Process
Analyzer
Technology

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To Julia, Stephen, and Nicholas,
with love and appreciation
for their support and encouragement.

Preface

Process stream analysis, the use of analytical instrumentation for continuous on-line measurement of the quality of industrial process streams, is an important part of the wide field of process instrumentation. The technique first became important in the process industries in the late 1950s and early 1960s. Since then, the technology has expanded enormously and continues to do so.

Process analyzers, while having a chemical basis in the theoretical sense, embody the practical electronic aspects of process instrumentation. Consequently, the analyzer engineer must have an in-depth knowledge of both chemistry and instrumentation, a rather unusual combination.

Successes that can be attributed to the use of process analyzers include savings in production, product giveaway, operating manpower, and energy conservation. In fact, many of today's complex processes could not operate at optimum efficiency without analyzers. Although the theoretical aspects of analytical techniques used in the plant laboratory are the subject of many excellent textbooks, comparatively few cover the subject of on-line process analyzers in detail, especially from the practical application standpoint.

Handbook of Process Stream Analysis, first published in 1973 tried to close this rather large gap and make life a little easier for the field analyzer engineer. Since 1973, we have seen many significant changes in this area of technology. The advent of the microprocessor in the early 1970s and its subsequent commercialization created a major revolution in the instrument world, leading to the programmable controllers and digital instrumentation systems used so extensively today. Likewise, the microprocessor has had a major impact on the design of process analyzers, providing for the first time the capability for carrying out multianalyzer control, internal self-diagnostics, report writing, and digital data transmission. The extensive use today of computers for advanced process control and optimization has markedly increased the importance of process analyzer technology, since it is essential that process stream quality data be available on a timely basis for use in process control algorithms.

This major revision, which includes the addition of several new chapters and reorganization of others, surveys the process analyzer scene today, at the same time maintaining an emphasis on practical aspects of the subject. The title of the book has been changed for two reasons. First, in view of the significant increase in the volume of material, it is no longer a "handbook" but a "reference book." Second, and more important, I feel strongly that the subject has now progressed in stature sufficiently to justify calling it a technology in its own right.

Although process gas chromatographs (GCs) are still the most extensively used of the chromatographic techniques for on-line analysis, liquid chromatography is gradually becoming accepted as an on-line analytical technique. In addition, capillary gas chromatography (GC^2) is now finding extensive use in on-line applications. For this reason, Chapter 1 is now titled "Chromatography" and includes information on these new areas, as well as a deeper treatment of column engineering, from a practical sense.

Spectroscopy has probably seen as much change as any other analytical technique in recent years. It is a wide and varied subject, each individual technique almost a specialist technology in its own right. During the past decade, we have also seen major developments in on-line spectrometric analyzers; techniques such as mass spectrometry and x-ray fluorescence, hitherto restricted to the laboratory, have now migrated into the on-line process field. Such development is still proceeding today and will almost certainly continue in the future. Chapter 10 has thus been expanded to reflect this situation.

The subjects of air quality and water quality monitoring have become extremely important from an industrial/environmental viewpoint, with interest and concern being shown by academia, industry, and government worldwide. A separate chapter has been devoted to each of these subjects, the complexity and variety of water quality monitoring being shown by the length of the chapter. The subject of pH measurement has been included here, since its primary application is in water quality monitoring.

In recent years there has been an increased awareness of the fundamental importance of the sample handling system and its vital contribution to the overall performance of the total analyzer system. Chapter 20 therefore deals with the subject in far greater detail than before, with an emphasis on the practical aspects. Again, because of their important contributions to overall performance, the subjects of design and installation, calibration, maintenance, and performance evaluation of analyzer systems are dealt with in new chapters. A separate chapter is also devoted to analyzer data systems in view of its importance in today's world of computer control.

Combustion efficiency monitoring and control has also become an important aspect of process plant operations, from energy conservation, environmental, and operating efficiency standpoints; a separate chapter is devoted to the subject.

Those involved in process analyzer technology today agree that the main

justification for installing on-line process analyzers is their contribution to efficient control and optimization of industrial processes. Therefore, no book on process analyzer technology would be complete without mentioning this very important subject. Rather than trying to cover the thousands of industrial applications in which analyzers are used, in Chapter 24 I have dealt briefly with major applications in the petroleum and petrochemical industries, with which I am intimately familiar. Many of the concepts outlined here will apply equally well to analyzer applications in other industries. The subject of pH control, unique in the process control field, is also dealt with in Chapter 24.

The list of manufacturers' names and addresses is missing from this revision for two reasons. First, the list would be much longer than ten years ago. Second, and more important, documentation in the process analyzer area has improved so much in the past few years that I considered it unjustified. I recommend two sources of information to the reader:

- The Instrument Society of America (ISA) *Directory of Instrumentation,* which names parent companies, and U.S. and international representatives. No analyzer engineer should be without this book.
- *Anadata,* published by Xertex Corporation, United Controls Division, which lists commercially available process analyzers in specification form, by measurement parameter. Again a useful document, but a full-time occupation for Xertex!

Once again I am indebted and wish to express my thanks and appreciation to the many process analyzer manufacturers and analyzer systems specialists in the United States, the United Kingdom, and Europe for their interest in and support for this project and for their permission to publish illustrations, photographs, and specification data concerning their equipment. Without their help it would not have been possible to write this book. Unfortunately, it would also have been impossible to include every process analyzer commercially available today; some arbitrary selection had to be made. Therefore I wish to express my regrets and apologies to any manufacturer whose equipment is not covered in any great detail, or not at all. I have attempted, at the end of each chapter where appropriate, to cover in a summary table all process analyzers of a specific type. It is a fact of life, based on the rapidity with which technology is advancing today, that these tables may be incomplete.

I also wish to acknowledge the Exxon Chemical Company for the inclusion of material in Chapters 1 and 20. This material has been used successfully over the past few years, as part of a training course for Exxon's analyzer engineers and maintenance technicians.

Finally, and by no means least, a word of thanks to microprocessor technology. With the help of a personal computer and an excellent word process-

ing software package, many hours of hard labor were saved in preparing the written script in a form that would not have been possible on a conventional electronic typewriter.

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April 1986

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Chromatography

1.1 INTRODUCTION AND HISTORICAL BACKGROUND

Chromatography, a physical process by which a mixture of chemical compounds may be separated, has rapidly become one of the most successful analytical techniques, both in the laboratory and for on-line process analysis.

The chromatographic process works in a discontinuous manner, similar to a batch distillation. A small sample is taken and the individual components of the mixture are retained on the column to different extents, as if they were distilled off one by one. Because of its nature, the separation normally takes from 1 to 10 min. As the components emerge from the process, they are individually measured and reported.

Note that this is a *physical* process; no chemical change is involved. In practice we are usually talking about gases simply dissolving in liquids or being attracted to the surface of solid materials.

The invention of chromatography is attributed to the work of the Russian biochemist Tswett [1], who was interested in the green coloring matter found in plants. In 1903 he reported the separation of different plant pigments, which were visible as colored bands when a solution of chlorophyll was washed by a suitable solvent through a tube containing an adsorbent such as powdered chalk. In a paper published in 1906 [1], Tswett named this technique "chromatography" (literally, color writing).

Not a lot more was heard about chromatography until a technique known as partition chromatography was introduced by Martin and Synge [2] in 1941, using a liquid moving phase. The method was further developed by Martin and his co-workers to a special form of the technique known as paper chromatography. For this highly successful contribution to the field of biological and medical research, Martin and Synge received the Nobel Prize in 1952.

The possibility of using a gaseous mobile phase instead of a liquid phase was mentioned in the 1941 paper of Martin and Synge, but there was no follow-up of this suggestion. Eventually, James and Martin [3,4] started to elaborate on it in 1949 and the results were presented at the Analytical Chemistry Congress at Oxford, England, in 1952. One of the characteristic features of the method described was the very small samples used for estimations.

The simplicity and analytical power of the method were instantly recognized. Because of its promise, the technique received much attention and its development was very rapid. Since 1952, growth in both the theoretical and practical aspects of the technique has been tremendous. Not only has it provided a simple solution to many complex routine laboratory analyses, but, as we shall see later, it has provided an efficient method by which industrial processes may be monitored and controlled on line.

Chromatography is now recognized as one of the most important tools of

analytical and industrial chemistry, with the great advantage that separation and quantitative estimation of components in a sample may be carried out rapidly in a single operation.

1.2 TYPES OF CHROMATOGRAPHY

The basis of chromatography is that a discrete sample of the mixture to be analyzed is transported through a static medium by a moving carrier. The various types of chromatography are classified by the nature of the carrier (or *mobile phase*) and the nature of the static medium (or *stationary phase*). There are therefore four practical possibilities:

Mobile Phase	Stationary Phase	
Liquid	Liquid	LLC
Liquid	Solid	LSC
Gas	Liquid	GLC
Gas	Solid	GSC

Tswett's early work is an example of liquid-solid chromatography.

In this chapter we are primarily concerned with gas-liquid, gas-solid and liquid-liquid chromatography. The last of these is currently in the same phase of development as GLC was in the early 1960s as far as on-line process analysis is concerned. The technique is beginning to make itself felt in the specialty chemicals industry now that component reliability is increasing. It remains to be seen whether LLC will become as popular as GLC.

1.3 THE BASIC GAS-LIQUID CHROMATOGRAPH

The basic components of a simple gas-liquid chromatograph are shown in Fig. 1.1. The *carrier gas*, which is normally nitrogen, helium, or hydrogen, continuously flows through the *column*, where the separation occurs. Samples, which can be either gas (typical volume 0.5 ml) or liquid (typical volume 1μl), are periodically injected into the carrier gas by a specially designed *sample injection valve*. Liquid samples must vaporize immediately on injection and pass through the system in the vapor phase.

After separation, the components emerge from the column and pass to the *detector*, which produces a signal proportional to the instantaneous concentration of sample components in the carrier gas. When this signal is graphed against the time from sample injection, the characteristic *chromatogram* record is obtained.

Since the sample volume, columns and detector are temperature-dependent in operation, they are installed in a temperature-controlled enclosure known as the *oven*.
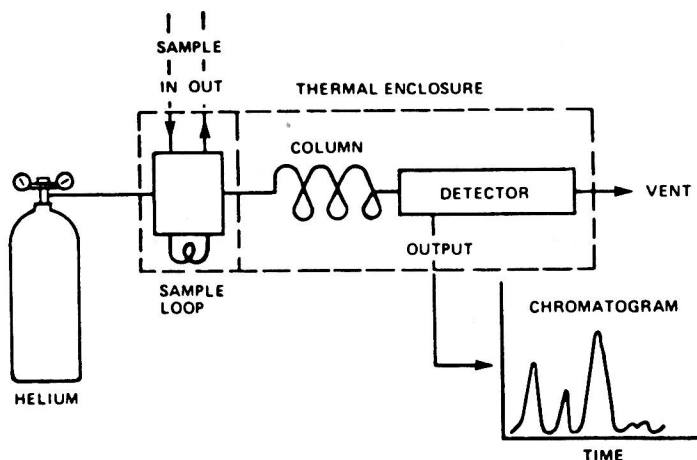
FIGURE 1.1   The basic gas-liquid chromatograph.

1.4   BASIC THEORY OF CHROMATOGRAPHY

The following discussion of the chromatographic process is a simplification, but it gives an insight into what actually occurs inside the chromatographic column. Although gas-liquid chromatography is considered initially, the general principles apply also to the other types previously described.

To understand gas-liquid chromatography, we need to know how gases and liquids interact. Consider what happens when a glass of water is gently heated. Long before the water boils, small bubbles of air appear and cling to the sides of the glass. This illustrates the basic fact that *gases dissolve in liquids*. Clearly, gas solubility decreases as the temperature increases.

Pressure also has an effect on gas solubility, as may be seen by opening a bottle of champagne or a can of beer. More important, the amount of carbon dioxide dissolved far exceeds the amount of air that can be dissolved in water. This second important fact, that *different gases dissolve to different extents in the same liquid,* is the fundamental basis of gas chromatography.

To explain the mechanism, we start by considering how a single gas behaves in a model of the chromatographic process. Imagine a liquid and some air in a completely closed vessel, as shown in Fig. 1.2*a* and then think what would happen if some carbon dioxide (or other gas) were added to the air. The carbon dioxide starts to dissolve, but soon reaches a point where the tendency for more to dissolve is exactly balanced by the tendency for some of the already dissolved gas to come out of solution. This equilibrium condition is shown in Fig. 1.2*b*.

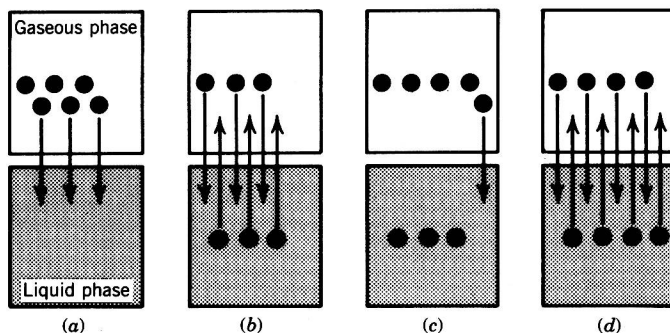The ratio of the amount of carbon dioxide in each phase at the equilibrium

FIGURE 1.2 Static model of the chromatographic process. (*a*) CO_2 molecules introduced; (*b*) dynamic equilibrium; (*c*) more CO_2 introduced; (*d*) new equilibrium. (Courtesy of the Foxboro Company)

point is known as the partition coefficient (K), where

$$K = \frac{\text{conc. of gas in the liquid phase}}{\text{conc. of gas in the gas phase.}}$$

The actual value of K is an indicator of how soluble the gas is in the particular liquid phase. In Fig. 1.2 it is assumed that $K = 1$, that is, half the gas is dissolved and half remains in the gas phase.

From the preceding discussion we know that the solubility will be constant if the pressure and temperature remain constant. Therefore, if more carbon dioxide is added to the system (within certain limits), half of it will dissolve to re-establish the equilibrium shown in Fig. 1.2*d*.

1.4.1   A Model of the Chromatographic Process

So far, we have considered only the static equilibrium of a gas-liquid system. However, in a gas-liquid chromatograph the carrier gas is moving continuously over the stationary liquid phase. How can we study what is happening when the situation in the column is continuously changing? Admittedly this is not easy; even complex theory does not completely explain the process. However, we may achieve a good understanding by the simple expedient of breaking down the movement into a series of separate steps, rather like taking a motion picture and playing it back frame by frame. We can then look closely at what is happening at each stage of the action.

In Fig. 1.3 it is assumed that the column is divided into a series of closed compartments, similar to those considered in Fig. 1.2. For the moment we will restrict our interest to what happens if a pure gas, such as carbon dioxide, is injected into the carrier gas. The flowing carrier gas transports the sample into the first "compartment." At this point we will imagine that the
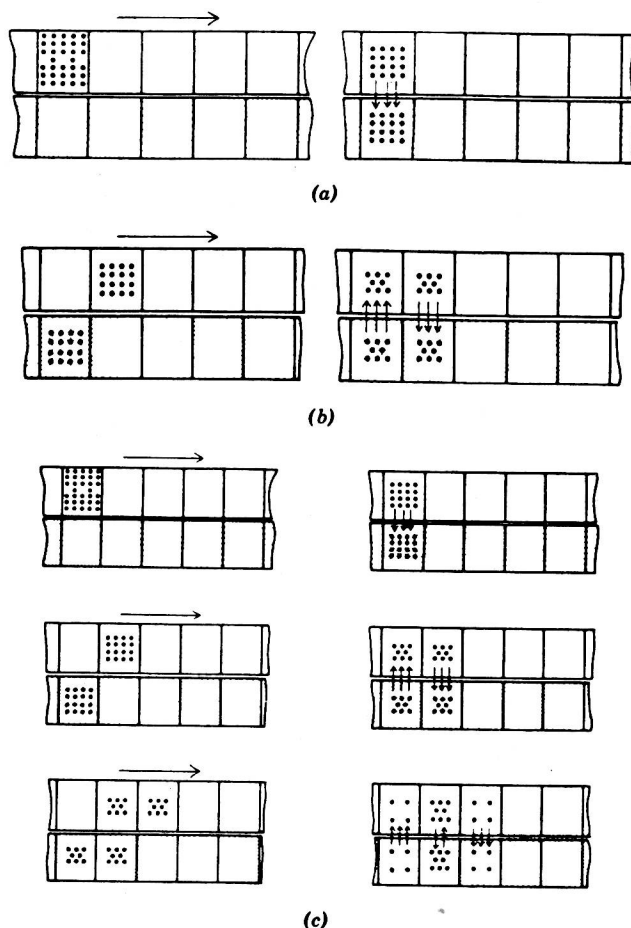
FIGURE 1.3 Gas-liquid equilibria. (*a*) First equilibrium; (*b*) second equilibrium; (*c*) third equilibrium. (Courtesy of the Foxboro Company)

carrier gas flow is stopped and the compartments sealed. We now have a situation similar to the previous assumption; equilibrium will soon be reached with half the sample dissolved in the liquid phase and half remaining in the gas phase, as shown in Fig. 1.3*a*. Once equilibrium is attained, assume that the carrier gas flow is re-established, allowed to move a distance equivalent to one compartment, and stopped again for examination. The sample in the gas phase is carried along with the carrier into the second compartment, disturbing the equilibrium and leading to the formation of two new equilibria as shown in Fig. 1.3*b*.

If the process is allowed to continue in this start-stop fashion, during each movement the leading edge of the component band will encounter a fresh liquid phase and divide by two, while the trailing edge of the band, dissolved
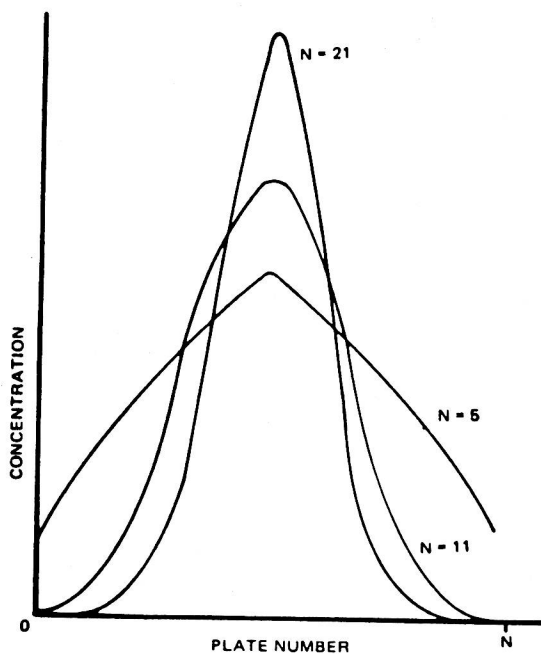
FIGURE 1.4 Graphical presentation of 5, 11, and 21 equilibria.

in the liquid, will be flushed by clean carrier gas and similarly divide by two. Intermediate compartments will reach equilibrium by partial readjustment.

Fig. 1.3c shows the development of the first five equilibria and these results are presented graphically in Fig. 1.4, together with the results that would have been obtained if the process had been continued for 11 and 21 steps. Note that in each case the sample is distributed through all the compartments, with the maximum amount at the center. For large numbers of equilibria, however, the amount of sample in the outside compartments is negligible and the distribution at the center begins to resemble the characteristic shape of a chromatogram peak.

1.4.2   Relationship to Theory

The description just given is very close to what actually happens in a chromatographic column. The curves model the distribution of a component along the column after the passage of the carrier gas. Clearly, the width of a peak in this model is dependent on the number of compartments into which the column is divided. Had we continued the process through 100 compartments, the peak would have been quite narrow.

The idea of separate compartments is, of course, purely imaginary, but it does explain chromatographic behavior reasonably well. It is possible to
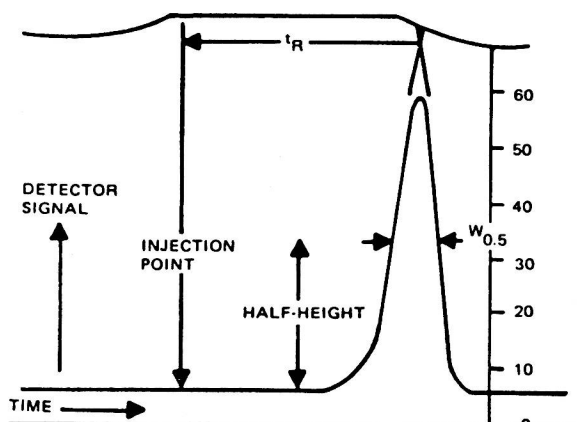
FIGURE 1.5   Data required for calculation of column efficiency.

calculate the number of theoretical compartments from the actual chromatogram peaks obtained; the measurements necessary to do this are shown in Fig. 1.5. The compartments are known as "theoretical plates," analogous to the theoretical plates of a distillation column. The number of theoretical plates (N) is calculated from the chromatogram measurements by the expression

$$N = 5.54(t_R/W_{0.5})^2$$

where t_R = retention time from injection and $W_{0.5}$ = peak width at half height.

Although this is only a discontinuous model of a continuous process, it is nevertheless a powerful and well used one. Most of the advanced theory is concerned with how other operating factors affect the number of theoretical plates. This is because the theory that helps us to design columns with more "plates" will lead to narrower peaks and more efficient separation of components. For this reason, N is used as a measure of column efficiency.

1.4.3   Achieving Separation

The preceding discussion has shown how a peak is formed as the component is carried through the column. The peak may be narrow or wide according to how many times it has reached equilibrium during its passage. However, this idea of theoretical plates does not explain how separation is obtained. Note that in Fig. 1.4, where component distribution is shown for 5, 11, and 21 plates, the peak *position* does not change. This is because an assumption was made that $K = 1$. For more soluble gases (K greater than 1), the peak would be left of center, whereas for less soluble gases (K less than 1), the peak would be right of center, as shown in Fig. 1.6.
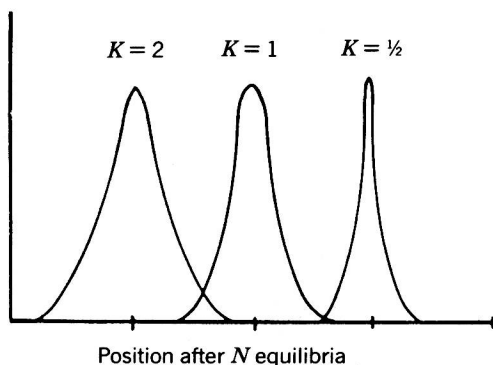
Position after N equilibria

FIGURE 1.6 Principle of chromatographic separation.

This result is to be expected. More soluble gases will be retained longer on the column than those that are less soluble. Thus, it is simply the solubility of the gas in the liquid that determines peak position in the chromatogram and not some mysterious chemical process.

Resolution as used in chromatography is defined as the distance between two peaks in the chromatogram and describes how column efficiency determines their width. Both of these factors are important in obtaining complete resolution and will be discussed in more detail later.

1.4.4 Gas-Solid Chromatography

The previous discussion dealt with gas-liquid systems. In gas-solid chromatography there is neither liquid nor solution. Instead, the carrier gas is in contact with a solid of high surface area. Sample gases are attracted to such surfaces and reach an equilibrium very much like that shown in Fig. 1.2.

Thus, the mechanism is essentially the same, with the "degree of attraction" to the surface replacing solubility. Gas-solid interactions are very strong and the technique is generally only useful for the common inorganic gases and light hydrocarbons. In addition, these solids irreversibly retain water and other substances, which leads to changes in their retention behavior. For these reasons, gas-solid chromatography is used in process gas chromatographs only when no other way of effecting the desired separation can be found.

1.5 LIQUID CHROMATOGRAPHY

Liquid chromatography has been known even longer than gas chromatography, but its use has largely been confined to the laboratory until quite recently. As mentioned previously, process liquid chromatography is now at about the same stage as process gas chromatography was 20 years ago.