*Journal of Chromatography*, 249 (1982) 167–173
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM 15,227

## Note

# New injector design for splitless capillary column gas chromatography

CARL-GUSTAF V HAMMAR
*The Ohio State University Department of Anesthesiology, 410 West 10th Avenue Columbus OH 43210 (U S A)*

(First received May 4th 1982, revised manuscript received July 21st, 1982)

Recent advances in capillary column technology has made capillary column gas chromatography more attractive than ever, although more or less serious imperfections of the sample introduction techniques may restrict its full utilization Various methods have been developed to circumvent inadequate injector designs Split injection[1,2], pre-column sampling[3] and the so-called falling-needle technique[4] are examples of methods that are designed to reduce or eliminate the problem with the solvent The so-called solvent front effect technique[5–8] takes advantage of the presence of the solvent, which in fact aids in utilizing the high resolution of the capillary column This latter technique is employed mainly in connection with splitless injection and enables injection of microliters of sample The relationship between the boiling point of the solvent and the initial column temperature is essential in this technique A quite thorough evaluation of various parameters of the technique has been performed by Yang *et al.*[9] using a Varian splitless injector with septum and injector purge They conclude, for example, that the initial column temperature should be 15–30°C below the boiling point of the solvent; that sample sizes between 0 1 and 10 μl can be injected; that the rate of sample injection should be about 1 μl/sec, that the period of time in which the syringe needle is resident in the injector should not be less that 20 sec and that the injector purge delay time should not be less than 40 sec

This paper presents an injector design that eliminates most of the drawbacks of the conventional sample introduction systems with their rudiments from the era of packed column gas chromatography and allows an uncomplicated introduction of a sample.

## EXPERIMENTAL

### *Instrumentation*

In a Varian 3700 gas chromatograph, equipped with flame ionization detectors and a make-up gas device, was a Varian splitless injector (with septum purge but no injector purge) installed. The dual-pen recorder was a Varian 9176 with one channel adjustable span.

0021-9673/82/0000–0000/$02 75 

## RESULTS AND DISCUSSION

*The Varian splitless injector*

This commercially available injector consists of a metal body in which a glass-lined stainless-steel tubing is inserted. The carrier gas enters through the intermediate space, which is enclosed by metal surfaces (Fig. 1). The capillary column is connected to the glass-lined insert. A part of the carrier gas flow is purging the septum to prohibit the septum bleed to enter the column and to avoid memory effects. The purge flow is controlled by a fix restriction.

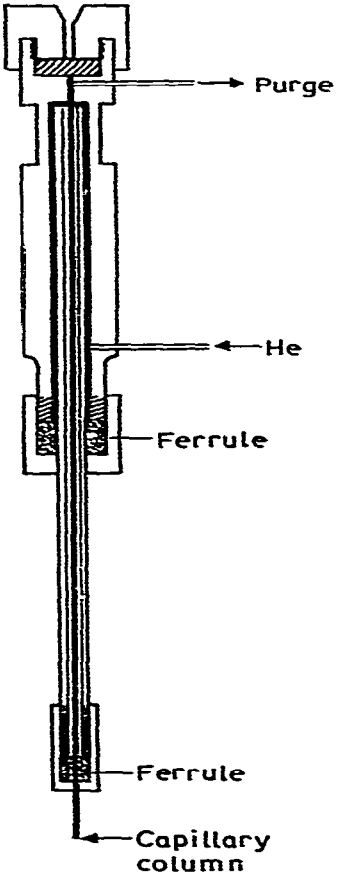


Fig. 1. The Varian splitless injector for capillary column gas chromatography Shaded areas indicate the volumes that are accessable to the carrier gas and vaporized sample

Extracellular fluids (from biopsies and cell cultures), which had been electrophoretically extracted and fractionated[10,11], were analyzed regarding their contents of low-molecular-weight organic compounds. A very limited fraction of acidic metabolites, derivatized in N,N-dimethylformamide with N-methyl-N-(*tert.*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA, Regis), was analyzed by capillary column gas chromatography employing the Varian splitless injector. Unacceptable chromatograms, similar to that in Fig. 2 (upper panel), were obtained.

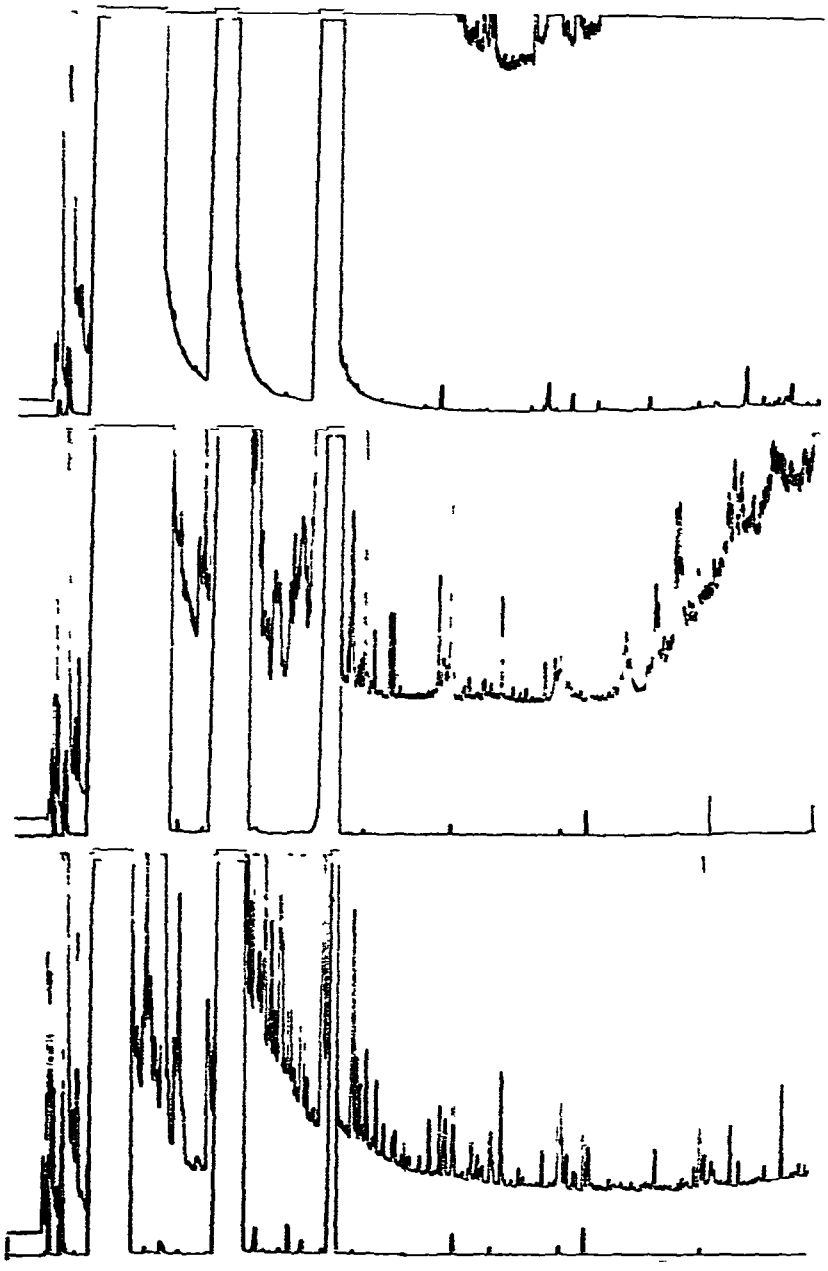

Fig. 2. Splitless injections (2 μl) of the same MTBSTFA-derivatized sample dissolved in dimethylformamide and chromatographed on a 30 m × 0.25 mm Durabond DB-5 column (J & W Scientific), but with different injectors. The oven temperature was 100°C during the initial 8 min and then increased at 4°/min to 300°C. The injector temperature was 220°C and the detector temperature was 310°C. The velocity of the helium carrier gas was about 20 cm/sec. The chromatograms were recorded at a span ratio of 1:50. Upper panel: injection with the Varian splitless injector, middle panel: injection with the modified Varian injector; lower panel: injection with the novel, pre-evacuated injector.

Tests with pure and non-polar solvents, such as isooctane, showed that a decent solvent front could not be obtained at high attenuation (*e g*, $2 \cdot 10^{-11}$ A). The insert was replaced twice with new, cleaned and silanized ones and various column temperatures, sample volumes, rates of injection and periods of time in which the syringe needle resided in the injector were tested without any acceptable result. In most cases a second and even a third small shoulder appeared, which together with the wide and tailing main solvent front strongly indicated problems with dead volumes and back flush.

The shaded areas in Fig 1 show the volumes, which are filled with carrier gas and during an injection will contain the vaporized sample. From the viewpoint of dead volumes the space between the insert and the injector body is excessive and in particular the volume between the gas inlet and the ferrule. During the vaporization process part of the sample will expand into this space and be exposed to a large, hot metal surface and with the well known risk of decomposition of sensitive organic compounds. Another remarkable dead volume is between the extended inner tubing of the insert, the nut and the ferrule for the connection of the capillary column.

*The modified Varian splitless injector*

The following modifications were made to reduce the dead volumes to improve the performance of the injector. The purge outlet was replaced by the carrier gas inlet and the original inlet was plugged. The inner diameter of the inlet tubing was reduced to diminish the risk of back flush. The space between the insert and the injector body was eliminated by sealing the top of the insert to the inner top of the injector body with a graphite disc. A hole was made in the center of the disc for the passage of the syringe needle. The dead space in the nut for the column attachment was filled with graphite by wrapping a small piece of graphite band around the protruding part of the insert. The dead volume was now reduced to the volume between the septum and the entrance of the column and which is enclosed by glass walls except for a short distance in the injector body between the septum and the insert.

The result of this modification is shown in Fig. 2, middle panel. Tests with non-polar solvents showed a greatly improved shape of the solvent front; total elimination of the third shoulder and an almost eliminated second one. The wide shape of these latter shoulders indicated bleeding from volumes not flushed by the carrier gas. This was substantiated by removing the graphite filling in the lower nut which caused the last eluted shoulder to reappear.

The rate of injection and the time the syringe needle was kept in the injector had no longer any influence upon the appearance of the chromatogram. Thus, it is most likely that the syringe needle has to be kept in the injector for a period of time to reduce the tendency of back flush into both the dead volume between the insert and the injector body and the inlet tubing. The slow rate of injection avoids a fast buildup of pressure, which increases the back flush. Even though the performance of this modified version of the Varian injector could be regarded as substantially improved, it was still unsatisfactory.

*The pre-evacuated injector*

The new design of an injector for splitless injection, as shown in Fig. 3, allows the introduction of a sample into a closed and evacuated volume. The vaporization

process is not hampered by an initial pressure; the sample is not diluted and spread out in volume and time by the carrier gas flow during the vaporization and the risk of back flush is reduced.

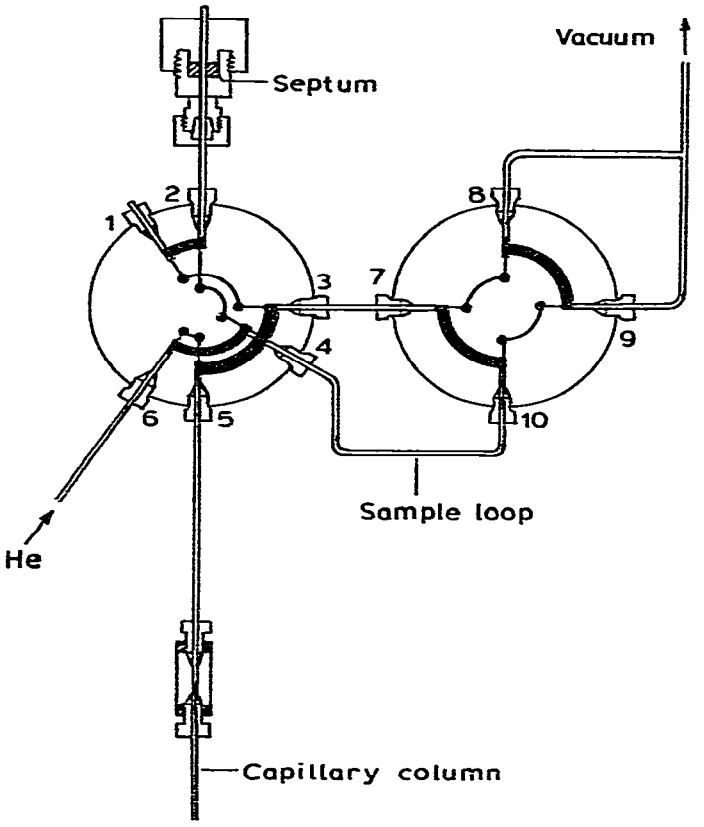


Fig. 3 The design of the novel pre-evacuated injector (For details, see text)

The injector was constructed by means of two zero-dead-volume, high-temperature valves (Valco Instruments Co.) and glass-lined stainless-steel tubing (Scientific Glass Eng ). The valves were mounted on an L-shaped bar as close to each other as the nuts at the ports 3 and 7 (Fig 3) allow Two holders (aluminum) for two Varian injector heaters (85 W each and coupled in parallel) and a temperature probe were mounted on the L-shaped bar, which was fastened to the frame of the gas chromatograph at the location of the original injector. The entire construction (valves, sample loop and heaters) was insulated with insulation material.

The length of the glass-lined tubing (0.4 mm I.D.), which serves as transfer line from the injector to the capillary column, was made as short as possible by mounting the zero-dead-volume connector (1/16 in.) close to the ceiling of the oven. The septum holder was made of a reducing union (1/4 to 1/16 in.) and the bottom of which had been flattened. In the center of the septum nut (made of aluminum) a glass-lined tubing (0 3 mm I D ) was soldered to guide the syringe needle through the septum and to hit the 0.3-mm hole of the glass-lined tubing, which is connected to port 2 of the

six-port valve. The length of this tubing was adapted to the length of the syringe needle so that, when fully inserted, the tip of the needle is 1–2 mm from the core of the valve rotor. Port 1 has a short and plugged glass-lined tubing (0.3 mm I.D.). The glass-lined tubing (0.7 mm I.D.) connecting port 4 with port 10, the sample loop, was arbitrarily cut to a length of 10 cm. Thus, the injector volume is about 40 μl. A single stage, oil vacuum pump (ultimate vacuum of 10 Torr) was used to evacuate the injector through ports 8 and 9.

The injector is operated in three sequential modes: evacuation, sample loading and injection. During the evacuation ports number 1 and 3; 2 and 4; 5 and 6; 7 and 8; 9 and 10 are connected (indicating by thin lines in Fig 3). The injector system is evacuated all the way from the septum while the column is supplied with carrier gas. The injector will be ready for the loading of the sample by switching the four-port valve to the position, which connects ports 7 with 10 and 8 with 9 (thick lines in Fig. 3). The vaporized sample is injected, without removing the syringe needle, by switching the six-port valve to the position where ports 1 and 2; 3 and 5; 4 and 6 are connected (thick lines in Fig. 3). The carrier gas is now diverted so it will push the volatilized sample out of the injector and onto the column. A negligible small fraction of the sample will be trapped and lost in the volumes at the ports 1 and 2 as can be seen in Fig. 3. The syringe needle is left inserted during the sample loading and injection to diminish the dead volume and reduce the sample loss. Depending upon the velocity of the carrier gas the sample is transferred to the column in 10–20 sec. Usually after 30–60 sec, the six-port valve is reversed first followed by the four-port valve. The injector will then be evacuated, while the chromatographic process continues uninterrupted.

The performance of this injector is exemplified in Fig. 2, lower panel. Besides the noticeable differences in sharpness of the solvent and the two reagent peaks, a steady baseline is achieved. The peaks with longer retention times, particularly in the upper panel, are mainly ghost peaks with a characteristic non-reproducibility. There are fewer of those in the middle panel, and none in the lower panel.

The internal volume of the injector was arbitrarily chosen (see above) and has not been evaluated regarding a likely optimal ratio between its volume and the injected sample volume, but has been found satisfactory for sample volumes up to 0.5 μl. Larger volumes (up to 2 μl) have been injected with good reproducibility but with loss of linearity. A wider range of linearity should be achievable by increasing the volume of the sample loop. The loss of linearity is most likely due to leakages developed at the high pressure created by the injection of too large a sample volume. Incomplete volatilization due to excessive pressure cannot explain non-linearity as the entire sample should be vaporized as soon as the pressure is released by opening the valve to the column.

Even though the two valves are quite costly as well as the pump, it falls short of the price tag of most commercially available injectors. The performance of this new injector surpasses at least the commercial one used in this laboratory. The pre-evacuated and closed sample loop ensures efficient volatilization of the appropriate sample volume at reasonable temperature without a dynamic dilution by the carrier gas. The excellent reproducibility may be attributed partly to a clean injector (exposure to continuous vacuum) with no hot metal surfaces. Additional factors such as hardly any exposure of the septum; no unnecessary and unflushed dead volumes and most likely very little back flush make this injector reliable and easy to operate.

## REFERENCES


1 I. Halasz and W. Schneider, *Anal. Chem.*, 33 (1961) 979
2 L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum, New York, 1965
3 L. German and E. C. Horning, *Anal. Lett.*, 5 (1972) 619
4 M. L. J. van der Berg and Th. Cox, *Chromatographia*, 5 (1972) 301
5 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 584
6 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 587
7 K. Grob and G. Grob, *Chromatographia*, 5 (1972) 3
8 K. Grob and K. Grob, Jr., *J. Chromatogr.*, 94 (1974) 53
9 F. J. Yang, A. C. Brown, III and S. P. Cram, *J. Chromatogr.*, 158 (1978) 91
10 C.-G. V. Hammar, presented at the Symposium *Drug Metabolism and Drug Design —Quo Vadis?* *Clin-Midy Research Center, Montpellier, France, November 26–27 1981*
11 C.-G. V. Hammar, *Anal. Biochem.*, in press