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DESIGN OF AND EXPERIENCE IN OPERATING TECHNOLOGICAL PREPARATIVE INSTALLATIONS

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SUMMARY

Examples are given of the use of gas chromatography under industrial conditions for producing thiophene, indole and xylene on columns 500 and 1200 mm in diameter with annual capacities of from 100 to 1000 tons. Some problems associated with designing industrial columns are considered, including optimization of temperature conditions.

INTRODUCTION

During the past decade, gas chromatography (GC) has been adopted in industry as a method for separating mixtures. The efficiency of chromatography can be greater than that of distillation if a highly selective sorbent is used. This has been observed for such mixtures as benzene-thiophene, benzene-cyclohexane and α - and β -pinenes. The possibility of separating multicomponent mixtures in one cycle, small losses of the compounds being separated with almost 100% extraction, the absence of toxic discharge and the high degree of automation are among the advantages of chromatography.

In this paper several examples of industrial application of chromatography in the U.S.S.R. and some aspects of designing columns and selecting appropriate thermal conditions for their operation are discussed.

INDUSTRIAL APPLICATION OF CHROMATOGRAPHY

In the U.S.S.R. chromatography was first introduced under industrial conditions in 1970 when an installation for producing high-purity reagents was put into service¹. About 30% of the operations performed were by GC; seven Etalon-2 chromatographs with columns up to 100 mm in diameter were being used. More than 100 reagents were produced (99.8% pure) and the total output capacity was 500 kg per year.

This example illustrates one of the current trends in the industrial application of chromatography: a great variety of reagents is produced in relatively small amounts

on columns with relatively small diameters (100–200 mm). The technology of the process is close to that of ordinary laboratory chromatography. Since several mixtures are separated in the same installation, it must be flexible to ensure easy change-over of the operating conditions. Similar experience in designing and operating such installations has been gained by French researchers².

A second trend is the production of large amounts (several tons) of compounds in installations designed for separating one particular mixture. A number of such installations have been built and operated for a long time³. The first was designed for separating commercial 95% thiophene from a benzene fraction containing 10–12% of thiophene. The column (5 m × 250 mm I.D.) had an annual throughput capacity of 120 tons. The separation factor, α , of the mixture was 1.4, the volume of a single sample was 2.5–3.5 l and the cycle duration was 12–15 min. Maximum throughput capacity is attained when the process is performed in two stages: preparation of a concentrated thiophene fraction (70–75%) and its subsequent purification to give the final product. The efficiency of separation and main parameters of the column remained virtually unchanged over an operating period of two years.

Later an installation with columns 1.2 m in diameter and 2.4 m in length was put into service for producing 99.8% toluene, its annual throughput capacity being 1200 tons. The content of toluene in the raw material was 99%, the volume of a single samples was 30 l and the carrier gas flow-rate was 240 m³/h. The column operated for 1.5 years with the same sorbent. The height equivalent to a theoretical plate (HETP, H) at a dose of 0.04 kg/m² was 8–12 mm.

At present an installation is in service in which indole is separated from an indole fraction containing about 4% of the desired product. The column is 520 mm in diameter and 1.5 m in length, single batches amount to 1.5–2.0 kg and the annual throughput capacity is 100 tons. Separation is performed in two stages: preparation of crude indole (*ca.* 75% pure) and subsequent purification to commercial indole (92% pure). The columns operate at 220°C. The HETP of the column, determined under the same conditions as for the column 1200 mm in diameter, was 7–10 mm.

Operating experience on the above installations has demonstrated the potential of chromatography under industrial conditions. Such application create a number of engineering problems related to evaporation of the sample, detection, automation of the process, collecting of the fractions and circulation of the carrier gas.

We shall discuss two aspects closely connected with column operation: construction of a column, and reduction of column efficiency caused by heating of the sorbent bed by the gas flow from the evaporator.

CONSTRUCTION OF INDUSTRIAL COLUMNS

In designing industrial columns one must optimize the length of sections, as well as the shape of the bottom and cover plates for each section. Usually sections are interconnected by means of transition pipes of small diameter.

Giddings and co-workers^{4,5} have shown that on increasing the length of a column the HETP first rises and then attains a constant value. From this it was concluded that it was reasonable to use short sections so that the limiting value of HETP could not be attained. The theory presented in ref. 4 was based on the assumption that in large-diameter columns the velocity profile of the carrier gas is parabolic. It was of

interest to verify the applicability of this theory to those cases in which such a profile does not exist.

The presence or absence of the velocity profile is determined by the method of filling the column. Earlier⁶, it had been shown by means of a laser anemometry technique that if the packing is compacted by tapping the column walls a velocity profile is always formed with an enhanced velocity near the walls. This method (No. 1) was adopted as a reference. We usually pack large-diameter columns by loading in portions and compacting with a plunger with simultaneous pumping of the column with a vacuum pump (No. 2). In this case (see ref. 6) there is virtually no velocity profile along a cross section of the column.

A chromatographic column 100 mm in diameter was assembled from sections 400 and 750 mm in length connected through flanges without any transition pipes or partitions. A sample of *n*-pentane was introduced through an evaporator at 70°C; the column temperature was 25°C. The carrier gas flow-rate was constant at the column exit (10 l/min). Spherochrom-1 (grain size 0.5–1.0 mm) with 20% of dinonyl phthalate was used as sorbent. Upon lengthening the column the sorbent in the lower sections was not re-packed: after filling with sorbent and measuring the HETP of one section, we removed the cover plate, levelled the sorbent bed and lengthened the column by connecting the next section filled with the sorbent.

For comparison, experiments were also performed with columns consisting of sections 750 and 400 mm in length connected by transition pipes (150 × 6 mm O.D. × 4 mm I.D.). Each section was filled separately with a sorbent by method 2.

The dependence of H on the column length for both filling methods is shown in Fig. 1. As is expected from the theory⁴, in the case of method 1, H first increases with increasing column length and then attains a constant value. In method 2, H

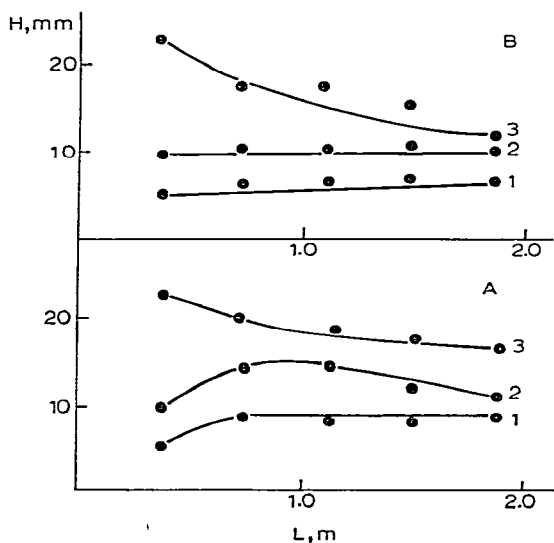


Fig. 1. Relationship between HETP and column length when packing is compacted by tapping the column walls (A) or by a plunger with vacuum pumping (B). Sample volumes of *n*-pentane: 0.5 ml (1); 5 ml (2); 10 ml (3).

undergoes only a slight linear increase with increasing column length. This may be due to the fact that as the bed becomes longer the rarefaction created by the pump diminishes and the packing becomes looser. Separate experiments have shown that compaction without pumping lowers the efficiency.

Introduction of large amounts of sample does not affect the character of the dependence of H on column length.

The data obtained show that sections 1.0–1.5 m in length can be used for industrial columns. The HETP values for continuous columns and for columns assembled from short sections are almost the same:

Column length (mm)	1150	1500	1900
H of a continuous column (mm)	6.2	7.1	6.7
H of a sectional column (mm)	6.9	5.7	6.5

These results mean that it is possible to simplify considerably the construction of industrial columns. Such columns are usually heated with the aid of jackets.

The shape of cover and bottom plates of columns also deserves attention. Usually, preparative columns have conical covers and bottoms, the height of the cone increasing considerably with the column diameter. As a result, the overall dimensions of the entire installation grow. The use of flat or frustoconical covers and bottoms would substantially reduce the overall dimensions of the installation and simplify the technology of manufacturing the columns.

Investigations were carried out on a column (100 cm \times 140 mm I.D.) with the same sorbent as in the previous experiment. The column had a welded conical bottom and a removable cover fixed with flanges. A 100 mm high cone (cone angle 60°), a 50 mm high frustum of a cone (diameter of the upper base 80 mm), a 30 mm high spherical segment (radius of curvature 100 mm) and a flat cover were studied. The diameter of the inlet pipe was 6 mm in all cases; the gas flow could be switched so that the removable cover was either at the inlet or at the outlet of the column. The flow-rate of the carrier gas was varied from 4 to 10 l/min, and the volume of pentane as sample was 1.5 and 10 ml. Table I lists typical data for a 1 ml sample volume and various gas velocities.

TABLE I
EFFECT OF COVER CONSTRUCTION ON HETP OF THE COLUMN

Flow-rate of carrier gas (l/min)	Flat		Spherical segment		Frustum of a cone		Cone	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
4	2.8	3.1	3.7	3.8	3.8	3.9	3.1	3.1
6	3.4	3.3	4.2	4.1	3.9	4.6	3.4	3.5
8	3.9	3.4	4.3	4.3	3.9	4.8	4.0	3.8
10	4.3	3.5	4.5	4.6	4.1	5.3	4.1	4.4

As can be seen from the Table, each type of cover gave approximately identical HETP values; in some cases the use of the flat cover somewhat increases the column efficiency, which may be due to difficulties encountered when filling the covers and to their enhanced hydraulic resistance.

A disc-shaped reflector (diameter 70 mm) arranged in front of the hole in the flat cover and an air gap between the cover and the packing surface exerted almost no effect on the efficiency. This was the case for a high-quality column packing when HETP was 4.0 mm. At a higher HETP value caused by poor-quality packing both the reflector and the gap improved the efficiency.

In all the above examples of industrial application of chromatography, columns with flat covers were employed.

TEMPERATURE GRADIENTS IN LARGE-DIAMETER COLUMNS CAUSED BY GAS FLOW FROM EVAPORATOR

Under the usual operating conditions of a preparative installation the evaporator temperature (T_{ev}) exceeds the column temperature (T_c) by about 50°C. In the case of direct connection of the evaporator to the column the temperature of the gas entering the column also exceeds T_c which, in its turn, causes heating of the initial sorbent zone. The poor conductivity of the sorbent results in temperature gradients in the column, which decrease the column efficiency. Experiments have confirmed that the greater the column diameter the greater is this effect. This might be one of the reasons for the difficulties encountered when we tried to obtain reproducible HETP values for the large-diameter columns.

When designing industrial installations⁷ it was proposed that an additional heat exchanger be placed between the evaporator and the column to act as a heat compensator. To measure the temperature distribution in a sorbent bed, an installation was assembled with a column (750 × 100 mm) fitted with eleven thermocouples as shown in Fig. 2. The experimental conditions were as follows: Spherochrom-1 (0.5–1.0 mm) with 20% dinonyl phthalate; $T_c = 20^\circ\text{C}$; $T_{ev} = 70^\circ\text{C}$; carrier gas (nitrogen) flow-rate 10 l/min. Fig. 3 shows temperature vs. time curves where $\Delta T = T_r - T_0$ and T_r is the current temperature and T_0 the initial temperature. Zero time was adopted as the moment the carrier gas entered the heated evaporator. It follows from the curves that stationary temperature conditions characterized by both the longitudinal (ΔT_l) and transverse (ΔT_a) gradients are established in the column after

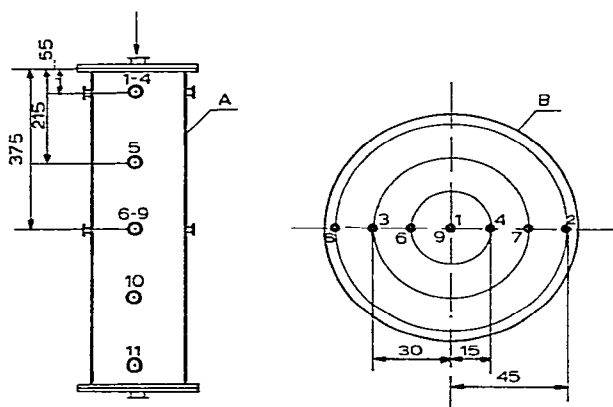


Fig. 2. Location of thermocouples along the length (A) and cross section (B) of the column.

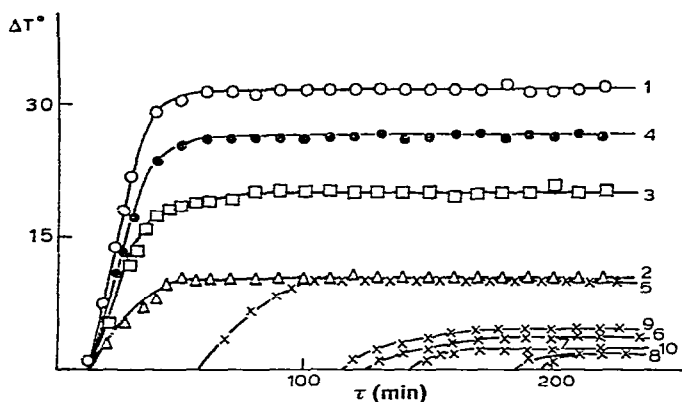


Fig. 3. Curves of temperature vs. time. Number on the curves correspond to those of the thermocouples (see Fig. 2).

a certain time (in our case, 220–250 min). It should be noted that the eleventh thermocouple did not record any deviation from T_0 during the whole period of measurement (*ca.* 300 min). Along the column the temperature varied approximately exponentially (Fig. 4). The shape of the transverse profile (for the first cross section) is shown in Fig. 5. A change in the carrier gas flow-rate, liquid sample volume (10 ml of *n*-pentane every 10 min) or in the shape of the inlet cover (flat or conical) affected the time of attainment of the stationary state but did not change the type of temperature profiles. The time dependence of HETP (Fig. 6) is in fair agreement with the temperature curves. The HETP value almost doubles up to 250 min, after which a thermal equilibrium is attained in the column and HETP remains constant.

Let us now evaluate the contributions of longitudinal (ΔH_1) and transverse (ΔH_2) temperature gradients to the HETP value. Evidently, the additional dispersion of a band because of the transverse temperature gradient is due to the different velocities of zones which move along the cross sectional areas at different temperatures.

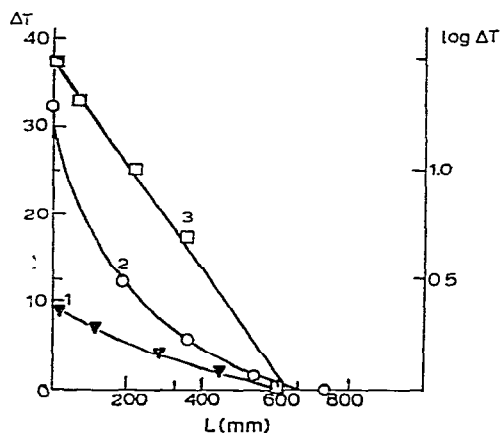


Fig. 4. Dependence of ΔT on L for column wall (1) and centre of the column (2) and dependence of $\log \Delta T$ on L for centre of the column (3).

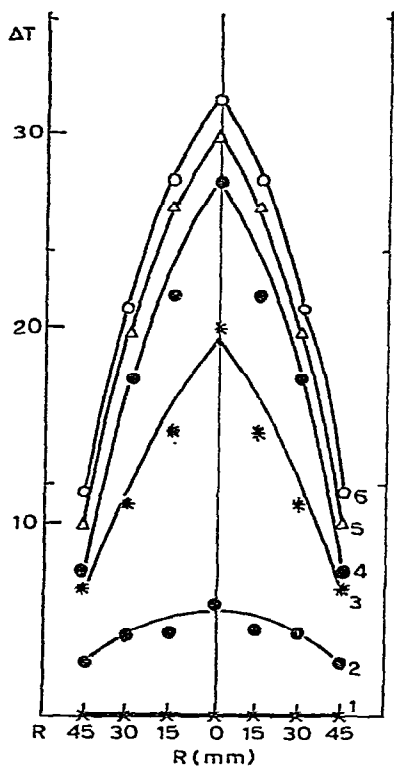


Fig. 5. Change in temperature profile along the column cross section (first section) as a function of time: 0 (1); 20 (2); 30 (3); 40 (4); 50 (5); 70 (6) min. R = Column radius.

The value of this contribution depends on the shape of the temperature profile. Giddings^{8,9} has derived an equation for calculating ΔH_a

$$\Delta H_a = \frac{q^2}{(2 + q)^2} \cdot \frac{\bar{v} r_0^2}{24 D_g} \quad (1)$$

where \bar{v} is the mean velocity of the carrier gas, r_0 is the column radius, D_g is the coefficient of gas diffusion and q is the term characterizing the temperature profile

$$q = (1 - R_w) (\Delta Q / RT_w^2) \Delta T \quad (2)$$

where $R_w = \bar{u} / \bar{v}$, \bar{u} is the mean velocity of the component, ΔQ is the heat of vaporization of the sorbate, R is the gas constant and ΔT is the difference between the temperatures of the centre and wall (T_w) of the column.

From the logarithmic dependence of ΔT on column length, L (Fig. 4), we calculated the mean value, $\Delta \bar{T}$, as a logarithmic ($\Delta T_{1g} = 7.7^\circ$) and \bar{T}_w (linear dependence on L) as an arithmetic mean ($\bar{T}_w = 296^\circ\text{K}$). A value of $\Delta H_a = 4.1$ mm was obtained from the following values of the parameters in eqns. 1 and 2: $\bar{v} = 3.02$ cm/sec; $\bar{u} = 0.333$ cm/sec; $D_g = 0.087$ cm²/sec (*n*-pentane in nitrogen at 20°C); $\Delta Q = 6.165$ kcal/mol of *n*-pentane and $r_0 = 5$ cm.

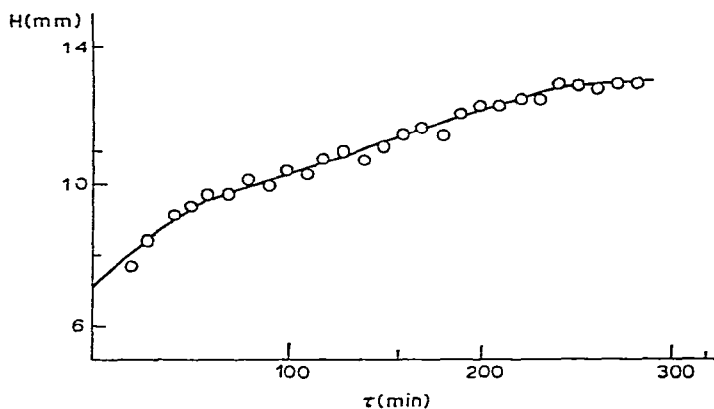


Fig. 6. Dependence of HETP on time. Sample: 0.5 ml *n*-pentane. Nitrogen flow-rate 10 l/min.

The longitudinal temperature gradient gives rise to a velocity gradient, Δu , of the component along the column. Giddings⁹ has developed a theory of dispersion in a column with a longitudinal gradient, according to which band dispersion in a gradient column is always greater than in a non-gradient column

$$\bar{H} = L \int_0^L \frac{H}{R_w^2 v^2} dz / \left(\int_0^L \frac{dz}{R_w v} \right)^2 \quad (3)$$

where z is a longitudinal coordinate.

In our case, when the temperature change along the column length is close to exponential and the temperature dependence of u is exponential ($u = v/Ae^{Q/RT}$, where A is an entropy factor and Q is the heat of sorption), integration of eqn. 3 presents certain difficulties. To simplify the evaluation of ΔH_1 , we divide the column into two equal parts, for each of which dispersions and peak retention times are σ_1^2 , σ_2^2 and t_1 , t_2 , respectively.

Then:

$$\bar{H} = H_0 2(t_1^2 + t_2^2)/(t_1 + t_2)^2 = H_0 f \quad (4)$$

When $t_1 = t_2$, *i.e.*, in the absence of a gradient, $f = 1$ and $\bar{H} = H_0$. In all other cases $f > 1$ and $\bar{H} > H_0$.

Let us assume that the temperature along each part is constant and can be regarded as an arithmetic mean of the temperatures at the ends of the parts. For the first part we have initial temperature 325°K, final temperature 300°K and $\bar{T}_1 = 311^\circ\text{K}$; for the second part initial temperature 300°K, final temperature 293°K and $T_2 = 296^\circ\text{K}$. Using the ratios of the component velocities, u_0/u_1 and u_0/u_2 , and the experimental values $Q = 6500$ kcal/mol and $u_0 = 0.254$ cm/sec ($T_c = 293^\circ\text{K}$), we can calculate u_1 and u_2 and t_1 and t_2 ($t_1 = 112$ sec, $t_2 = 119$ sec). Taking into account $H_0 = 7.1$ mm (Fig. 6), we have $\bar{H} = 8.2$ mm, *i.e.*, $\Delta H_1 = 1.1$ mm. Thus, the calculated value of the total increase of HETP due to the transverse and longitudinal temperature gradients will be $\Delta H_T = 5.2$ mm and the experimental $\Delta H_T = 5.9$ mm, *i.e.*, the difference between these values is about 12% which is quite satisfactory. The evaluation of ΔH_1 can be made more accurate if the column is divided into a greater number of parts.

It has already been noted that the stationary temperature gradient is established over a definite length of the sorbent bed (*ca.* 600 mm in our case) and, therefore, with increasing length the relative contribution of ΔH_T to diffusion of the zones must diminish. This is confirmed by comparison of the time dependence of H for columns of different lengths (Fig. 7): $\Delta H_T = 21, 15$ and 7 mm for $L = 400, 750$ and 1500 mm. Linear extrapolation of the dependence of H on L shows that when $L \approx 2$ m, ΔH_T tends to 0, *i.e.*, for columns longer than 2 m the contribution of ΔH_T to H becomes negligible. However, these data refer to columns 100 mm in diameter, and with increasing diameter the length at which ΔH_T will not affect the column efficiency will exceed practical values.

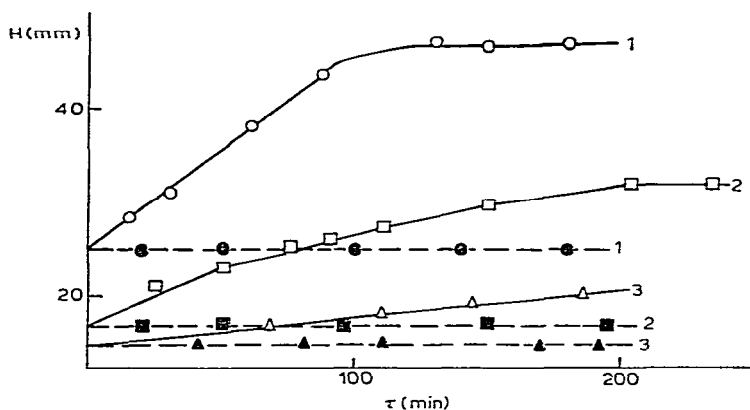


Fig. 7. Dependence of HETP on time for columns 400 (1), 750 (2) and 1500 (3) mm in length with a heat compensator (---) and without it. Sample: 10 ml *n*-pentane. Nitrogen flow-rate 10 l/min.

Therefore, when the column diameter is more than 50 mm it is desirable to add a heat compensator to a conventional preparative chromatograph in order to cool the gas flow leaving the evaporator down to the column temperature. The effect of a heat compensator on HETP is shown in Fig. 7. When a copper-coil heat exchanger cooled with water at a temperature of 18–22°C was placed between the evaporator and the column the HETP was independent of the length and remained constant during the whole observation period.

It should be noted that there may be operating conditions under which cooling of the gas flow from the evaporator will result in partial condensation of the mixture being introduced in the heat compensator. In this case the evaporator must operate only during sample introduction, and in periods between introductions, the gas flow bypass the evaporator.

CONCLUSION

Present-day engineering advances allow the construction of industrial gas chromatographic installations with capacities of several tons of product per year. The main problem is to find mixtures which could be economically separated by this method. Another problem consists of developing methods of calculation for such installations and in finding ways of enhancing their efficiency and capacity.

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