handbook of PROCESS STREAM ANALYSIS

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HANDBOOK OF PROCESS STREAM ANALYSIS

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Author's Preface

Process stream analysis, an important part of the very wide field of instrumentation, has expanded enormously in recent years and is still continuing to do so.

Process analysers, whilst having a chemical basis in the theoretical sense, embody the practical aspects of process instrumentation. Important criteria from an operational standpoint are reliability, accuracy and the ability to provide operating personnel with continuous information on process stream quality. At present, on-line analytical instruments are accepted as a necessary part of process instrumentation. Large savings in production, quality and operating manpower are attributed to their use, as a result of which certain complex industrial processes cannot operate at optimum efficiency without them.

Although the theoretical aspects of analytical methods, as used in the laboratory, are the subject of many excellent textbooks, few deal with instruments for on-line process analysis and, if there is a mention, the subject is covered all too briefly.

In this book I have attempted to survey modern analytical instrumentation as designed for continuous on-line operation, with an emphasis on the practical (applicational) aspects. At the same time, however, the theoretical basis of the techniques is covered in sufficient detail to give the reader a sound, fundamental working knowledge of these techniques.

The text is intended to provide useful information for practising chemical engineers, industrial analysts, instrumentation and control engineers, contractors, designers etc. in a wide variety of industrial fields and for senior undergraduates who are specializing in control, chemical or electrical engineering. In addition, the information will be of value to instrument construction and maintenance personnel.

Each chapter deals with a particular analysis technique (e.g. specific gravity, viscosity, vapour-phase chromatography etc.). Initially the theoretical basis of the technique is discussed, followed by a description of the basic laboratory method of measurement (where applicable) and how this method has been adapted or modified to provide a basis for on-line process analysis. There then follows a description of the main type of process analysers commercially available, giving details of operating principle and performance characteristics. The chapter closes with a survey of the potential industrial applications. The final chapter deals with the subject of sample handling system design, a very

important aspect of process analyser systems design. At the end of the book there is a set of specification tables, listing the operational and performance data for all process analysers described in the text. It has not been possible to include descriptive information for every process analyser currently available commercially. This would have been an impossible task, in view of the rapid developments that have taken place in this field. Nevertheless, the text covers operating principles and specifications of over 200 of the most important instruments.

I am indebted to a large number of the instrument manufacturing companies in the United Kingdom, Europe and the United States of America for their interest in this project and their permission to reproduce illustrations and photographs. Without their advice and co-operation this book could not have been written. My thanks also go to Miss Janet Phelan for her invaluable help in preparing the typescript and to Dr R. A. Chalmers for his excellent advice and painstaking review of the complete manuscript.

Kenneth J. Clevett
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Chapter 1

Vapour Phase Chromatography

1.1 Introduction

The term chromatography is used collectively to describe a group of methods which possess a number of common features, although, at first sight, they may appear to have little connection. Vapour phase chromatography, the subject of this chapter, has rapidly become one of the most successful analytical techniques in spite of its relatively recent introduction.

All chromatographic techniques involve the physical separation of components of a sample by transport through a column (or the equivalent of a column). The sample may be a liquid or a gas (vapour). The column contains a substance, known as the stationary phase, which may be either a solid adsorbing agent, or a liquid partitioning agent. The sample is transported through the column by the mobile phase, which may be either a gas or a liquid. When the stationary phase is a solid the technique is known as adsorption chromatography. Four fundamental combinations may therefore be obtained, as shown in Table 1.1. In this chapter we shall be concerned with only one of these combinations, namely gas-liquid partition chromatography or more simply GLC.

Table 1.1. *Methods of chromatographic separation*

Mobile Phase	*Stationary Phase*	
	Solid	*Liquid*
Gas	Gas-Solid Chromatography (GSC)	Gas-Liquid Chromatography (GLC)
Liquid	Liquid-Solid Chromatography (LSC) (adsorption chromatography)	Liquid-Liquid Chromatography (LLC) (paper chromatography)

Separation processes embodying the basic principles of chromatography were mentioned as early as the sixteenth century A.D. However, the technique, as we now know it, was first used by Tswett in 1906 for separating the components

of plant pigments [1]. He obtained discrete bands of coloured materials and named the separation method chromatography (literally: colour writing). Subsequently this became rather a misnomer since the method may be used to separate colourless components.

Partition chromatography in general was introduced by Martin and Synge [2] in 1941, using a liquid moving phase, and 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 fields 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 (GLC –gas–liquid chromatography) was mentioned in the 1941 paper of Martin and Synge, but no follow-up of this suggestion resulted. Eventually James and Martin [3, 4] started to elaborate the suggestion in 1949 and the results were presented at the Analytical Chemistry Congress at Oxford in 1952. One of the characteristic features of the method described was the very small size of samples used for estimations.

Since 1952, growth in both the theoretical and practical aspects of the technique has been tremendous. Not only has the technique provided a simple solution to many complex routine laboratory analyses, but, as we shall see later, it has provided a method whereby industrial processes may be monitored and controlled on-line in terms of quality.

GLC is now regarded as one of the most promising tools of analytical and industrial chemistry, with the great advantage that separation and quantitative estimation of components in a sample may be achieved in one operation.

Chromatographic separations may be carried out by three techniques: elution analysis, frontal analysis and displacement analysis. In practice the elution technique is the most widely used and will be the only one considered in this chapter. For a complete description of these techniques the reader is referred to the extensive literature on the subject.

In the elution method, a stream of carrier gas flows through the column. The sample is injected into the carrier-gas stream at the column inlet and passes through the column under the influence of the carrier gas. As the sample components move through the column they are selectively retarded by the stationary phase, and consequently pass through the column at varying speeds, emerging from the column in the inverse order of their retention by the stationary phase. The process is shown schematically in Fig. 1.1.

On emerging from the column, the gaseous phase passes through a detector where the individual sample components register a series of signals which appear as peaks on a recording device, connected electrically to the detector. The area under each peak is a quantitative indication of the concentration of the particular component in the original sample.

1.2 Theory of gas-liquid chromatography

GLC is a physical method of separation whereby the sample components can be separated and distributed between two phases, one being a stationary bed of large surface area, the other a gas which percolates through the stationary bed.

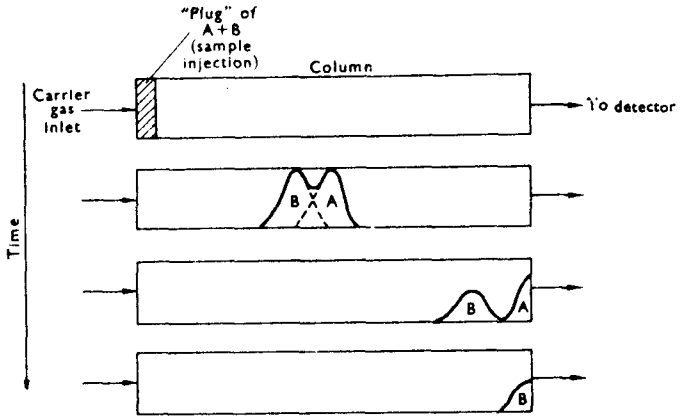

FIG. 1.1 Column separation process

The stationary bed consists of an inert support impregnated with the partitioning liquid.

GLC may be likened to a distillation process, since both depend on the repeated distribution of a sample between two phases, one of which is gaseous. In distillation, the two phases, liquid and vapour, are formed by the introduction of heat. Separation is achieved by the upward movement of the vapour under a pressure gradient and downward movement of the liquid under gravity. However, quantitative separation is rarely achieved unless the relative volatilities of the components differ greatly, and the extent of separation can be improved only by repeating the equilibrium step many times. To achieve this repetition, the distillation column is provided with plates whereby the liquid from each equilibrium step may be collected and the vapour allowed to percolate through this liquid. The process is likewise analogous to an extraction process whereby separation is obtained by means of a series of mixers and settlers.

Whereas in distillation and some extraction processes the sample forms a major part of the system volume, in GLC the sample volume is very small. Consequently, GLC columns are much more efficient, achieving greater separation of sample components, since the contact between phases (theoretical plates per unit length of column) is far greater. The chromatographic column, therefore, may be considered as a device in which a number of elementary separation processes are linked together. In theory, and sometimes in practice, distillation and extraction processes may be carried out in a number of discrete steps, in each of which complete equilibrium is established. Such a step is known as a theoretical stage, or plate. However, in the chromatographic column, and in the majority of distillation processes, the phases are continuously in motion and therefore complete equilibrium cannot be established. Nevertheless, the theoretical plate concept may still be usefully applied by referring to the length of the column over which a single plate separation is achieved, as the height equivalent to a theoretical plate (HETP). This factor is of great importance in gas chromatography.