THE DESIGN AND CONSTRUCTION OF A TWO-INCH PREPARATIVE GAS CHROMATOGRAPHIC COLUMN*

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(Received November 1st, 1960)

INTRODUCTION

Our interest in the field of acrylic and related monomers is, of course, well known. In this connection, it soon became apparent that a preparative gas column capable of producing pure samples of these monomers would be extremely useful. It further became apparent that the obtaining of these pure samples would greatly aid in the study and understanding of the reaction kinetics of polymerization. With these points in mind, it became almost a necessity either to purchase or design and construct a preparative gas column.

DISCUSSION

We have been interested in gas chromatography for approximately 5 years. Since our initial venture into gas chromatography, outstanding progress has been made in the development of the analytical gas–liquid chromatography instruments: The argon and flame ionization detectors and the capillary columns were developed to such a state that extremely small traces of material may be fully investigated. These methods are not amenable to sample isolation, and therefore, find use only in analytical investigations. It was felt that while these instruments were indeed a boon to the analytical investigations of odors and flavors, they are practically useless for obtaining workable quantities of pure samples. At the initiation of this project very few instrument companies had any suitable apparatus that would fit the job. Perhaps the first commercial preparative column was the 1-inch, 3-meter column designed by Perkin-Elmer Corporation as an accessory to their standard analytical instrument. Podbielniak has the Chromachron and very recently Beckman announced the sale of the Megachron. These are very fine instruments in themselves, but it was felt that the design and construction of our own column would give some insight into the cause and possible solution of some of the difficulties concerned with large scale gas chromatography.[1-3]

The design of the preparative gas column was based on a scale-up of our own "home made" analytical model, which consists of a 12-ft. 1/4-in. O.D. column, a Gow-Mac Thermal conductivity cell and the necessary power supply and recorder.

* Presented at the second Delaware Valley Regional Meeting, February 25, 1960.

It was intended that a charge of 5 ml of total sample would be a suitable size to inject for separation. The figure calculated by scaling up from the 1/4 in. column, resulted in a preparative column of 2 in. diameter. The exact figure is less than 2 in. but it was decided that the extra size would allow 5 ml of sample to pass without unduly overloading the column. This figure was arrived at by the following calculations. The small column has an I.D. of 4.5 mm and a load limit of about 50 mg. To allow for 5 ml of sample, a column capable of handling 5000 mg should be used. The calcultations based on the ratio of the diameters squared,

$$\frac{x^2}{(4.5)^2} = 100, \text{ hence } x = 45 \text{ mm}$$

resulted in a column 45 mm in diameter. The capillary was chosen since the detection of samples in large volumes of high velocity gas streams has proven very difficult. The Gow-Mac thermal conductivity cell was chosen since it has been our experience that these units are quite sturdy, have excellent sensitivity over a wide temperature and are reasonably stable over long periods of time. It was also decided that the detector system would consist of a capillary by-pass and a Gow-Mac thermal conductivity cell. These were then the basis of the design and construction of a 2-inch column.

CONSTRUCTIONAL DETAILS

The column proper consists of a 2-in. I.D. stainless steel pipe, 9 ft. long, with the ends sealed with stainless steel caps (Fig. 1). One cap acts as a sample inlet and the other cap was modified to act as the outlet. A piece of 1/2 mm capillary stainless steel tubing acts as a capillary by-pass to the stainless steel detector cell (Fig. 2). All connecting tubing is either plastic or stainless steel.

Fig. 3 is a diagram of the inlet system. This was threaded onto one end of the column proper and is individually heated with a 6-ft. heating tape and powered by a Variac. The temperature is maintained approximately 50° above column temperature to insure rapid and complete vaporization of the sample.

The stainless steel helices used to pack the inlet cap weigh approximately 100 g, which was considered sufficient to insure good vaporization without any appreciable cooling of the injection block.

Fig. 4 is a diagram of the outlet and condensing systems used for the recovery of the separated fractions. At present, there is only one trap since we are mainly concerned with the isolation of the main constituent. More could be added without any difficulty.

The detector cell is a Gow-Mac TE-II design; stainless steel, hot wire filament powered by a Gow-Mac power supply. The cell is housed in a specially designed unit which consists of a large Dewar flask and a heating unit. This unit plus the outlet system are heated individually with their own power supply and are maintained approximately 50° above column temperature. The output of the cell is connected to a 0.5 mV strip-chart recorder running at a chart speed of 6 in. per hour.

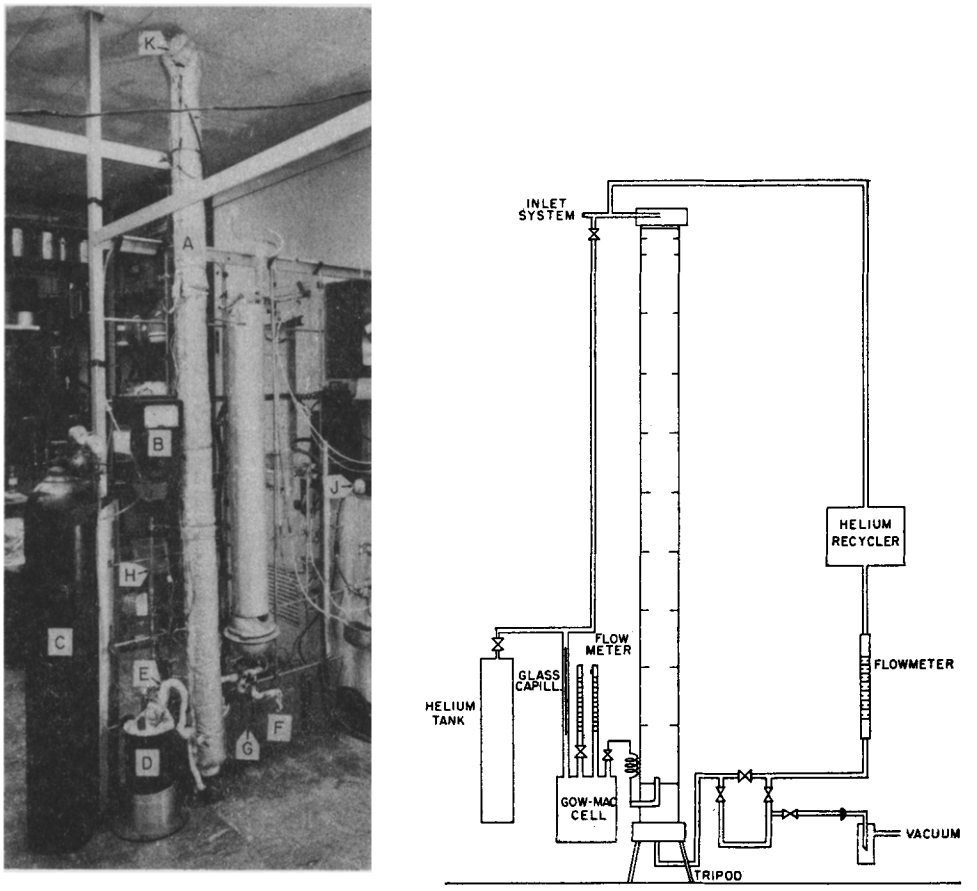

Fig. 1. Two-inch gas preparative column. (A) Column proper showing heating mantles. (B) Multipoint thermocouple meter. (C) Helium cylinder. (D) Detector and housing. (E) Capillary by-pass. (F) Helium recycler. (G) Outlet and condensing system. (H) Flow meter for capillary flow control. (J) Detector power supply. (K) Sample inlet.

Gas circulating system

The original column was set up to use nitrogen gas but the rapid rate of flow very soon depleted the cylinder. The annoying task of replacing a new cylinder every morning, was soon alleviated by a helium gas recirculating system designed and built by our Instrument Laboratory. This unit consists of 2 pressure gauges, 3 traps, 4 valves, a compression pump and a surge tank. In operation, the helium cylinder gauge is set such that the circulator high pressure gauge will register at 15 lb./in.^{2}. The second gauge is set by valve at 15 in. of water. The purpose of the second gauge and valve is to by-pass some of the gas from the high side of the compressor to prevent a vacuum on the outlet side of the column. The four valves are used to control the inlet, the outlet and by-pass stream, and also as a vent to flush contaminants out of the apparatus. The 3 traps are made of brass and are filled with activated charcoal, dehydrite,

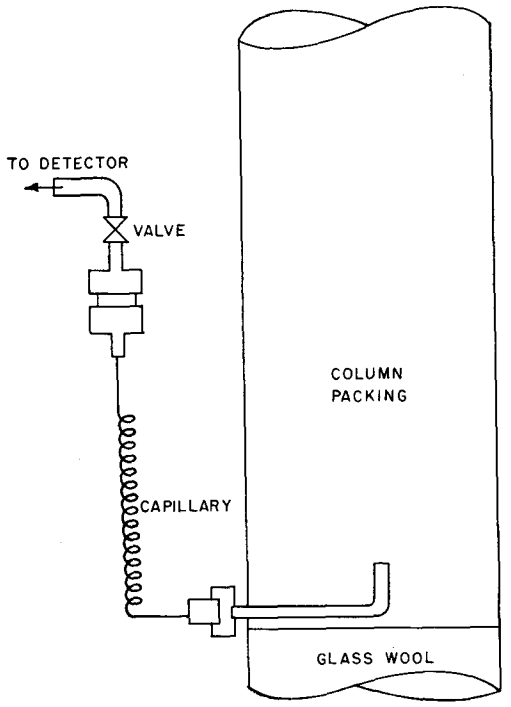

Fig. 2. Capillary by-pass system.

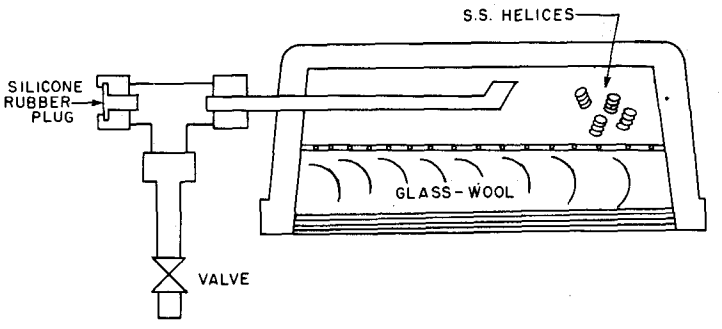

Fig. 3. Sample inlet system.

and ascarite, respectively. During operation of the column, these traps are immersed in a dry-ice acetone bath. To be absolutely certain that no contaminants re-enter the gas stream, a 4th trap of molecular sieves was separately added just previous to the main traps. This trap is continuously immersed in liquid nitrogen during operation and is quite useful since it will rapidly condense and hold most of the contaminants thereby facilitating clean-out. It is essential that these traps be purged at least once a week if the column is used heavily, since any sample that is not adsorbed by the trap will be recirculated and thereby show up as an impurity in the next fraction collected. Of course, this problem will change according to the demands put to the column.

Condensing system

The condensing system consists of 4 valves and a 1/2 in. copper U-tube filled with stainless steel helices (Fig. 4). During operation, previous to condensing the sample, the carrier gas stream is passed through valve 1, while valves 2, 3, and 4 remain closed. During condensation the U-tube is immersed in dry-ice acetone, valve 2 and valve 3 are opened and valve 1 closed. The point to condense the sample is determined by the appearance of the peaks on the strip-chart recorder. After the sample has passed, valve 1 is reopened and valves 2 and 3 are closed. The system is then evacuated by opening valve 4 and valve 5. The dry-ice bath is removed and the receiving trap immersed in liquid nitrogen. As the U-tube warms to room temperature, the condensed sample will be transferred to the receiver trap. Finally, a hot water bath is placed around the U-tube to complete the transfer of sample from the U-tube to the receiving trap.

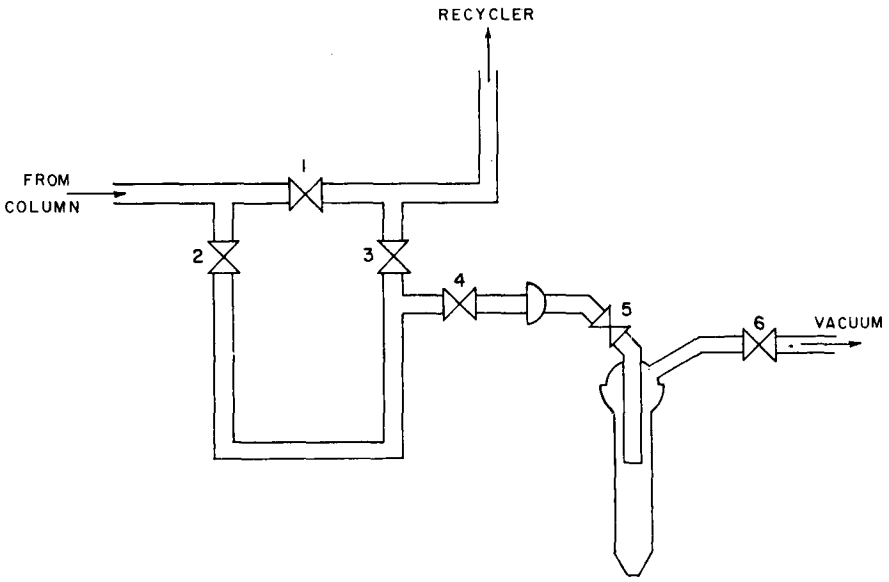

Fig. 4. Condensing and recovery system.

The efficiency of the trap represents about 95 % recovery, based on the recovery obtained when 3 ml of benzene was injected. It was necessary to design this type of condensing system since the entire apparatus is essentially closed and any direct condensing system without subsequent transfer might seriously disturb the equilibrium of the entire system.

Gas flow and pressure regulation

The gas flow and pressure regulation of the entire apparatus is controlled by the gas recycling system. The pressure in the preparative column is maintained at 15 lb./in.^{2}

by the compressor and a flow of 4.5 on the predictability flow meter, which corresponds to 1200 ml/min of He, is regulated by a valve on the helium recycler. Approximately 15 in. of water is maintained on the recycler by-pass valve situated on the high side of the pump for the reason explained above. To maintain a constant flow of 75 ml/min of gas through the sample side of the detector cell, a down-stream differential flow controller was used. A system of valves and a flow meter also control the flow of 75 ml/min of gas through the reference side of the detector cell.

Temperature control

There is no elaborate or precise temperature control in the entire system, although reasonable precaution was taken to insulate the entire apparatus from rapid temperature changes. The column proper is heated to 70° by 3 Glas-Col mantles wired in parallel and powered by a 15-A powerstat. The inlet system, outlet system, condensing system, and detector cell are individually heated by heating tapes controlled by powerstats and all are maintained approximately 50° above the column temperature. Iron constantan thermocouples were placed at various points of the apparatus and under steady state conditions, the following temperatures were recorded on a multipoint thermocouple meter:

Position		°C
Outlet		130
Condensing		125
Inlet		120
Cell		155
Column	1	65
	2	75
	3	70
	4	75
	5	75

The above description completes the details of construction as the column now stands.

PACKING THE COLUMN

One final detail remains to be described and this is the packing of the column. At present the column is packed with approximately 5 lb. of 20% N,N-bis-(2-cyanoethyl)-formamide liquid phase on 30–60 mesh crushed firebrick. The above liquid phase was developed in conjunction with Dr. NEWMAN BORTNICK. It was selected for a very special purpose but has proven to be extremely useful in many other types of separation. It has an excellent column life even to approximately 125°. It is expected that a brief note describing the characteristics of this liquid substrate together with other liquids developed in our laboratory will soon be submitted for publication. By far the most difficult task of the entire project was the packing of the column. Many different methods were tried in an attempt to obtain a reasonably efficient column. A brief description of these methods together with some of the reasons for trying them follows.

The first method of packing was merely pouring in the packing with simultaneous vibration while the column was connected to a vacuum pump. The column was vibrated until no more settling was noticed. This method was tried initially since this is the method used on our analytical columns and appeared to give reasonably good results. The column was then set up and put into operation. The first sample through the column was a sample of *n*-hexane. The peak from this first sample was very broad and indicated that the column was operating very inefficiently. The column was then shut down and another method of packing tried. The second method was to pour in approximately 250 ml aliquots of packing and then tamping with a specially designed tamp. The complete operation was performed with a vacuum pump on the outlet side until the entire column was full. The reason for this method was that if the column was packed in discrete sections, any channelling that might occur in the previous method of packing would now be isolated to one small section of the column. It seemed unlikely by this method of packing that the entire length of the column would channel in the same direction. The results of this method were also very poor as indicated by broad peaks and poor separation between peaks.

The third method of packing was by slurry. It is well known that the best method of packing liquid chromatographic columns is by slurry and, therefore, by reason of analogy a slurry-packed gas column might work equally as well. Before packing, 1 lb. of the liquid substrate was added to the solvent to prevent complete removal of the substrate from the firebrick. The column was slurry-packed with *n*-hexane, all the drainings collected, and the remainder of the hexane blown off with nitrogen. The solvent was evaporated and the residue weighed. The final weight of residue was 1.25 lb., leaving 0.75 lb. of liquid substrate on the firebrick. This then represented a 15 % column rather than the usual 20 %. The apparatus was completely assembled, a sample injected and the resulting chromatogram recorded. The results were again very discouraging indicating poor efficiency characterized by broad flat peaks.

At this time, it was decided to study the flow properties of gases through large diameter columns. A 2-in. glass column, 3 ft. long, was packed with firebrick and then saturated with hexane. A water aspirator was connected to the bottom of the column and the flow pattern observed as the hexane evaporated. The flow pattern observed was in the shape of an inverted bowl with the gas traveling faster at the walls than at the center. It was apparent then that if the samples were traveling down the column as inverted bowl shaped bands, the recorded curve should be broad and have overlapping peaks even though good separation may have been accomplished. The reason why the peaks would overlap is shown in Fig. 5A. During the preliminary experiments the capillary by-pass was connected to the outlet side of the column so that the entire sample had to pass through the outlet before being detected. If the capillary were placed at the center of the packing, such that only the dome section of the bowl passed the capillary system, the recorded curves should approach those of an analytical column (Fig. 5B). To test this approach, the column was dismantled and the capillary fitting added to the column so that the entrance to the by-pass was exactly in the center of the packing at the bottom of the column. The column was repacked, and a

sample of benzene and toluene introduced. The resulting curves showed a very marked improvement. The difficulty of this arrangement, however, was the fact that the recorded curves did not truly represent the samples as they emerged from the column. This discrepancy was found by connecting the capillary by-pass first to the center of the packing and then to the tubing on the outlet side. The curves from the

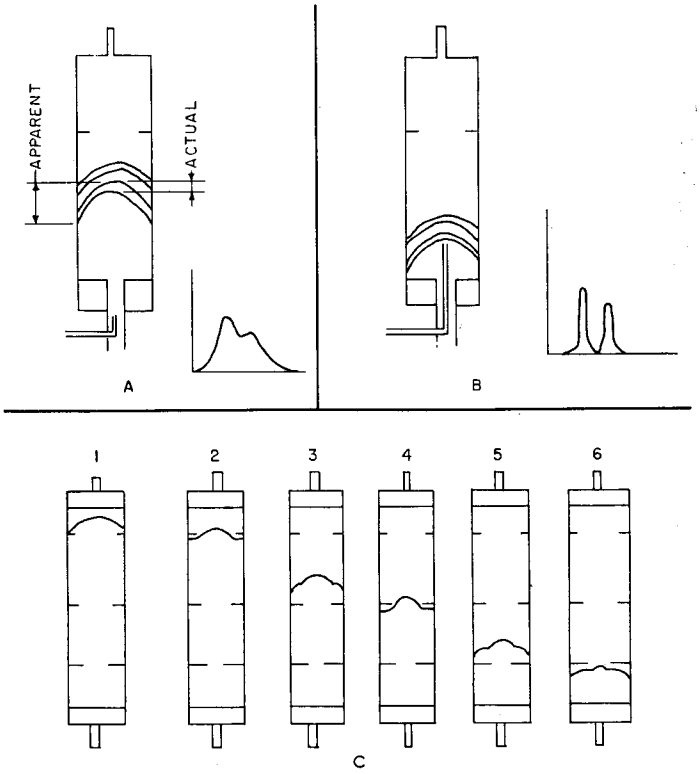

Fig. 5. Flow pattern.

center capillary showed definite peak separation, whereas the curves obtained by the capillary connected to the outlet side were overlapped and broad. It was apparent then that the assumption that these bands were moving as inverted bowls was reasonably correct. Once again, the column was dismantled and the packing removed. This difficulty brought to mind the discussion of GOLAY[1], who expressed the thought that "mixing washers" would be necessary for the efficient operation of large columns. With this thought in mind, the following experiment was attempted.

Filter paper rings were cut to the exact size of the column and then saturated with substrate. These rings were graduated in size starting with a ring 2 in. O.D. and 1 7/8 in. I.D. and ending with a ring 2 in. O.D. and 1 3/8 in. in I.D. The rings were spaced 1 ft. apart along the length of the column. The column was packed by filling with vibrating to a depth of 1 ft. and then adding a saturated ring, another foot of packing and then another ring with an opening smaller than the previous ring, the

largest aperature ring at the top and the smallest aperature ring at the bottom. After the column was packed in the above manner, the apparatus was completely reassembled and put into operation. Fig. 5C depicts a series of drawings illustrating my conception of the flow pattern of the sample bands as they pass over these rings. It is felt that since the carrier gas is flowing more rapidly along the walls of the pipe, a packing containing a homogeneous concentration of substrate will cause the bands to travel as an inverted bowl. If, however, it were possible to put a concentration gradient of liquid substrate across the radius of the column, then the sample bands should be more strongly adsorbed at the walls than at the center and, therefore, the sample bands should at least approach a straight line. Lacking suitable means of putting a concentration gradient across the column, the concept of saturated rings was employed.

The first drawing, Fig. 5C (1), shows the sample going on the packing. As the sample travels down the column, the bands start to distort, Fig. 5C (2). Passing the first and largest aperture, the ends of the bands are retarded slightly since there is a higher concentration of substrate even though the carrier gas is moving more rapidly at the sides than at the center of the packing. As the sample travels down the column, Fig. 5C (3–6), the bands become more distorted and will, therefore, require a greater amount of substrate at the wall to correct the distortion. This was the reason why the rings were graduated in size starting with the largest aperture near the inlet and going to the smallest aperture near the outlet.

When the column reached equilibrium, the previous experiment of connecting the capillary to two positions was repeated. A sample of benzene and toluene was injected and as was expected, the recorded curves from the center capillary showed good peak shape and high resolution. The capillary was then connected to the outlet tubing and another sample injected. The chromatogram obtained was very gratifying indeed. The peak shape was very good and the resolution was also very good. A calculation of the theoretical plate efficiency showed about 500 plates.

EXPERIMENTAL

Once the point had been reached where the column was shown to be reasonably efficient, a systematic investigation of the effects of the various parameters of gas flow, pressure, and sample size on the efficiency of the column was begun. Table I is a summary of the study of theoretical plate efficiency *versus* the flow rate through the column at 15 lb./in.^{2} at the inlet and at a constant cell flow rate through the detector. Table II is a study of the efficiency *versus* the flow rate through the detector at constant column flow rate. The operating conditions based on the above experiments were finally set at 15 lb./in.^{2} a flow rate of 1200 ml/min through the column and 75 ml/min through the cell. Table III is a study of the efficiency *versus* pressure at a constant flow rate through the cell and column. Table IV shows the changes in efficiency and separating power *versus* sample size. Table IV also indicates that even though the theoretical plate efficiency decreases rapidly, the separating power of the substrate remains fairly constant.

TABLE I*

VARIATION OF THEORETICAL EFFICIENCY PLATES WITH VARYING FLOW RATES

(Detector flow rate constant at 75 ml/min)

	Flow rate ml/min	*Theoretical efficiency (plates)*
2	270	284
3	590	395
4	1000	540
5	1450	459
6	1900	454
7	2360	323
8	2820	242

* 0.5 c.c. benzene.

TABLE II*

VARIATION OF EFFICIENCY WITH VARYING FLOW RATES THROUGH THE DETECTOR

(Column flow rate constant at 1200 ml/min)

Flow rate ml/min	*Theoretical plates*
20	522
41.3	522
58.0	496
80.0	526
300.0	506
480	560

* 0.5 c.c. benzene.

TABLE III*

VARIATION OF EFFICIENCY WITH VARYING HELIUM PRESSURE AT INLET

(Column and detector constant at 1200 ml/min and 75 ml/min respectively)

Per cent/in² at inlet	*Plates*
5	430
10	498
15	526
20	496
25	472

* 0.5 c.c. benzene.

TABLE IV

VARIATION OF PLATES AND SEPARATING POWER WITH SAMPLE SIZE (BENZENE AND TOLUENE) AT CONSTANT PRESSURE (15 lb./in.^{2}) AND CONSTANT FLOW RATE (1200 ml/min)

Sample size(c.c.)	*Sensitivity (%)*	*Separating power**	*Plates*
0.2	15.0	1.65	615
0.4	7.5	1.66	595
0.8	3.75	1.66	515
1.6	1.88	1.65	332
3.2	0.94	1.66	256
5.0	0.47	1.65	178

* $\frac{rt_2 \text{ vs. air}}{rt_1 \text{ vs. air}}$

in which rt_2 = retention time of peak 2 from air peak; rt_1 = retention time of peak 1 from air peak.

RESULTS

Figs. 6–9 are typical chromatograms obtained with the 2-in. column. Fig. 6 is a chromatogram of ethyl, *n*-propyl, and *n*-butyl acetate. Fig. 7 is a sample of aromatics and Fig. 8 is a sample of alcohols. Fig. 9 is a chromatogram of a sample of 2B alcohol.

Sensitivity

As seen from the chromatogram of 2B alcohol the maximum sensitivity of the apparatus is 3400 divs./ml of benzene. Under steady state conditions, short term noise is $\pm$ 1.5 divs. at 100% sensitivity. Long range noise is 1 div./h at 10% sensitivity.

Cost

A brief rundown of the cost of the various items used in the construction of this column are listed below:

9 ft. of 2-in. stainless steel pipe	$ 75.00
2 stainless steel caps at $ 6.50 each	13.00
4 stainless stop-cocks at $ 6.00 each	24.00
Assorted stainless steel tubing	10.00
1 Gow-Mac cell	65.00
1 Dewar	15.00
1 Power supply and att. (for cell)	100.00
1-20 A powerstat transformer	50.00
3 Glas-Col mantles each $ 65.00	195.00
3 Flow meters	30.00
5 lb. firebrick	60.00
Miscellaneous	25.00
Helium recycler	200–250.00
3–7 A powerstats	55.00

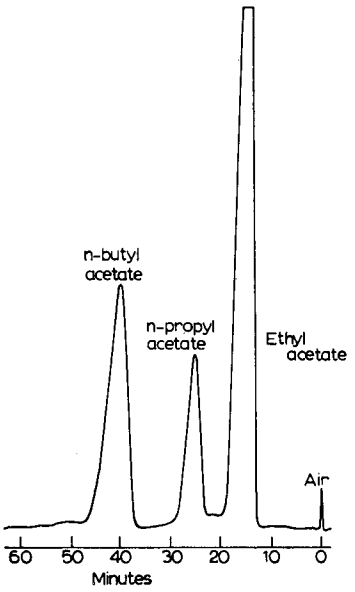

Fig. 6. Chromatogram of ethyl, *n*-propyl, and *n*-butyl acetate.

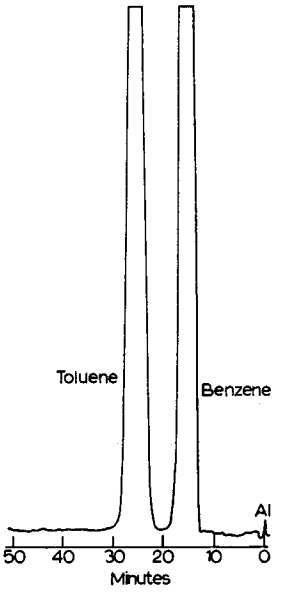

Fig. 7. Chromatogram of a sample of aromatics.

2-in. prep. column. Packing: N,N-bis-(2-cyanoethyl)-formamide. Flow: 1200 ml He/min (column); 75 ml He/min (capillary). Temp. 70°. Sensitivity: 10% on 0.5 mV F.S.D. Sample 2 ml. Pressure: inlet 15 lb./in.^{2}; outlet 12 lb./in.^{2}. Bridge current 150 mA.

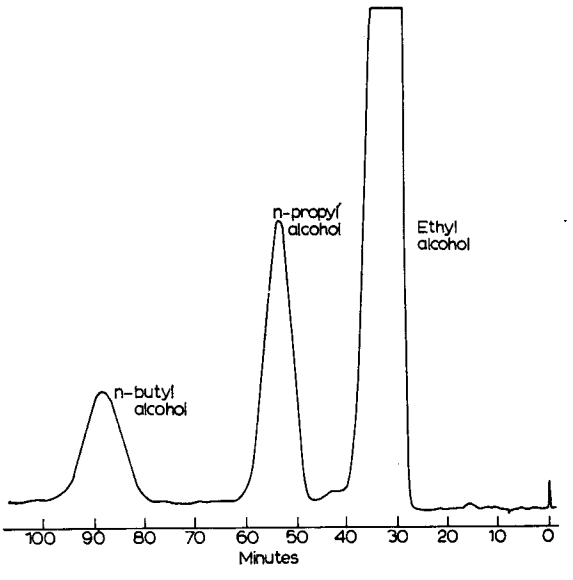

Fig. 8. Chromatogram of a sample of alcohols.

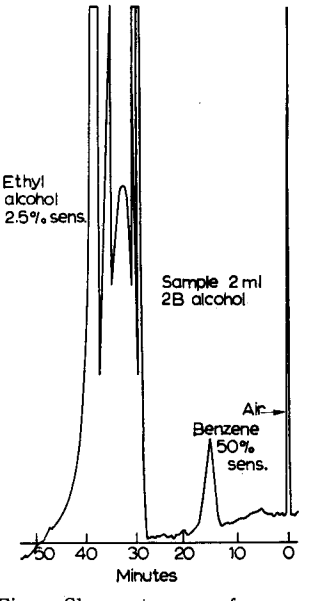

Fig. 9. Chromatogram of a sample of 2B alcohol.

2-in. prep. column. Packing: N,N-bis-(2-cyanoethyl)-formamide. Flow: 1200 ml He/min (column); 75 ml He/min (capillary). Temp. 70°. Sensitivity: 10% on 0.5 mV F.S.D. (Fig. 8) Sample 2 ml alcohol. Pressure: inlet 15 lb./in.^{2}; outlet 12 lb./in.^{2}. Bridge current: 150 mA.

CONCLUSION

The design and construction of a 2-in. gas chromatographic column has been described in full detail. A method of eliminating the wall effect due to large diameter packing has been extended and suitable experimental data to partially substantiate the proposal has been presented. The proposal has by no means been rigorously proven but is only extended as a possible explanation of the observed experimental data. This column has currently been in use for the past year and has performed quite efficiently in a wide variety of situations.

ACKNOWLEDGEMENTS

My sincerest thanks to my fellow co-workers for many suggestions and especially to Mr. DONALD GREENWAY, my assistant, who so patiently packed and unpacked this column so many times and to our instrument group for the helium recycler.

SUMMARY

Factors which control the design of a large column, such as column size, sample size, carrier gas flow, temperature, injection system, and condensing system are discussed. Other points of interest such as capillary by-pass and sample detection, packing problems, gas recycle, study of efficiency *versus* flow rate and efficiency *versus* sample size are also treated. A brief survey of the cost of materials is given.

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