

Gas Chromatography

INTRODUCTION

Prior to the invention of gas chromatography by James and Martin (Biochem J., 1952, 50, 679), the separation of close-boiling volatile liquids was at best extremely difficult. Gas chromatography is a surprisingly simple technique with great versatility, and is now a given in the analytical chemist's arsenal for the separation and analysis of volatile mixtures.

The procedure involves vaporizing a sample and sweeping it through a column with a moving stream of gas termed the mobile phase or the carrier gas. The gases are commonly supplied by compressed gas cylinders. The sample is introduced into the injection port. The most common type of analysis involves the injection of 1 to 3 microliters of a liquid sample into a heated inlet, either manually or by an automated injection device. The injection port is interfaced to the column where the actual separation takes place. In most cases capillary columns are used to obtain the best possible separation. The downside to capillary columns is that they have a limited "capacity". In other words not much sample can be separated at a time. Therefore a split injection port is often used to allow only a fraction of the injected volume of sample onto the capillary column. The capillary column's inner walls are coated with either a porous solid or a viscous liquid material. This inner coating will interact with different solute molecules to different extents. Those molecules which interact more strongly with the stationary phase spend on average a higher percentage of their time associated with the stationary phase than those solutes which do not interact strongly. Those compounds which do not often associate with the stationary phase pass more quickly through the column than those compounds which have strong interactions with the stationary phase, and a separation of the components in the mixture is achieved. Since the compounds have different mobilities, they exit the column at different times; i.e., they have different retention times, t_R . The retention time is the time between injection and detection. There are numerous detectors which can be used in gas chromatography. It is a device that senses the presence of components different from the carrier gas (mobile phase) and converts that information to an electrical signal. For qualitative identification one must rely on matching retention times of known compounds with the retention times of components in the unknown mixture. It is important to remember that any changes in operating conditions will affect the retention time which will affect the accuracy of identification. Thus GC is most often used when one is performing a target compound analysis, where one has a good idea of the compounds present in a mixture so reference standards can be used for determining retention times. For a sample of largely unknown composition qualitative identification can be determined by gas chromatography-mass spectrometry. A mass spectrum of any or all peaks in the chromatogram is compared with spectra contained in spectral libraries on the system's computer.

Quantitative analysis is possible, but given the small amounts of sample that are injected onto the capillary column, without an automatic injector these volumes are impossible to reproduce. It is thus recommended that the method of internal standards be used for quantitative analysis (Skoog/Holler/Nieman, 5th Edition, pp. 18).

Gas chromatographs are really rather simple. The apparatus consists of a pressurized tank of carrier gas, usually He, a pressure regulator to control the flow rate of the gas through the chromatograph, a sample inlet, the column, a detector with associated electronics, some kind of interface to the outside world such as a recorder, and a flow meter to measure the flow rate of carrier gas. Chromatographs also provide heating for the column, the sample inlet, and the detector. The temperatures of these three components can usually be controlled independently.

Good separation of a given pair of compounds by gas chromatography depends on the choice of column (which has already been done for you) and on the efficiency of the overall GC system. The relative position of the various components in the sample on the chromatogram is affected by a solute-solvent type of interaction with the column substrate. Column efficiency is concerned with the broadening of an initially compact band of solutes as it passes through the column. The broadening is a result of column design and of column operating conditions.

Problems with separation occurs at primarily three places:

1. Sample injection. The sample should be injected all at once into the column and should be vaporized immediately. For this reason, good GC's have heated sample chambers. In other words, the sample should enter the packed column as a plug of gas. The size of the sample should also be small so as not to "overload" the column.
2. Column Characteristics. Assuming you have chosen an appropriate column that affords selectivity, flow rate is very important. If the flow of carrier gas were shut off, the band would eventually diffuse throughout the column. Even with carrier gas flowing, this longitudinal diffusion still takes place forward and backward, and results in band broadening. This undesirable diffusion depends upon the time that the band remains in the column, and therefore on the flow rate of carrier gas (at a given column temperature, column, and type of sample). If the flow rate is increased, the effect of diffusional broadening is diminished. At higher flow rates however, a second factor creeps in which increases the broadening; partition equilibrium between the mobile and stationary phase is no longer maintained. Therefore, there exists a flow rate for maximum column efficiency. The problem is thus how to find a flow rate which minimizes the peak broadening due to the mass-transfer rate and longitudinal diffusion simultaneously. This is a qualitative description of the van Deemter equation (discussed in Chapter 26 of Skoog/Holler/Nieman, 5th Edition, pp. 681-687).

3. Detector Volume. This you have no control over unless you are designing your own instrument. Once the band issues from the column, it should go immediately into a detector of small volume.

For samples with a broad boiling range, it is often desirable to employ temperature programming, whereby the column temperature is increased continuously or in steps as the separation proceeds. This is the answer, in gas chromatography, to what is called The General Elution Problem. This is treated quite nicely in your Skoog/Holler/Nieman text in Chapter 26 for chromatographic separations in general, pp. 689-693. Basically, the isothermal analysis of wide boiling range mixtures frequently leads to a very wide spread in retention times. The longer the retention time, the broader the peak, so for those components which take a long time to elute, detector sensitivity is diminished and analysis times can be very long.. With temperature programming, successively eluted substances experience increasingly higher average temperatures and so emerge from a column more rapidly than they would under isothermal conditions. So long as one does not experience peak overlap (i.e. resolution remains tolerable), temperature programming gives a superior separation.

General

- Separation and possible identification of all types of volatile organic compounds
- Qualitative and quantitative determination of volatile compounds in mixtures

Common Specific Applications

- Raw materials, intermediates and final product analyses in manufacturing industries
- Environmental, forensic, pharmaceutical, clinical/medical applications

Limitations

- Analyte must be volatile, so not conducive for analysis of large molecular compounds such as proteins and polymers

Complementary or Related Techniques

- Liquid chromatography provides analyses of non-volatile analytes such as proteins and polymers.
- Supercritical fluid chromatography provides analyses of volatile, non-volatile and thermally labile compounds

- Capillary electrophoresis provides superior analyses in many biological/pharmaceutical applications
- Ion Chromatography provides analyses of ionic compounds, as does capillary electrophoresis

References used to devise this web page:

1. "Handbook of Instrumental Techniques for Analytical Chemistry" Frank Settle, Editor: "Gas Chromatography", M.J. Van Sant, Prentice Hall, 1997, pp. 125-146.
2. "Principles of Instrumental Analysis", 5th Edition. Skoog, Holler, Nieman, Saunders College Publishing, 1998, pp. 673-724.

Additional references:

1. "Modern Practice of Gas Chromatography" R.L. Grob, 3rd Edition, New York, Wiley, 1995.

GC Links

General treatment of chromatography including an overview of plate and rate theory:

<http://ull.chemistry.uakron.edu/analytical/Chromatography/>

Tutorials on chromatography and molecular spectroscopy:

<http://www.shu.ac.uk/schools/sci/chem/tutorials/>