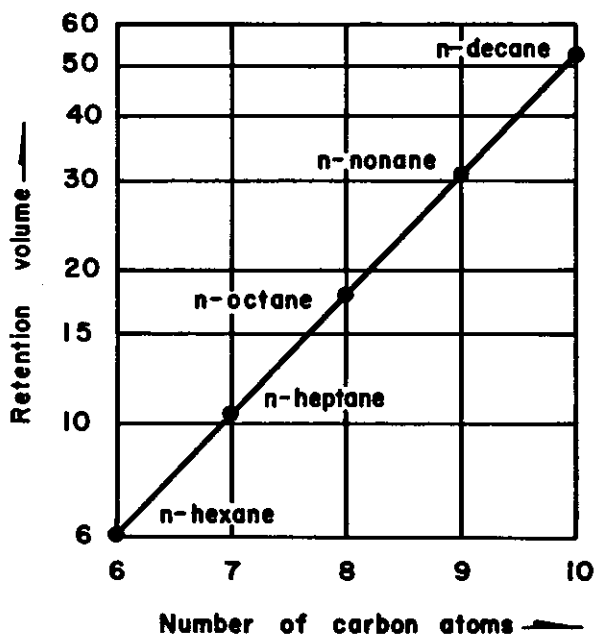
The collection system may be as original as the chromatographer can develop to satisfy the requirements of his analytical problems and instruments.

#### QUALITATIVE ANALYSIS

From the foregoing information it is obvious that practically any vaporous mixture can be separated by gas chromatographic techniques. One of the main problems, however, is the qualitative determination of the mixture components.

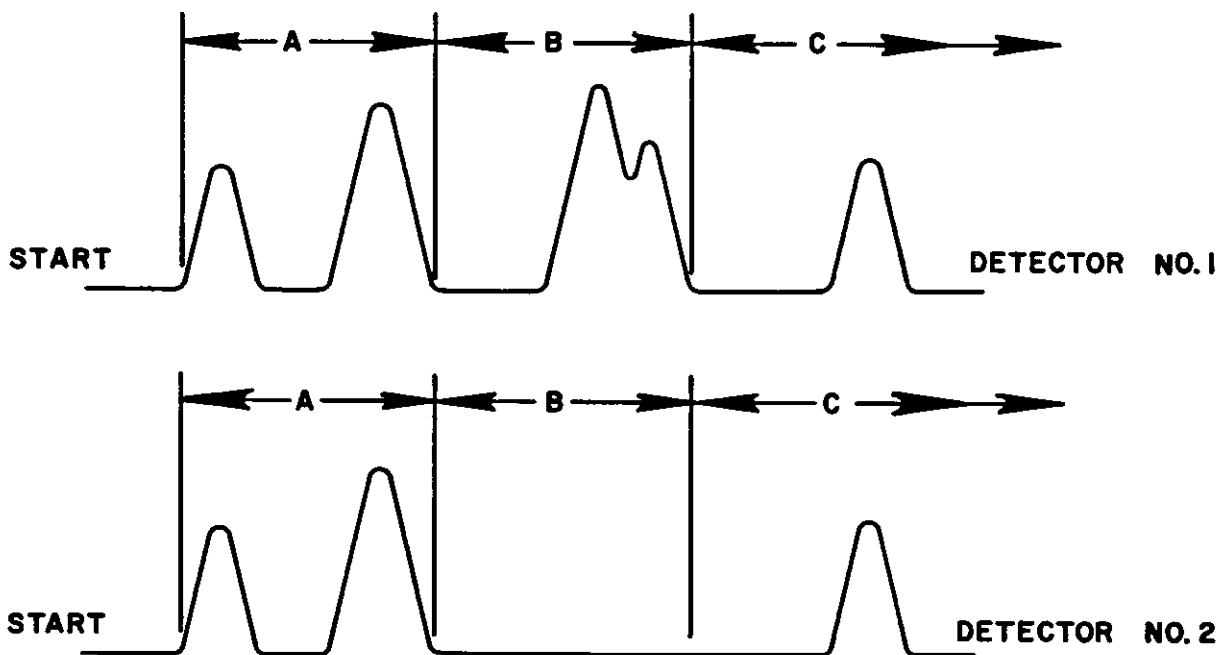
There are four basic methods which have been used for the identification of separated components: (1) comparison of known compound chromatograms with the unknown, (2) plotting of homologous series, (3) use of dual columns, and (4) identification by auxiliary instrumentation. When members of homologous series are chromat-

ographed under reproducible conditions, the results can be plotted as the number of carbon atoms versus log of retention volume. The plot can then be used for a determination of the carbon content of the component of interest. An example is shown in Figure 21-11.



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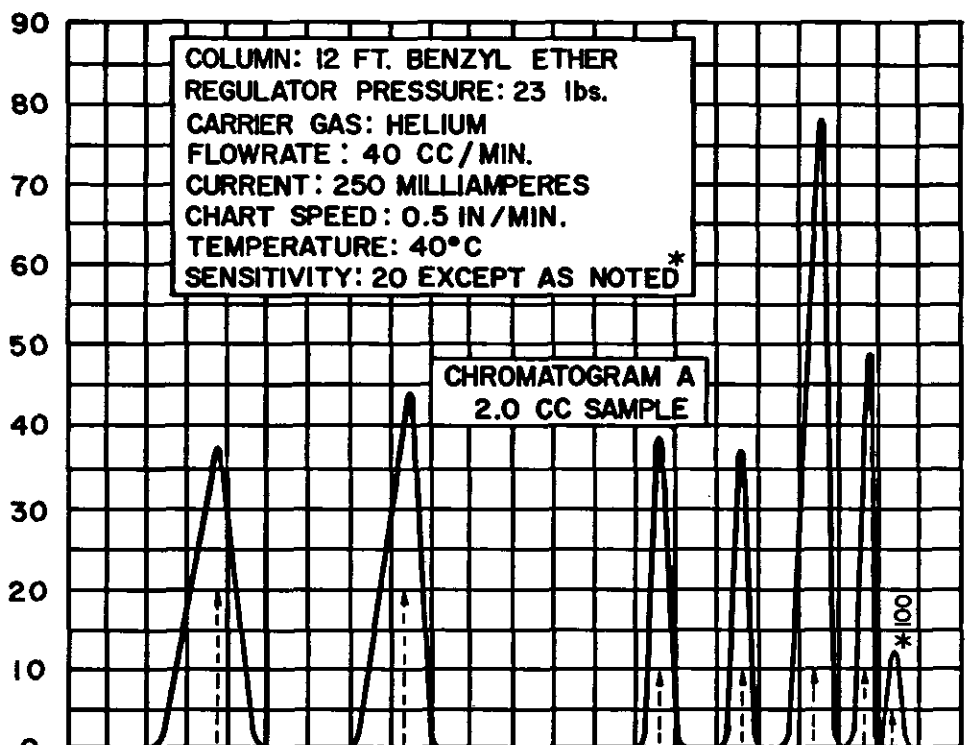
Figure 21-11. Example of Plot to Determine Carbon Content of Component.



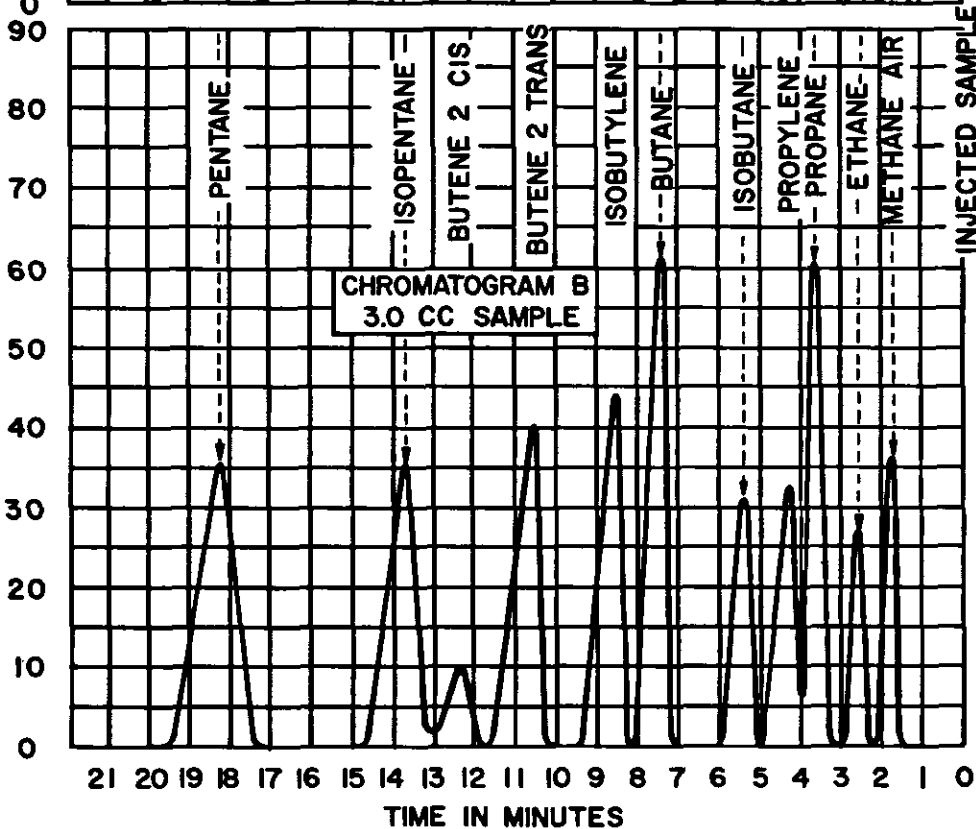
Prepared by Sandia Laboratories draftsmen.

Figure 21-12. Dual Detector Response.

UNKNOWN



KNOWN



Beckman Instruments, Inc.: Bulletin #756A. Fullerton, California.

Figure 21-13. Illustration of Use of a Known Sample to identify the Components of the Unknown Sample.

When dual columns are used different retention times of the individual components are obtained. The use of dual detectors results in a different response to the sample components due to the specificity of the detector. Figure 21-12 illustrates the dual detector response.

A more specific method for qualitative analysis is the use of auxiliary instrumentation such as infrared, ultraviolet or mass spectrometry. The sample components are trapped at the outlet from the gas chromatograph, transferred to the appropriate instrument and subjected to a qualitative analysis by the independent technique.

The separation achieved depends upon the column, the temperature, the detector and flowrate of the carrier gas. Therefore, it is imperative that all these parameters be kept the same for both the sample and the standard used for the determination of component peak location. It is important to know that the unknown component is eluted in the same time as a known compound. It is also important to know that no other compound can appear at this location with the parameters used. Figure 21-13 illustrates the use of a known sample to identify the components of the unknown sample.

### QUANTITATIVE ANALYSIS

The prime application of gas chromatography is, of course, quantitative analysis. It is well known that the area under a chromatographic peak is proportional to the amount of the responsible sample component in the carrier gas stream. This means that the use of gas chromatography for quantitative analysis requires a knowledge, first, of the area of the peak and second, the proportionality factor to convert this measurement to a concentration unit.

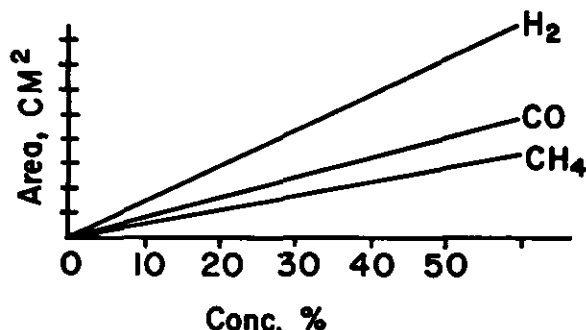
Areas can be determined by any of the following methods:

1. Automatic integrator
2. Polar planimetry
3. Cutting out the peak and weighing the chart paper on an analytical balance
4. Multiplying the peak height by the peak width at half the peak height
5. Calculating the area of the triangle formed by the two tangents drawn through the inflection point of the peak, using the base line as the base of the triangle.

The most commonly used of these methods are 1, 2 and 4. The areas are expressed in any convenient unit, the most common unit being  $\text{cm}^2$ . In the ideal case, where detector response is the same for all components in a mixture, a simple relationship is used to calculate percentage. As an example, assume that we have an ideal four-component mixture of methane, ethane, propane and butane. The areas are 2.50, 1.25, 5.00 and 0.625  $\text{cm}^2$ , respectively. The total area = 9.375  $\text{cm}^2$ . The percentages are then: methane = 26.67%, ethane = 13.33%, propane = 53.33% and butane = 6.67%, making the total 100%. The ideal case, however, does not always apply. The response factors are different for individual compounds, and this must be taken into consideration before calculation of percentage values.

The sample components may also be collected at the detector outlet and analyzed by means of infrared or ultraviolet spectrophotometry, mass spectrometry or computer coupling.

The most popular method of quantitation in the laboratory is by means of standard curves prepared by plotting the detector response versus concentration as shown in Figure 21-14.



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Figure 21-14. Plot of Detector Response Versus Concentration.

### OPERATION OF THE GAS CHROMATOGRAPH

#### Selection of Parameters for Operation

*Carrier Gas* — the choice depends on cost, availability, nature of sample, safety and the type of detector.

*Type of Column* — selection is dependent on the polarity and volatility of the packing as compared with the substances to be separated, (see section on "Columns").

*Detector* — selection is based on sensitivity for type of sample component to be analyzed, (see section on "Detectors").

*Temperature Controls* — the setting for the temperature of the injection block is determined by the boiling point of the least volatile compound in the sample. In general, it is maintained at a temperature of 50-100 degrees C above the column temperature, which may be maintained at the limit specified for the packing it contains. The detector must also be maintained at a specified temperature which is dependent on the type of detector used and the analysis performed. All temperature controls are set and allowed to stabilize before injection of the sample.

#### Column Preparation

Many liquid phases require conditioning before use. This is accomplished by heating the column at a slightly higher temperature than the intended operating temperature for six to twelve hours to "bleed off" any excessive coating in the column.

#### Sample Collection Methods

Samples of contaminated air may be collected in many ways, some of which are:

- (1) Glass or metal double-valved sampling flasks through which the sample is drawn by means of a small carbon vane pump or double-ended squeeze bulb.

- (2) An evacuated glass or metal single-valved flask or bulb, into which the sample is drawn.
- (3) Plastic or rubber bags which may be used for nonreactive gases are filled using either a double-ended squeeze bulb, for small volumes up to 1 liter, or by carbon vane pumps, for volumes up to 20 liters.
- (4) Adsorption on active solids while drawing the contaminated air through the solid contained in a sampling tube.
- (5) Absorption in a suitable solvent using standard air sampling equipment (i.e., impinger or bubbler).
- (6) Collection in large volume gas tight syringes which are then capped to prevent leakage.

There are two methods for the collection of air samples which are to be transported over long distances for analysis. The method of choice is to collect the air contaminant directly onto an active solid contained in a sampling tube. An alternate method is to first collect the air sample in a glass, metal, rubber or plastic container and then the air is passed through a tube containing an active solid adsorption of the contaminant. In either case the tube is sealed and sent to the laboratory for future analysis. Air volumes must always be recorded so that concentrations can be calculated.

#### Sample Preparation

Some substances, such as gases, can be injected directly into the chromatograph, but ordinarily, there may be some preliminary purification needed

which may be simple or complicated, depending on the compound to be analyzed. Because some substances in a mixture are similar, they cannot be separated from each other unless they are first converted into derivatives such as acetates or esters, thus producing larger molecules which may be separated more easily. Finally, after purification and derivative formation, the sample must be added to a suitable solvent which will volatilize at the temperature of the injection chamber. The solvents most frequently used for this purpose are acetone, alcohol, chloroform and hexane. In most cases, nanogram amounts of a sample are injected by means of a micro-syringe calibrated in microliters.

It is apparent that the preparation of the sample for analysis can be a tedious, time-consuming task and this phase is one of the few disadvantages of gas chromatography.

#### Presentation of Chromatographic Data

The precise reproduction of one's analyses or those of other investigators requires all of the pertinent information to be made available. The following data must be included in chromatographic reports: type of sample, instrument used, identification of the column and the conditions of operation, date of analysis, results and name of operator. Figure 21-15 illustrates a convenient tabulation report form.

#### CALIBRATION

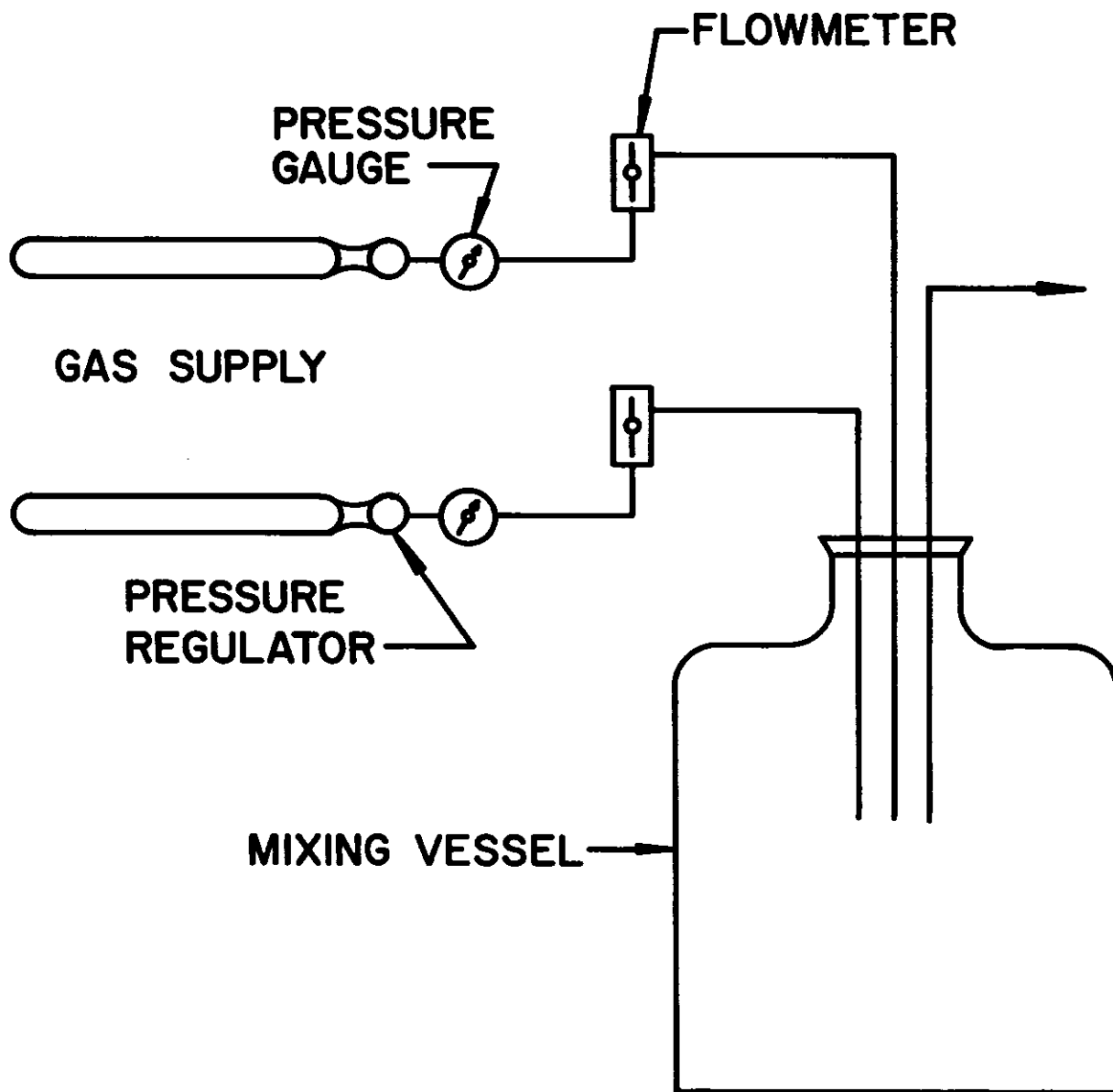
For accurate quantitative analysis the gas chromatographic system must be calibrated using

Operator _____	Date _____
Column	Detector _____
Length _____	Voltage _____
Dia. _____	Sensit. _____
Liquid Phase _____	Flow Rates, ml/min
Wt. % _____	Hydrogen _____ Air _____
Support _____	Scavenge _____
Mesh _____	Spht _____
Carrier Gas _____	Temperature, °C
Rotometers _____	Det _____ Inj _____
Inlet Press _____ psig	Column Initial _____
Rate _____ ml/min	Final _____
CHART SPEED _____	Ratio _____
SAMPLE _____	Solvent _____
Size _____	Conc. _____



known concentrations of the components of interest. Several methods are available for preparing known concentrations of gases and vapors for this purpose.

A simple system for the preparation of known concentrations of gases by a dynamic method is shown in Figure 21-16 where known amounts of the gas (A) are mixed with a diluting gas (B) to



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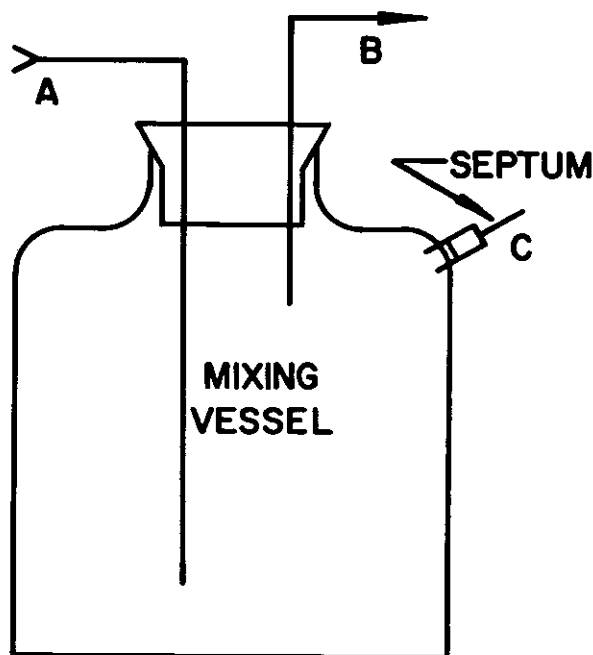
Figure 21-16. Dynamic Method.

yield the required concentration (C).

A second method which may be used for the preparation of known concentrations of either gases or vapor in air is the static method where a known volume of gas or volatile liquid is introduced (with an accurate volume measuring device) through a septum into a previously evacuated rigid container of known volume. The gas or vapor is then mixed with the diluting gas and stirred by either mechanical or thermal methods and samples are withdrawn from the vessel for use in calibra-

tion. This static system is shown in Figure 21-17, which illustrates the known gas (A), the diluting gas (B) and the known gas concentration (C).

Samples from either type of calibration system can be introduced directly to the gas sampling valve of the chromatograph or they may be contained in a plastic or rubber bag from which the samples may be removed using gas tight syringes to transfer them to the chromatograph. These standard samples are chromatographed and the detector response is plotted versus concentration.



Prepared by Sandia Laboratories draftsmen.

Figure 21-17. Static System.

For an accurate calibration, the concentration of the known mixture must be determined by standard chemical methods. Infrared spectrophotometry is a convenient procedure for determining the concentration of many components.

There are several companies which market pressure containers of gases in labeled concentrations in nitrogen or other diluents; these may be used in the calibration of gas chromatographic systems. These mixtures are very convenient, but the concentrations must be verified by independent analyses before using for calibration purposes.

### SPECIAL TECHNIQUES

#### Displacement Chromatography

Samples collected on active solids may be analyzed chromatographically by a technique called displacement, where the sample collection tube is inserted just ahead of the chromatographic column. A solvent vapor, for which the active adsorbent has a greater affinity than for the sample components, is passed through the collection tube displacing the sample onto the chromatographic column. This technique, when properly applied, presents essentially a plug of the sample to the column, by concentrating the sample as the displacement vapor replaced the components on the active solid.

#### Long Line Sampling

It is possible to sample gaseous contaminants in air over relatively great distances by using 0.5-inch I.D. tubing and moving the sample through the line at 1 liter per minute using a large capacity vacuum pump. Line losses are negligible if the sample lines have been pressure checked before

samples are taken. Sampling distances up to 6500 feet have been used.<sup>11</sup>

#### Portable Chromatographs

There are available many very good portable chromatographs which may be taken to the work areas for sample analyses. The difficulty, however, arises in obtaining a large enough sample for analysis of trace contaminants. A sample concentrating chromatograph has been developed (personal communications) which samples the air through a small tube of activated silica gel. After the sample has been collected valves are changed and the air contaminants are released from the adsorbent by heat and presented directly to the gas chromatographic column for analysis. The versatility and applications of the portable chromatograph are progressing at an encouraging pace fortunately, as this type of unit is needed greatly throughout the whole environmental health field.

#### Process Chromatography

The process unit is capable of performing repeat analyses of stream effluents, liquid or gaseous, for many components. This type of analysis can be programmed and the data fed to a computer for analysis; the results may be fed to a control system where necessary adjustments are made in processes if the analysis indicates the need. Process control by gas chromatography has wide-spread use in the chemical industry.

#### Pyrolysis

Pyrolysis, the thermal decomposition of samples, is an important new branch of the identification methods. This technique may be used in the identification of polymers, high molecular weight organic and inorganic compounds, and also low boiling compounds, by producing the characteristic breakdown products. It has also been used in the characterization of microorganisms.<sup>12</sup> Essentially, the technique employed is similar to that used in displacement chromatography but the displacement column is replaced by a combustion oven located just ahead of the partitioning column of the instrument. The output display has been called a pyrogram, which has an extremely complex nature. Since pyrolysis reactions are unpredictable the pyrolysis conditions must be very closely regulated for reproducible analyses.

#### Miscellaneous

Some recent applications have been published based on the work of investigators in the fields of air pollution, clinical medicine, toxicology and allied areas.

*Air Pollution* — Using a two section column, Bethea<sup>13</sup> was able to determine nitrogen dioxide with a lower detection limit of 200 ppm. Gas chromatography of gases emanating from the soil has been successful in separating the component mixture using a three column system equipped with a thermal detector.<sup>14</sup> A short silica column has been used to determine nitrogen dioxide at 50-60 degrees with hydrogen as a carrier gas.<sup>15</sup> Nitrogen dioxide has been collected and concentrated on Molecular Sieve 5A and determined by chromatography on a Poropak Q column<sup>16</sup>. Lawson<sup>17</sup> has determined nitrogen oxides in air by gas chromatography.

**Medicine and Toxicology** — Many articles are being published on the determination of alcohol in breath samples, using various chromatographic methods. Lowe<sup>18</sup> reviewed the determination of volatile organic anesthetics in gases, blood, and tissue by gas chromatography. The direct determination of organic solvents in blood was described by Schlunegger.<sup>19</sup>

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*Pyrolysis*

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