Dean Rood

The Troubleshooting and Maintenance Guide for Gas Chromatographers

Fourth, Revised and Updated Edition

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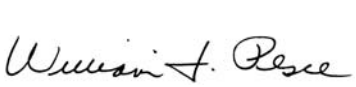

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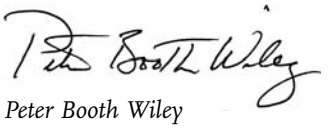

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Preface

Even though gas chromatography (GC) is considered a very mature and highly developed technology, advances continue to be made in the areas of hardware, electronics, software and columns. In some cases, these advances have reduced the occurrence of problems and made their detection easier and more certain. In other cases, greater complexity has been introduced with its own set of problems and solutions. Regardless of the age or complexity of the GC instrument, many of the same problems occur and the underlying causes are often the same. In addition, the guidelines and techniques used to care and maintain the instruments and columns are the same.

With this thought in mind, much of the core information in this edition does not differ significantly from the previous one; however, there are a number of noteworthy additions and enhancements. The majority of the figures are new and improved especially in the injector and detector chapters. A complete section on pressure and flow programmable injectors has been added. Due to its popularity and specific requirements, an Appendix on high speed GC using small diameter columns is new to this edition. Column, hardware, carrier gas and sample considerations and issues are presented in a concise and direct format to ensure successful high speed GC applications. Finally, an extensive Appendix on the basics of quantitative GC is new and relatively unique. This Appendix covers important quantitation definitions, calibration curves, the selection and use of quantitation techniques such as internal and external standards, and several standard preparation techniques. Numerous examples are provided to aid in understanding.

The information contained in this book encompasses nearly 25 years of in-depth experience in the field of GC along with the wisdom passed along from 1000's of personal interactions with GC practitioners around the world. It is often practical information mixed with a touch of theory such as presented and discussed within these pages that most often proves to be the most useful and helpful.

Sacramento, CA, March 2007 *Dean Rood*

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Intentions and Introduction

There already seems to be a number of excellent references on gas chromatography (GC), so why this book? Well, there are several reasons. There is a large number of gas chromatographs in use. If is often stated that gas chromatography is the most common instrumental analytical technique in routine use. The availability of easy to operate, affordable and feature laden instruments has made GC a powerful analytical technique accessible to nearly every laboratory.

Commercially available capillary columns of high quality have existed for about 25 years. For a number of reasons, many GC users are not extremely experienced in the practice of capillary gas chromatography. Many of these users do not possess a level of comprehension of the technique that allows them to prevent and solve many of the problems that commonly occur. Much of this comprehension comes from years of experience and the problems that accompany that experience. The combination of accessible instruments and capillary columns along with inexperienced users has created the need for practical information on the care, maintenance and troubleshooting of capillary columns and instruments.

One of the goals of this book is to provide practical information that will maximize both capillary column lifetime and the performance of the gas chromatographic system. The other goal is to provide an efficient and logical troubleshooting guide with the real intention to reduce or prevent performance breakdown problems from occurring. An in-depth knowledge of chemistry and chromatography (and other foreign languages) is not required. This book, in no shape or form, attempts to thoroughly explain every detail about capillary gas chromatography; it is intended as a practical guide so that the urge to hit the GC with a hammer as a last resort does not occur. In-depth technical information about GC techniques, instrumentation, specific applications and other gory details can be found in the books listed in the reference section.

Many generalizations and simplifications have been exercised to keep the information in a basic and widely digestible form. Again, this book is intended for the average GC user and not those whose entire life revolves around capillary gas chromatography. The topics covered within these pages are based on the most common problems, questions and misconceptions about capillary gas chromatography. These topics have been assembled and presented in an unique, practical and concise format suitable even for the most inexperienced GC user.

References to specific models of GCs and columns from specific manufacturers have been avoided where possible. Any differences are usually minor and often inconsequential in nature. The operating principles, proper techniques and practices, and underlying theory are the same regardless of the instrument or column manufacturer.

1
Introduction to Capillary Gas Chromatography

1.1
What Is Gas Chromatography?

In a broad sense, gas chromatography is a very powerful and one of the most common instrumental analysis techniques in use. When properly utilized, it provides both qualitative (i.e., what is it?) and quantitative (i.e., how much?) information about individual components in a sample. Gas chromatography involves separating the different compounds in a sample from each other. This allows the easy identification and measurement of the individual compounds in a sample. The compounds are separated primarily by the differences in their volatilities and structures. Many compounds and samples are not suitable for gas chromatographic analysis due to their physical and chemical properties.

1.2
What Types of Compounds Are Suitable for GC Analysis?

For a compound to be suitable for GC analysis, it must possess appreciable volatility at temperatures below 350–400 °C. In other words, all or a portion of the compound molecules have to be in the gaseous or vapor state below 350–400 °C. Another characteristic is the compound must be able to withstand high temperatures and be rapidly transformed into a vapor without degradation or reacting with other compounds. Unfortunately, this type of information about a compound is not readily available in references or other sources; however, some estimates and generalizations can be made from the structure of the compounds.

Compound structure and molecular weight can be used as indicators of potential GC analysis suitability. Compounds with very low volatilities are not suited for GC analysis since they do not readily vaporize. Compound boiling points are not always good indicators of volatility. There are many high boiling compounds that can be analyzed by GC. As a general rule, the greater the molecular weight or polarity of a compound, the lower its volatility. Both factors have to be considered. For example, a large, non-polar compound may be more volatile than a small, polar compound. Also, one polar group on a large molecule has less of an influence than one polar group on a small molecule.

Hydrocarbons with molecular weights over 500 are routinely analyzed using standard GC systems, and hydrocarbons with molecular weights over 1400 have been easily analyzed using the properly equipped GC and type of column. The presence of polar functionalities such as hydroxyl and amine groups severely decrease compound volatility. Some small molecules such as sugars and amino acids can not be easily analyzed by GC due to the large number of polar groups.

As a rule, inorganic compounds are not suitable for GC analysis. Metals and salts do not possess the required volatility. Many organo-metallics have sufficient volatility for analysis due to the high organic content of these molecules. Most organic compounds are suitable for GC analysis; however, there are many exceptions. Many biomolecules and pharmaceuticals are thermally sensitive and degrade at the temperatures used in gas chromatography. Some compounds react with the materials used in gas chromatographs and columns and can not successfully analyzed by GC. There are no realistic, absolute guidelines that can be used to determine whether a compound can be analyzed by GC. Overall, it has been estimated that only about 10% of all compounds can be analyzed by GC.

1.3 The Basic Parts of a Gas Chromatograph

A gas chromatographic system is comprised of six major components: gas supply and flow controllers, injector, detector, oven, column, and a data system (Figure 1-1). In most cases, the injector, detector and oven are integral parts of the gas chromatograph; the column, gases and recording device are separate items and are often supplied by a different manufacturer. All of the components are further described in individual sections or chapters with the exception of the oven and recording devices.

1.3.1 Gas Supply and Flow Controllers

High purity gases are supplied from a pressurized cylinder or gas generator. Pressure regulators on the cylinders or generators control the amount of gas delivered to the gas chromatograph. Flow controllers or pressure regulators in the gas chromatograph control the flow of the various gases once they enter the instrument.

The column is installed between the injector and detector. Gas at a precisely controlled flow is supplied to the injector; this gas is called the carrier gas. The carrier gas flows through the injector and into the open tubular column. The gas travels the length of the column and exits through a detector. To function as desired, most detectors require specific gases at the proper flow rates.

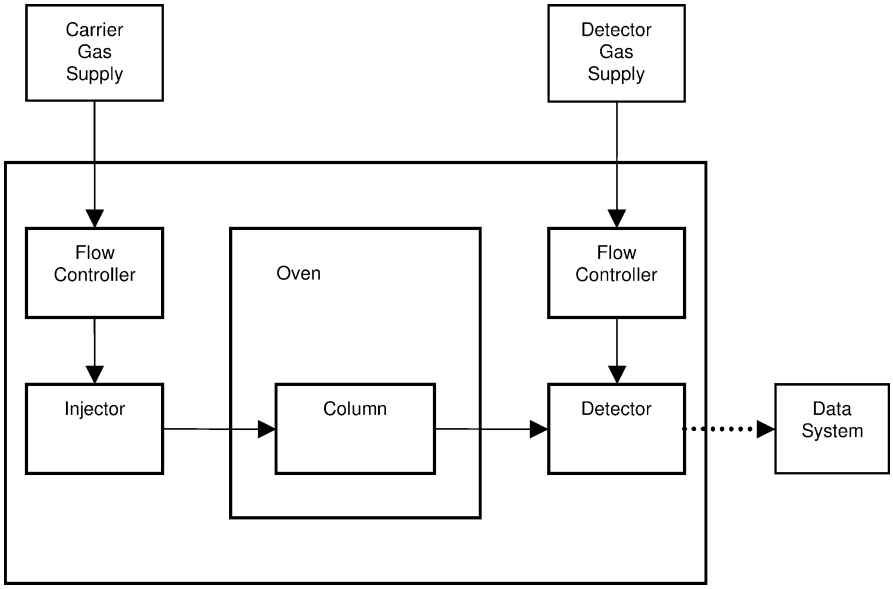


Figure 1-1 Block diagram of a typical gas chromatograph. Solid arrows denote gas flow paths and dotted arrows denote electronic signal flow paths.

1.3.2 Injector

The injector introduces the sample into the open tubular column. The injector is a hollow, metal cylinder containing a glass liner or insert. The column is inserted into the bottom of the injector so that the column end resides in the lower region of the glass liner. A liquid, or sometimes a gas, is introduced into the injector through a resealable septum using a small syringe. The injector is heated to 100–300 °C, thus any volatile sample components are rapidly transformed into a vapor. The carrier gas mixes with the vaporized portion of the sample and carries the sample vapors into the column.

An on-column injector deposits the sample directly into the column without a vaporization step and it is used for select types of samples. In some cases, non-syringe techniques utilizing specialized equipment or devices (e.g., purge and trap, headspace, and valves) can be used to introduce a sample into a column.

1.3.3 Capillary Column and Oven

The column resides in an oven whose temperature is accurately controlled. If unimpeded, vaporized compounds move through the column at the same rate as the flowing carrier gas. However, the interior walls of columns are coated

with a thin film of polymeric material called the stationary phase. This stationary phase impedes the movement of each compound down the column by a different amount. This behavior is called retention.

The length and diameter of the column, the chemical structure and amount of the stationary phase, and the column temperature all affect compound retention. If all of these factors are properly selected, each compound travels through the column at a different rate. This makes the compounds exit the column at different times. As each compound leaves the column, its presence and amount are measured by the detector.

1.3.4 Detector

As each compound exits the column, it enters the detector. The detector interacts with the compounds based on some physical or chemical property. Some detectors respond to every compound while others respond only to a select group of compounds. The interaction generates an electrical signal whose size corresponds to the amount of the compound. The detector signal is then sent to a recording device for plotting.

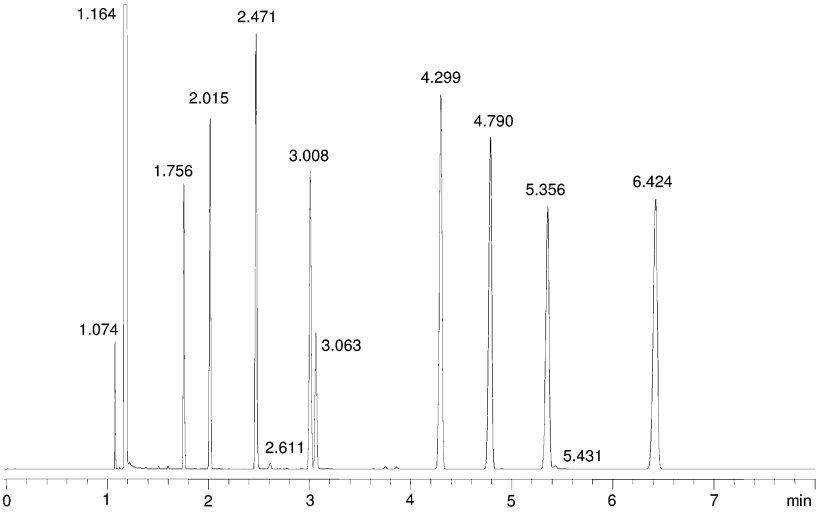
1.3.5 Data System

The recording device plots the size of the detector signal versus the time elapsed since sample introduction into the injector. The plot is called a chromatogram and appears as a series of peaks (Figure 1-2). Except very old recorders, some type of report is provided by the data system.

The most common data recording devices are computer (PC) based. Older GC systems may use an integrator or a strip chart recorder which produce printed versions of the chromatogram and report with little or no data storage and recall capability. PC based data system are extremely powerful and offer numerous data plotting, reporting and storage options, thus their popularity. Most computer data system can also control and automate the operation of the GC.

1.4 The Chromatogram

In the ideal situation, each peak in the chromatogram represents a single compound in the sample. It is not unusual for more than one compound in a sample to interact with the column in the same manner, thus each compound has the same retention. This results in a single peak that represents more than one compound (complete co-elution). In some cases, the interactions are very similar, but not identical. This results in two peaks that partially overlap (partial co-elution). Using the proper column and operating conditions minimizes dual



Retention Time	Area	Height	Width
1.074	19485	38020	0.0084
1.164	36605766	36035875	0.0167
1.756	12011	14998	0.0133
2.015	17933	18513	0.0153
2.471	24445	23052	0.0164
2.611	405	282	0.0224
3.008	20025	15747	0.0196
3.063	9160	7206	0.0204
4.299	36815	19872	0.0288
4.790	36378	17617	0.0329
5.356	31780	13923	0.0354
5.431	396	178	0.0340
6.424	40605	14352	0.0402

Figure 1-2 Chromatogram and report.

peak identities or overlapping problems, but there are cases where complete separation is not possible.

Each peak in the chromatogram is assigned a retention time. It is the time required for a compound to travel through the column. The data system usually calculates and prints the retention times and size for each peak on the chromatogram or in a table (Figure 1-2); additional information may also be included in the report table. Retention times are usually reported in minutes and the peak size in an unitless area or height value.

Identifying the compounds corresponding to each peak in the chromatogram is accomplished by comparison to a previously generated reference chromatogram. A prepared solution containing known amounts of each compound (commonly called a standard) is analyzed to obtain their respective retention times and peak

sizes. Using the same column and GC parameters, the sample is analyzed. If any of the peaks in the sample have the same retention times as those in the standard, there is a good probability that the sample contains one or more of the compounds. If the peaks in the sample do not correspond to those in the standard, the sample does not contain any of the compounds.

To determine the amount of a compound in the sample, the size of its peak is used. The size of a peak is proportional to its amount in the sample or standard. Since the standard contains a known amount of each compound, the peak sizes can be used as a reference. The size of the peak in the sample is compared to the size of the corresponding peak in the standard. A simple ratio is set up for quantitation. For example, if the peak in the sample is two times larger than the peak in the standard, the injected portion of the sample contains two times the amount of the compound than the amount known to be present in the standard.

There are numerous situations where peak misidentification or quantitation errors can occur. Adhering to good GC practices will minimize the occurrence of these types of errors. Additional information on quantitative GC can be found in Appendix F.

1.5 The Mechanism of Compound Separation

How does the column work? What happens inside the column? How do the compounds move through the column? Why do some compounds stay in the column longer than others? How does the sample get into the column? These are some of the most basic questions asked about gas chromatography. Knowing the answers does not automatically make a chromatographer produce better results, but the knowledge is very valuable in solving and preventing problems, selecting columns, and understanding unexpected results. Complicated discussions involving thermodynamics and molecular interactions are necessary to fully answer these questions. Fortunately, comprehension at this level is not necessary to become an excellent chromatographer. A basic understanding of the concepts, and not the intricate details, provides a chromatographer with all of the information necessary to produce the most consistent, trouble free and best results.

1.5.1 A Simple Description of the Chromatographic Process

The separation of a sample into its individual compounds by a capillary GC column can be described by a very simple concept. The sample containing a mixture compounds enters the column and collects in the front of the column (Figure 1-3a). Then the molecules of each compound start to collectively move down the column at a different rate (Figure 1-3b). The fastest moving molecules reach the end of the column first, enters the detector, thus corresponding with the first peak in the chromatogram (Figure 1-3c). The next fastest compound molecules follows,

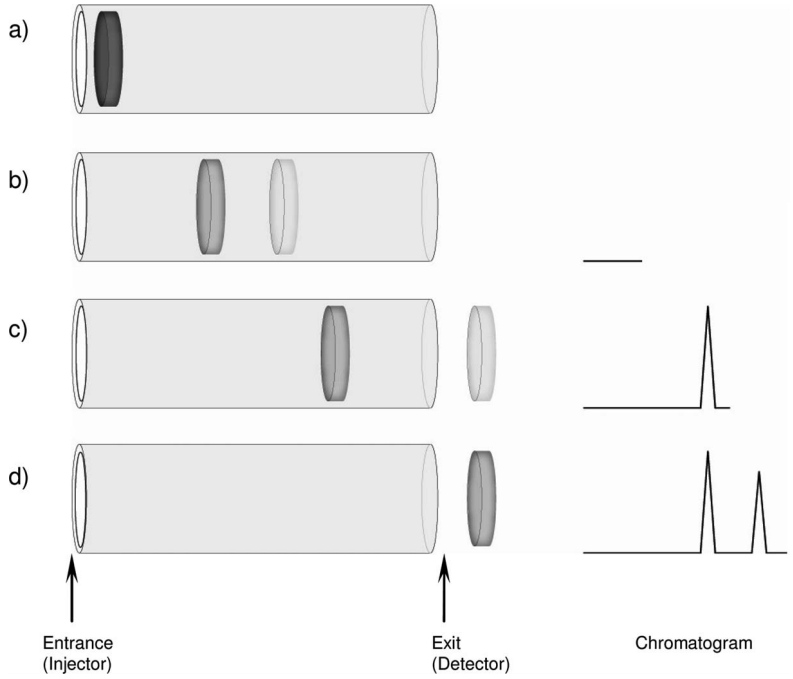


Figure 1-3 Separation of the sample in the column.

and this process continues until all of the remaining compounds have left the column (Figure 1-3d). Since the compounds each leave the column at different times, they are separated. Any compounds that travel through the column at the same rate are not separated and have the same retention times.

1.5.2 A Detailed Description of the Chromatographic Process

Capillary columns are composed of three distinct parts. The tubing is fused silica (glass) with an outer protective coating. The inner walls are coated with a thin film of polymeric material called the stationary phase. The sample compounds interact with the stationary phase, and this interaction is responsible for the separation properties of the column.

Once in the column, the molecules for each compound distribute between the mobile phase (carrier gas) and the stationary phase (Figure 1-4a). Molecules in the mobile phase move down the column; molecules in the stationary phase do not move down the column (Figure 1-4b). The carrier gas transports the compound molecules down the column. Simultaneously, the molecules are moving in a random motion. Eventually, each molecule comes into contact with the stationary phase. Each one enters the stationary phase when this occurs. For every molecule entering the stationary phase, another one leaves the stationary phase to take

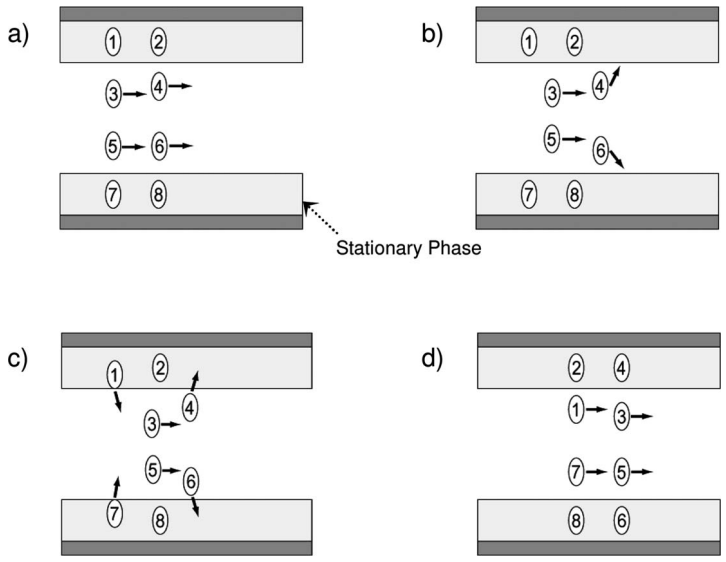


Figure 1-4 Movement of molecules down the column. Longitudinal cross-section view of a column.

its place in the mobile phase (Figure 1-4c). This maintains the same overall distribution of the molecules between the two phases. The process of exchange between the phases is repeated thousands of times for each molecule. The net effect is the movement of the molecules down the column (Figure 1-4d).

The rate of molecule movement down the column depends on the distribution of the molecules between the stationary and mobile phases. The greater the percentage of molecules in the mobile phase, the faster the molecules travel down the column. This results in a short residence time for the molecules in the column and a short retention time for the corresponding peak. Separation of two compounds occurs when the distribution of their molecules between the stationary and mobile phases are different. If the distributions are the same, co-elution occurs.

The distance or time between the various groups of molecules (with each group representing one compound) as they exit the column determines the amount of separation between the peaks. While this separation distance is important, there is more to chromatography than just separation. The length of column occupied by the molecules for each compound is critical. A narrow band of compound molecules occupying a short length of column is desired. If the width of the molecule bands is narrow, a large separation between the band of molecules is not needed to prevent overlap of the different compound molecules (Figure 1-5a). If the width of the molecule bands is broad, the same amount of separation results in an overlap of the different compound molecules (Figure 1-5b). When the molecule bands are broad, greater separation is need to prevent overlapping of the molecule bands (Figure 1-5c).