

# **EXPERIMENTAL GAS CHROMATOGRAPHY**

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## PREFACE

The tremendous impact that gas chromatography has had on chemical analysis should be obvious to all chemists. Not only is it an efficient, useful, and widely applicable tool, but it is also fast and inexpensive. In spite of these advantages, the incorporation of gas chromatographic experiments into college and university courses has been limited. Few experiments have been written for instructional purposes, and the novice has been given little encouragement and information regarding the techniques. Perhaps this is the natural result of the very rapid growth in this field of analysis.

This manual is intended to give the beginner information that will enable him to build a simple, but very useful, gas chromatograph and to perform several experiments that will illustrate the principles and usefulness of gas chromatography. The kit contains all the necessary components and chemicals except those normally found in the laboratory.

It will be necessary to locate the following apparatus not included in the kit:

1. Oven or cabinet for detector cell and column
2. Storage battery
3. Carrier gas and regulator (two-stage reducing valve)
4. Recorder, potentiometric type, 0-10 mv with strip chart

The experiments have been designed to provide illustrations of gas-liquid and gas-solid chromatography using four (4) basic columns provided with the kit. These experiments can be adapted to a variety of teaching situations — analytical, organic, or physical. Each experiment can be performed independent of the others, but attention is called to inter-relationships between experiments where they exist. Directions are given in enough detail for a novice. On the other hand, questions are posed which should stimulate the student to carry out further experimentation on his own. This can be done once the basic techniques and principles are learned. In most cases, provision has been made to allow an entire class to use the instrument even when the ratio of students to instruments is high.

The manual includes a brief introduction to gas chromatography and thermal conductivity, including definitions and techniques. Short discussions accompany each experiment; however, no attempt has been made to cover the field of gas

chromatography comprehensively. Instead, references are given to original sources, and students should be encouraged to consult them.

An instructor's manual has been prepared for use with the student's manual. It includes additional sources of information, data on retention volumes, typical chromatograms, suggestions for assigning unknowns, interpretation of student results, etc.

The author wishes to express his gratitude to the GOW-MAC Instrument Company for its cooperation, to his colleagues and students at Drew for their respective contributions, and to Daniel Ottenstein for reading and commenting upon the manuscript.

This Manual is dedicated to Dr. Harold M. McNair, whose encouragement provided the stimulus for me to build my first gas chromatograph.

JAMES M. MILLER

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# CHAPTER I

## AN INTRODUCTION TO GAS CHROMATOGRAPHY AND THERMAL CONDUCTIVITY DETECTION

One of the newer methods of chromatographic analysis, and one which has become very popular, is gas chromatography (GC). This popularity has resulted from its wide applicability, short analysis time, low cost, simplicity of apparatus, and necessity for only small samples. It can be adapted to qualitative and quantitative analysis.

Chromatography can be defined as a method for separating the components of a mixture by allowing them to distribute themselves between two phases, one of which is stationary and the other mobile. Chromatographic methods can be classified according to the state of the two phases; for example, "liquid-liquid" and "liquid-solid." The name "gas" chromatography denotes that the mobile phase is a gas. Hence we have "gas-liquid" chromatography (GLC) and "gas-solid" chromatography (GSC). In the case of GLC, the stationary liquid phase is held immobile on an inert "solid support."

The basic processes responsible for separations by GLC and GSC are partition and absorption, respectively. They represent another way of classifying chromatographic methods — by the process responsible for the separation. GLC is more popular and useful than GSC and therefore future discussion will be confined to GLC unless otherwise indicated.

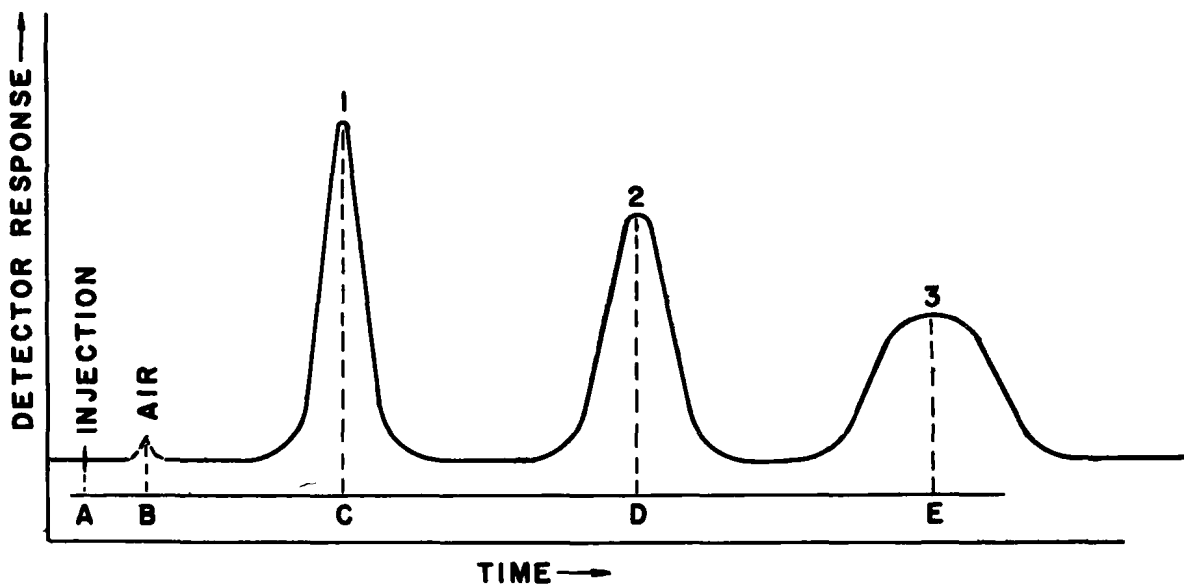
There are three techniques for doing GC — by elution, displacement, and frontal analysis. Of these, elution is most common and the only one we will consider. By this technique, a gas sample is admitted to the head of the gas chromatographic column which is packed with a stationary phase on an inert support. The mobile gas phase (carrier gas) is passed through the column and tends to sweep (elute) the sample gas along with it. The sample gas, however, partitions between the two phases (gas and liquid) and thus spends some of its time in the liquid phase (in solution). Obviously, when the sample is in solution, it will not be swept along with the carrier gas, and the time it spends in the column will depend upon the amount of time it spends in the liquid phase. This in turn depends upon the relative affinity of the sample for the liquid phase and is commonly expressed as the partition coefficient. A separation between two or more components of a sample can therefore be effected when their partition coefficients differ.



Under ideal conditions, each component of a sample should be eluted from the column in a small volume of the continuously flowing carrier gas. All that is necessary is to detect its presence at the column exit. Since this is easily accomplished, it is possible to measure the time that was necessary to elute a given substance from the column. This is called retention time,  $t_R$ . It is a constant for a given substance, under a given set of instrumental conditions, and hence can be used to identify that substance.

For a sample which contains three components, the detector at the column exit might give a response like that shown in Figure 2. The three components have been separated in the column according to their partition coefficients and emerge at the exit at different times. The distance A-C represents the retention time for component 1; A-D for component 2; and A-E for component 3. The three retention times are independent of one another and interactions do not occur between the three components. If these three compounds were part of a list of compounds whose retention times were known on this column, they could probably be identified from their respective retention times.

The peak at B in Figure 2 is due to air. Usually air is included in the sample intentionally so that retention times can conveniently be measured from the air peak. When this is done, the distance B-C is called the "adjusted retention time,"  $t'_R$ . This unit has significance, since for most columns, air does not dissolve in the



TYPICAL CHROMATOGRAM

FIGURE 2

liquid phase and passes through unsorbed. Thus, the distance A-B measures the time it takes a nonsorbed substance to pass through the column.

A more fundamental unit than retention time is retention volume,  $V_R$ . This measures the volume of carrier gas necessary to elute a given compound and is independent of flow since:

$$V_R = t_R F_c \quad (1)$$

In this equation,  $F_c$  is the volumetric flow rate of the carrier gas measured at the outlet pressure and column temperature. Accordingly, a term "adjusted retention volume,"  $V'_R$  can be defined:

$$V'_R = t'_R F_c \quad (2)$$

Also, the product of  $F_c$  and  $t_R$  for air is given the special name, gas holdup,  $V_M$ . This is the volume of carrier gas required to transport a sample from point of injection to point of detection. It represents the "interstitial" volume in the column, and the "free space" in the injection port and detector. It follows that:

$$V'_R = V_R - V_M \quad (3)$$

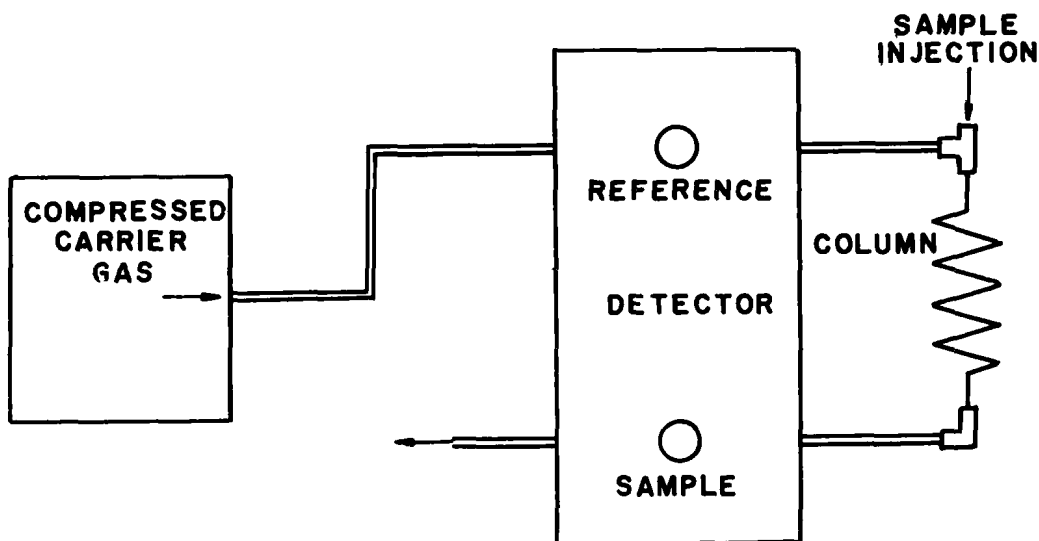
Other terms and units were recommended by the IUPAC in 1959 in order to decrease the confusion caused by the various notations used by different authors. Several summaries are available and should be consulted.<sup>1</sup>

Inspection of Figure 2 shows not only that the three components have different retention times, but also that their peaks have different widths. More specifically, the width increases as the retention time increases. This "peak broadening" has been explained by two theories. One, called the "Plate Theory," describes the chromatographic process relative to a distillation column. It uses the concept of a "theoretical plate" (see Chapter V) and predicts that the peaks should have Gaussian or Poisson shapes.

The other approach is called the "Rate Theory." It was developed by van Deemter et al.<sup>2</sup> and deals with the kinetic factors in the column. Broadening of the peaks is attributed to non-equilibrium conditions in the partitioning process, diffusion in the column, and similar factors. This theory is summarized in the van Deemter equation (see Experiment 1). It has served to stimulate chromatographers to improve the performance of their columns, and it is still a very important equation for describing column properties. However, it is not an exact equation and several investigators have proposed additional terms designed to improve its accuracy.

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<sup>1</sup>References for this chapter are listed on page 10.



FLOW DIAGRAM OF A GAS CHROMATOGRAPH

FIGURE 3

The basic flow diagram of a simple gas chromatograph is shown in Figure 3. The heart of the gas chromatograph is the column,<sup>3</sup> as has been discussed. Physically it is a tube of about 1/4 inch in diameter, varying in length from 2 to 60 feet. It can be made of glass, stainless steel, copper, or aluminum. The columns used in this manual will be made from 2 to 4 feet of 1/4-inch copper tubing. It should be noted, however, that in some cases copper is objectionable because of its reactivity.

Such a column is packed with the solid support (Chromosorb P)\* which contains the liquid (stationary) phase. The procedure is outlined in Chapter III. Textbooks should be consulted for further details concerning the selection of the solid support and the stationary liquid.<sup>4</sup> The column (and detector and injection port) is usually placed in an oven to extend the range of application to liquid samples.

\*Chromosorb P is a registered trademark of the Johns-Manville Company for their calcined diatomaceous earth designed for chromatographic use. Many similar products are sold under a variety of trademarks.

An arrow in Figure 3 indicates where a sample can be introduced onto the column. This is usually done with a syringe through a self-sealing septum. The sample may be a gas, a liquid or a solid (often dissolved in a solvent). In the latter two cases it is desirable to vaporize the sample rapidly to a gas. This flash vaporization causes the sample to enter the column more or less as a highly concentrated plug of vapor. This is referred to as "plug" flow and is more desirable than a slow introduction of the sample as represented by the "exponential" flow.<sup>5</sup> A liquid sample will exhibit the undesirable exponential flow to some degree (depending on its vapor pressure) unless it is rapidly vaporized.

The injection port of a gas chromatograph is therefore usually heated above oven temperature to facilitate plug flow of the sample into the column. The effect this has on a separation has been demonstrated by several workers.<sup>6</sup>

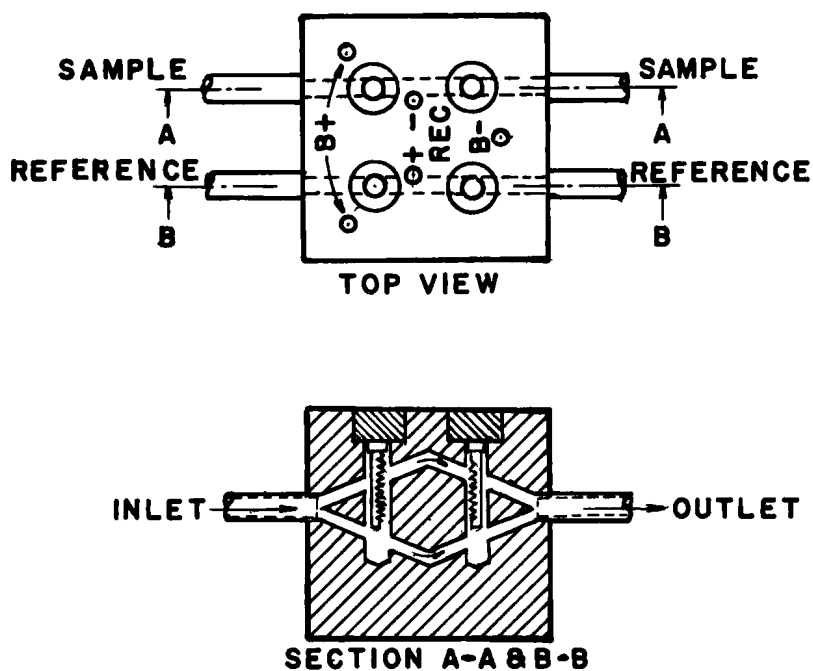
The carrier gas (mobile phase) must not dissolve in the stationary phase and hence is usually hydrogen, nitrogen, or one of the inert gases. It must also be pure and under pressure in order to be able to sweep through the packed column. It can be shown using the van Deemter equation, that heavier gases are preferred; but, when the detection system is thermal conductivity, these are not as desirable as lighter gases. In the United States, the gas most commonly used is helium.

The other component shown in Figure 3 is the detector. While this is not fundamental to the chromatographic process, it is a basic component in most gas chromatographs. Detectors can be divided into two types, integral and differential. The more important type is differential. Of the differential detectors, the most common one utilizes thermal conductivity and is the type used in these experiments. A differential signal is obtained because there are two detector elements, a reference and a sample (Figure 3). The output is always a ratio between the reference element (through which is passing carrier gas only) and the sample element (through which is passing carrier gas mixed occasionally with some sample).

A thermal conductivity (TC) detector\* consists of heat-sensing elements situated in a metal block which serves as a heat sink. The heat-sensing elements are either heated thermistors or resistance wires. The latter are more sensitive at high temperatures and are shown in Figure 4, a diagram of the TC cell supplied by Gow-Mac Instrument Company. The resistance of such a heated wire will change with temperature; its temperature will depend on the particular gas flowing in the cell. Different gases conduct heat away from the wire at different rates — i. e., they have different thermal conductivities. Some of these are shown in Table I. Therefore, if the gas is changed in a TC cell, the temperature and, hence, the resistance of the wire will change.

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\*A TC cell is also known as a katharometer.



DESIGN OF GOW-MAC HOT WIRE T.C. DETECTOR

FIGURE 4

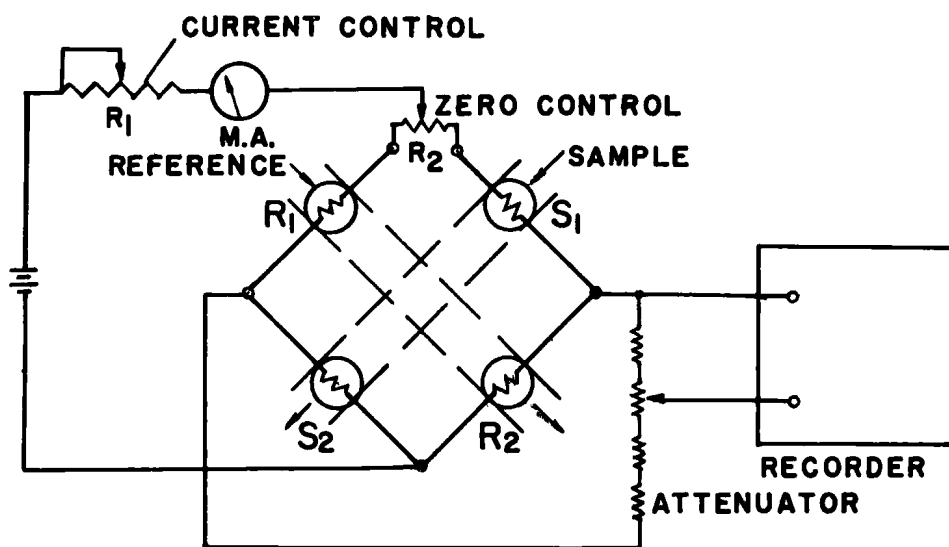
Table I

THERMAL CONDUCTIVITIES AT 0°C\*

Gas	TC x 10 <sup>7</sup> cal cm <sup>-3</sup> sec <sup>-2</sup> (°C cm <sup>-1</sup> ) <sup>-1</sup>	
	<hr/>	
Hydrogen	4160	
Helium	3480	
Oxygen	589	
Nitrogen	581	
Methane	721	
Methanol	345	
Benzene	220	
Chloroform	158	

\*Circular C564, U.S. Bureau of Standards.

To convert this resistance change to an output voltage, the reference and sample TC cells are incorporated into a Wheatstone Bridge Circuit as shown in Figure 5. Four filaments are used to increase the sensitivity. A current, regulated by variable resistor  $r_1$ , is supplied to the filaments by a DC source (e.g., battery) in order to heat them. With carrier gas flowing in both sides of the detector, the bridge is balanced using variable resistor  $r_2$ . Then when a sample is eluted, it changes the resistance of the sample filaments, the bridge is unbalanced, and the voltage so produced is indicated on a potentiometric recorder connected across the output.



**WHEATSTONE BRIDGE CIRCUIT FOR T.C. CELLS**

**FIGURE 5**

What is measured is the difference in thermal conductivity between the carrier gas in one side, and the carrier gas diluted with sample in the other. For maximum sensitivity this difference should be large, and hence the carrier gas used is preferably one with a thermal conductivity very different from most sample substances. Since most samples have low thermal conductivities, a high conductivity carrier gas like helium is preferred. Also, the detector will be more sensitive if there is a large temperature difference between the walls of the block and the filament. Although it would seem advisable to keep the block cool, it is usually

necessary to keep the detector block as hot as the oven, or hotter, in order to prevent condensation inside it.

The higher the concentration of sample in the sample side of the detector, the greater will be the difference signal. Therefore, the TC detector responds linearly with concentration and can be used for quantitative analysis.

The internal design of the cell is also critical. For fast response, the filaments should be placed directly in the flow. This results in an undesirable sensitivity to flow and pressure changes, so a compromise is effected (Figure 4).

Most commercial instruments are more complex than the one just described, and usually they permit more versatile operation. Nevertheless, a simple and adequate gas chromatograph can easily be built from available component parts. The construction of such an instrument is outlined in the next chapter.

This chapter has been only a very brief introduction to gas chromatography. The important terms and symbols used in this chapter are summarized in Table II.

Table II

TERMS USED IN CHAPTER I

Carrier gas (mobile phase)	The gas used to elute the sample as it passes through the column.
Stationary phase	In GLC, the liquid phase but not the solid support. In GSC, the active solid.
Solid support	The inert porous solid on which the liquid phase is sorbed.
Partition coefficient, $K$	$K = \frac{\text{weight of solute/ml stationary phase}}{\text{weight of solute/ml mobile phase}} .$
Retention time, $t_R$	The time required to elute a sample from the column, measured from the time of injection.
Adjusted retention time, $t'_R$	The time required to elute a sample from the column, measured from the air peak.
Flow, $F_c$	The outlet flow rate of carrier gas.
Retention volume, $V_R$	$V_R = t_R F_c$ . The volume of gas required to elute a sample from the column.
Adjusted retention volume, $V'_R$	$V'_R = t'_R F_c$ .
Gas holdup, $V_M$	The retention volume of a non-sorbed sample like air.

$$V'_R = V_R - V_M$$

Subsequent chapters provide information and experiments which will develop some aspects of gas chromatography more fully. However, it is expected that a book on this subject will be consulted for more complete information. A list of books is given in Appendix II.

## ADDITIONAL READING

With this introduction to GC, a good book in the field should be consulted, but short references of a more or less general introduction to GC are listed here in addition.

The reviews appearing every other year in the April issue of Analytical Chemistry should be consulted for recent developments. The most recent review is Anal. Chem., 34, 35R (1962). Other reviews can be found in Vols. 11 and 13 of Annual Reviews of Phys. Chem. and Vol. 2 of Chromatographic Reviews.

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