Making and Manipulating Capillary Columns for Gas Chromatography

by Kurt Grob

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Preface

I have repeatedly stated quite categorically throughout my professional career that I would never write a book. Why? I have always loved experimental work done by my own hands so much that I abhored every activity which took me away from the bench. Accordingly, I hated writing the (necessary) papers. I felt constantly tempted to consider symposia and conferences to be less necessary, and I missed most of them. So, why waste time by writing an even less necessary book?

The reason was a series of urgent appeals by many workers akin to myself. They blamed me for scattering my experience, without any guide to relative weight and topicality, over numerous papers. They wanted me to make it accessible from a single source, in other words to make it applicable. And they wanted me to fill in all the bits and pieces I had never included in a paper. Again in other words, they wanted a **complete description of my way of working.**

Finally, I gave in because of the present situation of our discipline. Most practicians of HRGC know they should really make their own columns in order to exploit the full potentialities of their branch. However, most of them succumb to the temptation of commercial columns. "Why should I worry about a thing I can buy"?, is the question they ask themselves. Some of them are wavering. The availability of a practical guide may give them the final impulse they have been waiting for. Hence my apostasy!

This brings us to the essential point. The book must fit the motivation. Rather than easy and exciting reading, it has to be a **laboratory guide** for individual column makers. What it recommends and describes **must work.** Accordingly, the descriptions have to be complete. They have to include all the know-how, the means, and the

manipulations which may contribute to the reliability of the procedures, and to the quality of the product. And this is where the basic problem lies. There are various approaches to column technology. Considering them all, as is normal in scientific literature, would confuse, rather than help, the practical user. My only solution to the problem is to concentrate on **my own approach**. In other words, the book gives no survey on how columns can be made, but describes comprehensively how we make them.

In keeping with the treatment of the practical work, no comprehensive survey of the **literature** is presented. The references are reduced to three groups. The first one consists of a few books and reviews which give access to more complete information. The second group cites pioneering work, *i.e.* the contributions which introduced the essential techniques of our actual work. The third one includes recent technical reports which give a specifically interested reader more details than can be included in this book.

I appear as the only author, since I assume the full responsibility for the subject matter. However, the book is the product of an extremely intense and fruitful **cooperation** with several experts, all of whom are true specialists in their particular sector. I would be unable to fulfill my task without collaboration. The reason is my repeated experience that a principle or a technique which worked brilliantly in our laboratory, worked less well, or even failed, when applied in a different environment. Hence my policy of not including any recommendation without having had it crosschecked and confirmed in other laboratories. Such cooperation has a second function. In the past years, my wife and I have been fully committed to column technological studies, and had little chance of evaluating our products beyond the basic testing. Obviously, **application** experience contributes greatly to the final judgment. We were fortunate to have friends who assumed this indispensable, complementary, function. The primary contributors were the following:

Wolfgang Blum, Basel, has been the main technological contributor. Most of the mechanistic studies were done in collaboration with him, and several essential ideas and methods are due to his untiring imagination and creativity.

Ian Davies, Stevenage, assisted in selecting and describing materials, tools, and manipulations.

Mario Galli, Legnano, besides contributing to the majority of topics, has specifically offered his large experience with handling fused silica.

Koni Grob, Zürich, was our most efficient source of information concerning the suitability of certain column types for specific applications. He also contributed numerous technological ideas.

Axel Habich, Zürich, has traditionally acted, and is still acting, as my scientific conscience. He has continuously and critically followed the development of this book, the internal structure of which is based on his ideas.

Willy Walther, Basel, has invested an impressive amount of skill, care, and patience in independently evaluating our techniques under the conditions of a large industrial research institution.

The realization of this book was supported in two important ways. It was **Anthony J. Rackstraw** of Hüthig, Heidelberg, who with indefatigable interest and patience managed to make my English readable while still preserving my intended meaning. He also spared no effort in materializing our sometimes strange ideas. Next to the language and the editorial presentation, there are the illustrations whose purpose is to replace practical demonstrations. We were fortunate to have the collaboration of an artist, **Harald Clausen**, Westendorf, who succeeded in illustrating arrangements and manipulations which could hardly have been presented in an equally convincing way in mere words.

I wish to thank my primary collaborator last. Whenever the personal pronoun "we" occurs in the text, it means my wife **Gertrud Grob** and myself. Without Trudy's work in the past 20 years, my work would not have been accomplished. This not primarily because she has assumed most of the practical activity. Even more important was her constant, encouraging and optimistic presence throughout all failures, successes, and decisions which I cannot imagine ever having managed on my own. It was thanks to her that the daily work occurred in a friendly atmosphere.

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Kurt Grob

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1 Introduction

1.1 Why Do Some Chromatographers Prefer to Make Their Own Capillary Columns?

What Points Favor Individual Column Preparation?

Asked why they make their own columns, different chromatographers will very probably give widely differing answers. While all the answers will stress the advantages ensuing from individual column preparation, the nature of these advantages may differ surprisingly. The variations directly reflect the individual chromatographer's scientific and economic priorities, as well as different conditions prevailing in his scientific environment in terms of organization, manpower, and facilities. Accordingly, it is virtually impossible to present the advantages in any generally valid order of relative importance.

Economy. In numerous laboratories, most of which have a relatively high column consumption, column preparation provides overwhelming economic advantages. Since there is some disagreement on this point, and since the discussion has hitherto been based primarily on general arguments, we prefer to describe a real-life, practical example. In a medium-size research institute it has become general practice to concentrate production of the necessary columns in certain periods, rather than to make single columns throughout the year (which may be equally satisfactory, depending on local conditions). In this institute preparation of six 25 m columns takes one operator two full working days (actually the work consists of short-time manipulations scattered over six to eight days). Thus, one 25 m column costs one third of a working day, plus the initiation time, the cost of the materials consumed, and the time and materials lost for unsatisfactory preparation. Compared to the labor costs, the initiation time and the cost of the materials are almost negligible provided the column consumption is not lower than about three columns a month. According to a recent inquiry in eight laboratories independently making their own columns, virtually all the columns produced nowadays (in contrast to previously) meet strin-

gent specifications, demonstrating that the cost of lost time and material is also very small. The overall result is that, depending on local conditions, a **self-made column costs 10-20% of a commercial one.**

The comparison may be greatly influenced by the fact that the price of a column from a commercial column manufacturer has to include all general expenses such as laboratory space, infrastructure, insurance, *etc.* In a research institute, these expenses are generated anyway by the regular research work, and are hardly influenced by whether or not some columns are made now and then, using the facilities available.

Large consumption. What we mean here refers to a particular way of using columns which is best explained by a practical example. Numerous laboratories have to analyze "difficult" samples, mostly of biological origin. The samples are known to be **"dirty"**, *i.e.* they contain traces of difficultly evaporable, polar, byproducts which "poison" the columns. The columns can only be protected by subjecting the samples to careful clean-up prior to analysis. However, this may cause severe artifact formation. Analyzing untreated samples means a great saving of time and labor, and produces much more reliable results. The attendant **short column lifetime** may be tolerable when fresh columns are constantly and cheaply produced. The example is extreme in that it implies that a column of constant specifications is constantly reproduced, possibly over years. The details of the preparation procedure have been perfectly optimized, and the laboratory staff have become so familiar therewith that column preparation continues almost automatically besides the regular analytical work. In fact, analysts working under such conditions state categorically that their work would be inconceivable with commercial columns.

Availability. It is a widespread and frequent problem in HRGC, particularly in research projects producing unexpected requirements, that the ideal column is never at hand at the right moment. It may be available in a matter of days. But there may be a delivery time of several months. Full control of availability is one of the most obvious features of individual column preparation.

Phase selection. The first task involved in solving a new analytical problem is that of selecting a stationary phase. There may possibly be analogies with earlier problems,

permitting a prediction with high probability of success. However, a reasonable prediction may be difficult in another case. The reaction of many chromatographers is then to use the column that just happens to be at hand. Many workers will hardly have any alternative.

A chromatographer making his own columns normally has quite a variety of column types in stock. He will know in a relatively short time how the sample behaves on different phases. One of the existing columns may be suitable, or the comparisons will allow extrapolation to a more promising column which can be prepared in a matter of days.

Optimization. A more careful choice may be desirable when a fresh problem resists ready solution, or when a new analysis is planned to become routine work over a long period, possibly over months or years. In the latter case it will pay to establish optimum conditions which means achieving sufficient resolution with sufficient quantitative reliability in the shortest possible analysis time, and under conditions assuring the best long-term performance of the column. An additional matter of choice may be the sampling technique (split, splitless, on-column), which will influence the selection of the column i.d., and may call for a column fitted with a retention gap.

Experimental optimization starts with **comparing available columns**, and extrapolating to more suitable ones by varying the stationary phase, film thickness, activity, and column dimensions. The task may include tailor-making several columns with various specifications. It is typically based on individual column preparation.

Tolerable risk. There are two main ways of ruining a capillary column, *viz.* by applying critical **conditions** (temperature, amount and nature of sample or solvent), or just by improper **handling**. Accordingly, the user of a commercial column may be afraid both of varying the conditions and of handling the column, as representing too great a **risk**. With easily replaceable, individually made columns, the risk is considerably lower, thus permitting the kind of broad study which is required to fully exploit the potential of the tool and the technique. In other words, commercial columns are precious while individually made columns are just tools, and the mentality of application corresponds to this difference.

Known design. Whenever a capillary column is used for more than just trivial analytical problems, it may be important to be familiar with the "inner workings" of the column. Details of its preparation contribute to certain features of its performance. An awareness thereof is the ideal basis of optimum column exploitation.

Quality. Column quality has a complex historical background. Not long ago, commercial columns were generally poor, whereas good columns had to be self-made. Within just a few years, the quality of commercial columns has improved dramatically. The change is even creating a tendency to view today's commercial columns as professional products and self-made columns as amateurish. Consequently, a chromatographer interested in individual column production may now ask, "is it difficult to match a commercial column?" Obviously, the discussed points favoring individual column production remain valid only so long as self-made columns continue to be superior or comparable in quality.

Several aspects have to be discussed in this context. First of all we can state it is easy to prepare the **workhorses** of HRGC, *viz.* the apolar, inert, high temperature columns, in a quality at least matching the corresponding commercial columns. This column type can solve the large majority of chromatographic problems.

Secondly, there are more sophisticated column types less easy to prepare in high quality. Here, the individual column maker has the options of learning to produce them or of relying on commercial products. Of course, there is no need for individual preparation of all column types.

Thirdly, there is one particular aspect of column quality which has much to do with individual column preparation. A gas chromatographer may have to handle **"difficult"** samples of low volatility, of high tendency to adsorption, and present in trace concentration. Under such conditions, the importance of column quality cannot be overemphasized. Even a slightly better column will clearly give better results. In contrast, **"easy"** samples yield symmetric peaks and straight calibration curves under ultra-trace conditions, even on very modest columns. In other words, some work can be done perfectly well with a very ordinary knife; an expensive surgeon's scalpel offers no advantages.

Commercial columns are expected to be of **top quality**. A vendor cannot afford to offer columns of modest quality (as it was done a few years ago). In contrast, the individual column maker can easily simplify or shorten his preparation procedures, and see what these **modest** columns are still good for. Adapting the expenditure on preparation to the required quality is a specific aspect of tailor-making, which is another specific point favoring individual column preparation.

Warning. In our experience, there are conditions under which individual column preparation does not unfold its full advantages. If only a few columns are made per year, the necessary know-how has to be reestablished for every new application. Wherever there is a rapid staff turnover, the experience, and the ideas behind the local installations are lost. Interest in individual column preparation is generally low in laboratories using mainly standardized analytical procedures, possibly even stipulating defined and commercially available capillary columns.

What Does General Column Technology Have to Offer?

Column preparation is the largest sector, but still only a sector, of column technology. Experience shows that column makers normally engage in other fields of column technology too, whereas most column buyers refrain from any column technological involvement. Some major fields of general column technology may be listed.

Coupling techniques. A column may be coupled to an identical or different column, to a precolumn or retention gap, or to various ancillary devices. Couplings have to be thermostable, and free of adsorptive effects and of dead volumes. The design and quality of **commercially available coupling** parts have greatly improved in recent years. However, simultaneous progress in column production and application techniques tend to outweigh the improvements, as the quality requirements grow too fast. At present there are numerous coupling problems which can be solved satisfactorily only by **manual** techniques.

Retention gaps. In addition to their original function of overcoming band broadening in space [1], retention gaps are becoming increasingly attractive for large-volume on-column injection. Whereas their original

length was 0.5-2 m, injections of 10-200 µl may require 5-25 m. Their proper functioning depends strongly on the nature of their **internal surface**, which is easily controlled by well-known methods of treatment. Extensive contamination may require frequent replacement. Both typical aspects, length and replacement, call for inexpensive material, which is obviously glass. It is hard to see how the elegant new technique can be implemented without individual column technology.

Splitters. Most stream splitters are used to transfer column effluents to different detectors, columns, or trapping devices. Not one of the new, highly refined, commercial splitters can compare with a hand-made splitter [2].

GC/MS interfaces, column switching parts. A few years ago, all these components were hand made. Meanwhile, impressive effort has been invested in producing these items in high quality, versatility, and ease of use. However, none of them is really free of minute dead volumes and adsorption effects, both of which can be overcome by **manual** techniques.

Headspace analysis. Direct thermal desorption from an adsorbent trap onto a capillary column is a technique which is not yet widely supported by commercially available materials. For the time being, it depends strongly on individual column technology.

Column washing. Washability is commonly understood as a principal feature of most modern capillary columns. Accordingly, washing should have become a widely applied, *trivial* manipulation. And yet most chromatographers don't wash their columns. This might appear regrettable as a failure to exploit the columns' full potential. From a more pragmatic standpoint, however, the fact may be considered to be fortunate. Column washing is **less trivial** than assumed. In particular, more polar and thicker coatings, both of which are of growing importance, can be severely damaged by improper washing although immobilization may be perfect. On the other hand, we know experienced column makers who routinely wash their freshly prepared columns immediately on conclusion of preparation. Their argument is that washing may, at least to some extent, and with certain column types, substitute conditioning. Accordingly, washing instead of long conditioning may mean **time saving**.

Column recoating. Recoating may be understood as partial column preparation (no surface treatment involved). It is especially attractive with polyglycol coatings using the rapid and easy dynamic coating technique. Laboratories which can solve their problems with such columns may be excellently served by this sector of column technology.

In conclusion, we wish to show that HRGC can be performed on two distinct levels. The first involves use of capillary columns practically without touching them. The second includes column technology. On the first level, just a small fraction of the full potential of HRGC is exploited, with the user remaining largely oblivious to the non-activated sector. Activating the full potential requires mastery of column technology.

1.2 Glass or Fused Silica?

Which Material Yields the Better Column?

Full awareness of the relative roles of the two major column materials is of cardinal importance. Since the available information is almost invariably beset with errors, we wish to discuss the comparison at length rather than give a short answer to the question. We may first look at the two materials purely from the standpoint of the user.

Assessing the relative suitabilities is very difficult, since essentially subjective arguments play an important role. The major suitability criteria may be listed.

Suitability criteria	Glass	Fused silica
1. Chromatographic quality of perfectly prepared column	no difference	
2. Effort required for surface treatment	significant	modest
3. Availability of coatings	unlimited	limited
4. Thermostability of tubing material	unlimited	limited
5. End treatment	required	not required
6. Convenience of installation	no difference	
7. Convenience of GC/MS coupling	difficult to judge	
8. Convenience of quick connection	good	modest

Criteria 1-4 are of a scientific, objective character. Criteria 5-8 have more to do with convenience and depend strongly on subjective evaluation. The individual criteria may be briefly discussed.