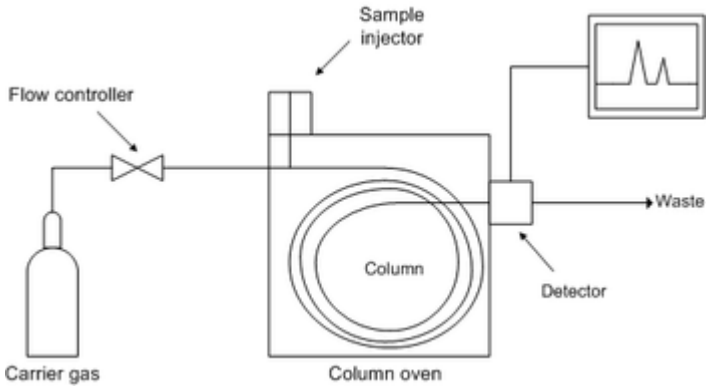
GC

Gas-liquid chromatography (GLC), or simply gas chromatography (GC), is a type of chromatography in which the mobile phase is a carrier gas, usually an inert gas such as helium or nitrogen, and the stationary phase is a microscopic layer of liquid on an inert solid support, inside glass or metal tubing, called a column. The instrument to perform gas chromatographic separations is called a *gas chromatograph* (also: *aerograph*, *gas separator*).

GC analysis



A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the *column*, through which different chemical constituents of a sample pass in a gas stream (carrier gas, *mobile phase*) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the *stationary phase*. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (*retention time*). Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature.

In a GC analysis, a known volume of gaseous or liquid analyte is injected into the "entrance" (head) of the column, usually using a microsyringe (or, solid phase microextraction fibers, or a gas source switching system). Although the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column.

Physical components

Inlets

The column inlet (or *injector*) provides the means to introduce a sample into a continuous flow of carrier gas. The inlet is a piece of hardware attached to the *column head*.

Common inlet types are:

- S/SL (Split/Splitless) injector; a sample is in introduced into a heated small chamber via a syringe through a *septum* - the heat facilitates volatilization of the sample and sample matrix. The carrier gas then either sweeps the entirety (*splitless* mode) or a portion (*split* mode) of the sample into the column. In split mode, a part of the sample/carrier gas mixture in the injection chamber is exhausted through the *split vent*.
- COC (cool on-column) inlet; the sample is here introduced in its entirety without heat.
- gas source inlet or gas switching valve; gaseous samples in collection bottles are here hooked up to what is most commonly a six-port *switching valve*: the carrier gas flow is not interrupted while a sample can be expanded into a previously evacuated *sample loop*. Upon switching, the contents of the sample loop are switched into the carrier gas stream.
- P/T (Purge-and-Trap) system; samples requiring preconcentration or purification can be introduced via such a system, usually hooked up to the S/SL port. The advantage of such a system is that no or few prior enrichment/purification steps in the laboratory are necessary.
- in addition, SPME (solid phase microextraction) offers a convenient, low-cost alternative to P/T systems with the versatility of a syringe and simple use of the S/SL port.

Columns

Two types of columns are used in GC:

- Packed columns are 1.5 - 10 m in length and have an internal diameter of 2 - 4 mm. The tubing is usually made of stainless steel or glass and contains a *packing* of finely divided, inert, solid support material (eg. diatomaceous earth) that is coated with a liquid or solid stationary phase. The nature of the coating material determines what type of materials will be most strongly adsorbed. Thus numerous columns are available that are designed to separate specific types of compounds.
- Capillary columns have a very small internal diameter, on the order of a few tenths of millimeters, and lengths between 25-60 meters are common. The inner column walls are coated with the active materials (WCOT columns), some columns are quasi solid filled with many parallel micropores (PLOT columns). Most capillary columns are made of fused-silica with a polyimide outer coating. These columns are flexible, so a very long column can be wound into a small coil.
- New developments are sought where stationary phase incompatibilities lead to geometric solutions of parallel columns within one column. Among these new developments are:
    - Internally heated *microFAST* columns, where two columns, an internal heating wire and a temperature sensor are combined within a common column sheeth (microFAST);
    - *Micropacked columns* (1/16" OD) are column-in-column packed columns where the outer column space has a packing different from the inner column space, thus providing the

separation behaviour of two columns in one. They can be easily fit to inlets and detectors of a capillary column instrument.

Because molecular adsorption and the rate of progression along the column depend on the temperature, the column temperature is carefully controlled to within a few tenths of a degree for precise work. Reducing the temperature produces the greatest level of separation, but can result in very long elution times. For some cases temperature is ramped either continuously or in steps to provide the desired separation. This is referred to as a temperature program. Electronic pressure control can also be used to modify flow rate during the analysis, aiding in faster run times while keeping acceptable levels of separation.

Additionally, choice of carrier gas is important, with hydrogen being the most efficient and providing the best separation. However, helium has a larger range of flowrates that are comparable to hydrogen in efficiency, with the added advantage that helium is non-flammable, and works with a greater number of detectors. Therefore, helium is the most common carrier gas used.

Methods

The method is the collection of conditions in which the GC operates for a given analysis. Method development is the process of determining what conditions are adequate and/or ideal for the analysis required.

Conditions which can be varied to accommodate a required analysis include inlet temperature, detector temperature, column temperature and temperature program, carrier gas and carrier gas flow rates, the column's stationary phase, diameter and length, inlet type and flow rates, sample size and injection technique. Depending on the detector(s) (see below) installed on the GC, there may be a number of detector conditions that can also be varied. Some GCs also include valves which can change the route of sample and carrier flow, and the timing of the turning of these valves can be important to method development.

Carrier Gas Selection and Flow Rates

The carrier gas is the mobile phase in a GC. Typical carrier gases include helium, nitrogen, argon, hydrogen and air. Which gas to use is usually determined by the detector being used, for example, a DID requires helium as the carrier gas. When analyzing gas samples, however, the carrier is sometimes selected based on the sample's matrix, for example, when analyzed a mixtured in argon, an argon carrier as is preferred, because the argon in the sample does not show up on the chromatogram. Safety and availability can also influence carrier selection, for example, hydrogen is flammable, and high-purity helium can be difficult to obtain in some areas of the world. (See: Helium--occurrence and production.)

The purity of the carrier gas is also frequently determined by the detector, though the level of sensitivity needed can also play a significant role. Typically, purities of 99.995% or higher are used. Trade names for typical purities include "Zero Grade," "Ultra-High Purity (UHP) Grade," "4.5 Grade" and "5.0 Grade."

The carrier gas flow rate affects the analysis in the same way that temperature does (see above). The higher the flow rate the faster the analysis, but the lower the separation between analytes. Selecting the flow rate is therefore the same compromise between the level of separation and length of analysis as selecting the column

temperature.
With GCs made before the 1990s, carrier flow rate was controlled indirectly by controlling the carrier inlet pressure, or "column head pressure." The actual flow rate was measured at the outlet of the column or the detector with an electronic flow meter, or a bubble flow meter, and could be an involved, time consuming, and frustrating process. The pressure setting was not able to be varied during the run, and thus the flow was essentially constant during the analysis.
Many modern GCs, however, electronically measure the flow rate, and electronically control the carrier gas pressure to set the flow rate. Consequently, carrier pressures and flow rates can be adjusted during the run, creating pressure/flow programs similar to temperature programs.

Inlet Types and Flow Rates
The choice of inlet type and injection technique depends on if the sample is in liquid, gas, adsorbed, or solid form, and on if a solvent matrix is present that has to be vaporized. Dissolved samples can be introduced directly onto the column via a COC injector, if the conditions are well known; if a solvent matrix has to be vaporized and partially removed, a S/SL injector is used (most common injection technique); gaseous samples (e.g., air cylinders) are usually injected using a gas switching valve system; adsorbed samples (e.g., on adsorbent tubes) are introduced using either an external (on-line or off-line) desorption apparatus such as a purge-and-trap system, or are desorbed in the S/SL injector (SPME applications).
The column(s) in a GC are contained in an oven, the temperature of which is precisely controlled electronically. (When discussing the "temperature of the column," an analyst is technically referring to the temperature of the column oven. The distinction, however, is not important and will not subsequently be made in this article.)
The rate at which a sample passes through the column is directly proportional to the temperature of the column. The higher the column temperature, the faster the sample moves through the column. However, the faster a sample moves through the column, the less it interacts with the stationary phase, and the less the analytes are separated.
In general, the column temperature is selected to compromise between the length of the analysis and the level of separation.
A method which holds the column at the same temperature for the entire analysis is called "isothermal." Most methods, however, increase the column temperature during the analysis, the initial temperature, rate of temperature increase (the temperature "ramp") and final temperature is called the "temperature program."
A temperature program allows analytes that elute early in the analysis to separate adequately, while shortening the time it takes for late-eluting analytes to pass through the column.

Application
In general, substances that vaporize below ca. 300 °C (and therefore are stable up to that temperature) can be measured quantitatively. The samples are also required to be salt-free; they should not contain ions. Very minute amounts of a substance can be measured, but it is often required that the sample must be measured in comparison to a sample containing the pure, suspected substance.

Various temperature programs can be used to make the readings more meaningful; for example to differentiate between substances that behave similarly during the GC process.

Professionals working with GC analyze the content of a chemical product, for example in assuring the quality of products in the chemical industry; or measuring toxic substances in soil, air or water. GC is very accurate if used properly and can measure picomoles of a substance in a 1 ml liquid sample, or parts-per-billion concentrations in gaseous samples.

In practical courses at colleges, students sometimes get acquainted to the GC by studying the contents of Lavender oil or measuring the ethylene that is secreted by *Nicotiana benthamiana* plants after artificially injuring their leaves. These GC analyses are done rather quickly (1 to 15 minutes per sample) and therefore suited for such courses.

One example of the use of gas chromatography is in the study of the selectivity of Fischer-Tropsch synthesis catalysts. The outlet from this process contains a number of light gases including H_2, CO, CO_2 and CH_4, as well as heavier parafinic and olefinic hydrocarbons (C2-C40+). In a typical experiment, a packed column is used to separate the light gases, which are then detected with a TCD. The hydrocarbons are separated using a capillary column and detected with an FID. A complication with light gas analyses that include H_2 is that He, which is the most common and most sensitive inert carrier (sensitivity is proportional to molecular mass) has an almost identical thermal conductivity to hydrogen (it is the difference in thermal conductivity between two separate filaments in a Wheatstone Bridge type arrangement that shows when a component has been eluted). For this reason, dual TCD instruments are used with a separate channel for hydrogen that uses nitrogen as a carrier are common. Argon in often used when analysing gas phase chemistry reactions such as F-T synthesis so that a single carrier gas can be used rather than 2 separate ones. The sensitivity is less but this is a tradeoff for simplicity in the gas supply.