



*JOURNAL OF CHROMATOGRAPHY  
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*selective gas  
chromatographic  
detectors*

*M. Dressler*

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# *selective gas chromatographic detectors*

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**ELSEVIER**

**Amsterdam — Oxford — New York — Tokyo 1986**

ELSEVIER SCIENCE PUBLISHERS B.V.  
Sara Burgerhartstraat 25  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

*Distributors for the United States and Canada:*

ELSEVIER SCIENCE PUBLISHING COMPANY INC.  
52, Vanderbilt Avenue  
New York, NY 10017, U.S.A.

Library of Congress Cataloging-in-Publication Data

Dressler, M., 1940-  
Selective gas chromatographic detectors.

(Journal of chromatography library ; v. 36)

Includes bibliographies and index.

1. Gas chromatography. I. Title. II. Series.

QD79.C45D74 1986 543'.0896 86-13366

ISBN 0-444-42488-1

ISBN 0-444-42488-1 (Vol. 36)

ISBN 0-444-41616-1 (Series)

© Elsevier Science Publishers B.V., 1986

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Printed in The Netherlands

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## PREFACE

In the last decade, specialized chromatographic literature and chromatographic practice have placed emphasis on the identification of individual compounds from complicated gas chromatograms. Of course, a gas chromatograph-mass spectrometer-data system has been the most efficient combination. However, much simpler techniques are provided by use of the so-called selective detectors. Selective detectors give a response only to certain heteroatoms, resulting in a simplified chromatogram. Many selective systems exist and some of them are manufactured commercially and employed in routine chromatographic practice.

Recently, new selective detectors have been developed and known detector designs have been innovated. The aim of this book is to collect and to collate up-to-date information on this topic to give the reader a detailed understanding of selective detectors in general, their principles, designs and analytical possibilities.

Throughout the preparation of the manuscript, I have appreciated the assistance of many people from the Institute of Analytical Chemistry of the Czechoslovak Academy of Sciences. Special acknowledgements are due to my colleague Dr. Josef Novák who read the manuscript and made valuable suggestions, and to Mrs. Melita Radevová for translation into English.

*Brno, March 1986*

M. DRESSLER

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## Chapter 1

## INTRODUCTION

Qualitative analysis by gas chromatography (GC) is based on the concept of the retention characteristics of sample compounds. The absolute values of the retention characteristics such as retention times, retention volumes or specific retention volumes, and also the relative values of these quantities such as relative retention times or volumes or Kováts retention indices are used. The retention volume,  $V_R$ , is determined by the quantities that characterize the chromatographic system, i.e., the dead volume of the column,  $V_0$ , the volume of the stationary phase,  $V_S$ , or the surface area of the adsorbent and the partition coefficient,  $K$ . The value of  $K$  depends on the substance being analysed and the stationary phase employed:

$$V_R = V_0 + KV_S \quad (1.1)$$

As the partition coefficient is a function of the thermodynamic properties of the system, the retention volume of a given solute in a given chromatographic system is constant at constant temperature and pressure, but it is neither selective nor specific. In addition, the separation power of any chromatographic column, even the best, is limited. This means that the column has a limited capacity for peaks and, therefore, the separation number (Trennzahl,  $TZ$ )<sup>1</sup>, given by the number of the separated peaks that can be placed between two successive peaks of neighbouring  $n$ -alkanes:

$$TZ = (d_2 - d_1) / \left[ Y_{\frac{1}{2}}(1) + Y_{\frac{1}{2}}(2) \right] - 1 \quad (1.2)$$

(where  $d_2 - d_1$  is the distance between the peak maxima of the  $n$ -alkanes and  $Y_{\frac{1}{2}}$  are the peak widths at half-heights) is finite. For complex mixtures (of natural or biological origin, for instance) not all of the peaks can be separated by the column even if the partition coefficients of the compounds differ. Consequently, from a theoretical point of view, only a negative result can be considered as conclusive in chromatography, i.e., that a compound  $a$  is not identical with  $b$  when  $V_{Ra} \neq V_{Rb}$ .

When performing qualitative analyses on the basis of retention data only, one should be aware of the risk that the chromatographic peak may not pertain to the

substance selected for calibration, although the latter has the same retention value, and even that it may not be due to a single substance but to two or more substances that have the same partition coefficients in the given system. Hence it has been generally accepted that the identification power of GC (and of chromatography in general) is far less than its excellent separation power. Therefore, a number of auxiliary techniques have been used for identification purposes, such as methods utilizing regularities in the partition coefficients within a homologous series which are known or can be predicted from experimental data. The retention values can be correlated with values characterizing the homologous series. Such values are either those that cannot be determined in any way from the chromatogram (e.g., molecular weight, number of carbon atoms or boiling point) or those found by chromatographic experiments (e.g., the ratio of the retention values on two stationary phases differing in polarity, or retention values measured at different temperatures)<sup>2,3</sup>. By interpolating these relationships, the retention value for a particular member of a homologous series can be obtained and compared with the retention value obtained experimentally. The agreement between the two sets of data increases the probability that the predicted identity will agree with that of the substance being analysed. However, these identification approaches are labourious and time consuming.

Reaction gas chromatography<sup>3,4</sup> is another approach used to facilitate the identification of individual components on a chromatogram. With this approach, the sample is subjected to selective reactions intended to remove selected types of substances from the chromatographic spectrum or to convert them into different substances. Subsequently, the chromatogram of the original sample is compared with those obtained after reaction. By introducing chemical reactions into the system, additional information on the identity of the sample compounds is obtained from the chromatogram, and the possibility of confusing the identities of the substances is again reduced.

The utilization of the detector itself for the identification of substances is an efficient approach to the application of auxiliary techniques for qualitative purposes. From the viewpoint of quantitative analysis, chromatography requires a detector that responds as far as possible to all types of sample compounds. If it is sensitive enough, the detector provides a record of all the solutes, thus making possible their subsequent determination. If, in addition, the detector response per unit solute mass (weight or number of moles) is similar for different types of compound, which is very advantageous for quantitative analysis, the detector itself provides no data for qualitative purposes.

The availability of a detector that gives a response that differs in some way for a certain type of compound from that for other compounds is obviously advantageous in qualitative analysis. Therefore, let us consider the ways in which the response of a certain detector can differ for different types of compounds.

It can differ, first of all, in the level of the response per unit solute mass. The ideal case would be represented by a detector responding to a certain type of compound only (e.g. to a certain kind of heteroatom in a molecule of these compounds). As will be seen later, no gas chromatographic detector meets this requirement. However, selective detectors<sup>5-8</sup> are available the response of which per unit mass to compounds containing a certain heteroatom differs considerably from the response to other compounds. In addition to the level of the response, the detector response to various compounds can also differ in polarity. Spectral detectors such as the mass or infrared spectrometer supply, in addition to the common chromatographic record, data for each peak that allow one to characterize the compound. It is therefore evident that the detector itself can contribute to the identification of chromatographed compounds, if a suitable selective detector is properly selected for a particular case and if optimum operating conditions for the chosen detector are maintained. In order to function properly, selective detectors must be operated under optimum conditions. In other words, there are a number of operating variables that can either adversely affect or even nullify the function of the selective detector.

Descriptions of the individual selective detectors and of the principles providing the basis for their operation, an analysis of the effects of the various operating conditions on the basic parameters of the selective detectors and consideration of the potential use of these detectors in qualitative analysis are the subjects of this book.

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## Chapter 2

## BASIC TERMS RELATING TO DETECTORS

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## 2.1. DETECTOR SENSITIVITY

Detector sensitivity is the basic term used in describing any detector. In spite of the frequent use of this term, there is great non-uniformity in expressing detector sensitivity in the literature<sup>1-9</sup>, which has resulted in misleading interpretations in many instances. Frequently, terms such as molar response, detection limit and minimum detectable amount are used to express detector sensitivity. In addition, different terms have been used for the same thing. For instance, the terms minimum detectable amount, minimum detectable quantity, minimum detectable limit, detection limit, minimum detectability and limit of detectability have been used to express the minimum detectable rate of introduction of solute mass into the detector.

The detector responds to an eluted sample compound, to the carrier gas and to other compounds that may be present and the response ( $R$ ) can be expressed by

$$R = R_i + R_m + R_x \quad (2.1)$$

Under stabilized chromatographic conditions, the response to the carrier gas ( $R_m$ ) and to the impurities ( $R_x$ ) is constant and can be compensated to zero by the applied counter voltage. Thus, the net response given by the detector during the passage of an eluted sample compound through the detector is equal to the response to that compound,  $R_i$ .