QUANTITATIVE ANALYSIS
BY GAS CHROMATOGRAPHY

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JOSEF NOVÁK

INSTITUTE OF ANALYTICAL CHEMISTRY
CZECHOSLOVAK ACADEMY OF SCIENCES
BRNO CZECHOSLOVAKIA

CHROMATOGRAPHIC SCIENCE

A Series of Monographs

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PREFACE

Traditional quantitative gas chromatography has hitherto
been conceived mainly from a practical point of view. (The
term "traditional" is used to indicate that those problems are
meant which are associated methodically with the traditional
instrumentation of gas chromatography, rather than the problems
of computer-aided processing of chromatograms.) However, this
conception skews the picture on the significance of quantita-
tive gas chromatography and affords no more than a cursory
understanding of this important discipline. Actually, quanti-
tative gas chromatography represents the only analytical vari-
ant of gas chromatography that per se provides unambiguous
results; in qualitative gas chromatography, unequivocal iden-
tification of components can be obtained only through combin-
ation with an independent analytical method.

The scope of quantitative gas chromatography is substantially broader than that of gas chromatography alone; in addition to the problems of the separation process, it is necessary to manage also the problems of the numerous gas chromatographic detectors and the arrangements for processing their responses. Thus, quantitative gas chromatography has associated with it a number of new conceptual qualities which cannot be done justice in a mere chapter of a book on the general subject of gas chromatography. At the present state of development of gas chromatography, quantitative gas chromatography has to be understood as a self-contained modern analytical discipline the theory of which is built up on the mastered principles of general gas chromatography. It is believed that this subject deserves a monograph of this size.

The book is designed primarily for those who have some acquaintance with gas chromatography, but it is hoped that it will prove useful also to the beginner in the field. Chapters 1-5 (about a third of the book) deal with the basic theory of quantitative gas chromatography. The goal of this part of the book is to demonstrate the properties of gas chromatographic detectors, present accurate relations between the integral detector response and the amount of solute component in the chromatographic zone, and show the possibilities of predicting the detector-response factors. Chapters 6 and 7 (also about a third of the book) concern the methodological aspects of the problems. Chapter 6 presents a consistent survey of conventional working techniques. Chapter 7 is devoted to special techniques, involving matters such as isolation of trace components from ballast material, accumulation of trace components, and analysis of multiphase systems. Special attention is given to quantitative head-space gas analysis; based on the standard addition technique combined with the mass-balance of solute in a two-phase system, methods have been formulated which enable

the determination of the content of a component in the whole
system to be carried out by virtue of the analysis of only one
of the phases. However, only general concepts of these methods
have been defined, and there is much left to be done in the
elaboration of procedures suitable for particular analytical
problems. Chapter 8 describes the problems and procedures of
processing chromatograms, and Chapter 9 deals with the analyti-
cal errors encountered in quantitative gas chromatography. The
problems of automatic processing of chromatograms are discussed
briefly in Chapter 8.

The material in this book has grown and matured since about
1960. It is a pleasant duty to thank Dr. Jaroslav Janák, who
has created a unique atmosphere for this work and for my pro-
fessional growth and was a good counsel at all times. The
method of equilibrium concentration of trace components has
arisen from enjoyable collaboration with Dr. Vladimír Vašák.
At a later stage of the development of this material, Dr. Peter
Boček was a significant participant in a trial on the reliability
of conventional techniques of quantitative gas chromatography.
The section on the automatic processing of chromatograms is
largely due to Dr. Stanislav Wičar.

Despite the care it has received, the book will certainly
have shortcomings. However, nothing is perfect in the world
of reality, and anything that should be made absolutely ideal
could never be finished. I shall appreciate any comments from
readers.

June, 1975   Josef Novák
Brno, Czechoslovakia

CONTENTS

Chapter 1

INTRODUCTION

Quantitative analysis by gas chromatography is a very broad problem that can be taken from several viewpoints and approached in various ways. This book is devoted primarily to the theoretical aspects of this problem; the main goal is to show that quantitative analysis by gas chromatography can be looked upon as a self-contained analytical discipline having its own consistent theory.

With the aim of making it possible to define precisely the concept of this discipline, a boundary was deliberately laid between the area associated directly with the chromatographic system proper and the area that can be considered to be more or less independent of this system. Under the term chromatographic system the arrangement is meant which corresponds to the concept of a standard analytical gas chromatograph,

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comprising the subsystems such as gas-flow control, column,
column-temperature control, and detector with the necessary
accessories. Hence, the first area covers those quantitative-
analytical aspects of gas chromatography which are directly
related to the properties of the subsystems. The second area
comprises the problems associated with the methods of instru-
mental integration of the detector response and computer-based
evaluation of the results of analysis. Although these methods
are of extremely great significance in quantitative analysis
by gas chromatography, and the respective instrumentation be-
comes gradually a standard outfit of the modern GC laboratory,
their theoretical background lies in the domain of the tech-
niques of computerization rather than in gas chromatography.

While the material pertaining to the first area has been
continuously developed and compiled since the very advent of
gas chromatography, the second area began to evolve later.
Thus, the problems of the first area are ripening gradually,
whereas those of the second follow the rapidly advancing de-
velopment of computerization techniques. In this book, the
primary focus is the first area; the problems of the second
area are discussed only briefly, in order to make the contour
of quantitative gas chromatography complete.

In the foregoing context, quantitative analysis by gas
chromatography can be defined as a method comprising the sep-
aration on a GC column of an n-component mixture to produce n
binary solute/carrier-gas mixtures, and the on-line determina-
tion of the solutes in these mixtures by a special analyzer,
the GC detector. The mixtures are represented by the indivi-
dual chromatographic zones. Owing to the nature of the chroma-
tographic process, the instantaneous solute concentration in
the column effluent displays a certain time dependence during
the elution of the chromatographic zone, which must be closely
followed by the detector. The magnitude of the record of a

chromatographic zone, regardless of whether it has been pro-
vided in an analog or digital form, is proportional to the con-
centration or mass of the solute substance in the zone.

It is only in some cases involving the use of integral
detectors that the overall detector responses (differences
between the responses at the end and the beginning of elution)
are related directly to the solute amounts in the individual
chromatographic zones and that the necessary proportionality
constants can be determined a priori by virtue of the chemical
reactions that are taking place in the process of detection.
A typical example thereof is the pioneer work by James and
Martin [1]. Still more straightforward cases are those involv-
ing the procedures described by Janák [2] and by Bevan and
Thornburn [3]; in these cases, the overall response is liter-
ally identical to the volume or mass of the solute substance
in the zone.

Unfortunately, in the majority of cases usual in gas chro-
matography, the situation is much more complicated. The most
important detectors are those of differential type, which ren-
ders it necessary to integrate the response in order to obtain
univocal quantitative data. Further, like the qualitative
data, which are to a certain extent stigmatized by quantitative
factors, the quantitative characteristics are dependent on the
quality of the material chromatographed. Examples are the de-
pendence of retention characteristics on the sample size
(dependence of the partition coefficient on the concentration
of solute in the sorbent) on the one hand [4] and, on the other
hand, the well-known variability in the sensitivity of a par-
ticular detector to various types of material. Such effects
are the usual sources of undesirable modifications of the
respective data and have to be eliminated. Only in special
cases can these secondary effects be utilized to advantage for
analytical purposes. Examples of the latter are to be found

in the use of selective detectors, e.g., electron capture [5],
alkali flame ionization [6], and coulometric detectors [7],
which make it possible to achieve quantitative determination
and group identification simultaneously. From the viewpoint
of quantitative analysis, of course, any detection specificity
calls for the introduction of corrections. This creates the
problem of defining the correction factors and the problem of
concentration units for expressing the results. A reliable
orientation in these problems can be gained only on the basis
of theoretical analysis.

Because of its inherent relationship with the problems of
detection, quantitative gas chromatography reaches into several
fields based on theoretical foundations entirely different from
those of the separation process. This fact and the outpacing
of the theory by practice, which has been prompted by the un-
usual attractiveness of gas chromatography, have resulted in
some vagueness, especially as concerns the corrections of
quantitative data of the chromatogram and the concentration
units to be used in expressing the results. Usual causes of
this vagueness have been, as a rule, unjustifiable generaliza-
tions made from empirical observations. Thus, for example,
one can find in the literature [8] a statement which claims
that the problem of concentration units is a matter which had
been solved, with reference to the paper by Hausdorff [9], who
found that in the gas chromatography of acetone and carbon
tetrachloride with hydrogen carrier gas and katharometer de-
tection the uncorrected peak areas are proportional to the
mole percentage of the components. A theoretical analysis [10]
shows, however, that the postulate, which is quite correct in
this specific case, cannot be generalized; both theory and
practice [11-18] have clearly shown that the proportionality
of uncorrected quantitative data to weight percentage of the
respective components has more general validity.

Quantitative analysis by gas chromatography imposes high requirements for instrumentation and necessitates meeting high demands on the sampling technique, sample adjusting and dosing, and the evaluation of the chromatogram. These aspects are quite general in nature, as discussed by Evans and Scott [19]. The relations between the properties of the detection and recording systems and the distortion of the chromatographic record were studied in detail by Sternberg [20], Hána [21], and McWilliam and Bolton [22].

In the existing monographs on gas chromatography, little space has been devoted to the problems of quantitative analysis. Their respective chapters give merely brief descriptions of the working techniques and the methods used for evaluating the chromatogram. The only book focused on the questions of quantitative gas chromatography is that by Kaiser [8]. A significant contribution to the field of quantitative gas chromatography has been Sternberg's study on detectors [23].

Gas chromatography can cover a considerable proportion of the problems of analytical chemistry. The scope of gas chromatography, with regard to the complexity of mixtures and character of material submitted to analysis, can be controlled within wide limits by the choice of the chromatographic system and operation conditions (capillary GC, temperature programming, high pressure, special modes of detection). The extent to which the versatility of gas chromatography can be utilized is determined by the existing degree of instrumentation refinement.
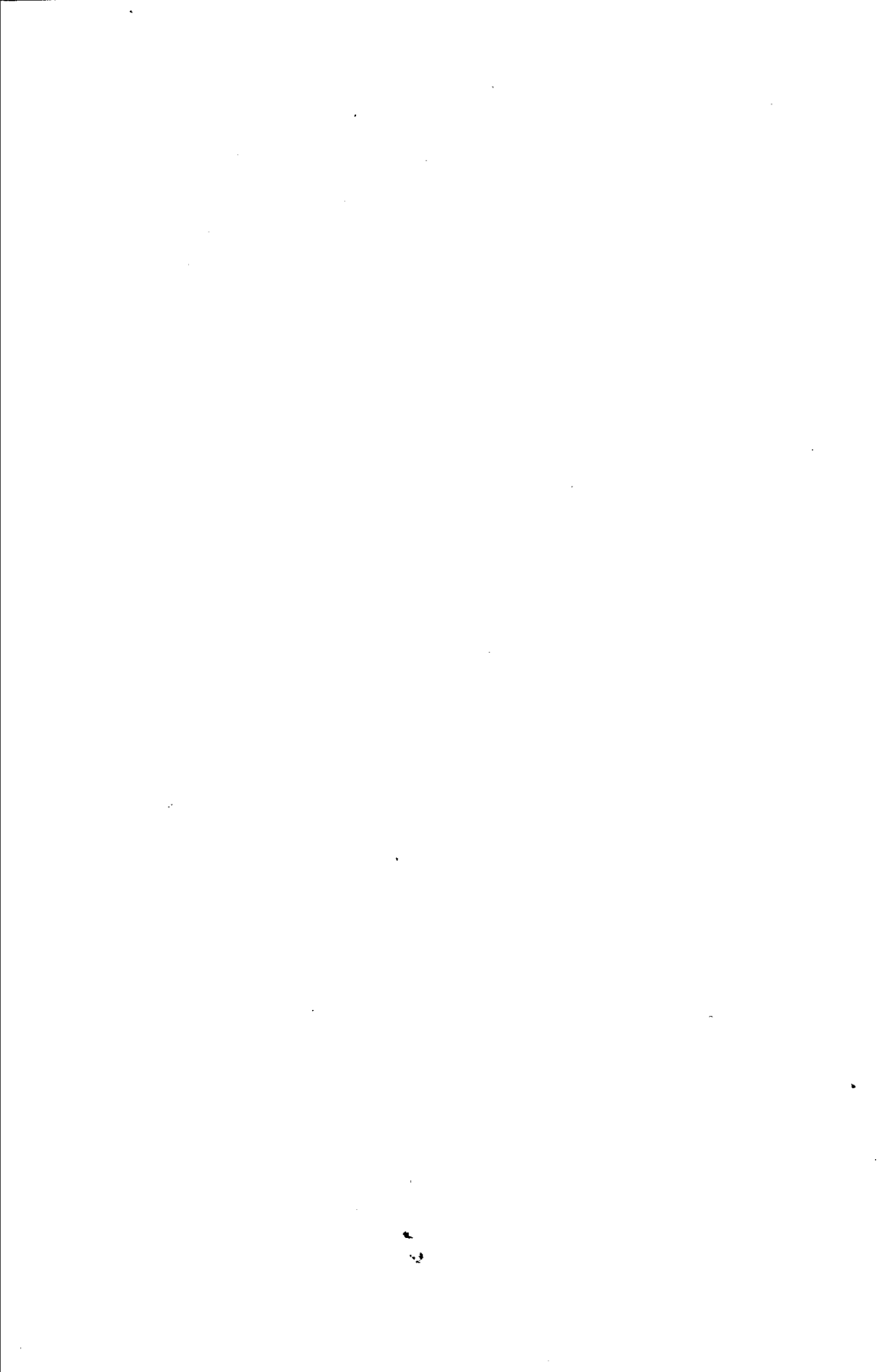
Chapter 2

CONCENTRATION OF THE SOLUTE COMPONENT IN THE ELUTED
CHROMATOGRAPHIC ZONE

After its introduction into the chromatographic column, the
solute component quickly distributes itself between the mobile
phase ($\underline{m}$) and the sorbent ($\underline{s}$). The distribution ratio is given
by the capacity ratio $\underline{k}$ defined by

$$\underline{k} = \frac{N_{i\underline{s}}}{N_{i\underline{m}}} = \underline{K}\, \frac{V_{\underline{s}}}{V_{\underline{m}}} \tag{2-1}$$

where $N_{i\underline{s}}$ and $N_{i\underline{m}}$ are the number of moles of the solute (i)
present in the sorbent and in the mobile phase, $\underline{K}$ is the parti-
tion coefficient of the solute in the given system, and $V_{\underline{s}}$ and
$V_{\underline{m}}$ are the volumes of the sorbent and of the mobile phase in the
column; $\underline{K}$ is given by $\underline{K} = (N_{i\underline{s}}/V_{\underline{s}})/(N_{i\underline{m}}/V_{\underline{m}})$. As long as the
chromatographic bed is homogeneous, the working conditions

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