OPEN TUBULAR COLUMNS

IN GAS CHROMATOGRAPHY

by L. S. Ettre

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With a Foreword by
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Foreword

For my past sins, Leslie Ettre has given me the privilege of writing a few words to preface his excellent little book. It gives me great pleasure to do so, because of the many years of fruitful collaboration we have had at Perkin–Elmer, because it is refreshing to see a treatise in gas chromatography in which the theoretical treatment has been bared to its essentials, without a mushrooming of formulae which, by means of an ever increasing number of parameters, account for more and more, and explain less and less, and because the author has recognized that the gas chromatographic column is a nearly passive element in its own right which deserves to have a treatise written nearly exclusively about it, just as electrical circuit theory can be discussed without elaborate references to vacuum tubes and meters.

I wish this conscientiously written volume the success it deserves.

M. J. E. GOLAY

Preface

Gas chromatography is a separation technique used primarily in analytical chemistry. Therefore, it is evident that special emphasis should be placed on that particular part of the apparatus in which the separation takes place. This part is the column, the heart of the gas chromatograph.

The goal of researchers in the field of gas chromatography has been—from the beginning—to understand the separation process so that they might design columns with the best possible performance. Such investigation led M. J. E. Golay in 1956–1957 to the development of a special column type. These columns are not filled with the ordinary column material, which consists of a solid support and a stationary (liquid) phase; rather the inside column wall itself serves as the support and is coated with a thin film of the stationary phase. As pointed out by W. W. Brandt [24], this invention "ranks as one of the two or three major original developments in gas chromatography since its discovery by James and Martin."

In the years since Golay's invention, these columns have found wide application in practically every field where gas chromatography is used. The publications on the theory, instrumentation, and applications of these columns are voluminous. However, with the exception of Kaiser's excellent book [160], originally written in 1961, the accumulated knowledge has not been summarized in one single publication.

In November 1963, the author had the honor to present a lecture at the Eastern Analytical Symposium in New York City, discussing in detail some theoretical and practical aspects of open tubular columns and their applications. In the following months, this lecture was repeated by invitation—with the content continuously updated—on six different occasions, including the yearly Gas Chromatography Institutes held at Canisius College, Buffalo, N.Y., and Fisk University, Nashville, Tenn. In the discussions following these presentations, it

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was often suggested that the text of the lecture be made available in printed form. This is how the idea for this book was born: it is based on these lectures, but the original text has been significantly enlarged and modified; furthermore, chapters discussing questions not included in the oral presentations were added in order to cover the subject completely.

This book was written for the *practical gas chromatographer*: its principal aim is to help him better understand this exceptional tool. After a brief introduction, some theoretical aspects are discussed in order to allow certain conclusions necessary in the actual application of these columns to be drawn. This treatment was felt to be most profitable since theory and practice cannot be separated. Subsequently, questions concerning the preparation of the various column types and special problems in connection with the gas chromatographic system in which these columns are used are discussed. Finally, a complete bibliography of publications dealing with the theory and applications of open tubular columns in gas chromatography, with a short subject index, is given. Bracketed numbers in the text refer to this bibliography, while other literature sources are given as footnotes.

Most of the chromatograms shown in the figures were selected to illustrate certain specific points discussed in the text rather than to show the analysis of typical samples, primarily because it is the author's experience from his long activity in gas chromatography that no "typical sample" exists. Also, the principal purpose of the chromatograms is to illustrate some practical applications, to draw attention to the most important fields to which open tubular columns can be successfully applied, and not to reproduce the best chromatograms ever published. It was felt that the basic goal of the book is not to give a collection of chromatograms but to help in better understanding the characteristics of open tubular columns.

The various units of measurement used by different authors in describing the columns and analytical conditions represented a serious problem. Although in this book the metric system is used whenever possible, data on column length and inlet pressure were left as given originally by the authors because the transformation of feet and pounds per square inch into the corresponding metric units would often result in irrational numbers. However, the internal diameter of the column is always given in metric units, in order to make comparison and calculation simpler.

Since this book discusses the open tubular columns, the instrumentation used to obtain the various chromatograms is not mentioned in the figure captions; however, it is summarized in the Supplement.

Great care was taken to establish a logical nomenclature. The symbols used are based on the recommendations of the various international symposia and the special I.U.P.A.C. Committee; symbols corresponding to terms not included in their treatment were established by selecting the most logical usage. In this respect, our goal was to have only *one* meaning for each symbol.

This book is based on both the literature and the experiences collected in the last eight years at the various laboratories of The Perkin–Elmer Corporation, where the original work of Dr. Golay was carried out. The author wishes to express his sincere appreciation to all colleagues and sources listed in the following pages who placed at his disposal various published and unpublished material. Special thanks are due to W. Averill, N. Brenner, R. D. Condon, and S. D. Norem at Perkin–Elmer and Dr. C. Horváth at the Research Laboratory of the Massachusetts General Hospital, Boston, who read parts of the manuscript and were instrumental, by their thoughtful advice and criticism, in molding its final shape; further, to the management of The Perkin–Elmer Corporation, Norwalk, Conn., for permission to write this book and for allowing the use of various company facilities. The fine cooperation of J. R. Piccolo and E. Hagenburger in the preparation of the illustrations and of Mrs. E. Barrett in typing the manuscript is particularly noteworthy. Last but not least, the efforts of Plenum Press in making possible the publication of this book in an unusually short time are greaty appreciated.

It is the author's sincere hope that this work will give the practical gas chromatographer a better understanding of the characteristics of open tubular columns and help him in improving his everyday work.

Norwalk, Connecticut
August 20, 1964

L. S. ETTRE

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Instrument News (The Perkin–Elmer Corp., Norwalk, Conn., USA): Figures 16, 17.

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Symbols

a	Constant in Eq. (50)
a_K	Constant in Eq. (51)
a	Accommodation coefficient in gas–solid adsorption chromatography
A	Peak area
b	Constant in Eq. (50)
B	Longitudinal gaseous diffusion term
B_0	Specific permeability
c	Concentration of the coating solution
c_{min}	Minimum detectable concentration in a given sample
C_G	Term of resistance to mass transfer in the gas phase
C_K	Mass transfer term for the kinetics of adsorption and desorption in gas–solid adsorption chromatography
C_L	Term of resistance to mass transfer in the liquid phase
d	Inside diameter of column tubing
d_f	Average thickness of the liquid-phase film
d_p	Effective particle diameter of the support
d_L	Density of the liquid phase
D_G	Gaseous diffusion coefficient
D_L	Liquid diffusion coefficient
f	A square root function of k [see Eq. (29)]
F_1, F_2	Factors used in chapter 2.322
$\bar{F}$	Average carrier gas flow rate
F_a	Carrier gas flow rate measured at column outlet and ambient temperature
F_c	Value of F_a corrected to column temperature
HETP	Height equivalent to one theoretical plate
$HETP_{min}$	The theoretical minimum value of the HETP curve
j	Carrier gas compressibility correction factor
k	Partition (capacity) ratio
K	Partition coefficient
L	Column length
m	Constant in Eq. (64)
M	Amount of coating in the column
n	Number of theoretical plates
n_c	Number of carbon atoms in a molecule
n_0	Number of theoretical plates calculated from Eq. (47)
n_{req}	Number of theoretical plates required in order to achieve a desired resolution for a given component pair
N	Number of effective plates

OPGV	Optimum practical gas velocity
p_a	Ambient pressure
p_i	Carrier gas inlet pressure
p_o	Carrier gas pressure at column outlet
p_w	Partial pressure of water at ambient temperature
Δp	Pressure drop along the column
PI	Performance index
q	Constant in Eq. (64)
r	Inside radius of column tubing
R	Peak resolution
R^*	Possible best resolution which could be achieved with a certain column for a given component pair
S	Total internal surface area of the column
t_M	Retention time of an inert component (usually air)
t_R	Retention time of the sample component (measured from start)
t'_R	Adjusted retention time of the sample component (measured from the "air peak")
Δt	Distance of two consecutive peak maxima
T_a	Ambient temperature (in °K)
T_c	Column temperature (in °K)
T_0	Initial temperature in programmed-temperature operation
T_F	Final temperature in programmed-temperature operation
$\bar{u}$	Average linear gas velocity
$\bar{u}_m$	Average molecular velocity
u_o	Linear gas velocity measured at column outlet (corrected to column temperature)
$\bar{u}_{opt}$	Optimum average linear gas velocity
u_s	Linear velocity of the coating solution at column outlet
v_{eff}	Effective volume of one theoretical plate
v_G	Volume of gas phase in one theoretical plate
v_K	Volume of the vaporized sample exclusive of the carrier gas
v_L	Volume of the liquid phase in one theoretical plate
V	Geometrical volume of the column
V_G	Total volume of gas phase in a column
V_L	Total volume of liquid phase in a column
V_s	Necessary volume of coating solution
w_b	Peak width at base (band intercept)
w_h	Peak width at half height
w_i	Peak width at the inflection points
$x_0, \ldots, x_3$	Distances on the chromatogram used for the calculation of the "air peak" time
α	Relative volatility
α^*	Smallest relative volatility which can be separated with a given resolution on a certain column
β	$= V_G/V_L$
ε	Interparticle porosity
η	Viscosity of the carrier gas
σ	Standard deviation of the Gaussian peak

Contents

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First Part

Introduction

1.1 ORIGINS

If the history of scientific developments were to be investigated, it would be found that many are the result of accidental inventions and that the number of significant developments which resulted from logical, theoretical considerations or were based on systematic outlines drawn up *prior* to the actual development is very small. It is interesting to note that both gas–liquid partition chromatography and the application of open tubular columns in gas chromatography are the result of such considerations. Martin and Synge, in 1941, in describing the method of liquid–liquid partition chromatography[1] predicted the possibility of substituting gas for liquid as the mobile phase; similarly, open tubular columns are the result of Golay's theoretical consideration of the behavior of packed columns.

In order to evaluate properly the importance of this new invention, one should look back to the years 1952–1957. Gas chromatography was introduced in 1952 by James and Martin,[2] but the real development started in about 1955 when more and more people became involved in investigations of this new technique. One of the most important questions with which the papers published at that time dealt was the theory of the chromatographic separation process, and the most important publication in this field, by van Deemter, Zuiderweg, and Klinkenberg,[3] describing the basic equation for the performance of a gas chromatographic column appeared in 1956.

[1] A. J. P. Martin and R. L. M. Synge, *Biochem. J.* **35**:1358 (1941).

[2] A. T. James and A. J. P. Martin, *Biochem. J.* **50**:679 (1952).

[3] J. J. van Deèmter, F. J. Zuiderweg, and A. Klinkenberg, *Chem. Eng. Sci.* **5**:271 (1956).

However, this work became really known only in 1957, after Keulemans' comprehensive book on gas chromatography was published.[4]

Parallel to these studies which had been carried out in Europe, the theory and practice of gas chromatography were also investigated in the United States. In the spring of 1956, Golay presented a paper[5] on a different theoretical approach to this problem. In this paper, based entirely on mathematical considerations, he developed certain equations that yielded a better understanding of the gas chromatographic process and drew some conclusions regarding the optimum operation of a gas chromatographic column.

In the months following the presentation of his paper, Golay continued his studies and started to investigate the relationship between the performance of a gas chromatographic (packed) column and such important parameters as the analysis time and the carrier gas pressure which are required for a given performance. In this investigation, a packed column was considered as equivalent to a bundle of capillary tubes coated with the stationary phase and with an inside diameter of the order of the support particles' size. Golay's rough theoretical calculations indicated that the diameter of the capillaries, which determines the resistance to gas flow, should also determine the order of magnitude of the height equivalent to one theoretical plate (HETP).

After checking these theoretical considerations with actual experimental data, an enormous discrepancy was found in that

> "the HETP was ten times greater than the packing granule dimensions while the characteristic dimension controlling the pneumatic resistance to flow was only one-tenth as large."

As Golay himself described later, during this experiment he happened to notice in the laboratory a rather long length of Tygon tubing and, in his own words [109],

> "... out of curiosity, I substituted it for the Celite column, just to see what the air peaks would look like. I was pleasantly surprised to discover that these air peaks were of the correct width predicted by the same rough theory.

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[4] A. I. M. Keulemans, *Gas Chromatography*, Reinhold, New York, 1957.

[5] M. J. E. Golay, 129th National Am. Chem. Soc. Meeting, Dallas, Texas, April 1956; *Anal. Chem.* **29**:928 (1957).

> The next thought was: if the air peaks have the correct width when the column is a length of plain tubing, why not coat the inside wall of this tubing with a retentive substance, and use it for a partition column?"

Golay's first report on his preliminary investigations was dated November 15, 1956. Due to its historical interest, it is reproduced in Figure 1.

November 15, 1956

From Marcel J. E. Golay

Subject: Progress report of gas chromatographic experimental work for September and October 1956

An enormous discrepancy with the theory evolved up to that time was the circumstance that the HETP was ten times greater (0.1 cm) than the packing granule dimensions while the characteristic dimension controlling the pneumatic resistance to flow (0.001 cm) was only one-tenth as large. It had been anticipated that these two quantities, two orders of magnitude apart, would be of the same order of magnitude.

Experiments with open cylindrical columns with an oil coating on the wall were initiated in order to unravel these discrepancies and to obtain a better insight into the separation mechanisms.

An initial experiment with a glass capillary, 1 meter x 0.08 cm, gave inconclusive results because of the near equality of the volumes in the injection block, in the column itself and in the detector (0.8 cm^3). An experiment with an uncoated 10 meter x 0.3 cm length of Tygon tubing gave a $\Delta t/t$ ratio corresponding very closely to the calculated number of theoretical plates of this column for the air peak (about 14,000).

Experiments were then initiated with two steel tubings, 12 feet x 0.055", wall coated with ethylene glycol by filling and wiping with a cotton wad drawn through the tubing. For these experiments, a new detector was constructed in order to reduce its volume.

Figure 1. Facsimile of M. J. E. Golay's first report on his investigations concerning open tubular columns.

A few months after this first internal report, Dr. Golay presented his first paper on the "Theory and Practice of Gas–Liquid Partition Chromatography with Coated Capillaries" [109] at the First Gas Chromatography Symposium of the Instrument Society of America, at East Lansing, Michigan, June 1957.

Golay's work is a classical example of how the proper application of theoretical conclusions can lead to an entirely new invention. This thought was also expressed by A. J. P. Martin, who characterized his paper as "the highlight of the meeting" and the use of open tubular columns as "a method which many of us are going to pursue with considerable enthusiasm from now on."[6]

One year after his first presentation, at the Second International Gas Chromatography Symposium, May 1958, in Amsterdam, The Netherlands, Dr. Golay followed up [110] with a more detailed theory and showed some practical applications of open tubular columns. At the same meeting, Dijkstra and de Goey [68] also demonstrated the possibility of using open tubular columns and described the dynamic coating method used most generally today.

Shortly after these presentations, various groups in different countries started to investigate the potentialities of open tubular columns, and a few months later the publications of Condon [54], Desty *et al.* [62, 64, 66], Kaiser and Struppe [162], Lipsky *et al.* [181, 182], Lovelock [187], R. P. W. Scott [243], and Zlatkis *et al.* [283, 284] gradually confirmed the value of the new concept. From then on, the line of development is unbroken, as more and more researchers and practical gas chromatographers clarified the various aspects of the theory, preparation, and application of these columns.

1.2 NOMENCLATURE

There is considerable confusion regarding the nomenclature of gas chromatographic separation columns built in conformance with Golay's work. They are often called "capillaries," although they are not at all restricted to "capillary" dimensions since "not the smallness but the 'openness' of these columns permits us to realize a two orders of magnitude improvement over the packed columns" [111]. Furthermore, the term "capillary" does not properly characterize this type of column since it has been clearly demonstrated recently[7–9] that *packed* columns of similar diameters as the "capillary capillary

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[6] A. J. P. Martin, in *Gas Chromatography*, ed. V. J. Coates, H. J. Noebels, and I. S. Fagerson, Academic Press, New York, 1958, pp. 237–247.

[7] I. Halász and E. Heine, *Nature* **194**:971 (1962).

[8] C. Cercy, S. Tistchenko, and F. Botter, *Bull. soc. chim. France* **1962**:2315.

[9] H. V. Carter, *Nature* **197**:684 (1963).

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