Packed versus capillary columns in gaschromatography

Citation for published version (APA):

Cramers, C. A. M. G., Rijks, J. A., & Bocek, P. (1971). Packed versus capillary columns in gaschromatography. *Clinica Chimica Acta*, 34(2), 159-167. [https://doi.org/10.1016/0009-8981\(71\)90169-0](https://doi.org/10.1016/0009-8981(71)90169-0)

DOI:

[10.1016/0009-8981\(71\)90169-0](https://doi.org/10.1016/0009-8981(71)90169-0)

Document status and date:

Published: 01/01/1971

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

PACKED VERSUS CAPILLARY COLUMNS IN GASCHROMATOGRAPHY

C. A. CRAMERS, J. A. RIJKS

Department of Instrumental Analysis, Eindhoven University of Technology (The Netherlands)

AND P. BOCEK

Academy of Science, Brno (C.S.S.R.)

SUMMARY

Three basic types of columns are currently in use:

- (a) packed columns
- (b) open hole tubular columns
- (c) packed capillary columns

A survey of the more important column characteristics is given in an attempt to clarify the confusion which still exists in comparing performance of columns of different design.

Column types are compared in steroid analysis.

Micropacked columns prepared according to a new technique compare favourably with other types of columns e.g. open hole tubular (Golay) columns.

INTRODUCTION

The heart of a gaschromatographic system is the column. Column performance sets limits to the separation attainable and determines time of analysis. Three basic types of columns are currently in use:

- (a) packed columns, since the introduction of G.C. by Martin in 1952 (ref. 1).
- (b) open hole tubular columns; Golay, 1957 (ref. 2).
- (c) packed capillary columns; Halasz, 1968 (ref. 3).

Practical factors such as column inlet pressure, required speed of sample introduction, required sample size (detection limit) are largely determined by properties of the selected type of column.

A survey of the more important column characteristics will be given below in an attempt to clarify the confusion, which still exists in comparing performance of columns of different design.

EVALUATION OF COLUMN POTENTIALITIES

Recalling from chromatographic theory three main factors determine gaschromatographic analysis (as demonstrated in Fig. 1):

Fig. 1. Effect of column efficiency and analysis time on detectability using a flame ionisation detector.

(a) *analysis time*. The residence time of the peak maximum in a column, the retention time t_R is given by

$$t_R = t_0 (1 + k) \quad (\text{Fig. 2})$$

where: t_0 is the gas hold up time, the retention time of an unretained component e.g. air; k is the capacity ratio which can be derived from the partition coefficient K ,

Fig. 2. Definition of "common" terms in gas chromatography.

by multiplication with the volumetric ratio of the stationary and mobile phases in the column

$$k = K \frac{V_{\text{liquid}}}{V_{\text{gas}}}$$

This ratio in packed columns usually of the order of 0.05–0.10, in open tubular columns considerably smaller values, 0.002–0.01 are common.

(b) *efficiency*, as expressed in the number of theoretical plates n . This number expressed the degree of band broadening a solute undergoes in a given column. The plate number can be derived from the chromatogram in the following way:

$$n = \frac{t_R^2}{\sigma^2} \quad (\text{Fig. 2})$$

The standard deviation σ (time units) is equal to half width at 0.607 of the height of a gaussian peak.

The plate number n can be related to the length, L , of a column by introducing the quantity, H , the height equivalent to a theoretical plate

$$H = \frac{L}{n}$$

H is dependent on a number of experimental parameters and is a function of the linear velocity, u , of the carrier gas. This function is shown in Fig. 3, the curve reaches a minimum in H (H_0) at a certain flowrate u_0 (the optimum flow rate).

(c) *resolution*, R , this quantity expresses the degree of separation of two components leaving the column shortly after each other.

$$R = \frac{t_{R2} - t_{R1}}{\sigma_1} \quad (\text{Fig. 2})$$

Using $t_R = t_0 (1+k)$ and the equation for n it follows

$$R = (\alpha - 1) \frac{k}{k + 1} \sqrt{n}$$

α being the relative retention of two components.

With this equation the number of plates required for a given separation (given α)

Fig. 3. Dependence of plate height H upon linear carrier gas velocity u .

can be calculated. The separation is almost complete if $R = 6$ and just acceptable for $R = 4$. Packed columns usually operate with relatively large values of the capacity ratio, k , the factor $k/k+1$ after approaches unity. For open hole tubular columns lower values of k are usual because of the lower value of phase ratio and the required plate number will be larger. In practice factors, such as pressure drop, detector sensitivity, time constants of detection and recording system, and the rapidity with which the sample may be introduced, all limit the plate number, resolution and speed of analysis attainable.

PRACTICAL LIMITATIONS

Pressure drop

In connection with his theory of open hole tubular columns Golay³ gave an expression for column performance based on the directly measured parameters of time and pressure:

$$\text{The performance index P.I.} = 31.2 \frac{H_0^2}{u_0} \frac{1+k}{k} \frac{\Delta P}{L}$$

L being the column length in cm.

The latter equation shows the importance of the pressure drop per unit length.

The performance index has the dimension of viscosity (g/cm sec) (pressure in dynes/cm²).

The P.I. has a minimum value of 0.1 when the carrier gas is helium. Values greater than this are usually obtained, although P.I.'s approaching 0.2 have been reported for open hole tubular columns.

Packed columns range from 20 to 1000 poises. P.I. shows a large dependence upon the product $t_R \Delta P$, which indicates the price one pays in waiting time and in pressure drop to obtain optimum performance of the column.

Speed of sample introduction

Up till now one important aspect has been left out of consideration, the capacity of the column, which determines the most practical parameter, the sample size. Schematically, a given quantity of sample can be introduced:

(a) as a narrow band of high concentration of (b) as a plug of correspondingly lower concentration.

(a) If the sample is fed into the column as a band of high concentration, the local conditions at least in the front of the column, will be such that the partition coefficient K becomes concentration dependent. Each part of the solute band will move at different speed. The result will be a band broadening, additional to the broadening effects discussed before (and expressed in the plate number n). The peaks become distinctly asymmetric.

(b) The sample is diluted with carrier gas before it enters the column. This causes additional symmetric band broadening. The variance σ^2 (sec²) of an eluting peak may be considered to be composed of the variance of the sample at the inlet σ_1^2 and the variances σ_c^2 due to column processes.

$$\sigma^2 = \sigma_1^2 + \sigma_c^2 \quad (\text{Fig. 4})$$

It is a trivial observation that the best resolution will be obtained at $\sigma_1^2 = 0$ (infinitely narrow sample band) $R_{\max} = \Delta t_R / \sigma_c$. For finite sample volumes R will be smaller than $R_{\max}$. However, from above eqn. and the definition of resolution it follows that for $\sigma_1 = 0.5 \sigma_c$ the resulting decrease in resolution will be only 10%. From this the permissible input width of the input peak σ_1 can be calculated.

From the definition of plate number, n , and the equation for retention time $t_R = t_0(1+k)$, where $t_0 = L/u$ it can be derived that:

$$\sigma_c = \frac{1+k}{u} \sqrt{LH}$$

Time constants

According to Schmauch² the time constant of a recording system including detector must be less than one fifth of standard deviation σ if the peak is to be truly recorded. Only for very fast analysis this will become a limiting factor.

Fig. 4. Speed of sample introduction and column efficiency.

Detector sensitivity

The signal of ionization detectors, commonly used, are proportional to the mass flow rates. This means the minimum amount of sample that can be detected is strongly dependent on the speed of passage of a peak through the detector and therefore on column dimensions. Columns of small diameter and accordingly higher optimal gas velocity enable the detection of smaller quantities.

Assuming an ionisation efficiency, η , of 0.25 Coulomb/g at C and a noise level of 10^{-13} A for a flame ionisation detector (as reported in literature) it can be calculated that the signal h ($\rightarrow$ Signal to noise ratio) to be obtained from a column is given by:

$$h = \frac{o}{\sigma\sqrt{2\pi}} = \frac{M \cdot (\%C) \cdot \eta}{12 \cdot \sqrt{2\pi}} \frac{u_0}{1 + k\sqrt{LH}}$$

M = weight of injected sample in g; h and o respectively are the height and area of a gaussian peak.

In Table I literature data together with results obtained in our laboratory on a new micro type of packed columns are summarized. For the sake of easier comparison all column lengths are chosen to be 5 m; H_2 is the carrier gas and squalane the stationary liquid phase. For the calculation of Resolution a solute pair with relative retention 1.10 is selected; the capacity ratio of the first eluting component is chosen to be 3.

The signal to noise ratio is calculated for a flame ionization detector assuming $\eta = 0.25$ Coulomb/g. at C and a noise level of the detector system of 10^{-13} A. The injected amount of sample is fixed on 10^{-9} g $\cdot$ C.

COMPARISON OF COLUMN TYPES FOR STEROID ANALYSIS

Considering above mentioned factors, it appears that open hole tubular columns are theoretically the most favourable ones and that the packed capillaries according to Halasz and the micro packed columns prepared in our laboratory take an intermediate position. The micro packed columns will be discussed in detail below. Besides these theoretical considerations there are, however, still many practical factors which anyhow do turn the scales to the packed columns, which in practice are used in 90%

TABLE I

COMPARISON OF COLUMN TYPES (see also text)

(L = 5 m, $\alpha = 1.10$, $k = 3$, $M = 10^{-9}$ g $\cdot$ C)

	<i>Golay</i>	<i>Capillary</i>	<i>Halasz</i>	<i>Packed</i>	<i>Micro packed</i>
i.d. mm	0.068	0.25	0.50	4.0	0.8
n	20,000	10,000	5000	7700	15,500
H_0 mm	0.25	0.50	1.00	0.65	0.32
u_0 cm/s	102	40	16	9	11
R	10.7	7.5	5.4	6.6	9.3
t_R s	20	50	125	220	182
ΔP atm	4	0.10	0.8	2.6	1.4
P.I	2	0.5	42	100	11
n/t s $^{-1}$	1000	200	40	35	85
σ_c s	0.14	0.50	1.70	2.50	1.46
σ_l s	0.07	0.25	0.85	1.25	0.73
S/noise	570	160	46	32	55

of the cases. The open hole tubular columns are used in most other cases, the packed capillaries according to Halasz are, for the major part, still in the developing stage.

With *packed columns* any support material can be used, these supports can be coated or impregnated previously with stationary liquid or used as such (e.g. porapak, mol.sieves). Packing of the columns as well as coating can be done in a reproducible way. Column overloading does not likely occur and therefore sample introduction offers no serious problems.

The choice of *open hole tubular (Golay) columns*, however is fairly restricted, especially glass columns for the analysis of sensitive biological materials are hardly commercial available. The coating of a glass column with an uniform layer of stationary liquid is difficult to achieve. Therefore, only a very limited number of stationary phases, suitable for work at elevated temperatures, is available. Stream splitting sample introduction systems, as commonly used in connection with open hole tubular columns, cannot be employed for steroids for many reasons, the most important being the intolerable waste of sample (only $\simeq 1\%$ of the sample enters the column). Direct sample introduction systems still are very much in the developing stage.

Packed capillary columns according to Halasz are manufactured by heating a packed glass column until the glass softens, then the column is drawn to a capillary tube and if desired wound up to a helix, of course the use of metals for this type of columns is prohibitive. Usually the packing of the drawn capillary is very irregular. Then a solution of stationary phase in a volatile solvent is forced through the column, the solvent is evaporated and the stationary phase remains in the column impregnating the support and covering the inner glass wall. The amount of stationary phase as well as the film formation on the inner wall of the capillary tube cannot be controlled sufficiently well. This makes the choice of available liquid phases smaller as in the case of open hole tubular columns. Another drawback is that the support material must be resistant to the heating, necessary to soften the glass. Therefore, the choice of support material is restricted; silanized support necessary for steroid analysis cannot be used. The permissible sample size is somewhat larger than with open hole tubular columns, therefore sample introduction gives less difficulties.

Micro packed columns

It is obvious it would be desirable that one disposes of packed capillaries with the theoretic advantages connected thereto, without having the practical objections with respect to nature of the support material, distribution of the packing, column material and the coating with stationary phase. Following a technique developed in our laboratory we succeeded to manufacture packed columns of diameters down to 0.6 mm (in glass and stainless steel). The columns are wound to a helix *before* packing. Any packing material can be selected; the support, usually silanized, is impregnated with the stationary phase of choice in a controlled weight percentage before packing. To decrease pressure drop per unit length the commercial available support material is carefully sieved to fractions with a small particle size distribution (< 20 microns). The fraction selected depends on the inside diameter of the column to be packed, a ratio of 5:1 of inside diameter/particle size seems to be optimal. Best results are obtained with Dow Corning silanized textured glass beads and with Spherosil (Pechiney St.Gobain), although supports like Chromosorb W result in good columns as well. The packing of the helically wound columns is established by maintaining a pressure

Fig. 5. Micro packed column. 0.05% PMPE on Dow Corning GLC 110 silanized textured glass beads. E = estrone; E-II = estradiol; E-III = estriol; ET = etiocholanolone; HET = 11-hydroxyetiocholanolone; A = androsterone; 11-KA = 11-ketoandrosterone; DHEA = dehydroepiandrosterone; PON = pregnanolone; PII = pregnanediol; APII = allopregnanediol; T = testosterone.

Fig. 6. Micro packed column. 0.05% SE-30 on Dow Corning GLC 110 silanized textured glass beads.

TABLE II

COMPARISON OF COLUMN TYPES USED IN THE AUTHORS' LABORATORY
(Solutes TMSi-derivatives of steroids or *n*-hydrocarbons; H₂ carrier gas).

	Δp atm.	k	H_0 mm	u_0 cm s ⁻¹	n	n/t s ⁻¹	P.I.	T
<i>Micro packed column</i>								
L = 14.3 m, i.d. 0.8 mm								
Support GLC-110 glass beads								
(140–160 μ)								
A 0.05% PMPE (Dehydro-epiandrosterone)	4	4.8	0.32	11.5	44 500	61	9.4	240°
B 0.05% SE-30 (Pregnanediol)	4	7.4	0.34	11.8	42 600	44	9.7	220°
<i>Packed capillary (Halasz)</i>								
L = 21 m, i.d. 0.55 mm								
Support Chromosorb W (140–160 μ)								
0.2 SE-30 (<i>n</i> -C-24)	1	2.5	1.19	4.8	17 600	11.5	61.3	260°
<i>Packed column</i>								
L = 2.8 m, i.d. 2 mm								
Support GLC 110 (140–160 μ)								
0.1% PMPE (Estradiol)	0.25	50	0.43	3.0	6 450	1.4	15	182°
Support Chromosorb W (140–160 μ) 0.5% PMPE (Estradiol)	0.33	20	0.46	4.9	6 000	5.0	16.6	215°
<i>Open hole tubular column</i>								
L = 23 m i.d. 0.25 mm SE-30								
(<i>n</i> -C-24)	0.30	1.6	0.46	16.4	50 000	137	0.9	254°

drop of ≈ 2 atm/m over the capillary tube, the flowing gas e.g. H_2 entrains the particles into the column.

During packing, preferably in small portions the column is subjected to ultrasonic vibrations in an ultrasonic cleaning bath.

The micro columns (up to 30 m length) prepared in this way possess a very uniform packing, the nature of which can be adapted exactly to the demands for a specific analysis. Their efficiencies make them very well suited for high resolution work in these cases where open tubular columns with an appropriate stationary phase are not available. As the packing may be prepared in large charges it is possible to produce columns with reproducible properties. The sample capacity is fairly large, commercially available direct sample inlets (Hamilton, precolumn inlet) can be used without loss in resolution.

Fig. 5 and 6 show the application of this column type to the analysis of steroids. These figures clearly demonstrate the advantage of using two stationary phases of different polarity as an aid in positive identification of sample components.

Table II compares above mentioned micro packed columns with conventional packed columns, prepared following the same packing procedure, a packed capillary (according to Halasz) and a open hole tubular glass column (coating procedure Tesarik⁴) For the open tubular column a direct sample introduction system described by Kuppens⁵ is used.

REFERENCES

- 1 A. J. P. MARTIN AND A. T. JAMES, *Biochem. J.*, 50 (1952) 679.
- 2 M. GOLAY, *Gas Chromatography* 1958, p. 36, D. H. DESTY (Ed.), Academic Press, New York, (1958).
- 3 I. HALASZ, *Chromatographia*, 1 (1968) 119.
- 4 K. TESARIK AND M. NOVOTNY, *Gas-Chromatographie* 1968, Deutsche Akademie der Wissenschaften, Berlin (1968).
- 5 P. S. H. KUPPENS, *Chemisch Weekblad*, 65/36 (1969) 7.

Clin. Chim. Acta, 34 (1971) 159-168