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A CHROMATOGRAPH INJECTION VALVE - AN APPARATUS FOR RAPID INSERTION OF MINIATURE GLASS SAMPLERS INTO THE CARRIER GAS FLOW OF A GAS CHROMATOGRAPH (U)

by

W.J. Fenrick and W.C. Carpenter

Project No. 13E01

December 1979

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(10) W.J. Fenrick [redacted] W.C. Carpenter

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ABSTRACT

An injection valve for the rapid insertion of miniature glass samplers into the column of a gas chromatograph has been designed and tested. The valve is constructed so that the carrier gas can be allowed to bypass the injection system and flow directly into the column or it can be diverted through a glass sampler tube where it entrains desorbed vapours and carries them into the chromatograph column. Diversion of the carrier gas is so rapid that the operational stability of the gas chromatograph is not affected. A description and general assembly drawing of the unit, together with experimental evidence of its performance, are presented.

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INTRODUCTION

For many years samples of atmospheric contaminants have been obtained by drawing the air through a glass tube packed with an adsorbent solid such as silica gel. Until recently the amount of contaminant has been determined by color reactions taking place within the sampler. In some cases the color is developed as the contaminant reacts with a coating on the adsorbent, while in others reagents are added to induce the color formation. With the advent of extremely sensitive liquid and gas chromatographic analytical methods it has become feasible to extract the adsorbed contaminant by various means for chromatographic analysis. Commonly the extraction is carried out by the use of solvents or by heating the sample in a gas stream and collecting the vapours in bubblers or cold traps. These methods are time consuming and subject to many sources of error. Frequently the result is a solution of the vapours, which is then introduced into the chromatograph. In the case of gas chromatographs, particularly, only a small percentage of the total solution can be used in an analysis, resulting in a corresponding loss of sensitivity.

If the sample could be totally desorbed directly into the inlet of the chromatograph the weaknesses of current systems would be largely overcome.

One type of the solid phase sampler is a 4 mm OD glass tube 40 mm in length. The central 20 mm holds the adsorbent which is kept in place by a suitable retainer, commonly cloth. A version of this sampler using specially shaped 600 mesh stainless steel screen to retain the packing will withstand the strong heating required to rapidly desorb the vapour loading. This "mini-tube" may be inserted into the sample inlet port of some gas chromatographs, where the sample is heated, desorbed and the vapours swept onto the column for analysis. However, to insert the mini-tube into the sample input port the port must be opened, resulting in loss of column pressure and interruption of column gas flow. This configuration is illustrated in Figure 1, which also shows that carrier gas may bypass the sampler by flowing around the outside of the tube. Disruption of the carrier gas flow affects the chromatograph operation to such an extent that in some cases the sample is lost before the operational stability of the column can be regained.

The chromatograph injection valve was designed to permit diversion of the carrier gas flow so that the mini-cube could be inserted with a minimum of column flow disruption, and to force the entire flow of carrier gas through the sampler. When the valve is in the bypass position (broken lines, Fig. 2), the sample chamber is isolated from the chromatograph column so that the chamber can be opened and the sampler inserted. As soon as the sample chamber has been resealed the valve rotor is rotated to the sample injection position (solid lines,

Fig. 2) and the desorbed sample is swept into the chromatograph column.

DESCRIPTION

A general assembly of the chromatograph sample injection valve is shown in Figure 3.

The valve operates as follows: the assembly is attached and sealed to the chromatograph sample port, No.1, by the adapter nut, No 2, and the septum, No. 3. The carrier gas supply line is coupled to the right angled Swagelok®[1] fitting, No.4, which conducts the carrier gas to the inlet port of the valve body, No. 5. If the valve lever, No. 6, is pulled forward into the horizontal position, the passages in the valve rotor, No. 7, will assume the position designated by the broken lines. With the valve rotor in this position, carrier gas entering the valve flows directly into the chromatograph input port, No. 1, while the desorption chamber is left sealed and isolated from the carrier gas flow. Alignment of the passages in the valve body, No. 5, and the valve rotor, No. 7, in either of its positions, is maintained by specially designed stops machined on the valve body working in conjunction with a specially designed washer, No. 26, which together control the angular travel of the rotor.

To insert the mini-tube, No. 8, into the injection valve, the rotor, No. 7, is placed in the bypass position and the desorption chamber is decoupled at the multiple thread, No. 9. The sub-assembly, consisting of parts 10 to 17,is then removed and the mini-tube, No. 8, placed over the stainless steel tube, No. 11, so that it comes to rest against the Teflon®[2] pad, No. 12. The sub-assembly is then quickly recoupled to the inner portion of the desorption chamber, No. 18, and securely tightened against the Teflon washer, No. 19. The mini-tube is

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[1] Registered Trade Mark of Crawford Fittings (Canada) Ltd.

[2] Registered Trade Mark of E.I. Dupont de Nemours & Co.

thus held between the Teflon pad, No. 12, and the septum, No. 23, by the compression spring, No. 15.

The desorption chamber is maintained at a suitable temperature by the heat sink assembly, Nos. 20, 20A and 20B, which is heated by the thermostatically controlled heater, No. 21. Because the desorption chamber is maintained at an elevated temperature, desorption of the sample begins immediately upon insertion of the sampler. This is the reason the coupling thread, No. 9, is specified to be a multiple thread so that the coupling can be sealed as quickly as possible.

As soon as the mini-tube is sealed into the desorption chamber the adsorbent is heated and the vapours desorbed. The valve lever, No. 6, is moved quickly from the horizontal to the vertical position. The passages in the valve rotor, No. 7, are then aligned as is designated in Figure 3 by the solid lines, diverting the carrier gas through the desorption chamber with little or no disruption in the operational stability of the chromatograph column. The carrier gas enters the desorption chamber through a small hole drilled in the wall of the inner portion, travelling through the annular space between the inner wall of the desorption chamber and the outer surface of the mini-tube until it reaches the area where the compression spring, No. 15, is located. All of the carrier gas must then pass through the centre of the sample holder, No. 13, and enter the mini-tube through the stainless steel tube, No. 11. Because the carrier gas is prevented from escaping from the mini-tube by the Teflon pad, No. 12, and the septum, No. 23, it passes through the adsorbent and sweeps the desorbed sample through the stainless steel tube, No. 37, onto the chromatograph column.

The sample injection valve assembly is attached to the chromatograph at three points, one being the sample port, No. 1, with the other two being standoffs between the chromatograph and the mounting plate, No. 24. A photograph of the assembly mounted on the front of a chromatograph is shown in Figure 4.

The rotary valve and desorption chamber sub-assemblies are fastened to the mounting plate, No. 24, by 4 binding head screws, No. 25, and are completely enclosed in the No. 20, 20A, 20B heat sink assembly, which it is necessary to produce in three pieces to permit complete enclosure over the valve rotor, No. 7, and the valve retaining components, Nos. 26 to 29. Two socket head cap screws, No. 30, are used to hold the two semicircular plates, Nos. 20A and 20B, in position while the main portion of the heat sink is held in place by a set screw, No. 31. The heat sink is covered with thermal insulation, No. 32, which is protected by the outer cover, No. 33.

The valve rotor, No. 7, is made of Vespel®[3], a polyimide resin developed by Dupont to operate without lubrication or appreciable out-gassing at elevated temperatures (260°C). In addition, Vespel is resistant to solvents and acids. All of these qualities contribute to the successful performance of the material for this particular application.

The design of the sample injection valve is such that "off-column" injections may be made without removing the valve from the chromatograph. The valve is assembled with a plain piece of glass tubing in the desorption chamber and the sample injected into the tubing, see Figure 4.

EXPERIMENTAL

The following experiment was conducted to evaluate the desorption and injection efficiency of the chromatograph sample injection valve.

Procedure

An adsorber of known and reliable characteristics (Tenax GC®[4]) was used to collect samples of triethyl phosphate (TEP) vapour,

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[3] Registered Trade Mark of E.I. Dupont de Nemours & Co.

[4] Registered Trade Mark of Enka N.V., The Netherlands.

which is also considered to be a material of known and reliable characteristics. The above combination of adsorber and adsorbate allows accurate prediction of the recovery data which should be indicated by the chromatograph and its associated data collection system.

Five injections each containing 10 nanograms of TEP in a suitable solvent were made through the valve and the areas under the resulting peaks determined.

After the standard injections were made the valve was set into the bypass position and the plain glass tube was removed.

Five mini-tube samplers, which have already been described, were used to collect TEP vapour samples from a controlled vapour source. Each mini-tube contained 10 nanograms of TEP.

In turn, each of the specially prepared mini-tubes was sealed into the desorption chamber, the valve switched to the sample injection position, the TEP vapours swept into the chromatograph and the areas under the resulting peaks determined.

Detector output was recorded on a strip chart recorder and also fed into a Peak-11 On-line Computer System. The peak area figures obtained from the computer as well as the GC parameters are shown in Table 1.

Conclusions

The data presented show that the injection valve system is capable of quantitatively transferring the contents of a sample contained in a mini-tube into a gas chromatograph for analysis, with a high degree of reproducibility.

APPLICATIONS

By making the appropriate changes in Parts Nos. 2 and 39 the valve may be adapted to fit a wide variety of instruments such as mass spectrometers and atomic absorption analyzers as well as most models of gas chromatographs.

To date, many applications have been found whereby samples of contaminated air can be taken in the field using the mini-tubes and the samples subsequently analyzed in the laboratory using this injection valve assembly. The system works extremely well for many vapours.

The valve and glass sampler combination is also useful as a pre-column to protect the chromatograph column when liquid samples are analysed. If the liquid samples are contaminated by non-volatile contaminants they will collect in the chromatograph column packing, to the point where the column must be repacked or replaced. If such samples are injected into the packing in a glass sample tube mounted in the desorption chamber of the valve assembly as is shown in Figure 3, the residue will collect in the packing material within the glass tube. After several samples have been injected into the packing material within the glass tube and the concentration of residue has reached a significant level the tube can be discarded and replaced with a clean one. Alternately, if the substance being sought is not exceptionally volatile, specific volumes of each liquid sample can be injected into the packing of separate sample tubes, analyzed individually and disposed of.

PATENTS

The chromatograph sample injection valve described in this note has been patented in both Canada and the United States. Entitled "Chromatograph Injection System" by Carpenter, Wilfred C., Schmitz, Gary N. and Fenrick, Walter J., all of Defence Research Establishment Suffield, Canadian Patent No. 1055723 was issued 5 June 1979, U.S. Patent No. 4,084,440 on 18 April 1978. Both patents are vested in Her Majesty in Right of Canada in accordance with the Public Servants Invention Act.

TABLE 1

EXPERIMENTAL DATA

Sample Number	Integrated Area Under Peak	
	Reference Samples	Mini-Tube Samples
1	790	820
2	830	840
3	820	860
4	840	860
5	890	860
Mean	834	848
S.D.	36	18

CHROMATOGRAPH PARAMETERS

Desorption Temperature -	210°C
Carrier - Nitrogen -	35 cc/min
Column -	1/8 in x 6 ft
Detector -	Flame Photometric

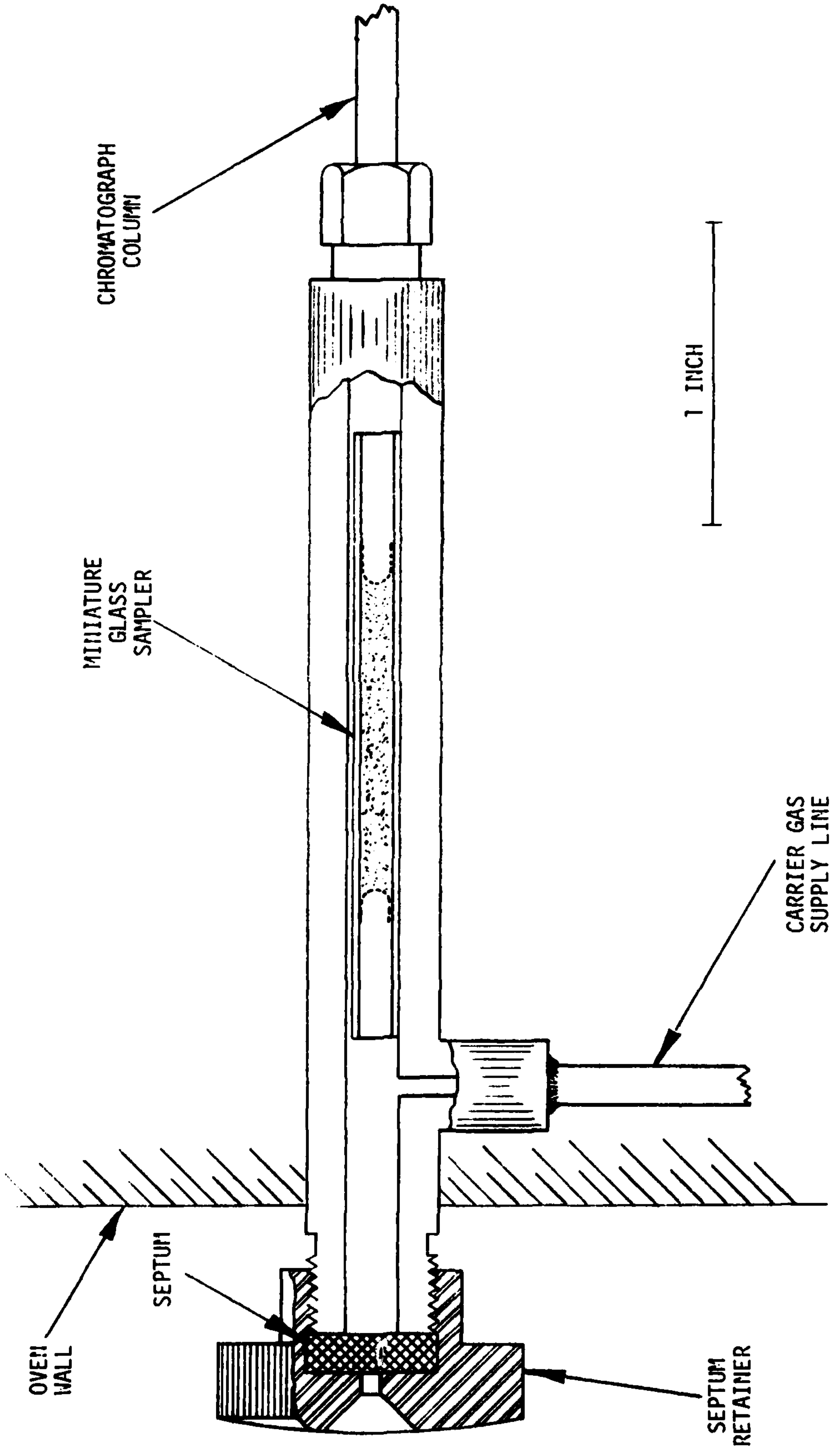

FIGURE 1 - MINIATURE GLASS SAMPLER AS INSERTED IN CHROMATOGRAPH SAMPLE PORT

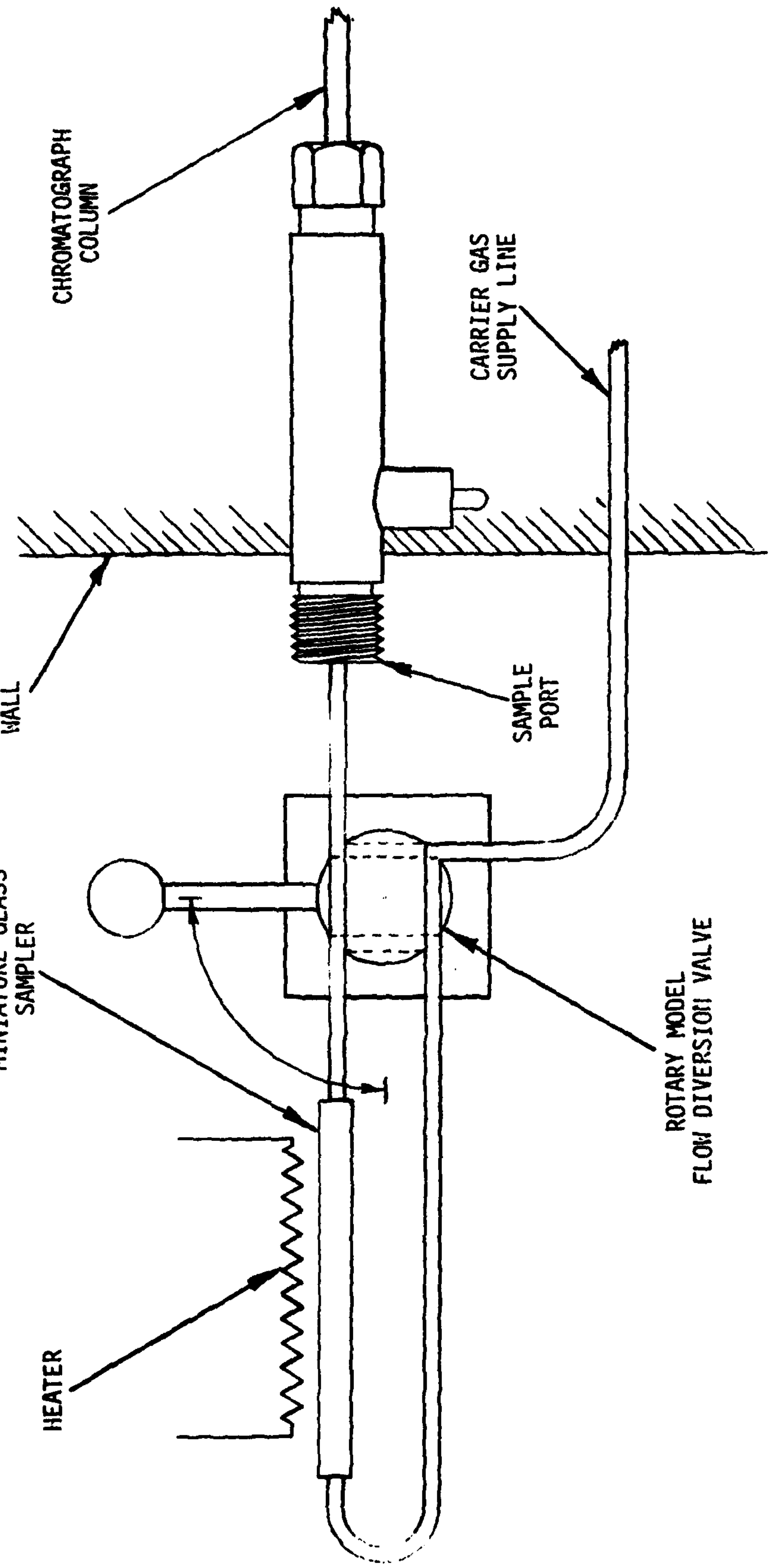

FIGURE 2 - SCHEMATIC DIAGRAM OF CHROMATOGRAPH SAMPLE INJECTION VALVE (ROTARY MODEL)

PARTS LIST FOR SAMPLE INJECTION VALVE

1. Chromatograph Input Port
2. Chromatograph Adaptor Nut
3. Septum
4. Elbow 1/16" N.P.T. to 1/16" Swagelok
5. Valve Body
6. Valve Lever
7. Valve Rotor
8. Miniature Glass Sampler
9. Multiple Thread
10. "C" Ring
11. Stainless Steel Tube
12. Teflon Pad
13. Sample Holder
14. Outer Portion of Desorption Chamber
15. Compression Spring
16. Septum
17. Septum Retaining Cap
18. Inner Portion of Desorption Chamber
19. Teflon Washer
20. 20A and 20B Heat Sink Assembly
21. Cartridge Heater
22. Thermocouple
23. Septum

PARTS LIST FOR SAMPLE INJECTION VALVE (Cont'd)

24. Mounting Plate
25. Binding Head Machine Screws (4 x 40)
26. Angular Travel Limiting Washer
27. Compression Spring
28. Washer
29. Roll Pin
30. Socket Head Cap Screw
31. Allen Screw
32. Thermal Insulation
33. Outer Cover
34. Binding Head Machine Screw (4 x 40)
35. Threaded Insert
36. Stainless Steel Tube
37. Stainless Steel Tube
38. Teflon Ring 0.625" OD x 0.569" ID x 0.065 Thick
39. Chromatograph Inlet Adaptor

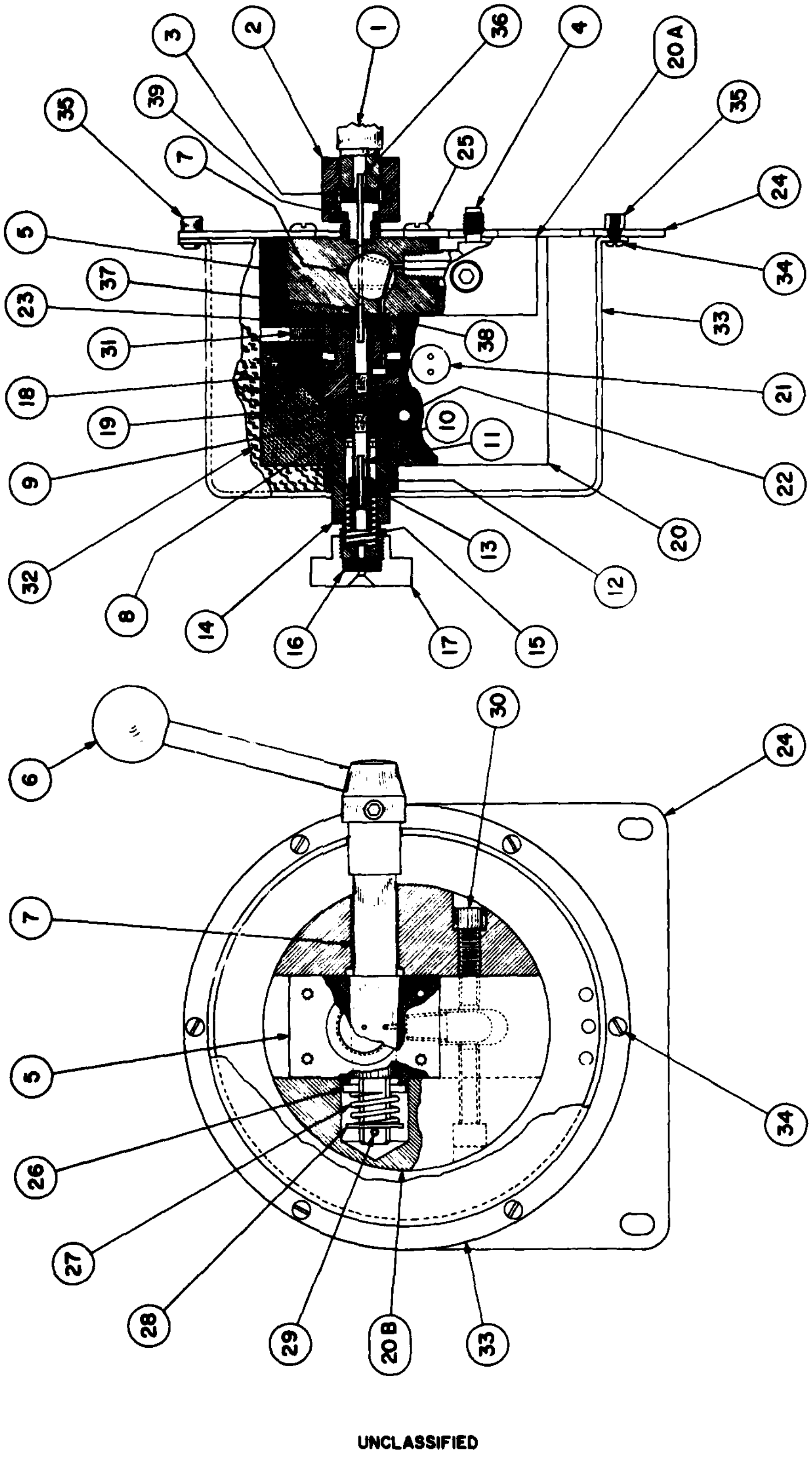

FIG. NO. 3 CHROMATOGRAPH SAMPLE INJECTION VALVE (ASSEMBLY)

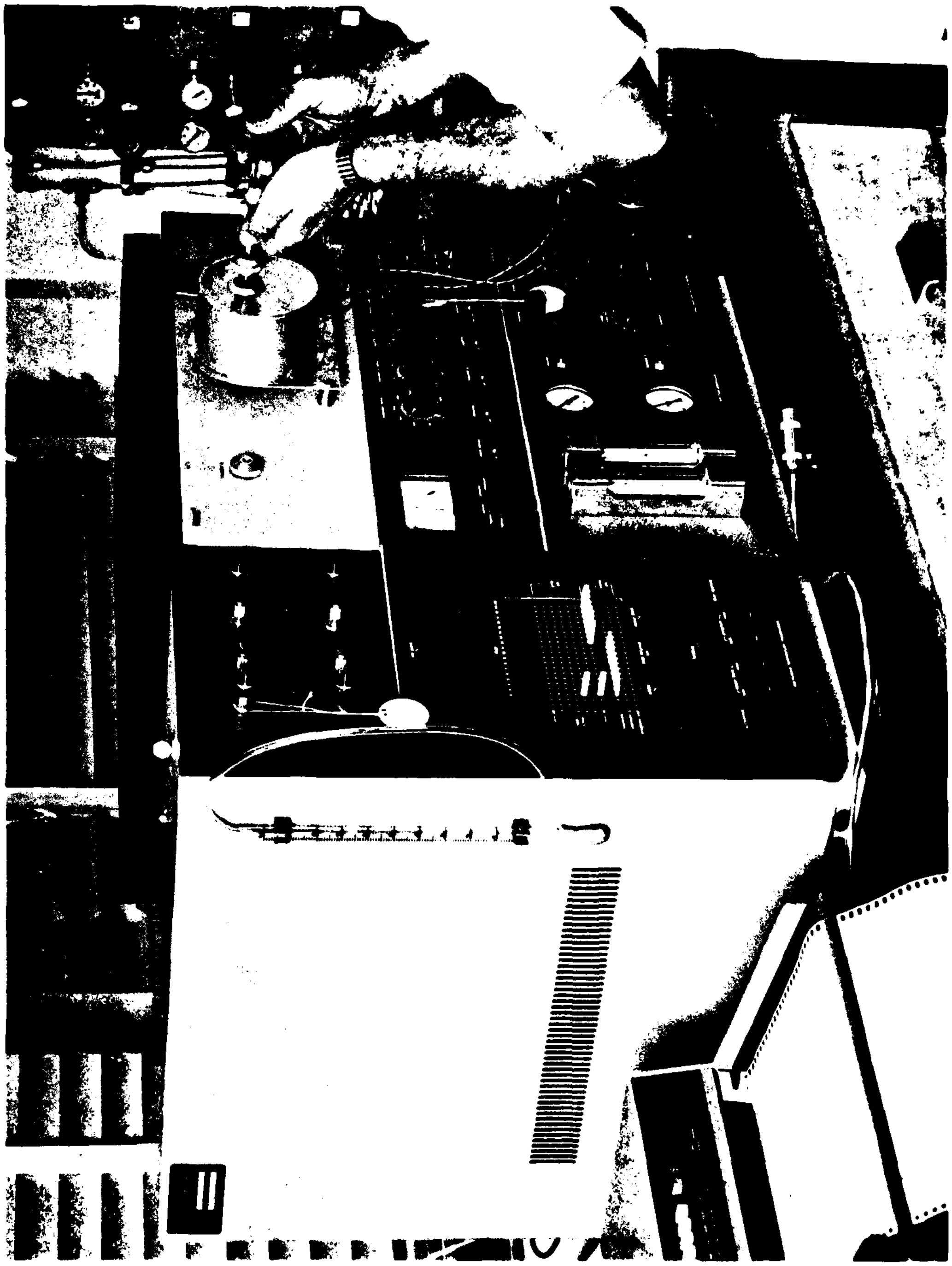

FIGURE 4 - INJECTION OF SAMPLE ONTO COLUMN THROUGH INJECTION VALVE

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