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Oppegaard

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[54] **INJECTOR AND SEPTUM FOR GAS CHROMATOGRAPHIC APPARATUS. AND OTHER EQUIPMENT**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **55/197;** 55/386; 73/422 GC

[51] **Int. Cl.**[2] **B01D 15/08**

[58] **Field of Search** ..... 55/67, 197, 386; 23/232 C, 23/259, 292; 73/422 GC

[56] **References Cited**

UNITED STATES PATENTS

2,584,397	2/1952	Pitman	23/259 X
3,205,711	9/1965	Harris	23/259 X

OTHER PUBLICATIONS

Gas Phase Chromatography (Vol. I) by Kaiser, Butterworth Inc., 1963, pp. 83 and 84 relied on.

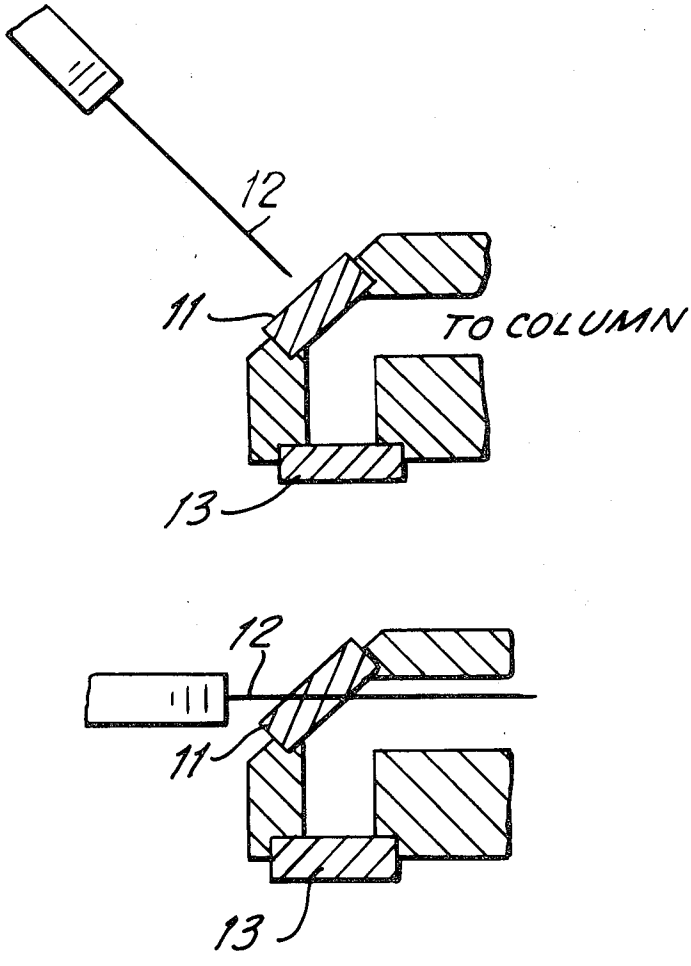
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[57] **ABSTRACT**

An injector arrangement in which an injector chamber is provided with at least two septa. The injector is for gas chromatographic apparatus and other equipment where a sample is to be introduced through a hollow needle which is pushed through a septum. The two or more septa are arranged in relative positions so that the hollow needle first penetrates one septum whereby the tip of the needle enters the interior of the injector chamber. Thereafter, the needle is forced through a second septum whereupon the tip of the needle appears on the outside of the chamber, where the needle can be cleaned. After the cleaning action, the needle is retracted so that the tip is returned to the interior of the injector chamber where the injection process can then proceed.

6 Claims, 2 Drawing Figures



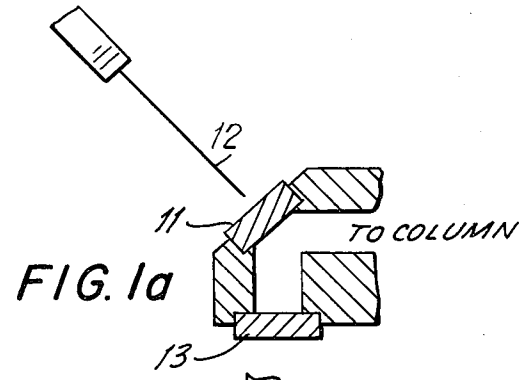


FIG. 1a

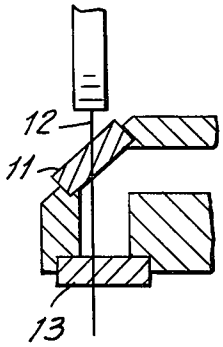


FIG. 1b

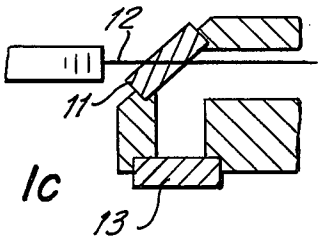


FIG. 1c

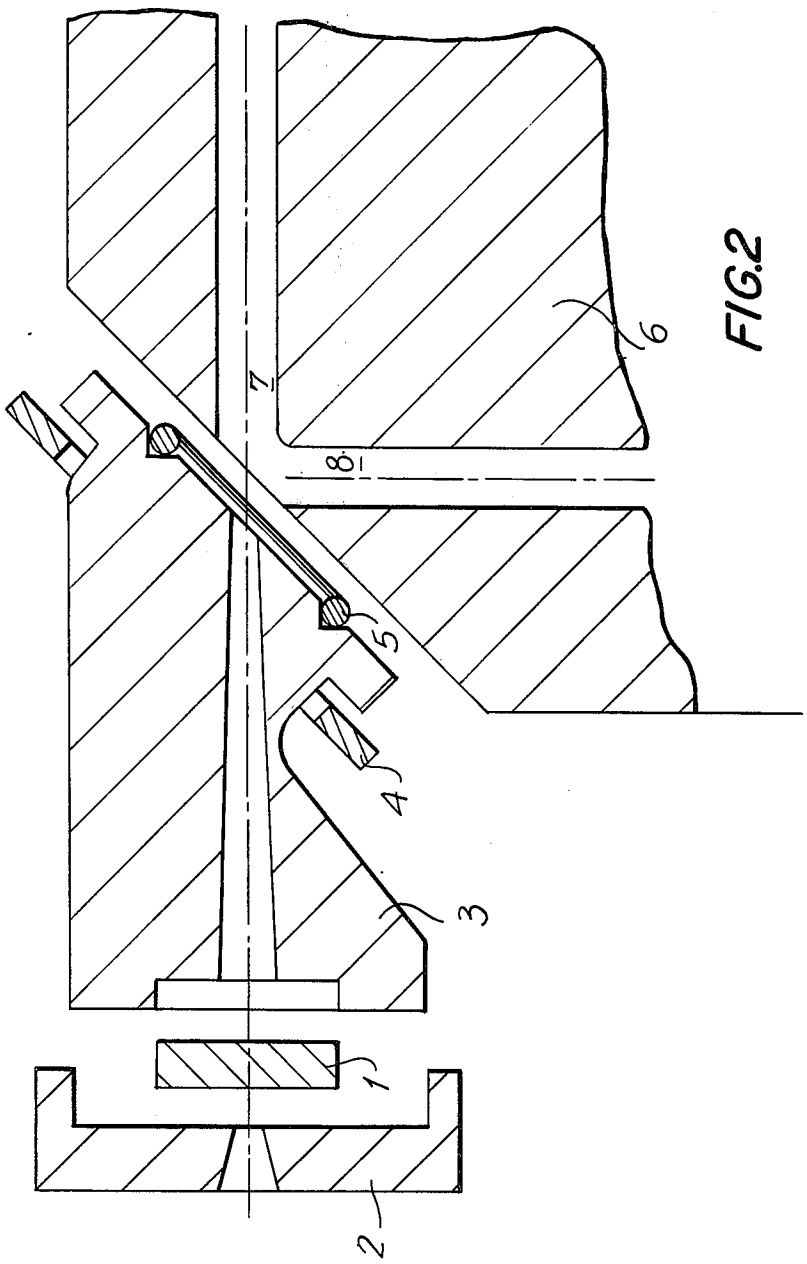


FIG.2

INJECTOR AND SEPTUM FOR GASCHROMATOGRAPHIC APPARATUS AND OTHER EQUIPMENT

In various types of apparatus a physical-chemical investigation of elements is performed after injection of a suitable amount of sample in some way. Many of these apparatus include closed systems, as in the application of pressure, vacuum or special gases within the detection system. Examples of such are chromatographs of gas or liquid type, elementary analysis instruments, instruments for determination of molecular mass, gas density, sorption conditions etc.

These instruments are often equipped with a septum through which the sample is introduced with a syringe. A septum is usually in the form of a disc of elastomer material installed in a suitable injector support. This septum separates the detection system from the environment, but the sample may be introduced by perforation by the needle of the syringe.

The combination septum/syringe is in use for injection of gases, liquids and solids into the above mentioned types of apparatus. It is especially popular for liquids because it has a range of advantages in comparison with other methods: It is quick; the quantity to be injected can be easily chosen and adjusted with accuracy (100 ± 2 percent in the microliter range); precision of the quantity to be injected is suitable for many purposes (100 ± 2 percent or better); and in the cases where this deviation is too large, internal standards can be used.

Poor materials, design and inefficient methods can, however, lead to serious sources of error and interference in connection with septum/syringe/injector. Many complications can be traced back to three simple reasons:

1. Leakage of gas through the septum, in or out;
2. Sorption of the substance being injected, onto the material of the septum;
3. Bleed from the septum material.

All three reasons, then, have a direct connection with the properties of the septum, but the syringe and injector are important decisive factors controlling how serious the complications can be. Certain firms manufacturing injection devices are clearly in considerable doubt over the application of septum/syringe/injection to automatic injection so they have instead chosen to use, for example, sample ampoules.

The present invention is based on the fact that many of the complications in turn are linked with problems which until now have been neglected. To simplify the further description the following will treat a particular instrument, a gas chromatograph, GC among the above mentioned group of apparatus.

Septum

A septum-less injector is referred to (van Swaay, Bacon: Journ. Chrom. 19(1965) 604), but the use of it is complicated and its reliability is dubious under varying circumstances. Hence, in commercial GC, the syringe injection is nearly always combined with a septum.

The ideal septum has physical properties which maintain the seal during and after repeated perforations, even when there is a great difference in gas pressure between the two sides of the septum. An ideal septum is also chemically inert; it neither takes up nor gives off substances. These physical and chemical properties should be maintained in a temperature range over several hundred degrees over an unlimited period of time.

The qualities demanded of the material, especially towards efficient coordination, are a long way from being reached in reality. The majority of attempts to achieve this high standard as nearly as possible have used one or another type of silicone rubber as the main component. Some septa are homogeneous; others are made up of different layers, sandwich septa; whereby it has been tried to combine the unlike qualities to advantage.

Mechanical Qualities of the Septum

In the homogeneous septa, mechanical qualities of high standard are aimed at by modifying the elastomer; however in the sandwich septa, soft elastomer is bonded between layers of harder material. The soft layer makes a tight seal around the syringe needle and makes sure that the seal is continuous when the needle is pulled out. The outer layers give mechanical stability, also at high temperatures.

Sorption onto Septum Material

Through faulty injector design, the septum under normal injection comes into contact with the injected substance. Sorption onto the septum material can as a result be a problem, something which is easier to understand when there is some similarity between the septum material and the stationary sorbent being used in the separation column of the instrument. Various complications are described in the literature.

Septa with improved sorption properties can be obtained by using materials such as PTFE, but because their sealing properties are rather poor, such materials are used only in a thin layer sandwich types. Due to reasons later discussed, the sandwich principle is not completely efficient in eliminating the sorption phenomena. By using certain types of rubber in the inner layers, in fact, the situation can be made worse.

Septum Bleed

In the production of synthetic elastomer, the monomer is usually used with other organic substances with comparatively high vapor pressures. It is not surprising that the latter substances can appear in the finished product. When a septum is used in a G.C. a series of unpleasant symptoms can arise from the septum giving off substances. Examples of this are unstable conditions and the so-called ghost-peaks. To avoid such complications attempts have been made to modify the elastomer and to apply certain post treatments. This will, however, usually result in a loss of other important material properties.

As previously mentioned, the sandwich principle is not entirely efficient in eliminating the sorption phenomena, nor is it completely effective in dealing with bleed. Further details are given later.

The bleed characteristics of seven commercial septum types have been studied by Smith and Sorrells (Smith, Sorrells: Journ. Chrom. Sci. 9 (1971) 15). The seven septum types studied include all major varieties such as homogeneous and sandwich types. None was judged to be satisfactory for sub-microgram analyses.

Injector

The use of the same type of septum in different GC-apparatus, can have very different effects. The consequences of the septum material's shortcomings are largely affected by the quality of injector design.

It is naturally desirable in an injector that the septum is placed so there is little chance of sorption of the injected sample. On the other hand, it is not desirable in the gas system that there are pockets of gas, dead volume, or areas where the injected substance can condense. The majority of injectors are a compromise. Furthermore, it is clearly an advantage that the surface area of the exposed septum is as little as possible. Such designs are described in various publications.

Factors causing septum bleed under the effect of injected solvents, on the whole can be viewed under the same conditions as sorption on the septum, and the injector design is influenced in the same way by these conditions. Septum bleed affected by temperature merits other considerations in design:

Obviously, the septum temperature should be kept as low as possible. But on the other hand, at such low temperatures there is a likelihood for condensation of the injected substance to occur and this must be prevented. On the understanding that septum bleed will always appear, a more radical injector modification can, however, be found. It prevents gas, which has been next to the septum, from entering into the column. The carrier gas stream is divided into two. The main stream enters the column as normal while a side stream moves toward the septum and so out of the system. This modification does not increase the dead volume of an injector, but the danger with such designs is clearly that parts of the sample can be lost. This is due to the expansion and back-flush; in other words, the sample is driven towards the septum and out, instead of going towards the column.

Syringe

Complications from both leakage, sorption and bleed occur to a degree as a result of the syringe's condition and use. The needle of the syringe is especially important. Syringe needles for GC use are usually made from stainless steel. Platinum is used only for extra special samples. Needles often have an outer diameter of 0.5 mm and an inner diameter of about 0.2 mm. Various needle tips can be obtained. Some manufacturers recommend a 17° bevel for ease of penetration, although bevels of 12° and 22° and needles with a 90° tapered tip are also available. Production techniques are advanced and special polishing operations produce needles with a smooth finish.

Unfortunately, the needles often suffer from rough handling during use. Several injectors are designed such that the needle can come up against various obstructions, such as edges and the ends of tubes. The needle can thereby be bent or damaged, becoming rough and result in scraping. A damaged needle results in a damaged septum. The manner in which a syringe needle perforates the septum affects gas leakage to a great extent, and a septum perforated by a bent rough needle has fewer chances of maintaining a tight seal.

There is a relationship between the condition of the syringe needle and complications from sorption and bleed.

This statement is the basis for the prsent invention and will now be explained in some detail.

Tearing of Septum Material

A close study of a septum taken out of use after a series of injections, clearly shows that some elastomer material has disappeared from the region of perforation. It is obvious that this may cause leakage, but what is surprising is that this fault has been neglected as the possible key to many of the complications which occur in connection with sorption and bleed from septum material.

Investigations, as microscope-studies, have now showed that a syringe needle when perforating the septum can tear off septum-materials. In some cases cylinders of diameter equal to the inner diameter of the needle have been punched out. However, it is seldom that the entire cylinder is cut out of the septum in this way. What does tend to happen is that granules and irregular bits are torn out and taken into the injector with the tip of the needle. When the syringe's piston is pushed in during injection, the bits of septum material are pumped out together with the sample. A considerable amount of the septum which has disappeared under repeated perforations in this way, consequently ends up in the actual analysis system.

Sorption of the sample on loose septum bits can take place freely in the analysis system. The granules come in very close contact with the sample and the surface area of irregular shapes is decidedly large.

Bleed from such bits of rubber can be considerable. If for example a silicone rubber type contains 100 p.p.m. volatile substances, one single cylinder such as mentioned above can have a bleed of 10 nanogram. It is therefore possible that sometimes there can be as much bleed as there is sample. One can imagine the number of difficulties which can arise from such contamination.

After repeated use of a GC instrument, a series of bits of rubber can have been taken into the system during injections. What happens further to these contaminations is controlled by operating conditions. The temperature of the injector is especially influential as at higher temperature the granules become changed and decomposed. Many publications have mentioned certain deposits in the injector zone and first part of the column. Usually, these deposits have been attributed to the injected sample. Probably the rubber particles have been more responsible for the deposits than the actual samples.

Injection by syringe offers many advantages, as mentioned, and so it is desirable to keep this method. However, bearing in mind the various complications discussed, it is necessary to make some adjustments. By modifications outlined in the present invention, wasted time can be avoided, the actual taking of measurement is made more reliable, and, in addition, one must take into account that certain samples are irreplaceable. This invention will prevent introduction of septum particles into the system when using syringe and septa.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1*a–c* are sectional views and show the penetration of a hollow needle through the septa for cleaning and injecting into the injection chamber, in accordance with the present invention;

FIG. 2 is a sectional view and shows the constructional details of an injector arrangement, in accordance with the present invention;

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The construction is based on the fact that bits of septum are torn out only when the needle is pushed in and not when it is retracted. This principle is illustrated in FIG. 1 and applies under different technical designs. The upper septum **11** is first (a) perforated by the syringe needle **12**, which is then rotated into a vertical position. The syringe needle is then (b) pushed out from the inside through the lower septum **13**. The bits or rubber can then be removed from the needle tip which is now accessible, and the syringe, can be rinsed with an appropriate liquid. Having eliminated the contamination, the sample can be taken up into the syringe in the usual manner. The needle tip is then drawn back through the lower septum, into the system again, and after being rotated to a horizontal position (c), the sample is injected without any danger of contamination from bits of septum material.

After injection, the needle can remain in the upper septum and it can also be driven out through the lower septum. The upper septum, therefore, only needs to be perforated once and the lower septum a number of perforations usual for an injector.

In FIG. 1, the syringe is rotated $\pm 45°$ from the original perforation position in the upper septum. Certain types of septum appear to tolerate such rotation and the seal remains acceptable. In practice, however, the degree of rotation can be reduced. It is also possible, for example, to use a special equipment, appropriately sealed, which holds the needle and septum in a fast position while being rotated itself. FIG. 2 illustrates an injector after the above principle.

In FIG. 2, a septum **1** is applied to a rotating support **3** by means of a septum nut **2** having threads, not shown. The rotating support **3** has assembled to it a clamping ring **4** with clamping bolts, not shown. An O-ring **5** serves as a seal. An injector block **6** is provided with a channel **7** leading to the column, and a channel **8** leading to the lower septum.

The problems of septum material in the analysis system can also be tackled by modification of septum construction. Even sandwich septa do not solve this problem since the main component of the septum can have such poor sorption and bleed properties that even a little material taken into the system can give rise to serous complications.

What is claimed is:

1. An injector arrangement for introducing samples into physical-chemical investigating apparatus by means of a syringe, comprising in combination:

an injector block;

a rotating support mounted on said injector block and adapted to receive a syringe;

an annular seal between said rotating support and said injector block;

a first channel extending through said rotating support and having an opening within said annular seal;

a first septum closing said first channel;

a second channel extending through said injector block and having an opening within said annular seal;

a second septum closing said second channel;

a third channel extending into said injector block and having an opening within said annular seal;

said first, second and third channels being so arranged with respect to the axis of rotation of said rotating support that said first channel can be brought into alignment with said second channel and third channel respectively, by rotating said rotating support, whereby in a first position of said rotating support a syringe needle can pass through both said first septum and said second septum, and after cleaning and retraction of said needle from said second septum the rotating support is rotatable to a second position in which said needle can be introduced into said third channel along a predetermined line for injecting a sample through said needle.

2. The arrangement as defined in claim **1** wherein said septa are self-sealing for maintaining a seal around said needle after penetration of said septa.

3. An injector arrangement according to claim **1**, in which said first, second and third channels are arranged with an inclination at approximately the same angle with respect to said axis of rotation.

4. An injector arrangement according to claim **1**, in which at least one of said septa is located at an end of its associated channel remote from said annular seal.

5. The injector arrangement as defined in claim **1** including gas chromatographic apparatus communicating and cooperating with said third channel.

6. The injector arrangement as defined in claim **1** including a syringe connected to said needle and filled with said sample.

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