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SEPTUMLESS DEVICE FOR INJECTING SAMPLES INTO A GAS CHROMATOGRAPH

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SUMMARY

A method and apparatus have been developed for injecting samples into the evaporator of a gas chromatograph. The evaporator is sealed only for the period of sample introduction subsequent to the physical communication of the evaporator with the sample carrier. Sample vapour is conveyed from the evaporator into the chromatographic column via a flow constrictor being communicated with the atmosphere subsequent to such a transfer, and the interior volume of the evaporator is back-flushed or blown off by a portion of the carrier gas flow entering the inlet port of the column.

INTRODUCTION

The most frequently used system for injecting liquid samples into a gas chromatograph consists of an evaporator with a septum made of a self-sealing material in conjunction with a microsyringe for sampling, dosing and injecting the sample through the septum. Practical experience with chromatographic measurements has shown that this system has some disadvantages that affect the accuracy, reproducibility and reliability of analysis. The septum is not infrequently responsible for the appearance of so-called "ghost peaks", which are pronounced during column temperature programming even when no sample is injected into the evaporator. There are at least four reasons for such contamination: release of gaseous substances by the septum under the action of the high temperatures developed in the evaporator; release of volatile components from pieces of the septum broken away therefrom, entrapped by the syringe needle and introduced into the evaporator together with the sample; residues of the previous sample absorbed by the septum due to contact with the sample vapour in the evaporator; and residues of previous samples accumulated when the septum material reacts with the sample in the syringe needle. Another important problem is the maintenance of the septum pressure-tightness after repeated piercing with a syringe needle.

In more recent years a method of introducing samples into a gas chromatograph has been developed in which a liquid sample is injected into the evaporator through the inlet port thereof provided with a sealed rotatable shut-off valve[1]. Prior to inserting the syringe needle into the evaporator, the latter is depressurized; after

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a sample has been injected and the needle removed from the evaporator, the inlet port is again sealed closed by means of the rotatable valve. this system suffers from the disadvantage that the rotatable valve is located in the immediate proximity of the heated area of the evaporator; the valve is intended to ensure a sealed closure of the inlet port of the evaporator without lubrication, by virtue of highly accurate mating of the polished surfaces thereof alone. Another disadvantage is in that only a syringe can be employed as the sample carrier, which limits the range of substances that can be subjected to analysis, as only liquid or gaseous substances can be introduced by means of a hypodermic syringe.

In this paper we describe an apparatus for introducing samples into a gas chromatograph of simple and reliable construction featuring no moveable elements and operable in the high-temperature zone of the evaporator.

EXPERIMENTAL

The septumless device for injecting samples into a gas chromatograph is shown in Fig. 1, in two operating positions: prior to injecting a sample (Fig. 1A) and during the injection (Fig. 1B). The septumless device consists of a conventional evaporator (1) with an added flow constrictor (2) of constant cross-section mounted at the inlet of chromatographic column (3). The conduit for feeding the carrier gas consists of a flow regulator and a flow divider (5). One outlet line of the flow divider communicates with the passage for evacuating from the evaporator the vapours through the flow constrictor into the chromatographic column and is provided with a shut-off valve (4), such as an electromagnetically controlled valve. Another outlet line of the flow divider communicates with the passageway for evacuating the vapours from the evaporator to the chromatographic column. It is arranged downstream of the flow constrictor and is provided with an adjustable flow constrictor (6). The sample carrier (7) is a syringe with a hollow needle (8) and a sealing element (9). Prior to the injection of a liquid sample (Fig. 1A), the flow of carrier gas follows a path from the flow regulator to exist the outlet line of the flow divider and is then conveyed continuously via the adjustable flow constrictor into the inlet port of the chromatographic column. Most of the flow enters (at a rate of 20–30 ml/min) the chromatographic column and then the detector. The remainder or smaller portion of the flow (1–5 ml/min) is conveyed via the flow constrictor to enter the evaporator. With this path of travel of the carrier gas the shut-off valve is closed, an optimal flow-rate is established in the chromatographic column, while a smaller portion of the carrier gas flow acts to back-flush or blow off the evaporator.

At the moment of sample injection (Fig. 1B), the evaporator is sealed with the sealing element fixed on the syringe, and the injection of liquid sample into the inner volume of the evaporator chamber is performed in the usual way. This is accompanied by switching over the shutt-off valve to the position illustrated. In this position valve 4 is opened for the flow of the carrier gas escaping from the flow divider to pass along the both outlets thereof, one path of the carrier gas flow being traceable via the adjustable flow constrictor to enter the chromatographic column, while the other carrier gas flow follows the path from the outlet of the flow divider to enter the evaporator. The vapours are entrained by the stream of carrier gas entering the evaporator and conveyed via the flow constrictor to the chromatographic column,

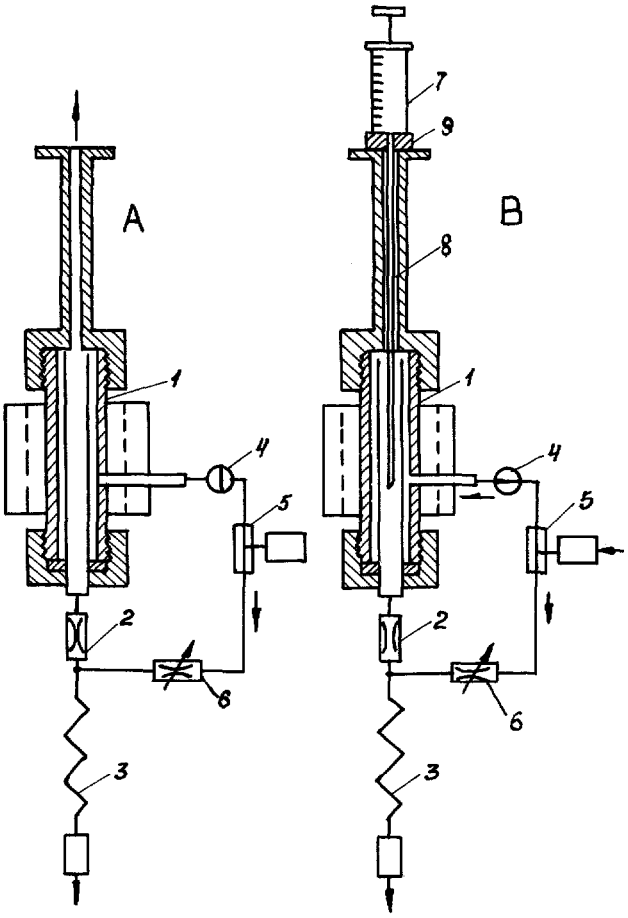

Fig. 1. Septumless devide for injecting samples into a gas chromatograph. (A) prior to injecting a sample, and (B) during the injection. 1 = Evaporator; 2 = flow constrictor of constant cross-section; 3 = chromatographic column; 4 = shut-off valve; 5 = flow divider; 6 = adjustable flow constrictor; 7 = microsyringe; 8 = hollow needle; 9 = sealing element.

wherein they are separated. After the sample has been injected, followed by separation of the sample mixture into constituents in the chromatographic column, valve 4 is closed and the needle of the syringe can be withdrawn from the evaporator. The sample injector is thus returned to the mode of operation shown in Fig. 1A, thereby back-flushing the passageways of the evaporator chamber to evacuate the sample residues therefrom.

The advantages of this device are illustrates by the chromatograms of the N-trifluoroacetylbutyl (N-TFAB) esters of amino acids, shown in Fig. 2. Chromatograms a–d were obtained while using conventional devices with a septum and e–h were obtained under the same conditions using the septumless device. The conditions of the analysis were as follows: Varian 3700 chromatograph with a flame ionization detector; gas flow-rates, nitrogen 30 ml/min, hydrogen 30 ml/min, air 300 ml/min; evaporator temperature, 300°C; column temperature, programmed from 100 to 200°C

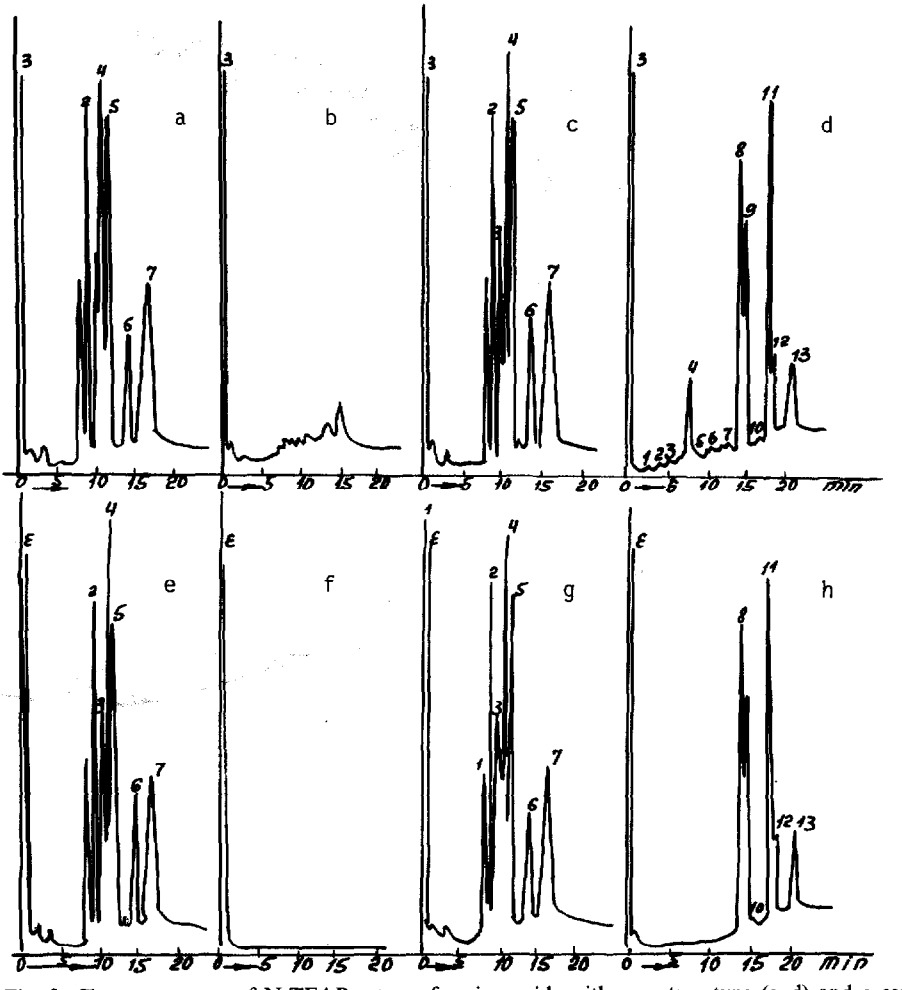

Fig. 2. Chromatograms of N-TFAB esters of amino acids with a septum-type (a–d) and a septumless (e–h) injection device. For an example, see text. Peaks: 1 = α-Alanine; 2 = valine; 3 = isoleucine; 4 = glycine; 5 = leucine; 6 = serine; 7 = proline; 8 = hydroxyproline; 9 = cysteine; 10 = asparaginic acid; 11 = methionine; 12 = phenylalanine; 13 = glutaminic acid.

at 4°C/min; column, 1 m × 2 mm I.D.; sorbent, 5% XE-60 on Chromton (0.16–0.20 mm).

Fig. 2b shows the chromatogram obtained on injecting pure solvent (ethanol) into the evaporator after analysing the mixture, the chromatogram of which is shown in Fig. 2a. The "ghost peaks" (1–7) due to residues of the previous sample can be clerarly seen. Fig. 2c shows the chromatogram of a mixture of compounds 1–7, obtained after repeated injection of the pure solvent into the evaporator many times. Fig. 2d shows the chromatogram obtained on injecting a mixture of six volatile N-TFAB esters of amino acids: hydroxyproline (8), cysteine (9), asparaginic acid (10), methionine (11), phenillanine (12) and glutaminic acid (13). This mixture was injected into the evaporator just after the injection of the mixture whose chromatogram is

shown in Fig. 2c. From the chromatogram it is clear that on injecting the new mixture "ghost peaks" (1–7) appear due to residues of the previous sample. Fig. 2e–h show the chromatograms of similar samples obtained when the septumless device was used. Fig. 2f and h show that the "ghost peaks" due to the residues of the previous sample are completely eliminated.

For the evaluation of the reproducibility of chromatographic analysis with the use of the septumless device for sample injection, series of analyses of a fatty acid mixture (acetic acid, propionic acid and butyric acid) were carried out under the following conditions: LKhM-80 chromatograph with a flame ionization detector; gas flow-rates, nitrogen 25 ml/min, hydrogen 30 ml/min, air 300 ml/min; evaporator temperature, 170°C; detector temperature, 210°C, column temperature, 160°C; column, 1 m × 3 mm I.D.; sorbent, Polysorb I; sample injection (1 μl volume), with Gasochrom-101 microsyringe.

Table I shows the reproducibility data (relative standard deviation, R.S.D.) for the analysis of the above mixture with reagard to peak height and peak area obtained with the use of a conventional sample injection system with a septum and with the septumless injection device. These data were obtained from ten analyses with each device. The results show that the septumless device gives much better reproducibility.

For the evaluation of the influence of sample size and pressure in the evaporator on reproducibility we carried out series of analyses of a model mixture of acetone in water. The conditions of analysis were as follows: LKhM-80 with a chromatograph flame ionization detector; gas flow-rates, nitrogen 25 ml/min, hydrogen 30 ml/min, air 300 ml/min; evaporator temperature, 90°C; detector temperature, 90°C; column temperature, 70°C; column, glass, 0.3 m × 3 mm I.D.; sorbent, 5% SE-30 on Inertone.

Table II shows the reproducibility data (R.S.D. with regard to peak height of acetone) for different conditions of sample injection. The results show that the reproducibility depends on the pressure in the evaporator and improves as the pressure increases.

As this device has no sealing septum which is constantly mounted on the injection port of the evaporator, samples can be injected using various known sample carriers. Fig. 3, shows another aspect of the arrangement for injecting liquid samples

TABLE I

REPRODUCIBILITY OF ANALYSIS OF ACIDS WITH DIFFERENT INJECTION SYSTEMS

Injection system	*Acetic acid*		*Propionic acid*		*Butyric acid*	
	R.S.D. (%)		*R.S.D. (%)*		*R.S.D. (%)*	
	Peak height	*Peak area*	*Peak height*	*Peak area*	*Peak height*	*Peak area*
Septum-type evaporator	2.49	6.05	2.95	5.2	4.46	4.81
Septumless device	1.04	3.23	0.75	2.06	0.62	0.67

TABLE II

REPRODUCIBILITY OF PEAK HEIGHT OF ACETONE UNDER DIFFERENT SAMPLE INJECTION CONDITIONS

Pressure in evaporator (atm)	*Sample size (μl)*	*R.S.D. of peak height of acetone (%)*
2.0	0.25	2.45
	0.5	2.28
	1.0	3.3
3.0	0.25	2.30
	0.5	2.16
	1.0	1.8
4.0	0.25	1.2
	0.5	0.93
	1.0	1.0

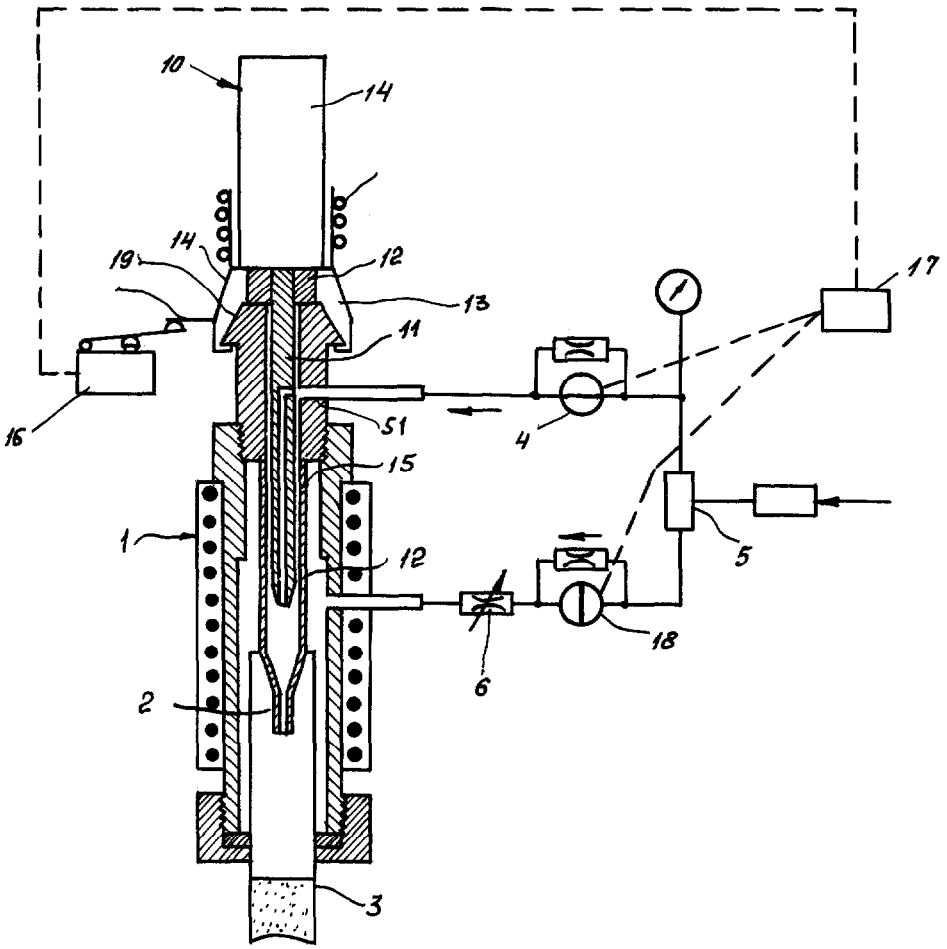

Fig. 3. Version of septumless device for injecting samples into a gas chromatograph. 1–9 = as in Fig. 1; 10 = micropipette; 11 = capillary tube; 12 = moveable sealing element; 13 = clamps; 14 = head; 15 = tubular element; 16 = microswitch; 17 = control unit; 18 = shut-off valve; 19 = rib.

into a gas chromatograph, in wich a micropipette (10) is used as sample carrier; components corresponding to those in Fig. 1 are indicated by the same numbers. The sample carrier in the arrangement in Fig. 3 is a capillary tube (11) fabricated from heat-resistant inert material, such as glass or stainless steel. This capillary is further provided with a sealing element (12) in the form of a sleeve of deformable inert material, such as rubber. The holder of the capillary is provided with clamps (13) in the form of plates of flexible material, such as steel. The evaporator has a head (14) extending away from the heated area thereof and rigidly connected with the tubular element (15), the passageway of the latter in combination with a passageway in the head serving for insertion of the capillary into the evaporator. Positioned in the immediate vicinity of the head of the evaporator is a microswitch (16), electrically connected to a control unit (17) for controlling the operation of shut-off valves 4 and 18, the control unit generally being a time relay. Extending from one of the plates of spring-biased clamps 13 is a rib (19) cooperating with the microswitch during pressurizing and depressurizing of the evaporator.

This arrangement operates as follows. Sample fluid is supplied into the calibrated passage of the capillary by virtue of capillary forces. The moveable sealing element blocks the lateral bore (20) of the capillary. Initially, or prior to the injection of a sample into the evaporator, valve 4 is closed, while valve 18 is open. The carrier gas travels along the outlet line of the flow divider to enter the interior volume of the evaporator, from which most of the gas flow (20–30 ml/min) is conveyed along the passageway into the chromatographic column, whereas a smaller portion (1–5 ml/min) passes through the flow constrictor and the passageway of the tube and head of the evaporator to be discharged into the atmosphere. At the moment of sample injection, the capillary is inserted into the passageway of the head of the evaporator and is moved as far as it can go. The moveable sealing element is thereby pressed against the head to provide a sealing engagement, thus blocking the entrance to the passageway of the head of the evaporator, while the hooked ends of the spring-biased clamps lock with the collar of the head of the evaporator. The rib is forced into enagement with the microswitch to close the contacts thereof and cause the control unit to issue a signal to the electrically controlled valves 4 and 18 for the valves to be switched into the position as seen in Fig. 3. In this position of the valves, a major portion of the carrier gas flow travelling along the outlet line of the flow divider enters the passageway of the evaporator head located opposite the lateral bore of the capillary to sweep a rationed amount of the liquid sample into the passageway of the tube, wherein it evaporates and the vapour thereof entrained by the stream of carrier gas is then carried via the flow constrictor and the passageway to the chromatographic column. On completing the injection the holder of the capillary tube is turned until the plates of the clamps are aligned with the grooves of the evaporator head. Then the rib of the clamps releases the contacts of the microswitch to switch valves 4 and 18 into the initial position preceding the sample injection (valve 4 closed; valve 18 open); the capillary tube is then withdrawn from the passageway of the evaporator head, thereby depressurizing the evaporator.

To compare the reproducibility of chromatographic analysis with the septumless device and known devices for sample introduction such as microsyringes and micropipettes, we carried out series of analyses of mixture of C_6–C_{10} normal hydrocarbons. The conditions of the analyses were as follows: LKhM-80 chromatograph

TABLE III

REPRODUCIBILITY OF ANALYSIS OF HYDROCARBONS WITH DIFFERENT SYSTEMS

Injection system	C_8		C_9	
	R.S.D.		*R.S.D.*	
	Peak height (%)	*Peak area (%)*	*Peak height (%)*	*Peak area (%)*
Septum-type evaporator	4.61	1.5	4.04	2.07
Evaporator with septumless device: syringe injection	2.7	1.03	2.1	1.4
Evaporator with septumless device: micropipette injection	2.07	0.6	1.96	0.56

with a flame ionization detector; gas flow-rates, carrier gas (nitrogen) 30 ml/min, hydrogen 30 ml/min, air 300 ml/min; temperatures, evaporator 150°C, column 65°C, detector 70°C; column, glass 1 m × 3 mm I.D.; sorbent, 5% SE-30 on silanized Chromaton.

Table III shows the reproducibility data (R.S.D.) for the analysis of the C_8–C_9 normal hydrocarbons mixture with regard to peak height and peak area with the use of a conventional system for sample injection with a septum and with the septumless injection device. In the latter instance the sample was injected with a Gasochrom-101 microsyringe and a micropipette. Series of ten analyses were carried out with each device. The results show that the use of micropipette (Fig. 3) in conjunction with the septumless device gave a much higher reproducibility.

CONCLUSIONS

The results obtained indicate that the septumless proposed device makes it possible to eliminate many of the difficulties associated with the use of septum in gas chromatographic evaporators. For injecting samples into the gas chromatograph with the use of proposed device one can apply sample carriers of various types such as microsyringes and micropipettes. The septumless device ensures a higher reproducibility, especially when a micropipette with a capillary volume is used as the sample carrier. The septumless device may be used for sample injection into capillary columns and is especially suitable for use in conjunction with autosamplers of various types.

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