Journal of Chromatography, 208 (1981) 67–70
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,478

Note

Variable-volume sample valve for high-performance liquid chromatography*

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In general, there are two main ways of injecting samples into a column in liquid chromatography: by syringe and by sample valve. The advantage of a syringe is the variability of the sample volume, minimum consumption of the sample and the possibility of direct sample injection onto the column packing. The sample is injected onto the column either through an elastic perforable septum or via a separating valve. In the latter case, either during the mobile phase flow, the syringe needle being sealed in front of the valve, or at stopped flow.

Syringe injection using a septum is the most useful method because injection via a separating valve is rather complicated and stopping the mobile phase flow is not always convenient. Septum injectors are suitable for polar mobile phases (reversed-phase chromatography) which do not attack rubber septums and for pressures up to $\approx$10 MPa. For non-polar organic mobile phases (normal-phase chromatography) which attack rubber, Kalrez septums (DuPont) or a septumless syringe injector[1] can be employed. However, at higher pressures it is necessary to apply stop-flow techniques if syringe injection is used. Such injectors are used very rarely[2] by the chromatograph manufacturers, even if they are hard to fault from a theoretical point of view.

Sample valves are not subject to any of the above limitations. However, simple six- and four-way valves with outer and inner sample loops exhibit several practical disadvantages, *e.g.*, a greater consumption of sample for washing the loop, it is difficult to change the sample volume and higher cost. The first two disadvantages may be eliminated by use of syringe-loaded injectors[3–5] which in fact operate as separating chambers for sampling by syringe. Apart from their high cost and a small loss of sample during loading of the loop, these injectors show no disadvantages and at the present time represent the best type of universal injector for high-performance liquid chromatography (HPLC).

The ability to vary the injected volume without making use of a loaded syringe can be achieved by a slight modification of a simple valve. The principle of operation

* Presented at the *6th International Symposium "Advances and Application of Chromatography in Industry", Bratislava, September 16–19, 1980.*

0021-9673/81/0000–0000/$02.50

of such a valve[6] is illustrated in Fig. 1. A four-port valve is provided with a scale in μl indicating the rotor position. The valve rotor has two pairs of interconnected grooves (C, D) into which the inlets (E, F, G, H) in the valve body lead. One groove (C) serves as a sample loop and the second (D) for connecting the pump with the column. By turning the rotor (B) against the valve body (A) it is possible to vary the length of the part of groove (C) connecting the sample inlet (G) with its outlet (H), the column being connected throughout with the pump via the second connecting groove (D). The fixed stop limits the rotor movement between the position of maximum sample volume (a) and the injection position when the lines to the pump and the column (E, F) lead into the disconnected ends of sample loop (C) and the sample inlet and outlet lead outside both grooves (position b).

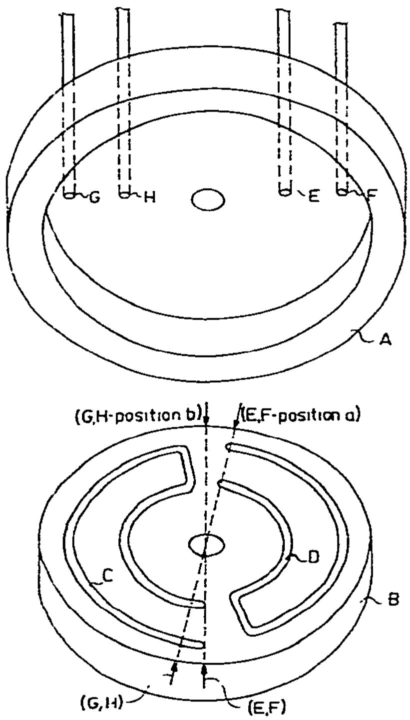

Fig. 1. Section through the variable-volume sample valve of the disk type: A = valve body; B = rotor; C = sample groove; D = connecting groove; E = mobile phase inlet; F = mobile phase outlet; G = sample inlet; H = sample outlet; a = position of loading of the sample loop with sample at maximum injection volume; b = position of injection of sample into the mobile phase.

The sampling is carried out in such a way that spreading of sample into the blind parts (closed arms) of the groove owing to air bubbles does not occur during loading. The loading position is therefore set in the direction from minimum sample volumes towards the value limited by the adjustable stop on the valve scale with simultaneous sample flow through the loading branch. By turning the rotor in reverse direction, the injection position can be set without interrupting the boundary between the sample and the mobile phase in the unloaded sample loop arms.

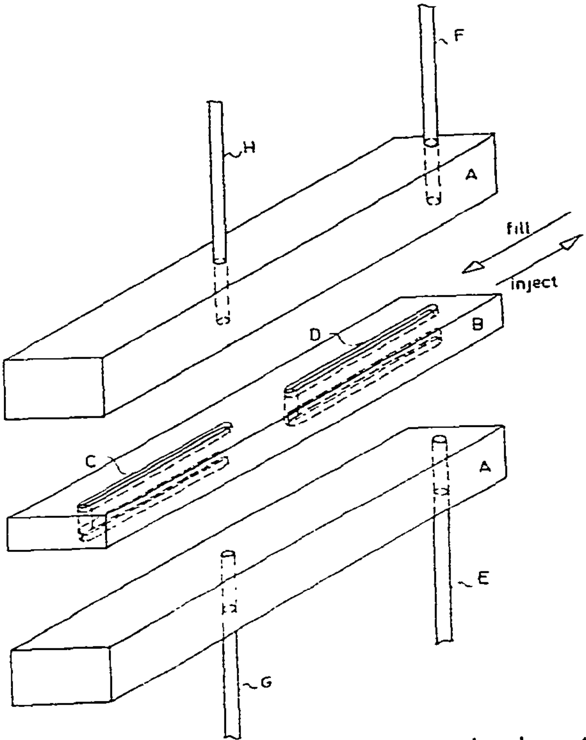

Fig. 2. Diagram of the variable-volume sample valve in the slide version; symbols as in Fig. 1.

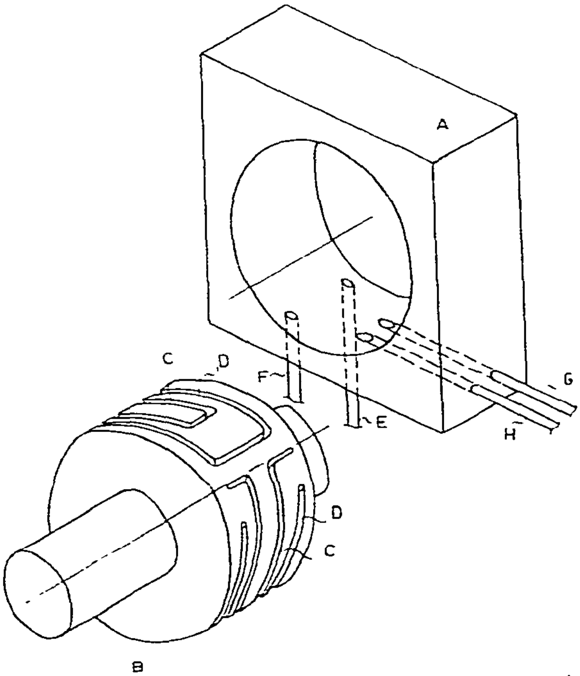

Fig. 3. Diagram of the variable-volume sample valve with radial sealing and decreased angle between the sample connections and the sample loop; symbols as in Fig. 1.

This principle can be applied, naturally, to any design and construction of valve (both axial and radial, rotary and slide) and the grooves which form the sample loop need not be on a common surface as is evident in Figs. 1–3.

The sampling precision is dependent on the length of the zone in which the sample is mixed with the stagnant liquid in the blind branches of the sample loop, and most importantly on the reproducibility of this mixing during repeated loading of the loop with the sample. The sampling precision can be improved by decreasing the angle between the input channels in the valve body and the groove forming the sample loop (Fig. 3) and by stabilizing the sample flow in loading by means of a restrictor inserted between the valve and the syringe exhausting the sample from the vessel through the loop.

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