New Developments and Experiences with Glass Capillary Column Production and Sampling Techniques

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Summary

An introductory discussion is given on the manufacture of glass capillary columns, including details of the methods of column testing and of the properties of the inner surfaces of glass capillaries. As a result a simple method for the testing of various kinds of support surfaces is presented which allows stepwise control of the column making procedure. A new kind of pretreatment of soft glass surfaces with HCl and HF at 450 °C is described which allows the production of non-polar columns with much improved tailing behaviour for strongly polar solutes. Concerning capillary column sampling a new technique of "direct" sampling without previous vaporisation of the sample outside the column is presented together with a double column system for "selective" sampling of complex mixtures.

Optimum gas chromatographic analyses of complex mixtures can only be achieved by using columns which combine high separation efficiency, excellent tailing behaviour, and temperature stability.

These requirements are met only by carefully prepared glass capillary columns the full efficiency of which can only be utilized if the instrumentation has been adequately designed. Older commercial instruments have to be replaced or reconstructed with regard to the special requirements of (glass) capillary gas chromatography. These are:

- the handling of very low carrier gas flows;
- wide range of sample volumes;
- steep peak profiles.

In our paper we intend to contribute to two areas of capillary gas chromatography which are column production including testing, and sampling techniques.

Glass capillary columns with improved tailing behaviour by coating soft glass capillaries, after a combined HCl + HF pretreatment of surfaces

The important aim of glass capillary column-making is to obtain temperature stable and homogeneous films of stationary liquids which are deposited on glass surfaces that should not contribute to the intermolecular interaction between solute and solvent i.e. to the polarity of the stationary liquid. In our opinion the requirements of glass surfaces are as follows.

1. There is no or neglible adsorption of solute molecules which causes peak tailing or even irreversible adsorption, especially when polar solutes have to be chromatographed on non-polar stationary liquids in thin films.
2. There is no catalytic activity of surfaces which may cause decomposition of solutes and/or stationary liquids especially at elevated temperatures.
3. The homogeneity and geometry (roughness) of support layers is suitable for generating "stable" films of the stationary liquid the variable thickness of which is the optimum for high separation- or "coating"-efficiency at not too low sample capacity e.g. not too high phase ratios.

Before reporting on our recent experiments on column making, we shall discuss the various test procedures for glass capillary surfaces and the ready-to-use column. In testing columns the symmetry of peaks of selected test compounds (contained in so called polarity mixtures) is studied at a defined temperature and sample load. Not so common is the evaluation of retention indices of these test compounds in order to characterize the polarity of the stationary phase which may be influenced also by the properties of the support surfaces. Irreversible solute adsorption in the subnanogram range restricts the application of gas chromatographic separations in ultra-trace analysis but has not been investigated by many authors. Investigations on solute decomposition which may be catalyzed by either basic or acidic surfaces is done with suitable test compounds like phenols and amines which are considered to be able to characterize the acidity or basicity of surfaces [1] via the observed tailing effects or with compounds like aldehydes and acetals which undergo typical decomposition reactions on "active" surfaces. It can be assumed that columns which exhibit tailing effects with peaks of polar test compounds also show catalytic decomposition, especially at elevated temperatures. Last but not least the temperature stability of capillary columns has to be tested under conditions which are typical for quantitative and qualitative practical applications. The loss of stationary liquid by decomposition at the highest

column temperature to be applied has to be kept as low as possible. The decrease of k'-values of special test compounds is a suitable relative measure for the loss of stationary liquid. The control of baseline drift and noise during temperature programming when using maximum detector sensitivity is another necessary method of column testing, quantitative figures are seldom given in the literature, however. It is important for the proper assessment of capillary columns that during and after extended isothermal and temperature programming the column tailing behaviour and polarity of the stationary liquid is controlled by using the common polarity mixtures under defined test conditions. The determination of retention indices of these standard compounds is strongly recommended.

An aim of our present work in glass capillary column production is the generation of support surfaces which show no or only minor influence on peak symmetry and polarity of even very polar solutes when using non or weakly polar stationary liquids like squalane, Kovats hydrocarbon, OV 101, SE 52, OV 17 and so on. It is of advantage, if additional intermediate deactivation procedures are not necessary, at least for the separation of not extremely polar classes of compounds. If the support surface has been deactivated with organic compounds before coating with stationary liquid, the tailing behaviour should not be made worse by heating the column to the maximum temperature of application. In our experience the usual deactivation of surfaces with Carbowax 20M or Emulphor 0 are not stable enough for extended use beyond 220 °C – at least on NaCl layers. This is true even after deactivation by heating to 260 °C according to *Aue*'s procedure. For the investigation of the surface properties of glass capillaries the above mentioned test methods which comprise studies of tailing and retention indices proved to be time consuming. Moreover, direct information on the properties of the support surface i.e. before coating is not available. Therefore we adopted a test method which allows the characterization of all kinds of surface such as untreated, HCl treated, $BaCO_3$ covered, deactivated or coated with a stationary liquid. Such a method could also be suitable for the purpose of controlling the column-making procedure from step to step without performing too elaborate and time consuming measurements.

A simple test method for the assessment of support surfaces in glass capillaries

The chromatographic system consists of a capillary column with a polar stationary phase like Carbowax 20 M or Marlophen on which peaks of a polar test solute are eluted with perfect symmetry. A piece of the capillary to be tested is connected to this (pre-) column by means of Teflon shrinking tube (see Fig. 1).

A dilute solution of the polar test compound (for example n-butanol) in a non-polar solvent (hydrocarbon) is injected into the pre-column. The n-butanol leaves this column with an ideal peak profile and then enters the capillary to be tested. The symmetry of the test peak can be spoiled by adsorption phenomena in the test capillary and in severe cases very broad and unsymmetrical profiles or even total adsorption of the solute are observed whereas well prepared surfaces do not cause any symmetry distortion. The sampling of the test solution is repeated several times in order to control repeatability of peak areas and peak symmetry which may be effected by deactivation of the surface by the test sample itself (see Figs. 2 and 3).

Several characteristic features of this test method may be mentioned.

1. Short pieces of capillary tubing (1–4 m) can be tested. Thus the homogeneity and quality of a surface treatment can be studied over the total length of a capillary by taking representative parts as test pieces.
2. Surfaces which have been generated by any kind of pretreatment procedure may be tested before beginning the time consuming coating procedure. The process of column making may be interrupted in the case of adsorptive surfaces.
3. When coating columns with polar stationary phases surface properties of the support can be studied without the interfering effect of deactivation by the stationary liquid itself.
4. A nearly Gaussian peak is generated by the pre-column from which symmetry distortions may be evaluated by mathematical methods using symmetry factors, peak area/peak height ratios etc. The non-polar solvent is separated completely from the test compound in the precolumn.

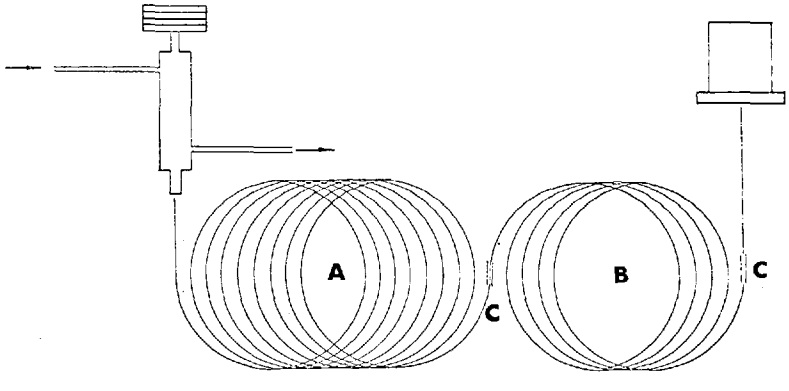

Fig. 1

- Test method for surface: Properties of representative capillary pieces before and after special treatment. A) precolumn: capillary column with ideal peak profile of test solute (for example: n-butanol). B) test column: 2 m length. c) Teflon shrinking tube.

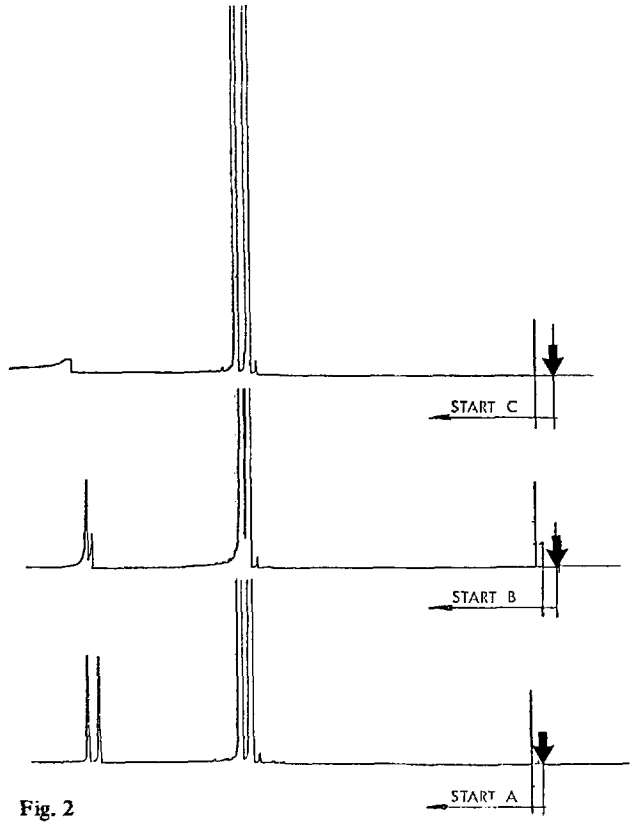

Fig. 2

● Peak symmetry of n-butanol after elution from representative pieces of insufficiently HCl + HF pre-treated soft glass capillary (160 m). A) 2 m piece from start. B) 2 m piece from middle. C) 2 m piece from end. (Test method see Fig. 1).

A similar test method for surfaces without a precolumn, however, has been used previously by *J. A. Luyten* [2], whereas *K. Grob* [3] has coupled Pt capillaries with a coated precolumn in order to study the adsorptive properties of Pt capillaries and their deactivation by the bleeding of the precolumn. The practical application of our method is illustrated in Figs. 2 and 3. In Fig. 2 three different pieces of a HCl + HF treated, soft glass capillary were taken for testing from beginning, middle, and end of a 160 m piece in order to study the homogeneity of the support surface along the total length of the capillary. In the example insufficient surface treatment was discovered. The peak tailing increases considerably from the beginning of the column towards the end. The test method was also used to study adsorption phenomena at column ends straightened in a flame for direct connection to injectors and detectors. No severe tailing effects were found with not too long pieces. Nevertheless deactivation of these ends before using the column may be of advantage. In Fig. 3 results of studies with various sorts of glass which had been treated with HCl or HCl + HF and by the *Grob* $BaCO_3$ method [4] are given. The surfaces were studied before "etching" or deactivation, after certain thermal treatments and after coating with non-polar or polar stationary liquids. The observed tailing effects are characteristic and can be correlated with those shown by the peaks in the chromatograms of polarity mixtures measured with completely manufactured columns (for comparison see chromatograms in Fig. 4). Furthermore, the retention indices of the test compounds supply important information when correlated with the tailing effects obtained in the surface test (see Tables II and III).

As a result of our experiments on column making using HCl + HF, we apply the following pretreatment which is especially suitable for coating with OV 101 or similar non-polar stationary liquids. The soft glass capillary is first HCl treated at temperatures up to 450 °C using a continuous flow of HCl from a cylinder. In the next step a HF/N_2 mixture is led through the column for a period of 1–2 hours at 450 °C. During the subsequent cooling period of 1/2 hour pure N_2

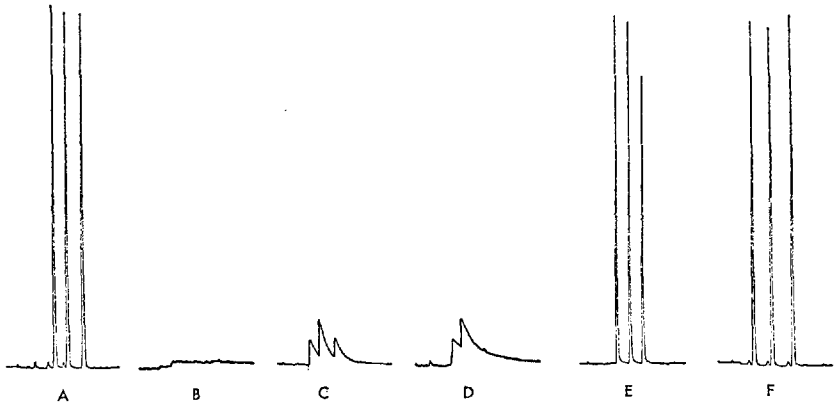

Fig. 3

● The influence of adsorption on peak symmetry of polar test solute on various glass capillary surfaces. (Test method see Fig. 1). A) no test column. B) Alkali-, Duran-, Pyrex glass (untreated). C) aqueous HCl treated Pyrex, same result with additional $BaCO_3$ (0.3) coating. D) soft glass, gaseous HCl-treated. E) soft glass, HCl + HF treated. F) soft glass, HCl + HF treated, CW 20M deactivated. For each test: three injections of n-butanol.

Table I

	Test capillary or column	Peak profile for n-butanol
Chromato-gramm	1: No test capillary	symmetrical peaks with all 3 injections
	2: 2 m untreated soft or Durane glass	strong adsorption with all 3 injections
	3: 2 m HCl treated soft glass	strong tail of butanol peak
	4: 2 m Pyrex treated with aqueous HCl	strong tailing
	2 m Pyrex covered with $BaCO_3$	strong tailing
	5: 2 m soft glass HCl + HF	minor tailing
	6: 2 m dito. Carbowax 20 M deactivated	no tailing

Table II. Influence of deactivation procedure on retention indices of selected test solutes with non-polar stationary liquid (OV 101). Column: 80 °C

	Butanol	Benzene	Cyclopentanone	1-Octene	n-Butylether
HCL pretr. + OV 101	–	658.2	–	788.7	878.1
HCl + HF pretr. + OV 101 + 280 °C	642.6	658.1	764.1	788.6	875.2
HCl + HF + CW 20M + OV 101 + 280 °C	647.3	659.4	766.5	788.8	875.5
HCl + HF + CW 20M + 280 °C + OV 101 + 280 °C	650.4	660.0	768.0	788.9	875.7

Table III. Polarity test of OV 101 column (HCl + HF pretreatment) with McReynolds compounds. Column: 120 °C

	McReynolds data* (OV 101)	HCl + HF + OV 101	Diff.
Butanol	647	641.0	– 6.0
Benzene	670	667.9	– 2.1
1.4-Dioxane	700	696.8	– 3.2
Nitropropane	719	713.5	– 5.5
2-Methyl-2-Pentanol	723	719.0	– 4.0
Pyridine	742	741.8	– 0.2
1-Iodobutane	822	819.3	– 2.7
2-Octyne	864	862.9	– 1.1

* McReynolds data: J. of Chr. Science 8, 685 (1970)

flows through the column. Afterwards the capillary is rinsed with diethyl ether for the removal of HCl and HF residues. By coating with OV 101 without previous deactivation columns are obtained from which n-butanol and cyclopentanone are eluted but show tailing.

Both test compounds are adsorbed irreversibly by HCl-pretreated OV 101 columns (see chromatogram a of Fig. 4) whereas by Carbowax deactivation of the HCl treated surface the excellent chromatogram b is obtained. By simple thermal conditioning of the HCl/HF treated OV 101 column for several hours at 280 °C without Carbowax deactivation considerable improvement of symmetry of the n-butanol and cyclopentanone peaks is observed (see chromatogram c, of Fig. 4). This observation supports the assumption that at high temperatures methylsilicones undergo simultaneous decomposition and chemical bonding of decomposition products to the surface similar to the Carbowax deactivation procedure of *Aue* [5]. Further reduction of tailing is achieved by Carbowax 20 M deactivation at 280 °C including removal of excess Carbowax by rinsing with a solvent and subsequent coating (see chromatogram d of Fig. 4). The Carbowax deactivation is very stable thermally on this special support, but as on HCl treated surfaces causes increase of polarity of stationary liquid as can be seen from the retention indices, preferably of the polar test compounds (see Table II). From Table III it may be seen that with our method of surface treatment and without additional Carbowax deactivation much lower retention indices of the McReynolds compounds are achieved than with packed columns.

In the chromatograms of Fig. 5 the tailing behaviour of different OV 101 columns was tested using two test

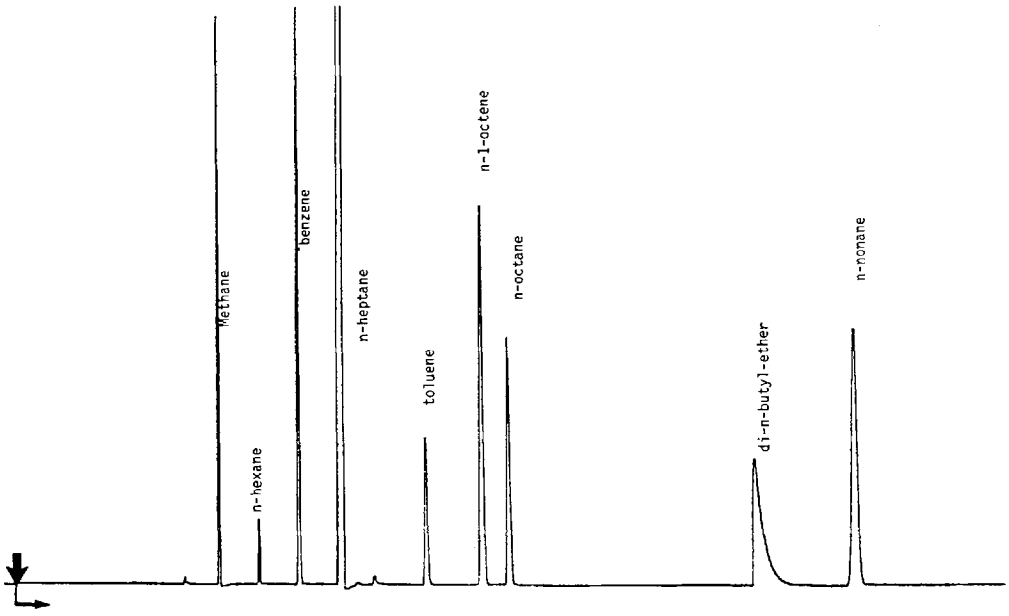

Fig. 4a

- HCl pre-treatment

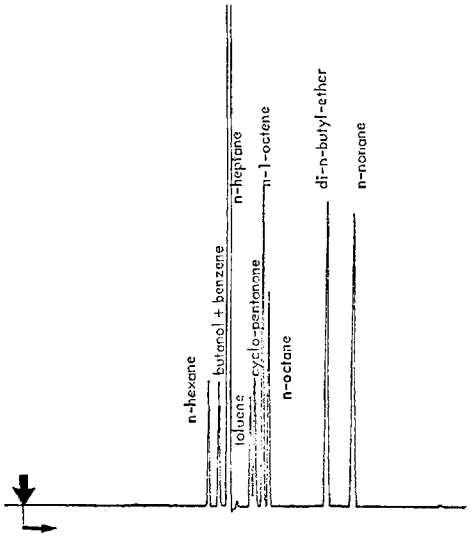

Fig. 4b

- HCl pre-treatment + CW 20M

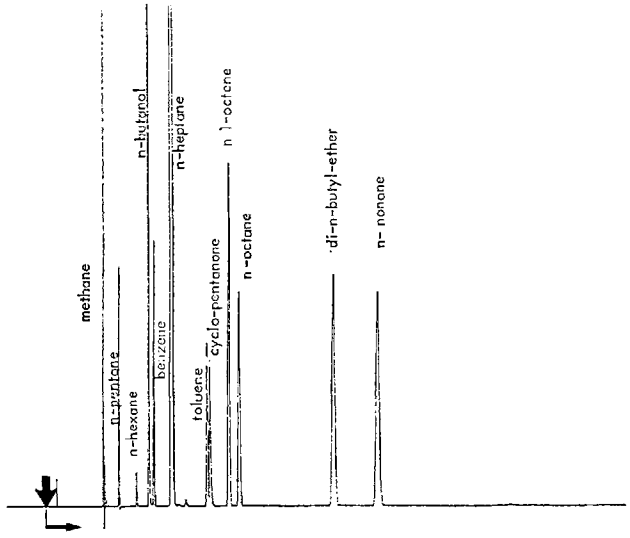

Fig. 4c

- HCl + HF + OV 101 + 280 °C

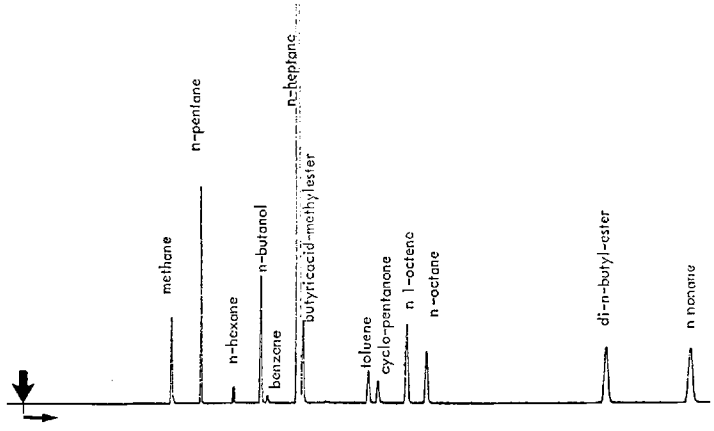

Fig. 4d

- HCl + HF + CW 20M + 280 °C + OV 101 + 280 °C

Fig. 4

- Test chromatograms of OV 101-columns with polarity mixture after various surface pre-treatment procedures.

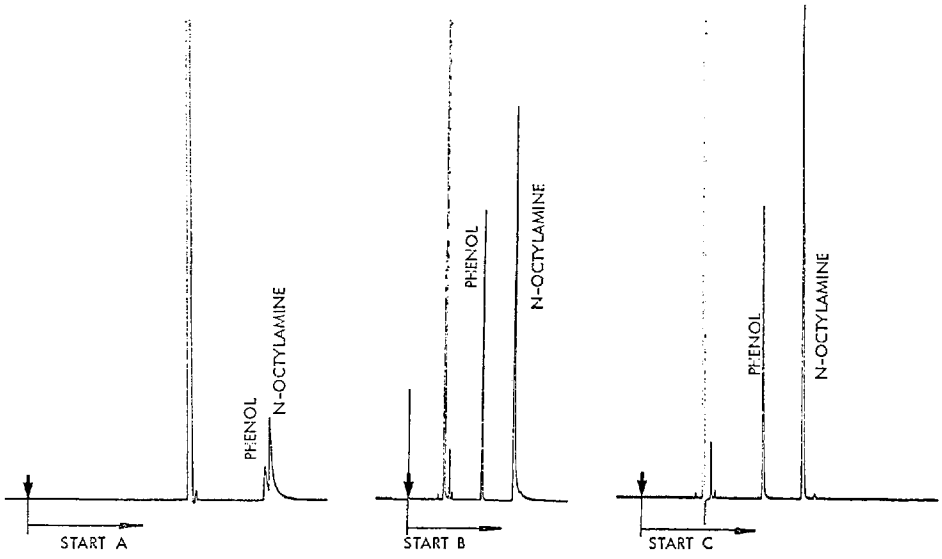

Fig. 5

• Tailing test with phenol and n-octylamine. A) 20 m OV 101, HCl pre-treated, CW 20M deactivated. B) 25 m OV 101, HCl + HF pre-treated + 280 °C. C) 20 m OV 101, HCl + HF + CW 20M + 280 °C + EMO + 280 °C.

solutes of much stronger polarity than n-butanol or cyclopentanone. Phenol and primary n-octylamine were selected. That the characterization of the acidity or basicity of surfaces can be measured by these compounds seems to be dubious, however, according to our experience. Nevertheless, every chromatographer knows that primary amines, for example, are the most critical compounds with regard to tailing behaviour especially on non-polar stationary liquids. Even on the less adsorptive HCl + HF treated surface tailing of n-octymalmine can be completely removed only be deactivation with Carbowax and Emulphor 0. It can be seen from comparison of chromatograms A and B that phenol and octylamine exhibit much stronger tailing on the HCl pretreated and Carbowax 20 M deactivated surface than on the HCl + HF pretreated surface without Carbowax deactivation.

Up to now the following stationary liquids could be deposited on new surfaces without any difficulties: OV 1, OV 3, OV 7, OV 17, OV 101, SE 52, OV 225, Kovats'-hydrocarbon, Marlophen, PPG, Carbowax 20 M.

For polar stationary liquids deactivation is not necessary. The separation efficiency of the columns coated by the dynamic mercury plug method was always between 2500 and 3500 theoretical plates ($k > 5$) per meter (in some cases even more) depending on the polarity of the stationary liquid. Thermal stability with regard to tailing behaviour and bleeding (drift) is excellent and superior to that of HCl pretreated columns. Aqueous samples can be analyzed without severe deterioration of tailing behaviour and separation efficiency. The same is true for HCl pretreated columns – contrary to statements made in the literature [5].

Finally, we would like to point out that we adopted the consecutive HF treating preferably in order to obtain less adsorptive surfaces, coating on which more thermally stable columns are obtained with regard to tailing and bleeding. The growth of any kind of SiO_2 whiskers which are considered by us to be very adsorptive, was carefully avoided. Therefore the capillaries were always HF-treated dynamically i.e. under flow conditions. Thus the SiF_4 formed by the reaction of HF with the glass surface is removed by the HF/N_2 flow. The method of HCl + HF surface treating is a gas phase reaction and can be applied also for very long capillaries (170 m) without difficulties.

The coating of all capillaries was performed by the mercury plug method described previously be the authors. Film thicknesses of 0.1–0.2 μ were obtained in most cases.

Sampling techniques in capillary GC

"Selective" sampling

The sample capacity of capillary columns is in the range of nanograms per component depending on the column diameter, film thickness and type of stationary liquid. Splitter injection is applied in the case of mixtures of several components present only within a limited range of concentrations. Sensitive and reliable detection of traces in diluted solutions requires the overloading of the column with the solvent or main components which may also be present in the sample, especially if "splitless injection" is used. Difficulties arise when main and trace components are closely located in the chromatogram. Peak broadening of the

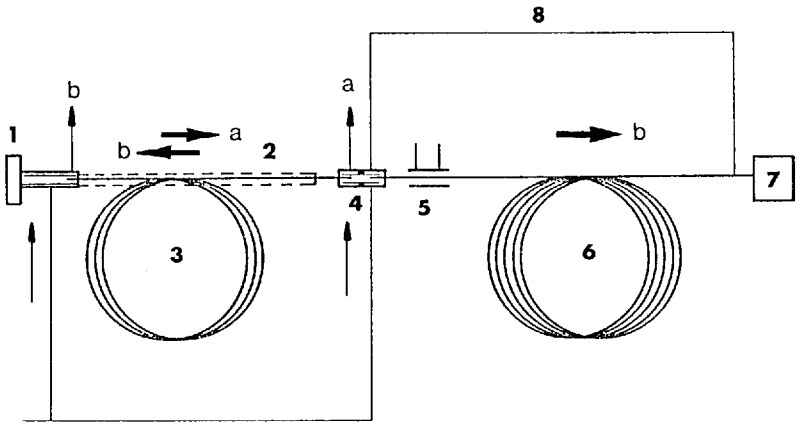

Fig. 6

- "Selective" sampling in double column systems with packed or capillary precolumn and capillary main-column. a) eluate transfer and cut, pre-separation, b) backflush, main-separation.
1. Injection port, 2. packed precolumn, 3. capillary precolumn, 4. coupling device, 5. trap, 6. main-column, 7. detector, 8. bypass.

overloaded peaks causes overlapping of the trace peaks thus complicating quantitative evaluation. The adjustment of the sample size to the concentration of every interesting component of a mixture would require the injection of different sample volumes which can be realized only by repeating the chromatographic separation. In many cases of practical analysis, however, only the trace components have to be separated and detected; therefore a "selective sampling" of the traces may be important. This means that the sample volume is chosen according to optimum detection of the interesting components. By means of multistage and multidimensional separations including heartcutting the disturbing major, or solvent components, are removed from the eluate by a pre-separation. The separation of the trace components is accomplished in the main column, without the interference difficulties of overlapping peaks. Moreover the performance of ionisation detectors like FID, N-, P-FID, ECD, GC-MS is no longer affected by solvents, derivatisation reagents or other major peaks. Intermediate trapping in capillary columns which has been described in previous papers, improves resolution and peak symmetry in the subsequent main separation and allows enrichment of traces by repetitive pre-separation. A simplified version of such a system which allows the application of the different, above mentioned, multistage sampling techniques is given in Fig. 6.

Type and length of precolumn have to be chosen with regard to the required separation efficiency and sample capacity. In the case of very dilute samples large volumes have to be injected and packed or microparticle columns should be used instead of the standard (0.2–0.35 mm i.d.) capillary columns because of their higher sample capacity. Some technical problems arise when widely differing carrier gas flows have to be used in the pre- and the main column. Intermediate trapping and re-injection improves the peak profiles arising in the pre-separation. This is important for an optimum separation with high resolution in the main column. The trapping can be performed at the beginning of the main column. Distortions of peak symmetry caused by poor sampling technique (including inefficient column coupling devices) are also removed by the re-injection procedure.

When using a double T coupling piece between the two columns the following steps of multistage gas chromatography are performed.

1. Pre-separation in a packed or capillary column.
2. Transfer of a selected part of the eluate to the main column. Solvents and other species of low retention are vented at the end of the precolumn whereas peaks with higher retentions are backflushed from the precolumn.
3. Trapping of the components contained in the selected part of the eluate at the inlet of the main column, mantled by a cold trap.
4. Re-injection by instantaneous heating of the cool part of the column.
5. The main separation is accomplished.

In our opinion this method of "partial" analysis of complex mixtures also solves many problems of sampling. The applicability of the method is of course influenced or restricted by the analytical problem. A sampling device which simultaneously allows backflushing of components with low volatility which normally are contained in every practical sample and removal of volatile (solvent-) constituents could be a useful standard part of future gas chromatographic equipment. Such devices could easily be used in an automated mode as well.

In our previous papers on intermediate trapping we used a construction by which either cooled or heated nitrogen was blown onto the part of the column acting as a trap. A new version was developed in cooperation with *Oreans* and *Mueller* by which electrical heating of the cooled trap from −60 °C to 180 °C in 1 second is possible. The construction of the trapping device and of the electrical unit for temperature programming and control is not described in this paper. Detailed information on different applications will also be published in the near future.

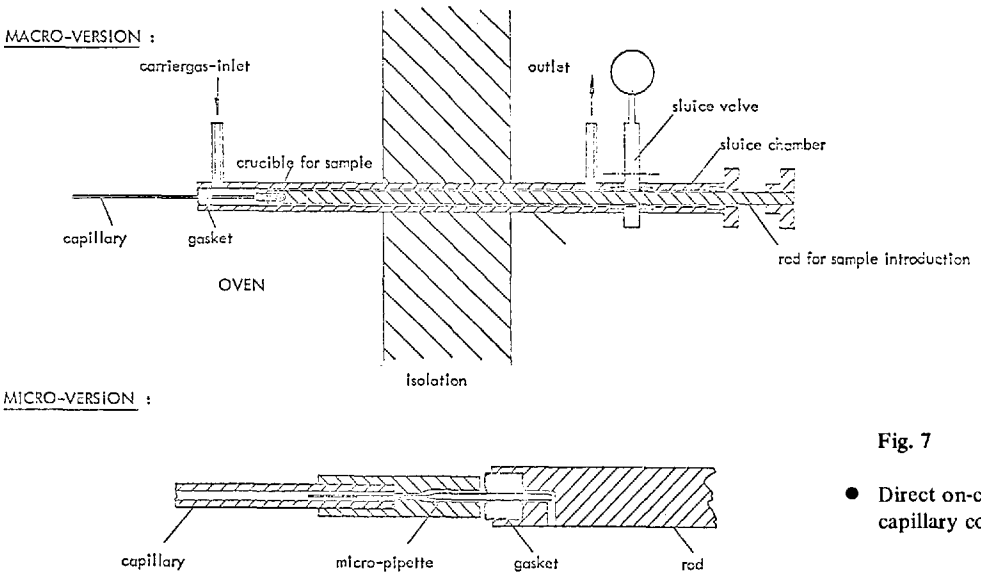

Fig. 7

- Direct on-column injection of liquid samples with capillary columns.

"Direct" sampling

All sampling techniques used in practice (split-, splitless-, moving needle injection etc.) include a previous vaporization of the sample in a separately heated injection port before the more or less homogenized sample/carrier gas mixture enters the column. In this paper we shall not deal with the quantitative aspects of capillary column sampling. They will be treated in a paper to be published in the near future. We looked mainly at the problems of sampling of very high boiling compounds and the decomposition of sensitive compounds. Depending on temperature, surface activity and residence time in the vaporisation chamber thermal or catalytic decomposition or conversion of the more sensitive components may occur.

Sample components with very high boiling points beyond 400 °C may be adsorbed at the surfaces of the vaporizer or the septum. In both cases non-representative sample composition is obtained after transfer into the column. The overloading of columns with large amounts of volatile solvents when using the "splitless" injection technique is not generally considered to be a severe restriction in difficult cases of trace analyses although detector performance and column coatings may be affected by too large amounts of solvents. Double column GC is the best method to be used then. For the sampling of high boiling compounds and for compounds which are easily decomposed, it may be of advantage to introduce undiluted and diluted samples directly into the capillary column without previous vaporisation or other transfer operations outside the column. We have developed two different devices for direct capillary column sampling by which sample volumes in the range between micro- and nanoliters may be introduced into a capillary column. In Fig. 7 the microversion and the macroversion of this technique are shown. A more detailed description of this technique is given in our patent application [8]. Further information on technical features and special applications will be published in the near future.

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Received: April 30, 1977
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