

THE APPLICATION OF GOLAY COLUMNS OF LARGER INTERNAL DIAMETER

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INTRODUCTION

The use of capillary columns for the gas chromatographic separation of volatile substances dates from the pioneer research of GOLAY¹ by whose name such columns are also sometimes recognized. The various applications of Golay columns have been described by numerous later authors², and, since it appears that no doubt exists as to the reproducibility of their manufacture³ and characteristic operational features for quantitative and qualitative analysis, the way is now clear for their general application in gas chromatography. The work described here is concerned with the use of Golay columns with internal diameters of 1.0 mm. The geometrical parameters, the separation efficiency, the loading capacity and the necessary initial instrumental requirements by which the first results were obtained are separately discussed⁴.

THEORY*

By analogy with the phenomena attending distillation and liquid-liquid partition, it is customary in gas chromatography (GC) to adopt the working hypothesis of the "theoretical plate height" (usually designated HETP) and the concept of the "number of theoretical plates (n)", factors which are interrelated with the column length L by the expression:

$$\text{HETP} = \frac{L}{n} \quad (1)$$

VAN DEEMTER AND GOLAY have furnished a further equation to provide a relation between the geometrical parameters and other variable quantities resulting from the use of the columns:

$$\text{HETP} = \frac{B}{u} + [C_G + C_L]u = \frac{2D_G}{u} + \frac{r^2}{D_G} \left[\frac{1 + 6k + 11k^2}{24(1+k)^2} \right]u + \frac{d_F^2}{D_L} \left[\frac{2k}{3(1+k)^2} \right]u \quad (2)$$

The minimum HETP is given by eqn. (3):

$$\text{HETP}_{\text{min}} = 2 \sqrt{[B(C_G + C_L)]} \quad (3)$$

* For a list of symbols used, see p. 450.

If one considers C_L to be very small compared with C_G (which is permissible to a first approximation), eqn. (4) follows:

$$\text{HETP}_{\min} = \frac{d}{2} \sqrt{\frac{1 + 6k + 11k^2}{3(1+k)^2}} \quad (4)$$

which provides a simplified, direct relation between HETP_{\min} and the column diameter d . This equation provides the reason for the concentration of our past work on the use of the smallest possible column diameter (in the region of 0.25 mm).

The further diminution of column diameter, to attain lower plate heights, is limited by purely practical problems of tube-stretching, the quality of the tube's inner surface, the loading capacity and the pressure gradient along the column length.

Since, in order to attain a small HETP, a small film thickness, d_F , of the stationary phase must also be chosen the loading capacity of the Golay column is perforce restricted. It is already evident that, for sample sizes of 0.5–1 μl , stream-splitting before the column in the ratio 1:100 to 1:200 must be adopted, to avoid "overloading". It is very difficult to separate such small samples of mixtures containing many, equally distributed components, and this at the same time gives rise to the need for a highly sensitive detector, *e.g.* a flame ionization detector (FID).

In three particular instances it is especially desirable to increase substantially the loading capacity of Golay columns:

(1) In the case of mixtures of widely differing component-concentrations (*e.g.* so-called trace analyses), the given sample size must be so chosen that the least abundant component present is estimable by the detector. In order to maintain simultaneously the main components in the linear part of the distribution isotherm, a highly sensitive detector (FID) must be combined with a column of greater capacity.

(2) At present the efficiency of GC in the separation of mixtures by the use of Golay columns is essentially higher than in the identification of single components. It is understandable, therefore, that identification is usually made by another method. Since it is not always possible to make use of a mass spectrometer⁵ for this purpose, it is necessary to collect the separated components at the base of the column. Although a higher concentration ratio between substance and carrier gas is obtainable in the case of Golay columns of small diameter, such small absolute sample sizes are not suitable for analysis by other chemical or physico-chemical methods. The combination of the separation efficiency of Golay columns with their ability to "prepare" components therefore primarily requires an increase in their loading capacity.

(3) The wide application of GC in industrial routine analysis demands a careful examination of the balance between the initial outlay on equipment and the issuing analytical results. Moreover, the high number of theoretical plates (from about 100000) of Golay columns, operable only in conjunction with an FID, is by no means essential for all analytical problems. In numerous cases numbers of theoretical plates from 20000–25000 suffice, and in this instance, macro-Golay-columns may be introduced without difficulty and run in conjunction with a simple thermal conductivity detector (TCD)⁴.

It is evident from these considerations that under three different sets of problematic conditions it is desirable to increase the loading capacity of Golay columns. This can

be achieved by raising the "working volume V_n " of a plate. For the latter, KEULEMAN'S⁶ equation applies:

$$V_n = \frac{V_G + KV_L}{n} \quad (5)$$

It is possible to increase the working volume under constant geometric conditions (constant V_G) by raising the volume V_L of the stationary phase. In the case of Golay columns this in effect means an increase in film thickness d_F . The stability of the film, however, decreases with increasing thickness, so that the manufacture of such "thick film columns" is not recommended. By changing the geometric parameters (e.g. by increasing the column diameter) one can profitably alter the gas volume V_G in a simple way. The volume V_L of the liquid phase is also increased, and the desired increase in plate volume is attained.

Equation (4) shows that an increase in $HETP_{min}$ is paralleled by a drop in the number of plates. Table I reports the gas volumes V_G attained in the case of different geometrical parameters.

For the successful application of Golay columns, the magnitude of the film thickness d_F in relation to the column diameter d , is of great importance.

TABLE I
GAS VOLUMES V_G OF GOLAY COLUMNS WITH DIFFERENT DIMENSIONS

Column radius r (mm)	Column length L (m)	Gas volume V_G (ml)
0.125	25	1.2
0.125	50	2.4
0.250	50	9.7
0.500	100	78.0

Since, in all analytical separations, the time required for analysis is an important factor, the interdependence of film thickness, column diameter, gas volume, and carrier gas flow, is discussed below, taking into consideration several k values for different substances.

From the simple relations:

$$k = \frac{t_r'}{t_M} = K \cdot 4 \frac{d_F}{d} \quad (6)$$

and:

$$t_M = \frac{V_G}{u} \quad (7)$$

the corrected retention time t_r' is obtained:

$$t_r' = K \frac{4d_F}{d} \cdot \frac{V_G}{u} \quad (8)$$

From eqn. (8) the following conclusions can be drawn:

Columns possessing a relatively high gas volume V_G will show a longer analysis time for a particular separation than columns with smaller gas volumes (if the ratio

d_F/d is initially taken as constant). If the carrier gas flow is not too small, the influence of V_G on the analysis time is reduced. Since, however, the flow cannot be chosen independently of the film thickness, owing to its influence on the plate height and on the resolving power, a definite limit to the film thickness already exists. Normally, this should be as small as possible (eqn. 2) as the plate height is then smaller, the efficiency of the column is only to a small extent dependent on the magnitude of the partition coefficient and of the carrier gas flow, and the latter can be relatively high without disadvantage. The reasons for a flat curve in the HETP/ u diagram becomes more apparent since, from eqn. (9):

$$u_{\text{opt}} = \frac{8D_G}{d} \sqrt{\left[\frac{3(1+k)^2}{1+6k+11k^2} \right]} \quad (9)$$

the optimum flow rate u_{opt} is proportional to $1/d$. The optimum flow rate, corresponding to HETP_{min}, therefore decreases with increasing column diameter. When working with optimum flow rate the analysis times increase with increasing column diameter.

This attempt to obtain the smallest possible d_F/d ratio militates against the desirability (also on practical grounds) of relatively high loading capacity of the columns. On the other hand, of course, in order to guarantee a complete coating of the tube wall, the film thickness must not fall below a certain value.

These considerations, which have been made essentially with regard to columns with the smallest possible HETP (highest possible number of theoretical plates), are completed by taking carefully into account a further feature, the resolving power. This is by no means always proportional to the number of theoretical plates of a column, but is dependent in many cases upon the form and nature of the film on the tube wall.

In conclusion, comparison of columns of diameter $0.25 \leq d \leq 0.5$ mm with those of diameter $d = 1$ mm, shows that on the grounds discussed above, the ratio d_F/d for the two column types differs only insignificantly. Since the surface area of the tube wall increases only linearly with increasing diameter, while the column volume is proportional to the second power of d , the columns of greater diameter yield a greater gas volume V_G in relation to the volume V_L of the liquid phase. The loading capacity is, for all substances, greater than that in the case of columns of small diameter, so that stream-splitting before the column can be avoided.

Especial difficulties arise in the theoretical interpretation of measurements on loading capacity. Experimentally the sample size is continually raised until a distinct deviation of the peak form from the shape of a Gauss curve is established. When such a "concentration" range is run, the linear part of the distribution isotherm falls off at a particular value of the sample size, so that the calculation of the number of theoretical plates and of the plate height respectively from the peak shape is no longer permissible. Therefore only the reciprocal value of the relative half-band width, *i.e.* the quotient $t_r/w_{1/2}$, was applied to the interpretation.

In the case of relatively high k values the change of t_r with the concentration is negligible, to a first approximation. Furthermore the quotient $t_{r2}/(t_{r2} - t_{r1})$ (t_{r2} and t_{r1} are the retention times of the two base points of a peak) once again indicates the change of the peak form with concentration.

The particular geometric parameters of the Golay columns under discussion yield a very small pressure gradient for the necessary flow rates (see Table II). Hence, for the first time in gas chromatography, columns are available, possessing an approximately uniform flow over the whole column length without special apparatus.

TABLE II
CARRIER GAS FLOW u (COLUMN EXIT AT NORMAL PRESSURE)
AS A FUNCTION OF THE INLET PRESSURE FOR A 100 M COPPER COLUMN
(1.0 mm I.D.), CARRIER GAS He, 40° COLUMN TEMPERATURE

p (kg/cm ²)	u (ml/min)
0.1	7.5
0.2	15.0
0.3	23.0
0.4	31.0
0.5	39.0
0.8	62.5
1.0	78.0
1.5	117.0

The advantages arising from the application of pressure in the column have already been described elsewhere⁴. In the work here described the results correspond to new experimental conditions.

APPARATUS

For the measurements, the Fractometer F6 (Bodenseewerk Perkin-Elmer & Co., GmbH., Germany) was used. Thermistors and hot wires were used as detectors, as also was an FID.

Columns were developed from copper tubing. The dimensions are reproduced in the various cases.

As stationary phases, squalane, apiezon L, apiezon M and polypropylene glycol were used.

RESULTS

The upper half of Fig. 1 shows the plate height HETP as a function of the linear flow u for three different film thicknesses (calculated from the coating process). The smallest film thickness gives the nearest approach to the ideal function in this respect. The loading capacity of the column is, however, like the resolving power (see the lower half of Fig. 1), so small that practical application is out of the question.

This example illustrates a criticism of the separating efficiency of these columns, namely that the HETP is not sufficient. In each case the resolving power must also be measured. There is no essential difference between the resolving power of the other film thicknesses, so that from the functional representation in the upper part of Fig. 1 the middle thickness is to be preferred.

The upper part of Fig. 2 shows the HETP as a function of the linear, pressure-corrected flow u for squalane as stationary phase, working with several absolute

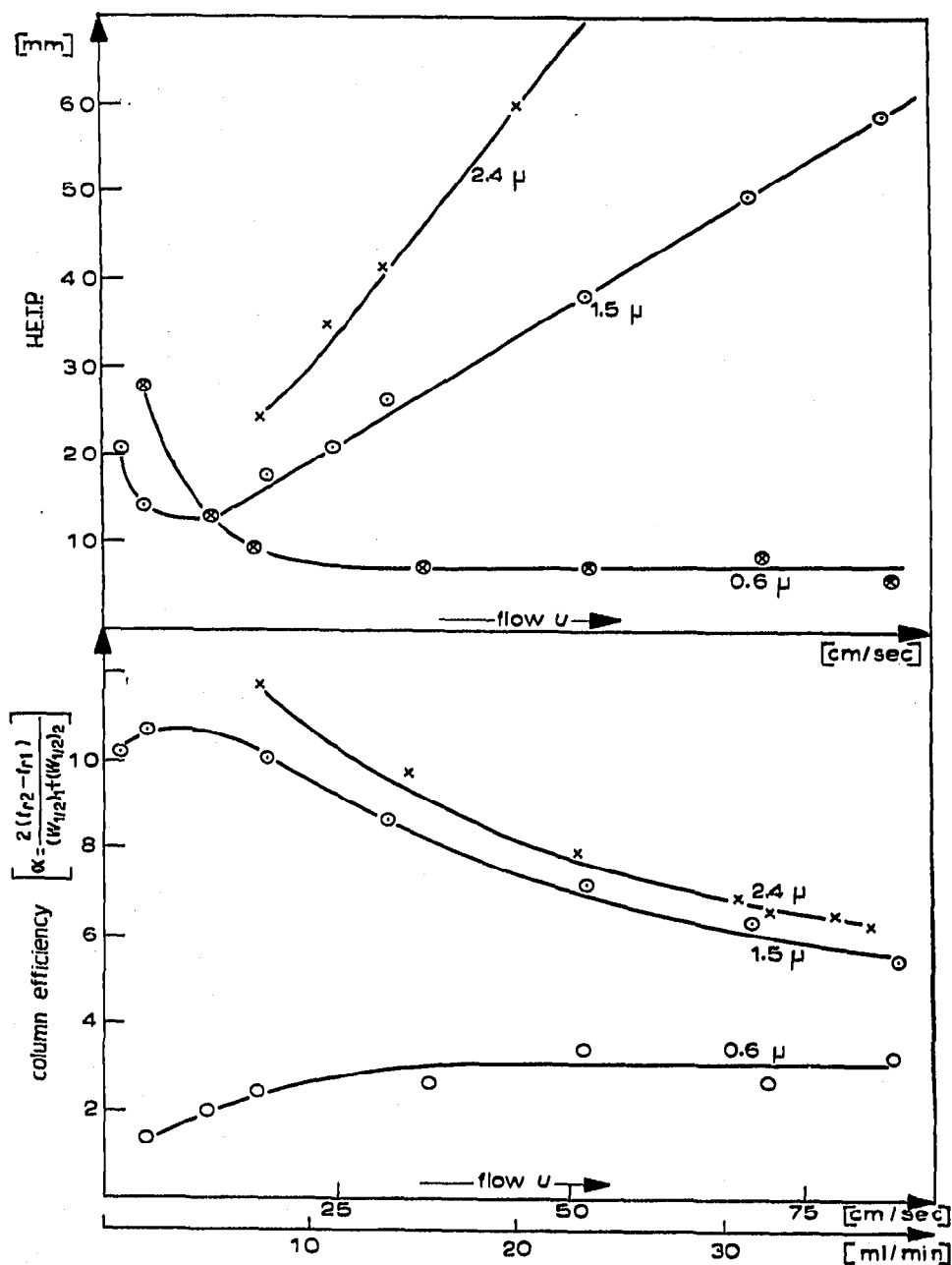


Fig. 1. HETP and column efficiency as a function of carrier gas flow (helium) for three different film thicknesses d_F . 100 m copper column (1.0 mm i.d.), Apiezon M as stationary phase; column temperature 40° ; sample 2,4-dimethylpentane, 0.1 μ l.

pressures in the column. In the lower part the retention times of the same measurements are represented as a function of the linear, pressure-corrected flow (in the form of $1/u$). These measurements show that results of the analysis are independent of the absolute pressure and that only the linear flow in the column is of significance. (It could be established—see also ref. 4—that the influence of the absolute pressure in a column on the half-band width—and therefore also on the HETP—is dependent on the ratio of component boiling-point to working temperature.)

The lower half of Fig. 2 also verifies eqn. (8), according to which the retention

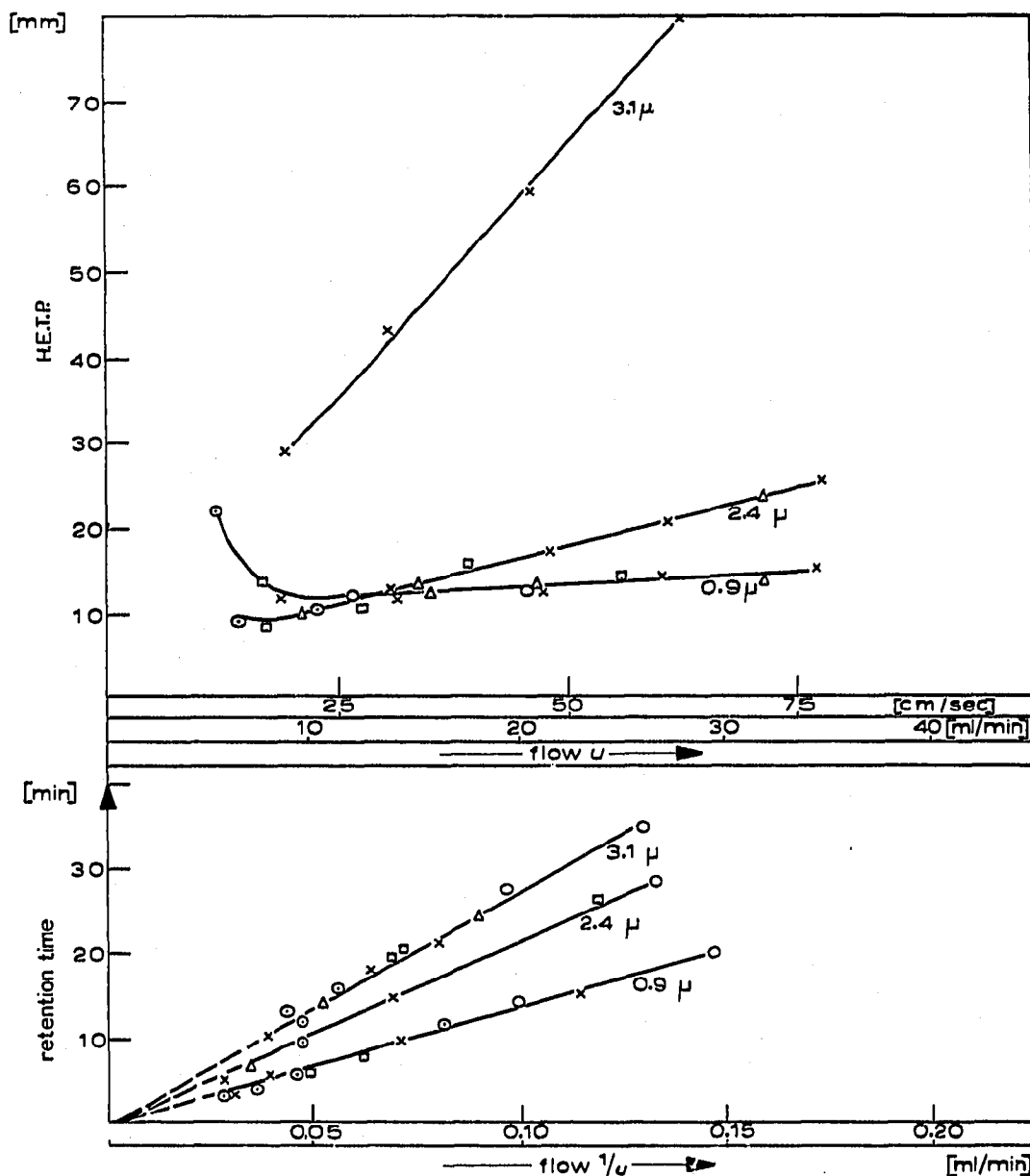


Fig. 2. HETP as a function of flow u , and retention time t_r as a function of flow $1/u$ for different pressures in the column. (x) 0.2 atm; (O) 0.5 atm; (Δ) 1.0 atm; (\odot) 2.0 atm, excess pressure. Film thicknesses d_F of 0.9; 2.4 and 3.1 μ . 100 m copper column (1.0 mm i.d.); stationary phase squalane; column temperature 40°; sample 2,4-dimethylpentane, 0.1 μ l.

time t_r for a particular column diameter d , a definite film thickness d_F , and for a constant gas volume V_G , must, for a particular substance, be independent of absolute pressure in the column, and only dependent on the flow, being proportional to $1/u$.

In Fig. 3 the reciprocal value of the relative peak-base width $t_{r2}/(t_{r2}-t_{r1})$ is represented as a function of the sample size. A distinct difference is evident in the loading capacities of the two columns with internal diameters of 0.5 and 1.0 mm respectively. Only the horizontal part of the curve corresponds to symmetrical peaks of a form similar to that of a Gauss function. With the onset of the fall-off of the curve, the peaks lose their symmetry and assume a near-triangular form⁴.

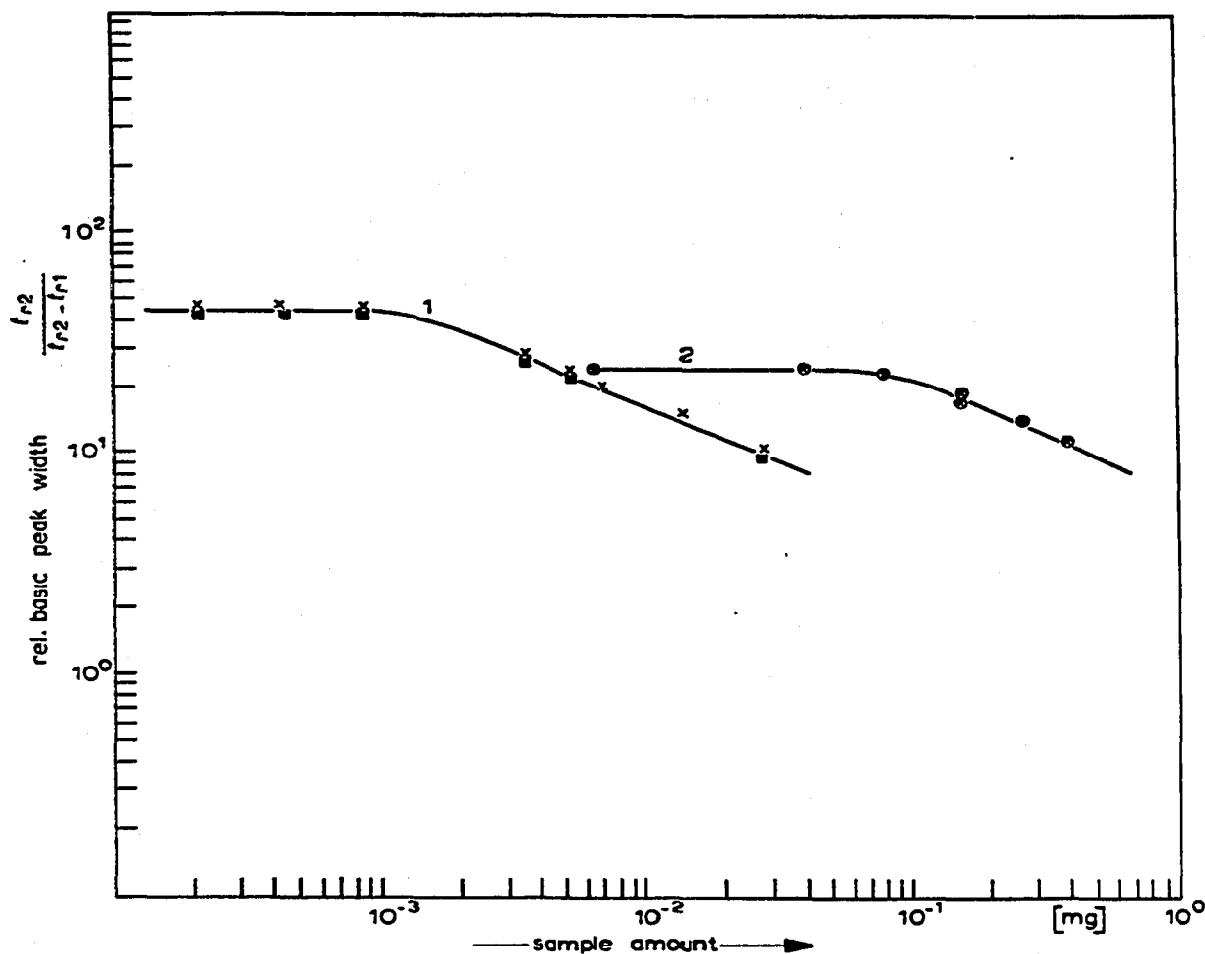


Fig. 3. Admissible sample size of Golay columns. Curve 1: 50 m copper column (0.5 mm i.d.); stationary phase 7:8-benzoquinoline; column temperature 70°. Curve 2: 100 m copper column (1.0 mm i.d.); stationary phase polypropylene glycol; column temperature 80°. (x) *m*-xylene; (□) *p*-xylene; (⊗) 3-methylbutanol-1.

Fig. 4 shows the resolving power $t_r/w_{1/2}$ as a function of the sample size (*n*-butanol) for two different layer thicknesses. The thicker films yield a higher resolving power for greater sample sizes. The differences in the case of small sample sizes are in agreement with theory. It should be pointed out at this juncture that these relations are highly dependent on the chosen sample and the working conditions, particularly the working temperature. This is also illustrated in Fig. 5. Here the resolving power for *n*-butanol is again reproduced as a function of the sample size. In the upper part the results at 100° are indicated, and in the lower part the working temperature was 120°. The pressure in the column served as a parameter.

The linear flow in the column was the same in each set of experiments. While working at the lower temperature, below the boiling point of *n*-butanol, the course of the function was approximately independent of the two pressures, while at 120° (b.p. of *n*-butanol 117°) the two curves overlap. Thus by the application of pressure one can also in this case obtain a good separating power with large sample sizes.

Fig. 6 shows how greatly the influence of pressure in the column is dependent on the ratio of working temperature to boiling point. The results shown are those obtained with ethanol at a working temperature of 120°.

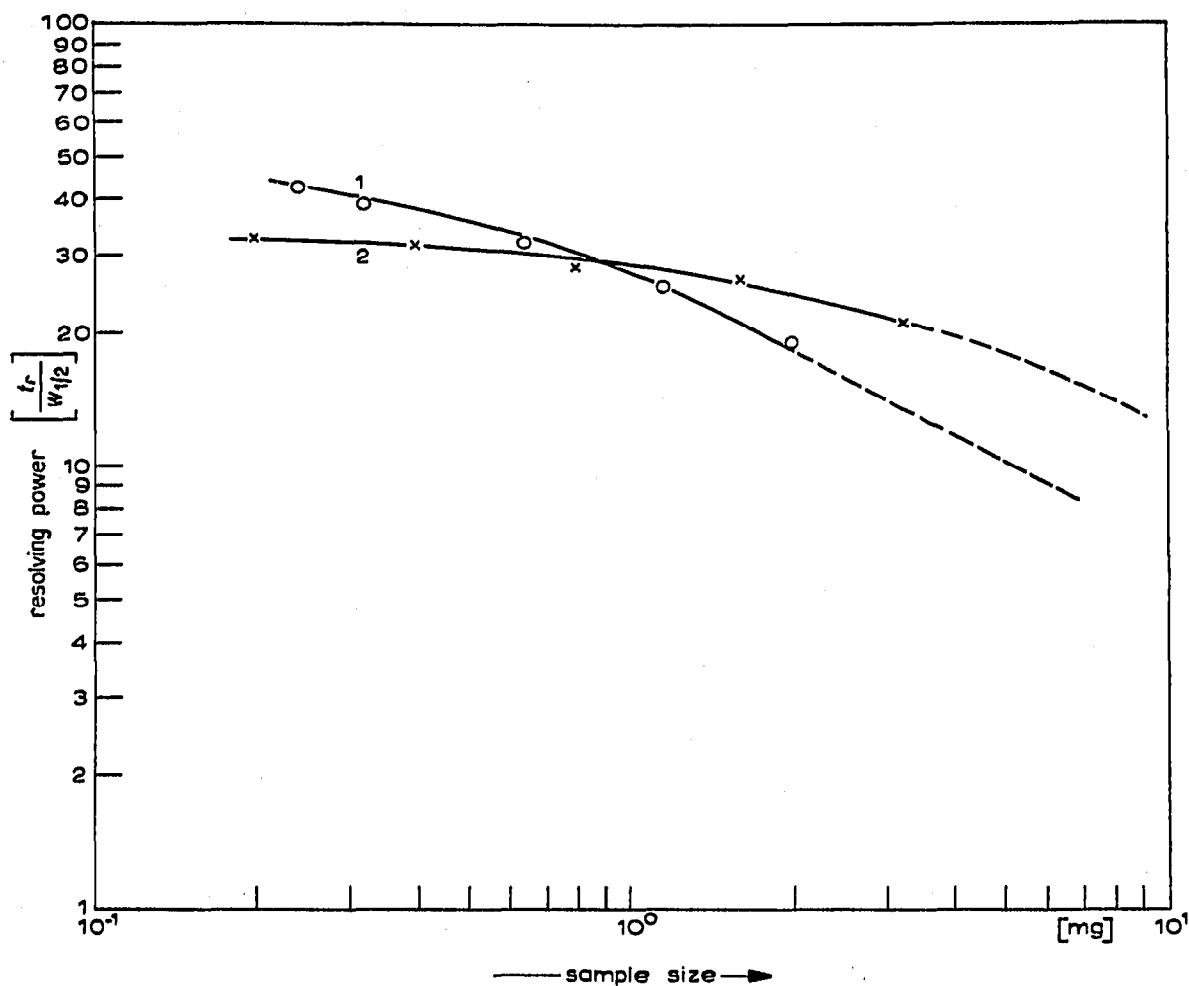


Fig. 4. Resolving power $t_r/w_{1/2}$ as a function of sample size (mg) for two film thicknesses d_F with *n*-butanol as sample. Curve 1: $d_F = 1.5 \mu$; curve 2: $d_F = 3.1 \mu$. 100 m copper column (1.0 mm i.d.); stationary phase polypropylene glycol; column temperature 100° .

DISCUSSION

The theoretical considerations and experimental results have shown that it is possible and advisable to use Golay columns of a relatively large diameter. With regard to the analysis time, which must lie within a definite limit, the carrier gas flow velocity must lie between 10–25 ml/min on account of the relatively large gas volume of these columns. Since such velocities greatly exceed the optimum flow velocity, the film thickness must be so chosen that the HETP increases only slightly with increasing flow. From this point of view the ratios d_F/d are taken with $\sim 1/1000$ maximum.

In order to achieve operative simplicity when using Golay columns of smaller diameter, e.g. by avoiding the necessity of stream-splitting and the use of the thermal conductivity detector, particular attention must be paid to the loading capacity of the columns. Since relatively thick films are desired, the d_F/d ratio should lie above $1/1000$.

It is therefore obvious that, in order to take both tendencies into account, it is necessary to effect a compromise. Indeed, by the choice, given a certain film thickness, of particular working conditions—e.g. the ratio of working temperature to boiling

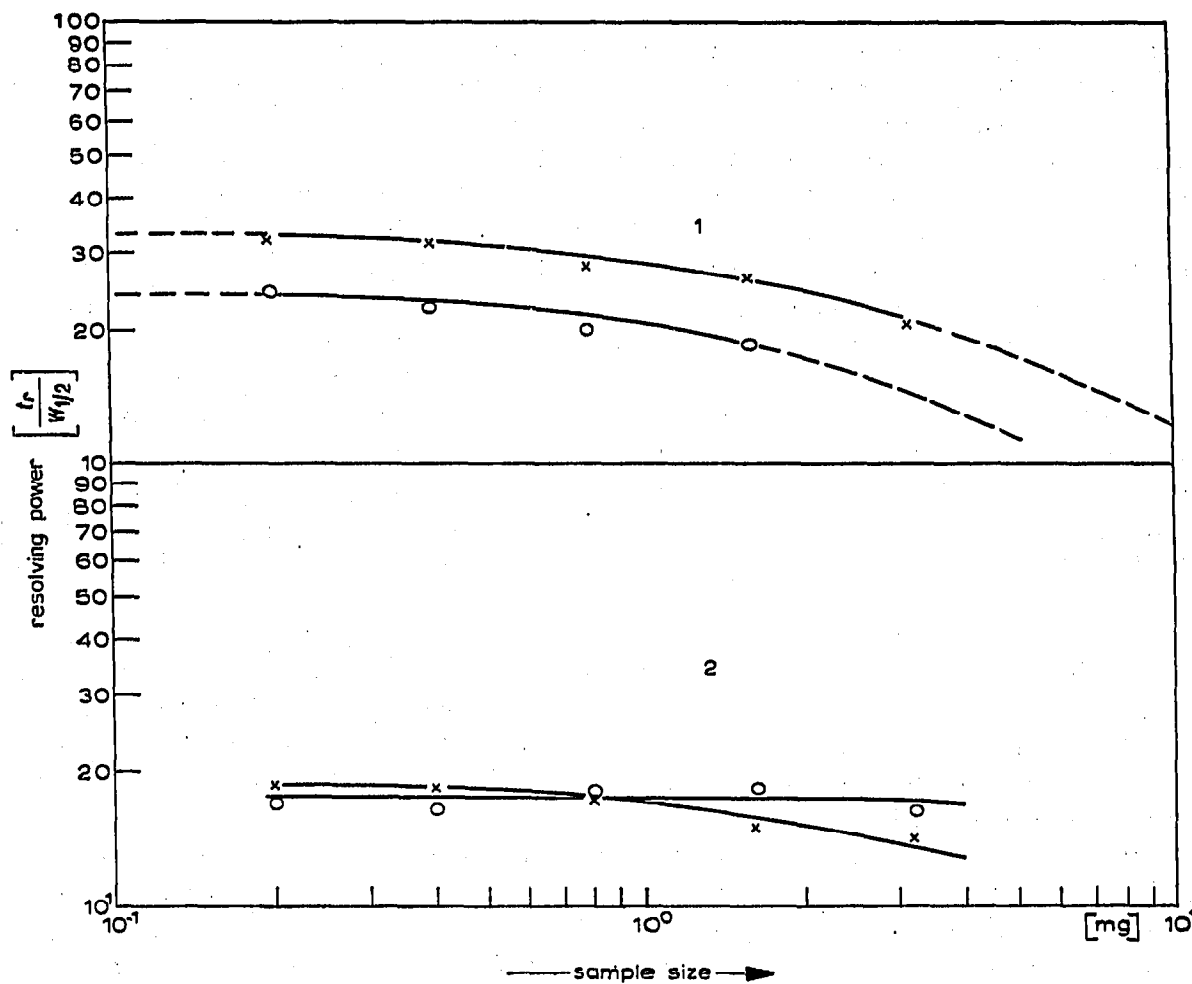


Fig. 5. Admissible sample size of columns (100 m copper; 1.0 mm i.d.; stationary phase polypropylene glycol; film thickness $d_F = 3.1 \mu$) for *n*-butanol as sample at 100° (curve 1), and 120° (curve 2). Excess pressure in the column (x) 0.5 atm and (O) 2.0 atm; 19.3 ml/min He; 20.0 ml/min He carrier gas flow.

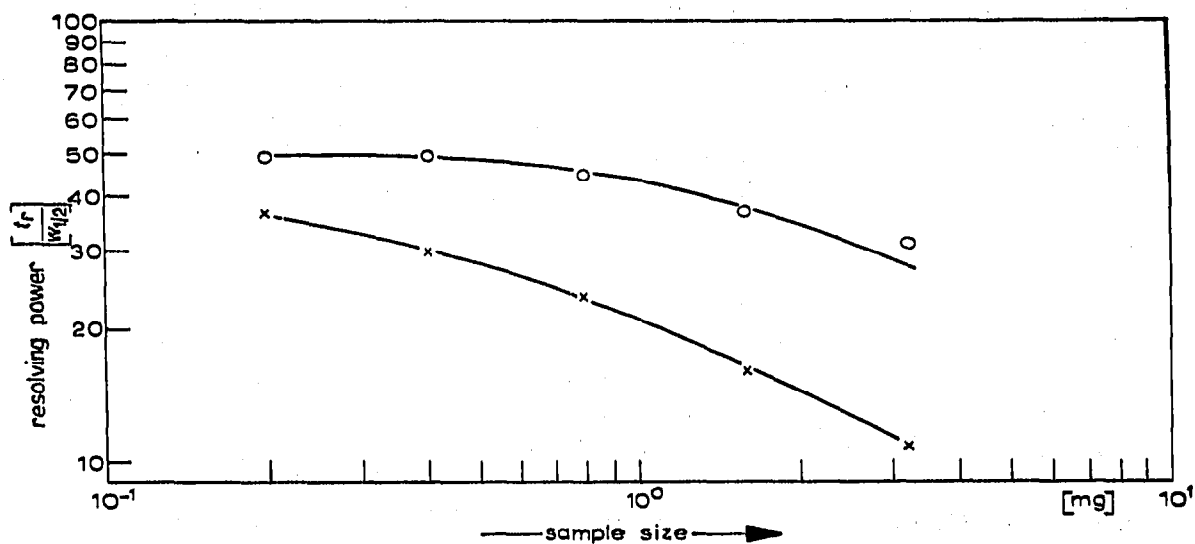


Fig. 6. Admissible sample size of columns (100 m copper; 1.0 mm i.d.; stationary phase polypropylene glycol; film thickness $d_F = 3.1 \mu$) for ethanol at 100° with 0.5 atm (x) and 2.0 atm (O) excess pressure in the column. Carrier gas flow 19.8 ml/min He in both cases.

point, and the application of pressure in the column—an increase in the loading capacity may be attained. For a theoretical description of the ensuing phenomena, e.g. peak form, loss of separating power under different working conditions and pressures, a further series of experiments must be carried out.

When the efficiency of Golay columns of large internal diameter is compared with that of those of small diameter, it is evident that in the former case a much smaller outlay on equipment is required (no FID, no stream-splitting). In the case of the bigger column the resolving power is smaller. Furthermore it is not possible to choose convenient and practicable sample amounts for analysis of component mixtures of wide boiling range ($\Delta T_s > 100^\circ$), for, with too much sample, apparent overloading effects ensue and the peaks lose their symmetry. As regards loading capacity, however, the bigger Golay column is a real improvement on the smaller. For trace analyses (that is, the analyses of mixtures of high concentration differences), the high loading capacity of the column can be combined with the high sensitivity of an FID. Owing to the large gas volume of the column, dead-space problems in the apparatus play only a small part.

Compared with packed columns, Golay columns of large diameter have the advantage of a higher separating efficiency, attainable in the same analysis time. The economic considerations of these columns should be emphasized, when the column is run to give the same resolving power as that of a packed column, namely that the carrier gas consumption is itself between 1/3 and 1/10 of that of a packed column. Resolving power is normally higher.

With increasing resolving power, the consumption decreases to about 1/20. The small flow velocities reduce the noise level and yield warming-up times favourable to the use of thermal conductivity detectors. The small pressure gradient across the big Golay columns leads to an approximately uniform flow throughout the whole column and reduces all leakage problems in the complete apparatus. The big Golay column is also of much broader application than the packed column:

(a) Carrier gas flows of 30–40 ml/min yield in shorter analysis time separations comparable to those of packed columns.

(b) Carrier gas flows of 15–25 ml/min yield in the same analysis time separations which are better than those of a packed column.

(c) Flows of less than 10 ml/min yield the maximum efficiency of the columns, which is essentially higher than that of a packed column.

The advantage of this column type therefore lies in the fact that, *with one column*, the working conditions can be so chosen as to yield the desired performance.

SYMBOLS USED

d	column diameter
d_F	film thickness of the stationary phase
D_G	diffusion coefficient in the gas phase
D_L	diffusion coefficient in the liquid phase
HETP	theoretical plate height
HETP _{min}	minimum theoretical plate height
K	partition coefficient
k	retention time ratio t_r'/t_M

L	column length
n	number of theoretical plates
r	column radius
t'_r	corrected retention time $t'_r = t_r - t_M$
t_M	retention time of a substance insoluble in the liquid phase
u	carrier gas flow velocity
v_n	volume of a theoretical plate
V_G	gas volume of a column
V_L	volume of the liquid phase of a column
$w_{1/2}$	half-band width
$t_r/w_{1/2}$	resolving power.

SUMMARY

The application of Golay columns of larger internal diameter is described from a theoretical and practical point of view. The influence of the geometry and of the ratio film thickness to diameter on the admissible sample size is discussed.

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