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A MULTIPLE COLUMN GAS CHROMATOGRAPH

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SUMMARY

In this article, we present the results of our study on the design, construction and use of a multiple column exploratory gas chromatograph. This device has a single oven and a single hydrogen flame detector, but has five valves, injection ports and columns in parallel, so that any one of the columns may be connected to the detector by switching its valve. Our purpose in developing this device was to provide a compact and inexpensive arrangement whereby a number of packings could be held immediately available in standby condition for a quick qualitative evaluation in the separation at hand. The design has also proved useful for preparative chromatography on a small scale.

One of the most time-consuming aspects of gas chromatography is the installation and conditioning of columns. Where a variety of columns are in intermittent use, considerable time is lost in making interchanges. We have tested a design in which five columns can be held at operating temperature with a normal carrier gas flow, and valved into operation as desired. Over a period of several years, we have found this method of operation to give satisfactory results.

Practical design considerations dictated that valving should take place at the low pressure, or at the detector end of the column. This implies that each column must have its own injection port, but that one detector system will suffice for all the columns in a single oven. If several columns are to be connected to a single detector, it may be desirable to provide a positive gas flow which will minimize dead spots and carry residual gases to the detector after a valve is closed. This is easy to do if a hydrogen flame detector is used, since column effluents can be valved into the hydrogen stream through very short connecting tubes.

The design adopted is shown schematically in Fig. 1. A pillar is used which contains five valves, injection and exhaust ports, connections to the individual columns, and a single detector mounted at the top of the pillar. Axial ducts in the pillar supply

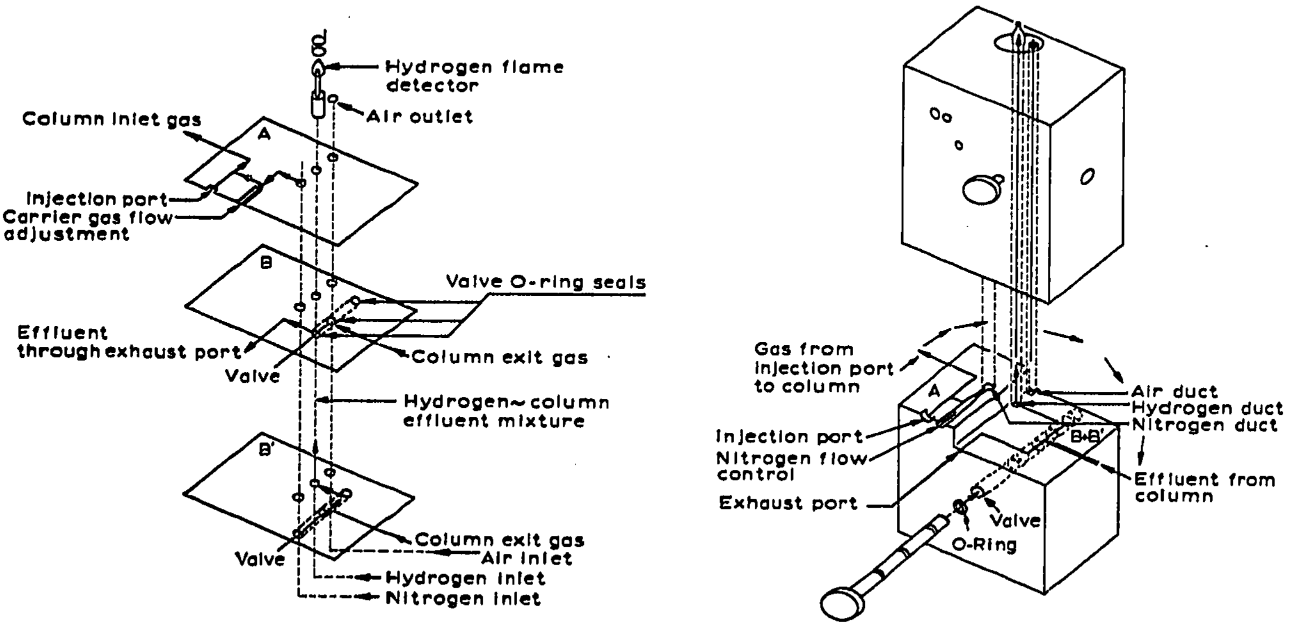

Fig. 1. A is a plane section through the column which contains the inlet port. B is a similar section through the exhaust port with the valve in closed position (*i.e.*, open to the exhaust port). B' is the same section, but with the valve open to the hydrogen (detector) duct. For each column in the chromatograph there is a plane A and plane B. The spacing between planes A and B is $\frac{3}{4}$ in., and between the adjacent A planes, $1\frac{1}{2}$ in. In order to provide proper heat circulation to the bottom column, the bottom A plane should be at least 3 in. from the floor of the oven.

hydrogen and air for the detector as well as carrier gas for the columns. Effluent from a column flows through its O-ring sealed valve and thence either to the exhaust port or to the hydrogen duct, where it mixes with the hydrogen and is carried directly to the detector.

The valve itself, which is built into the pillar, is a very simple arrangement of three ports and three O-rings, and is shown in Fig. 2*. This arrangement has been satisfactory for continuous operation at temperatures up to 150°, using silicone rubber or fluorocarbon O-rings (Parker compound Nos. S 455-7, S 318-6 and 77-545 (Viton) have proven satisfactory).

Above 150°, O-rings take a set and develop leaks. Therefore, for temperatures above this point we use a flat rotating graphite** disc to replace the O-ring valve. This has proved very satisfactory although its construction is a little more complicated then the O-ring type. Fig. 3a shows this type of valve and also outlines the arrangement of column connections, the mechanism for adjusting carrier gas flow and a simplified arrangement for conducting the carrier gas and the hydrogen streams.

The chief simplifications in construction involve the replacement of the dif-

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[*] The hole for the valve is finished by forcing an oversized hardened steel ball through it. This not only burnishes the hole to a high finish, but slightly relieves the edges of the ports, and minimizes the tendency to cut the O-rings. The O-rings need only press very lightly against the bore of the tube, since the pressure at the valve is very small.

[**] Teflon is not suited to this application. Above 250° it begins to deteriorate rapidly, and corrodes the ambient metal. Moreover, contact of the column gas stream with Teflon is deleterious (see ref. 1). While we expected that graphite might show adsorption of column effluents, in fact, we have not noticed this effect.

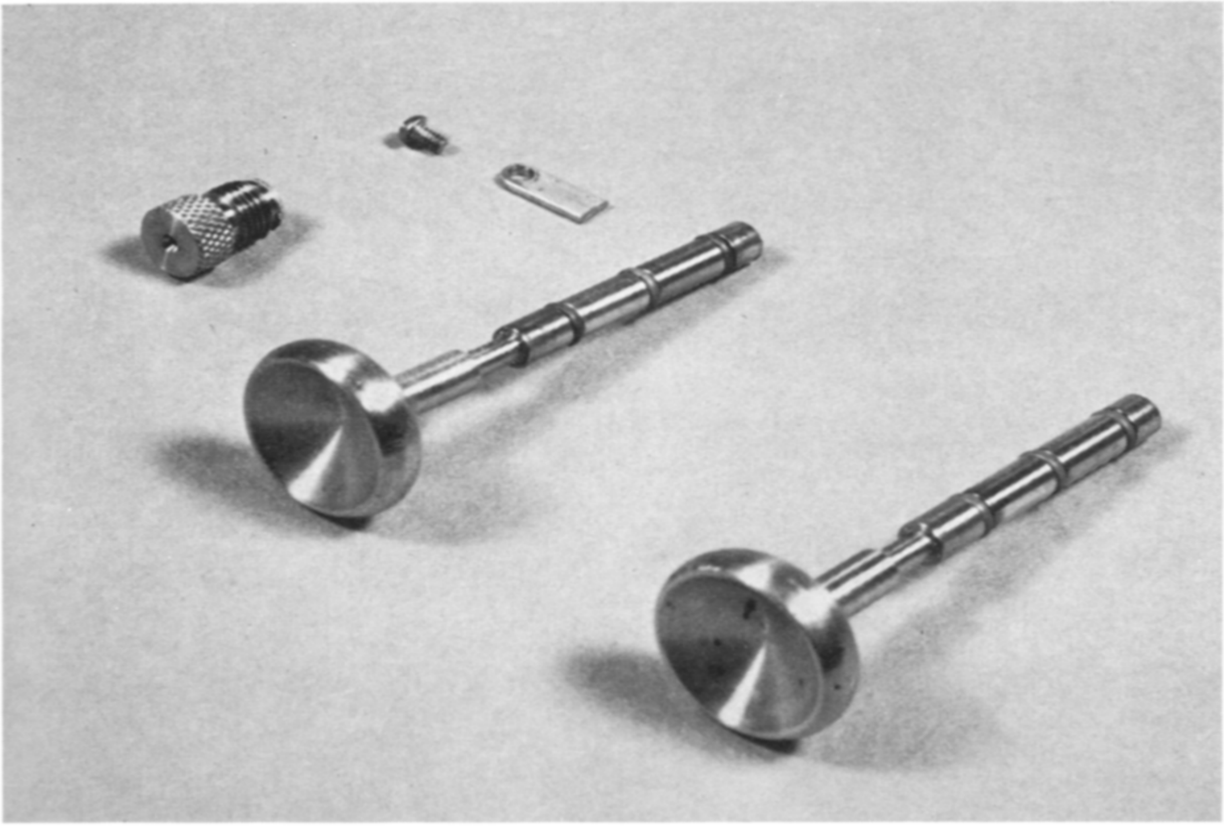

Fig. 2. Valves with O-rings for lower temperature application. The valve stems are $\frac{1}{4}$ in. diameter, relieved 0.010 in. between the O-rings. Movement of the valve is limited by the stop-tab shown. A septum retaining screw is also shown at the top of this figure. Although the valve handles shown here are of metal, they should actually be made of heat-insulating material.

ficult-to-make axial gas passages in the column by corresponding tubes fastened exterior to the pillar (E and F, Fig. 3a). It is feasible to furnace braze these carrier gas and hydrogen tubes to the back side of the column, and to drill into them at right angles to tap off for the various gas ports*. A second modification was introduced to overcome a problem with individual needle valves (D, Fig. 3a) which regulate the carrier gas flow for each column.

We have found it particularly unsatisfactory to attempt to regulate the carrier gas flow with a tapered needle which screws into the chromatograph pillar. Aside from the difficulty of getting the required finish in the hole, the needles tend to seize and break off—probably because when the column is heated there may be a lack of perfect concentricity of the needle stem threads with the carrier gas passage. The use of a steel ball in a tapered gas passage has been found to give far better results. This construction is detailed in the insert of Fig. 3b. If the ball N becomes wedged in the taper due to injudicious tightening of the screw, plug M can be removed and the ball tapped out with a punch.

Fig. 4 shows the appearance of a pillar for five low temperature ($\leqq 150°$)

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* Faulty brazing which leads to internal leaks between the ports in the individual tubes is not of consequence, although large pockets of trapped gas between the valve and the hydrogen stream could lead to peak tailing. We have not observed such an effect.

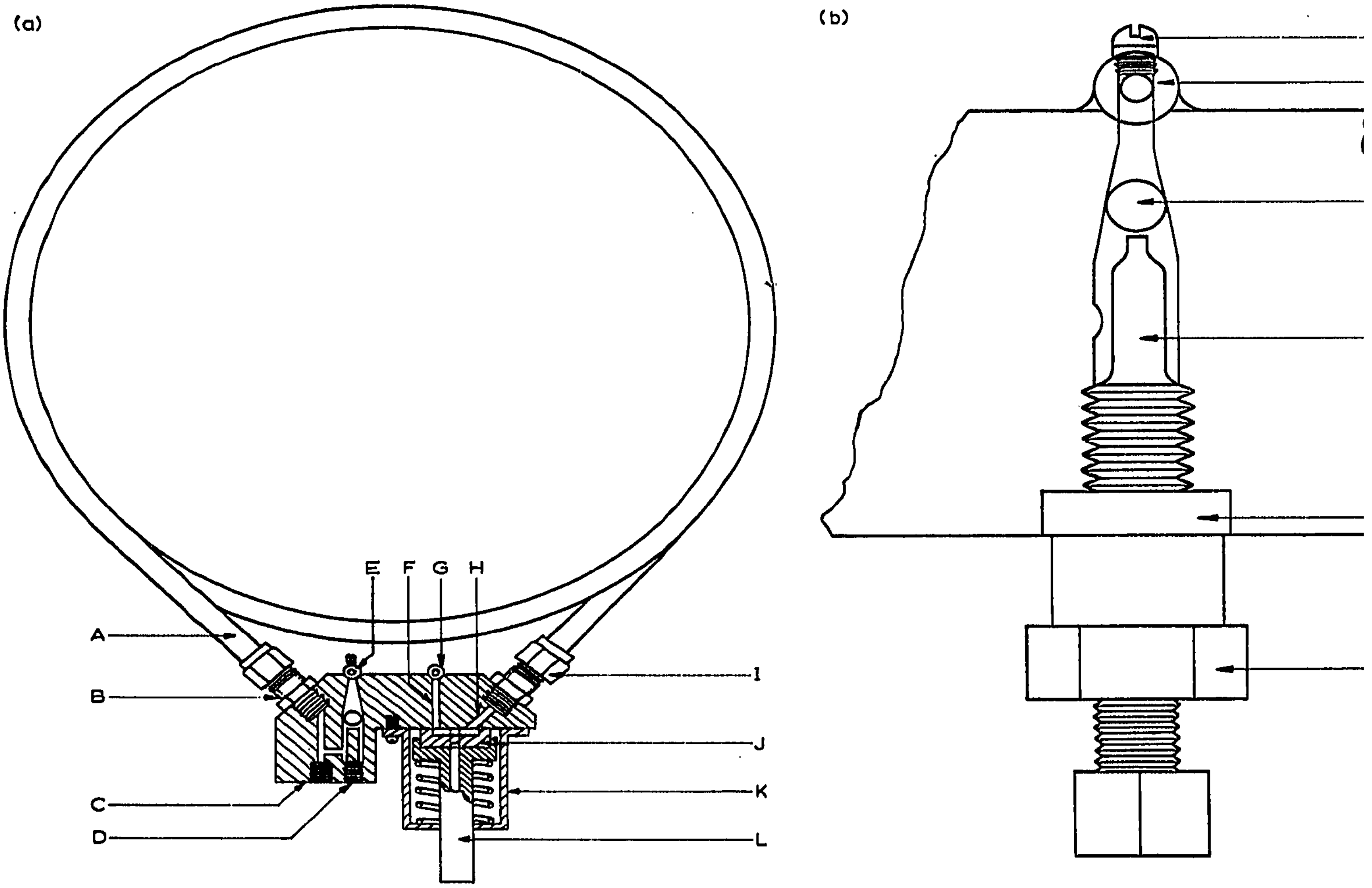

Fig. 3. (a) A valve for higher temperature application and the arrangement to the column. A = the circular column, B = column inlet, C = injection port, D = carrier gas flow control assembly, E = carrier gas supply tube, F = connecting passage, G = hydrogen supply tube (to detector), H = connecting passage, I = column outlet, J = carbon valve disc (showing valve in a position to connect column to detector), K = valve guide, L = valve stem. (b) Enlarged view of carrier gas flow regulator assembly. M = plug, E = carrier gas supply tube, N = ball, P = adjusting screw, Q = packing, R = gland nut.

columns. The valve for column 4 is in position to direct the column effluent to the detector. Fig. 5 is a corresponding view of a high temperature (150–300°) pillar utilizing an earlier version of the graphite valve shown in Fig. 3. In this type, the valve is essentially the same as the later version except that it is encased within the pillar rather than being on surface with the moving parts exposed. While this construction is quite satisfactory, it is very difficult to get a good finish on the bottom of the hole which forms the valve face, and the valve spring tends to lose its temper because of the high ambient temperature. The version shown in Fig. 3 represents a considerable simplification in construction and improvement in performance. Fig. 6 is a photograph of the component parts of this valve. Note the stainless steel stand-offs which insulate the valve guide from the pillar and help to minimize heat loss from the pillar. The valve stem is made of stainless steel for the same reason.

Inasmuch as the pillar contains the inlet and exhaust ports for each column,

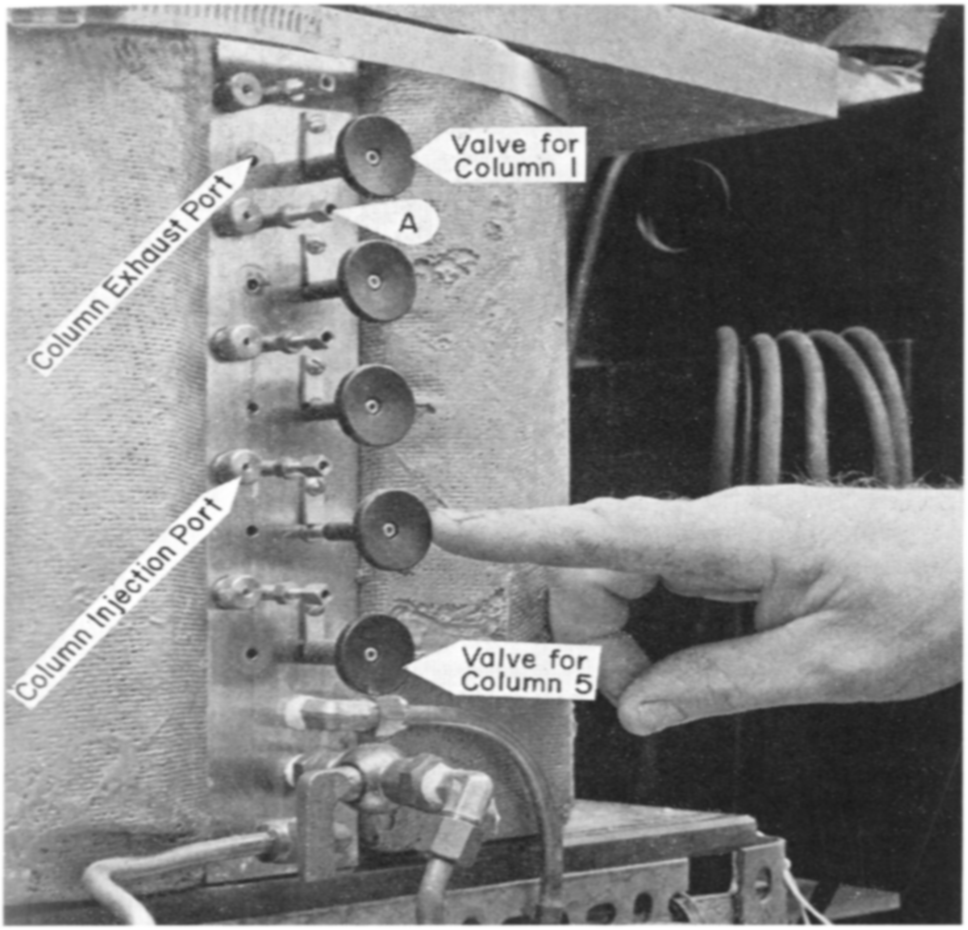

Fig. 4. Pillar for O-ring type valves for use at temperatures not exceeding 150°.

it needs to be heated somewhat above the ambient temperature for the columns. This is accomplished by means of small cartridge heaters placed immediately adjacent to each injection port. The top four ports use 65 W heaters, while a 130 W heater is used for the bottom port. These heaters are connected in parallel, and controlled by a single variable transformer. Since stainless steel is a relatively poor heat conductor, the heat loss from the pillar is not prohibitively great, and we have not felt that it is necessary to insulate its exposed face. However, in the external valve model, with more exposed components shown in Fig. 3, we have taken precautions to minimize the heat loss from this source.

In operations at 250 to 300°, septum life is annoyingly short, and we have found it advantageous to use a device for insulating the septum from the heat of the injection port. This is shown in Fig. 7. The device is constructed from very thin stainless steel hypodermic tubing to minimize heat transfer to the septum. Air is drawn through the cooling jacket and chimney by thermal convection, and the septum life is greatly prolonged. This device requires the use of a 3 in. injection needle. We have found Hamilton 2822-gage needles to be suitable for this purpose. Although this device may lead to the loss of a fraction of the material injected because of non-volatilization, in fact, we have not noticed that its use alters our results.

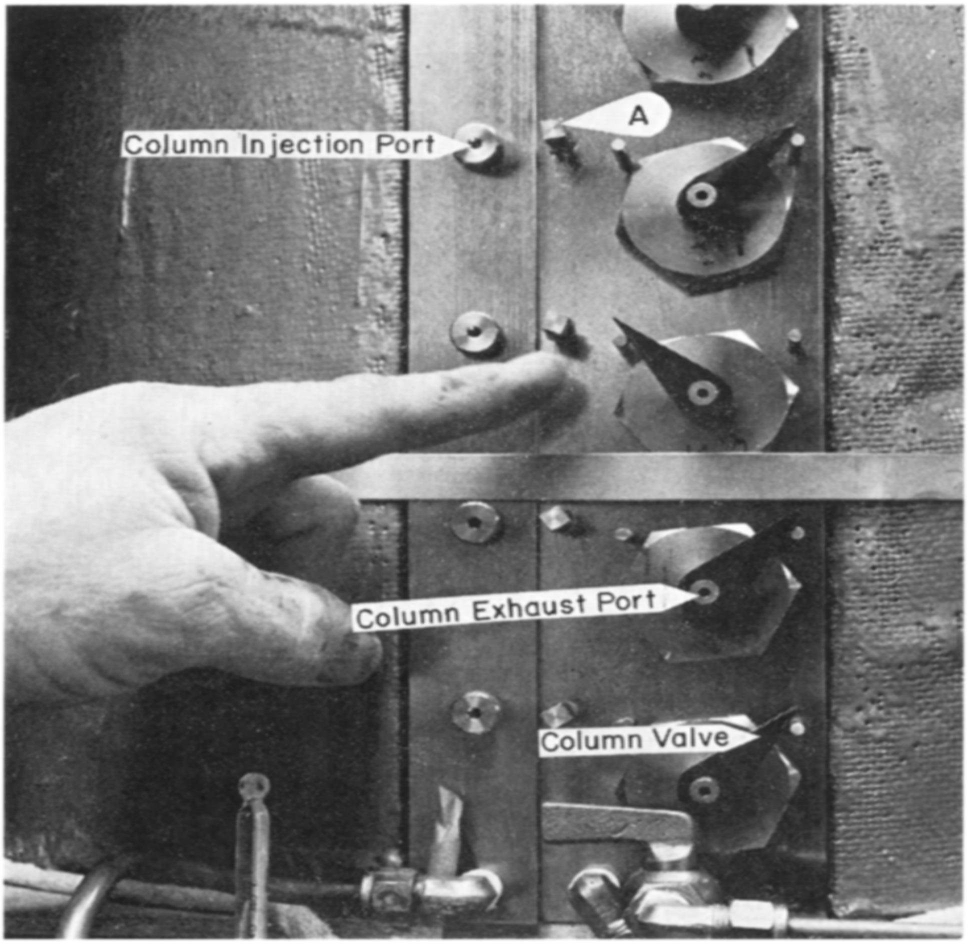

Fig. 5. Front view of a high temperature pillar. The third valve from the bottom is in open position. A is the needle valve for adjusting the carrier gas flow to that individual column. This pillar uses the earlier style internal graphite faced valve.

RESULTS

The aspects of this design which might be expected to affect the results and which require comment are (a) the valve and (b) the variable path length and nature of the passage through the effluent duct in the chromatograph pillar. With regard to the valve, we can see no effect. Retention times, peak shapes and peak yields are comparable to those obtained in a standard chromatograph. The variable gas passage does have a moderate effect on peak yield. Fig. 8 shows chromatograms run on the same column when the column was used at the top position (upper trace) and the bottom position (lower trace) of the chromatograph pillar. There is a moderate, reproducible decrease in peak yield in the bottom position, which varies slightly with the material which is being eluted. The average attenuations in peak (height, area) which we obtained were as follows: ethanol, (14%, 23%); benzene, (9%, 18%); ethyl acetate (14%, 18%); tetrahydrofuran (THF) (15%, 18%). (Since ethyl acetate and THF were not completely resolved, the combined peak area was used in each case.) While for precise quantitative analytical work these differences would be important, we do not regard them as significant in an instrument intended for ex-

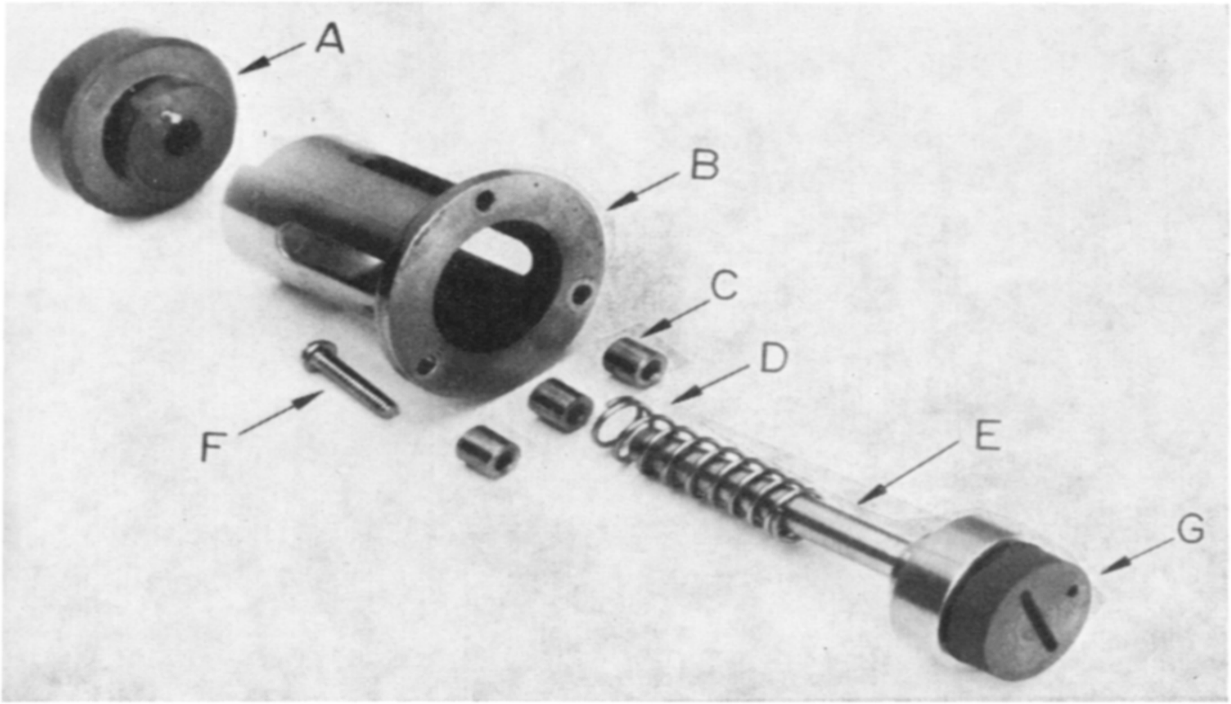

Fig. 6. Exploded view of high-temperature valve assembly. A = valve handle, B = valve guide, C = stand-offs for valve guide (not shown in Fig. 3), D = valve spring, E = valve stem, F = valve graphite disc. The slot in the disc carries gas from column to detector. The round hole near the periphery carries to the hollow stem of guide, E, whence it exhausts to the atmosphere (see exhaust port, Fig. 5).

ploratory work which is the primary objective of this design. Furthermore, these differences are constant and reproducible, so that any one column can be used in a quantitative way, as in the ordinary chromatograph.

At the time this test was made, the instrument had been in use for about two

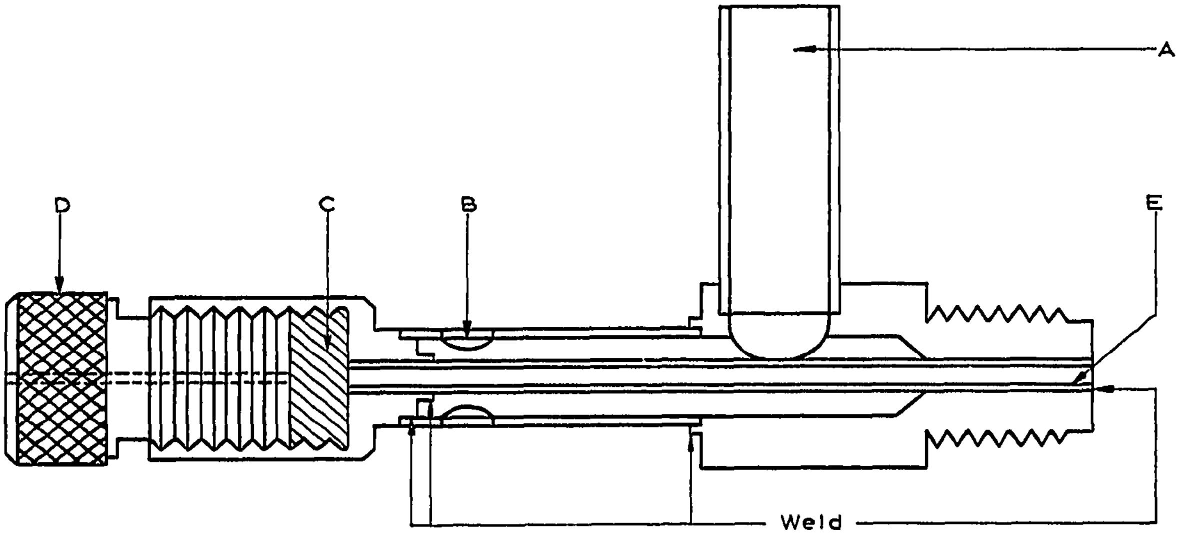

Fig. 7. Septum heat protector. A = chimney, B = air inlet holes, C = septum, D = septum retaining screw, E = injection passage.

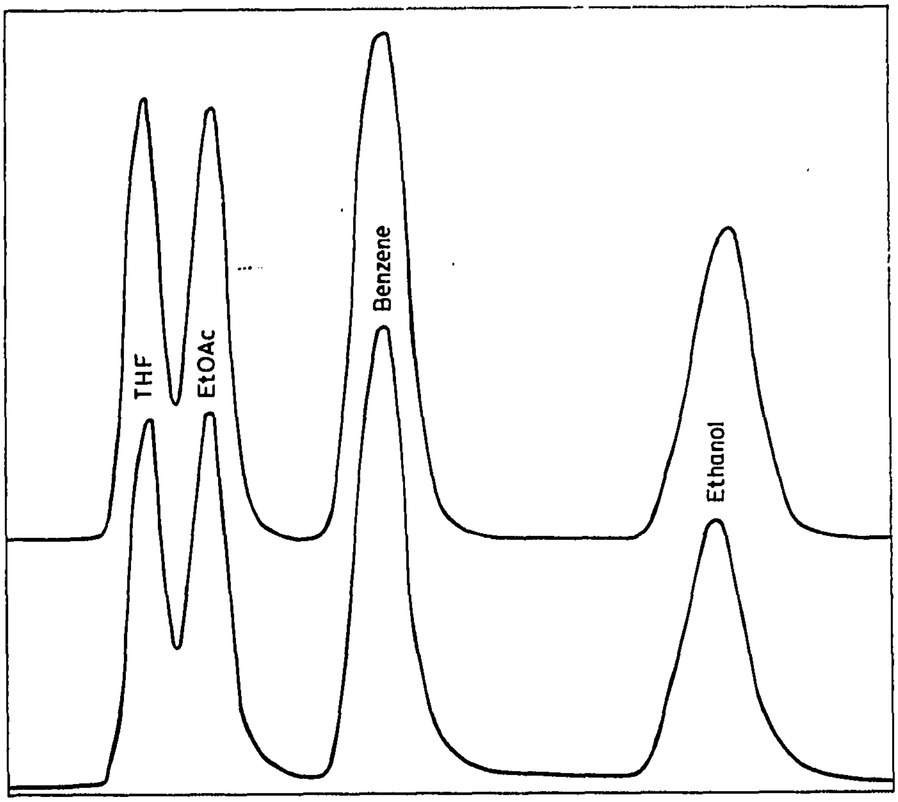

Fig. 8. Chromatogram run on the same column. Upper trace, column was used at the top position, lower trace, column was used at the bottom position.

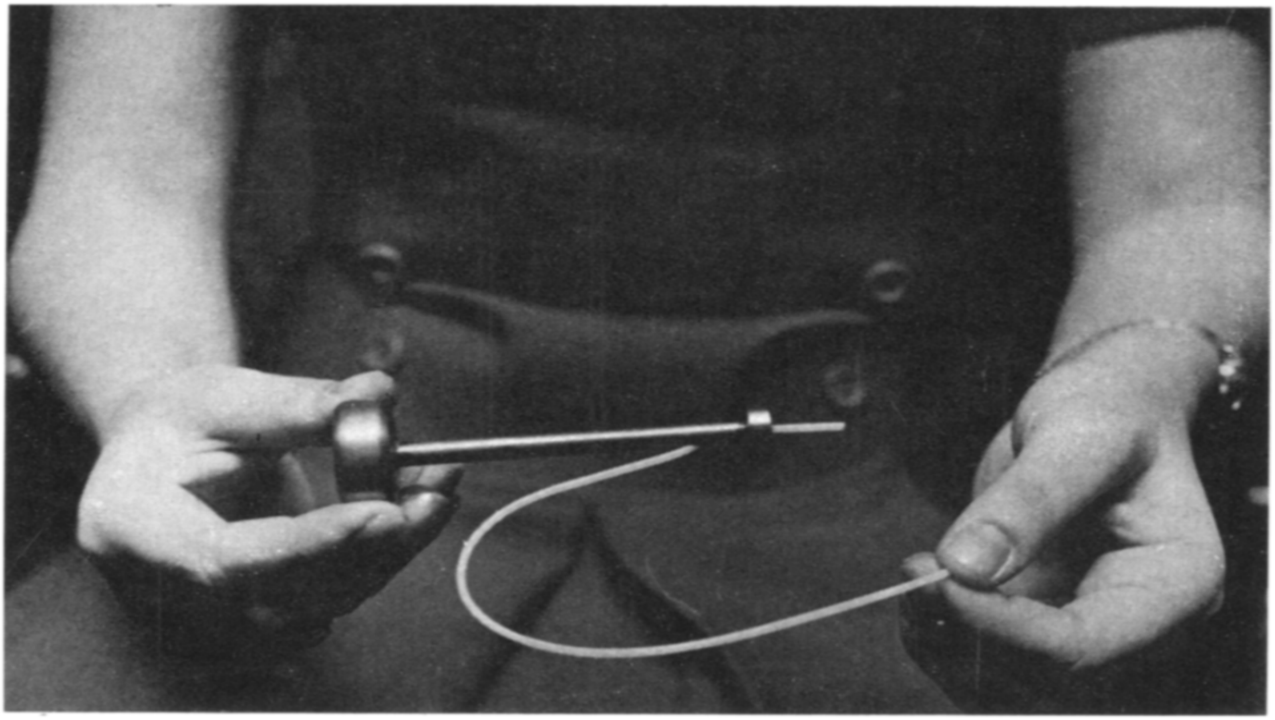

Fig. 9. Device for collecting chromatographed products.

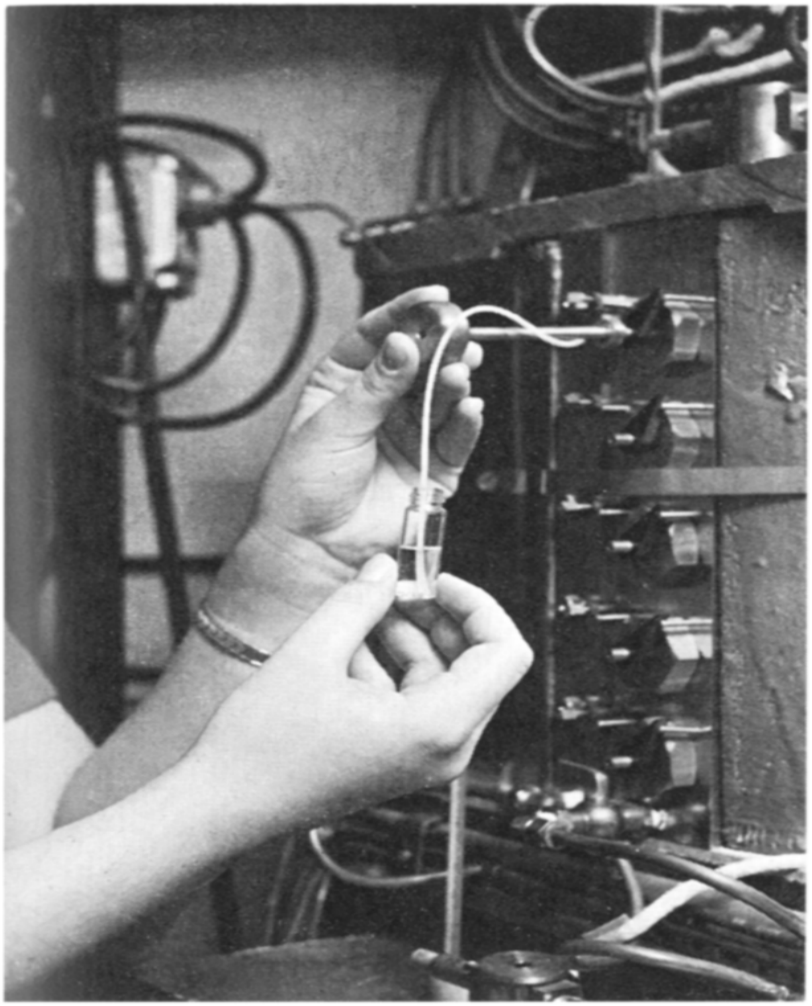

Fig. 10. Sample collection technique.

years, and we suspected that leakage at the valves might account for the attenuations seen. However, when we replaced the O-rings on all the valves in the pillar, the results were identical, indicating that valve leakage is not a significant factor in the operation of the instrument. Since the pillar used in this test was made by milling the gas passages in flat plates and subsequently bolting the plates together, the most likely place for leakage is at the seams between the plates. The brazed design discussed above obviates this source of leakage.

As with other chromatographs which have stainless steel injection ports, steroids occasionally give trouble, although at other times we obtain entirely satisfactory results. This effect, which has been noted by others[2] may be due to decomposition products in the injection ports left from previous injections, but as of now, we have no clear understanding of the phenomenon. At present, we are experimenting with the possibility of incorporating a glass vaporizing chamber within the pillar.

Use of the valve in preparative gas chromatography

The column effluent, when not directed to the detector, comes out of the front of the pillar, as illustrated in Figs. 4 and 5. It is a simple matter to collect manually condensable materials at this point using the device illustrated in Fig. 9. The small Teflon tube is inserted into the exhaust port of the column. The holder has a flat silicone-rubber gasket (not shown) made from a $\frac{3}{8}$ in. diameter flat septum, which tightly surrounds the teflon tube and permits a tight seal to the exhaust port.

A normal chromatogram is run and the width of the desired peak determined. The injection is then repeated, and when the desired peak begins to appear, the valve is turned to shift the column effluent to the exhaust port. The effluent is collected by bubbling the gas stream through solvent as illustrated in Fig. 10. We have also made use of a sintered glass bubbler to help break up the aerosol. At a time when the peak material would be expected to be 90% eluted, the valve can be returned to the detector position, so that the correctness of the peak collection can be affirmed. It is also possible to collect portions of peaks where the homogeneity of the effluent is in question. A single collection is usually ample for a mass spectrum determination, while for NMR determinations, twenty or more repetitive collections may be required.

REFERENCES

1 J. F. Arnold and H. M. Fales, *J. Gas Chromatog.*, 3 (1965) 131.
2 *Handbook of Silation*, Pierce Chemical Co., Rockford, Ill., 1970, p. 7.