



## Review

## Changes in the basic experimental parameters of capillary gas chromatography in the 20th century

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Studies of qualitative changes in capillary gas chromatography are of significant practical and scientific interest. This paper analyzes the evolution of the most important experimental chromatographic parameters over the last three decades and is based on the use of a new approach to scientometrical research that is referred to as applied scientometry. One essential feature of this approach is that it looks at the entire contents of each paper rather than only taking account its title, abstract, and references (as is typical for conventional scientometry). In this paper, we monitor how the most important chromatographic parameters, such as column length and diameter, layer thickness, stationary liquid phases, separation temperature mode, etc., have been evolving over the period 1970–2000. We used data from the following journals: *Chromatographia*, *Journal of Chromatography*, and *Journal of High Resolution Chromatography and Chromatography Communications*.

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## 1. Introduction

Contemporary analytical gas chromatography is, predominantly, capillary chromatography. The matter and character of the theory and experiment, equipment and application of capillary chromatography are closely bound to open capillary columns. That is why the evolution of capillary gas chromatography can be viewed as the evolution of a capillary column.

High-efficiency capillary gas chromatography has progressed a long way to become the main method of analytical and physicochemical research. Ettre has devoted an article [2] to its dramatic history, an example of the continuous successful scientific and technical evolution of a new analytical method. This evolution will undoubtedly continue in the 21st century. However, wishing to see into the future, one should take account of past evolution. Scientometric studies are of great interest in that they adequately reflect chromatographers' interest in the development and practical application of open tubular columns. Scientometric studies on chromatography have been carried out in our laboratory during the last decades [1,3–11]. Our first work on the use of applied scientometry in chromatography was published in 1972 [3]. Classical scientometry studies statistical structure and the dynamics of scientific data [12]. Based on the definition of scientometry given in Ref. [13], we suggest another extended definition. Scientometry is a scientific subject that analyses and compares (in graphical form also) scientific and technological information (STI) using mathematical methods including statistics and data analysis. The main task of the classic scientometry is to answer the question, "Who is doing what, and where?" based on STI. Two types of evaluation can be done using STI: "metric evaluation" of the flow of information (articles and journals) and "quality evaluation" of information processed in databases. Graphical representation focuses on presenting STI in the form of maps reflecting fields of research and

the participants (researchers, institutions, countries). The objective is to provide a representation of the structure of information at any given time in its development.

Such work is often limited to studies of the number of publications, co-authorship and quoting dynamics. Earlier we suggested broadening the concept of scientometry and considering a special field, which we called applied scientometry [1]. Applied scientometry is the field of scientometry that studies the dynamics of applied information in the use and development of analytical methods, engineering, etc. and studies time dependencies of general parameters of the selected scientific field. The main goal of applied scientometry is to quantitatively characterise the scientific and technical evolution and contemporary status of the selected scientific field. Apparently, new tasks require new approaches to processing scientific publications. In applied scientometry we can not just analyse scientific terms in titles, lists of references, authors, etc., as is typical in traditional scientometry. In applied scientometry you need to analyze the entire contents of a publication. This approach is undoubtedly more laborious, but gives more valuable information, because we can get specific technical data, that reflect technical evolution of the field of interest.

This paper aims at studying the evolution trends in gas capillary chromatography. But we find it necessary first to characterise the general evolution stages of gas capillary columns.

### 1.1. Gas chromatography invention by Golay

The scientific evolution of gas capillary chromatography is first of all associated with the name of Golay. The first theory of capillary chromatography and the first chromatogram obtained on an open column were presented by Golay at an international symposium in the USA in 1957 [14]. Unfortunately, this presentation did not attract attention to the new

column type, which can be explained, first, by Golay's revolutionary approach to the column design (a capillary column radically differs from a traditional packed column), any new idea is always taken sceptically, and second, by the absence of solid confirmation of the superiority of capillary columns in comparison with packed columns. One should note that data on a capillary column (91 m) published by Golay were not very impressive: column efficiency  $N=12\,000$  theoretical plates, height equivalent to a theoretical plate (HETP)=7.6 mm (our calculations).

Golay demonstrated the advantages of open columns later, in 1958, at a symposium in the Netherlands [15]. There he also showed the chromatogram obtained on a 45 m×0.25 mm column with a stationary liquid phase of 1% didecyl phthalate [16]. According to that chromatogram, the efficiency of the column was ~50 000 theoretical plates and HETP=0.9 mm (our calculations). That was a record efficiency value at that time in gas–liquid chromatography, and it was significantly greater than in packed columns.

### *1.2. Glass capillary columns—an important step in the development of inert capillary columns*

One of the most important features of gas chromatography is the separation of microsamples, which greatly increases requirements of the inertness of the inner surface of a capillary column. So, the use of more inert glass capillary columns in capillary chromatography was a great qualitative achievement. Etre in his recent work on the history of gas chromatography [2] shows a picture of Golay with a glass column in his hands (~1960). But the success in capillary chromatography could not have been achieved without the work of Desty et al., and first of all, without a glass column broach device developed by Desty et al. [17]. At the same time, a similar device was invented by Kreyenbuhl [18]. Unfortunately, glass columns had a number of drawbacks, the most noticeable being: (i) difficulties in everyday use (fragility, inflexibility); and (ii) insufficient sorption and chemical inertness.

Achievements in the use of capillary columns are described in a monograph by Jennings [19] and in other reviews [20–22].

### *1.3. Fused silica capillary columns*

First, we must note that Desty et al. [23] had previously suggested that quartz would be an appropriate material for capillary columns. But he considered quartz as just an alternative to glass, inflexible thick-walled quartz columns. Drawbacks of glass capillary columns were eliminated in fused-silica capillary columns, based on fibre optic technology. First columns had polymer heat-resistant coatings. This important step in the development of capillary chromatography was made by Dandeneau and Zerenner [24,25]

Advanced metal heat-resistant coating was invented a few years later in Russia (Russian Academy of Sciences) [26].

### *1.4. Immobilised phases as a condition of column durability*

Temporal stability of the stationary liquid phase (SLP) film on the inner surface of a capillary column is an essential condition for its successful use, because configuration changes in the SLP layer (appearance of drops and SLP layer thickening) lead to drastic reduction in column efficiency. The main criterion for film stability is its immobilisation. The most prevalent method of immobilisation is polymer molecules linking together and bonding to capillary column inner surface.

Madani et al. [27–29], Blomberg et al. [30,31], Grob et al. [32], Sandra et al. [33] and other scientists are the pioneers in the use of immobilised phases in capillary chromatography.

### *1.5. Capillary gas–solid chromatography—an important branch of capillary chromatography*

The practical importance of capillary gas–solid chromatography is unquestioned—it is used in medicine, pollution control and large-tonnage petrochemical industry.

The history and peculiarities of gas–solid capillary chromatography are observed in detail in a monograph [34]. Many people suppose that capillary gas–solid chromatography was first devised by Mohnke and Saffert [35]. However, the first paper in this field was published by the Russian scientists Kal-

manovsky et al. [36]. That is why we consider Russian and German scientists as the discoverers of capillary gas–solid chromatography. A great contribution to the development of gas–solid capillary column production technology was made by the Varian–Chrompack company [37]. This branch of chromatography is actively developed nowadays. At the 23rd International Symposium on Capillary Chromatography in Riva del Garda, ~8% of presentations were devoted to gas–solid capillary chromatography. We find it promising to use membrane materials as the chromatographic adsorbent. Polytrimethylsilylpropane (PTMSP) separates gases and organic compounds quite well, and capillary column production technology is remarkably simple [38]. Incidentally, PTMSP is probably the first soluble adsorbent.

## 2. Research methods

As mentioned above, our studies were carried out using applied scientometry [1]. In our scientometric research we used data from the following journals: *Chromatographia*, *Journal of Chromatography*, and *Journal of High Resolution Chromatography and Chromatography Communications*. In our opinion, these periodicals reflect the conditions and achievements of contemporary gas chromatography in corpora. We also used data from conferences on gas chromatography, in particular from symposia on gas chromatography at Riva del Garda, 1998 and 2000, and from catalogues of various chromatographic companies. As mentioned above, considering that titles and abstracts of chromatographic publications usually contain incomplete information on chromatographic processes, we used the whole texts of publications in our work. The data obtained were then summarized, and frequencies of various chromatographic parameters were calculated. Since instruments used in the chromatographic process do not vary significantly, we did not consider this parameter in our work.

Below you can find data on changes in the general parameters of capillary chromatography in the 20th century.

## 3. Results and discussion

### 3.1. Capillary column geometrical parameters

#### 3.1.1. Capillary column length

The length of a capillary column is one of the most important experimental parameters. As is well known, the total efficiency of a chromatographic system increases with the length of the chromatographic column. However, duration of analysis and the carrier gas pressure also increase.

Table 1 represents the dynamics of changes in the length of chromatographic columns over the last 30 years (1970–2000). As can be seen, in 2000 30-m columns (47%) were most frequently used, and 25–30-m columns were prevalent (73%). It is important to notice the decrease in the use of 30–50- and 50–100-m columns. We find the quite low values for 10-m and shorter columns surprising. Recently we have demonstrated the usefulness of 10–50-cm columns [39]. Estimates for the relative frequency of the use of columns with particular lengths can be found in Table 1 for the years 1970, 1980, 1990, and 2000. The column length of 11–24 m was not considered because in 1970 only it was essential (10%), but later this length was almost not used (2% in 1980 and <0.5% in 1990, 2000)

#### 3.1.2. Diameter of a capillary column

The chromatographic characteristics of a column are also greatly influenced by its diameter. The column diameter influences the following characteristics: (i) broadening of chromatographic zones, (ii) column load (SLP quantity per column length unit) and (iii) the retention factor.

Table 2 contains data on the dynamics of changes

Table 1  
Dynamics of the length of capillary columns (%)

Length (m)	Years			
	1970	1980	1990	2000
≤10	6	18	13	11
25–30	26	36	57	73
31–50	22	23	22	3
51–100	28	17	7	10
100 and more	8	6	1	3

Table 2  
Dynamics of the diameter of capillary columns (%)

Diameter (mm)	Years			
	1970	1980	1990	2000
0.2 and less	7	10	14	11
0.22–0.25	39	31	27	52
0.26–0.31	3	24	6	–
0.32	4	9	29	21
0.33 and more	44	26	24	16

in the column diameter. According to these data, the main tendency is the preferred use of 0.25- and 0.32-mm diameter. Frequency of the use of such columns in published works is 73%. These values can be explained by the existence of standards for capillary tube diameters. We should notice that researches are interested in small diameter (<0.2 mm) capillary columns which are more compact and can be used in express-analysis and for the development of highly efficient columns.

### 3.2. Stationary liquid phase and carrier gas

#### 3.2.1. Stationary liquid phase

The selectivity of a chromatographic system depends most of all on the nature of SLP. Table 3 contains data on the dynamics of SLP use in capillary gas chromatography.

According to Table 3, in the period from 1970 to

2000, considerable changes took place in the SLP used in capillary gas chromatography. Old SLP types were replaced by new ones; we divided them into eight groups. At present, the most prevalent SLP type is phenylmethylsilicones, containing less than 25% of phenyl. Their use increased from 4% in 1972 to 42% in 2000. The use of polyethers decreased by almost five times (32% in 1970 to 7% in 2000). The use of hydrocarbon phases has decreased almost to zero. In 1980s and 1990s 100% methylsilicone phases were popular (43 and 35%), but their use has returned to the 1970 values (16% in 1970, 21% in 2000). However, new SLP types appeared, for example, silicon chiral phases based on cyclodextrines and their carbon derivatives.

#### 3.2.2. Thickness of SLP layer in a capillary column

Thickness of the SLP layer influences broadening of chromatographic zones and column capacity. Unfortunately, earlier data on SLP layer thickness were not always included in papers (for example, in 1970 it was hard to find this parameter in publications). According to our data, the use of less than 0.1-mm thick SLP layers has decreased since 1980, while the number of columns with SLP layer thickness of 0.25 mm has increased.

It is important to notice that standard layer thicknesses (as other parameters) evidence that the over-

Table 3  
Dynamics of capillary column SLP use (%)

SLP	Years			
	1970	1980	1990	2000
100% Methylsilicone	16	43	35	21.5
Methyl[phenyl(≤25%)]silicone	4	12	26	49
Methyl[phenyl(>25%)]silicone	8	5	4	4
Methyl[cyanpropyl(25%)]silicone	–	–	6	5.5
Methyl[phenyl (7%), cyanpropyl (7%)]silicone	–	–	6	6
Polyethers	32	25	13	7
<i>Hydrocarbons</i>				
Apiesons	20	5	–	1
Squalanes	20	5	–	1
100% Dicyanalkylsilicone	–	–	0.7	4
Other	–	5	9	3

whelming number of columns are manufactured by companies, actually there are no home-made columns. Almost one half (47%) of all columns mentioned in papers in 2000 are columns with 30-m length, 0.25-mm diameter and 25- $\mu$ m SLP layer thickness. The proportion of such columns in common use is probably even greater, as their efficiency is  $\sim$ 100 000 theoretical plates, which is quite enough for most analytical tasks.

### 3.2.3. Use of various carrier gases

Carrier gas influences not only the kinetic, but also the equilibrium characteristics of capillary systems as well [40]. Using different carrier gases at permanent pressure we can smoothly vary selectivity of a gas–SLP chromatographic system. Table 4 contains data on the use of various carrier gases in capillary chromatography.

The variety of carrier gases used in capillary chromatography is wide. It includes traditional carriers such as nitrogen, helium and hydrogen, and gases like argon, ammonia, carbon dioxide, etc. and their mixtures as well. The most prevalent gas in 1990–2000 is helium (62–63%), its use having increased six-fold compared to 1970. Nitrogen holds the second place with 19%, its use having decreased, but now remaining stable. The use of hydrogen, which was very popular in the 1970s (48%) has recently decreased to 12–14%.

## 3.3. Experiment parameters

### 3.3.1. Separation temperature modes

The temperature parameters of chromatographic separation predetermine the success of a developed chromatographic method. The possibility of temperature changes during the separation process greatly

Table 4  
Dynamics of the use of carrier gases (%)

Gas	Years			
	1970	1980	1990	2000
N <sub>2</sub>	30	27	19	19
He	12	36	62	63
H <sub>2</sub>	49	24	14	12
Ar	5	9	2	3
CO <sub>2</sub>	2	2	2	1
Other	2	2	1	2

Table 5  
Use of temperature modes (%)

Temperature mode	Years			
	1970	1980	1990	2000
Isothermal	43	35	26	12
Programmed	57	65	74	88
<i>Temp. (°C)</i>				
100 and less	49.5	13.5	14	12.5
101–200	45.5	38.5	34	30
201–300	5	43	43.5	47
>300	–	5	7.5	10.5

improves and widens the abilities of gas chromatography.

Table 5 contains data on the use of different temperature modes. According to this table, temperature modes mentioned in most papers on capillary chromatography have changed significantly in recent decades. In 2000 only 12% of experiments were made at constant temperature (43% in 1970, 26% in 1990). Notice that most experiments were run in mixed temperature modes, where isothermal mode is replaced by temperature programming and vice versa.

More and more high-boiling compounds are analysed in capillary chromatography. In 1970 one half of studies were run at 100 °C or less, but only 13% in 2000. In 1970 the highest operating temperature did not exceed 210–300 °C in only 5% of cases, while in 2000 almost half the studies were conducted in this temperature interval. It is remarkable that more and more papers report operating temperatures higher than 300 °C (none in 1970, 10% in 2000).

### 3.3.2. Sample injection

The method of sample injection into the column influences such important parameters as efficiency, sensitivity, etc., and has been permanently improved not only by changes and the design of the injection device, but also by changes in injection methods. Thus, the traditional simple split injection method that was almost unique in the first stage of capillary chromatography evolution is now often replaced by the direct sample injection method. A new method is becoming more and more popular. Stream splitter turns on a fixed period of time later than direct sample injection (so-called split/splitless system).

Table 6  
Dynamics of the use of sample insertion methods (%)

Sample injection	Years			
	1970	1980	1990	2000
Split injection	90	76	47	29
Split/splitless	–	–	18	50
Direct/on-column	–	9	21	7.5
Other	10	15	14	13.5

The “tail docking” effect appears on the sample, and as a result the initial sample zone converges. This method is described in 50% papers in 2000. Table 6 contains data on the dynamics of the use of various sample injection methods. According to these data, the most popular method is split/splitless.

There is one more practically interesting and important method of sample injection with syringe-type device, when a linear absorber containing concentrated earlier admixtures moves from the needle to the high temperature zone in a vaporiser. In this case, admixtures are stripped and transported by the carrier gas to the capillary column. This graceful idea and device design were suggested by Pawliszyn [41].

#### 4. Conclusion

Capillary chromatography is one of the most demanded, informative and rapidly developing analytical methods. Chromatographic equipment is becoming better and better.

And the process of any science evolution has been figuratively characterised by A. Einstein: “Science is not, and will never be a completed book. Any new success brings up new questions. Any evolution uncovers new difficulties”.

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