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NEW INJECTION SYRINGE FOR GAS CHROMATOGRAPHY

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SUMMARY

A new syringe construction with a thin glass or fused-silica capillary needle is described. A gas-tight retractable needle shield allows injections through a silicone rubber membrane, without mechanically affecting the needle. Thus, sampling from closed vials can be performed as well as leak-free injections into pressurised systems.

The new sampling device was compared with a conventional syringe, equipped with a stainless steel needle, with respect to inertness in a heated inlet system. The thermolabile compound dibenzothiophene-5-oxide was injected in the splitless mode at 250°C and the reaction products were quantified. Considerably less degradation was observed when the new syringe was used, which reveals the catalytic activity of the metal needle, and shows the need for inertness of the complete sampling system.

With only a few modifications, the construction presented can be used for automated on-column injection, which will be described in a subsequent article.

INTRODUCTION

There are many methods for sample introduction in pressurised chromatographic systems, such as sample loops, valves, capsules, precolumns etc., but the predominant technique, at least in gas chromatography (GC), is injection of the sample through a silicone rubber membrane. Although it may be questionable whether the commonly employed syringe is really the most suitable sampling tool for modern precision GC, it is still used in a form basically similar to that used in the early days of GC. This is mainly because the concept is very simple, yet allows control of all important parameters such as sample size, injection speed and cross contamination. Moreover, samples can be taken from almost any type of vial or container without risking a change in sample composition. When only a limited amount of sample is available, total transfer can be achieved without excessive dilution and with a minimum of sample waste. Thus, there are several reasons to believe that the syringe will continue to be a major sampling tool in chromatography.

However, parallel with on-going developments of new chromatographic techniques, such as microbore columns and associated injection devices, it is necessary to evaluate critically and improve the present syringe constructions in order to allow a more compatible and accurate microsampling. In this context, the well established

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cold on-column injection technique, developed by Grob *et al.*[1] involved an important first step. A syringe needle with a reduced diameter was employed, which made possible direct deposition of the liquid sample into the capillary column. Another improvement was the use of thin glass tubing as a syringe needle[2], which allowed visual studies of the sample dispensing process as well as the choice of any desired inner and outer diameter of the needle. With the advent of polyimide-coated fused-silica tubing, a material with a better mechanical strength became available. After it was first suggested that fused silica could be used as a syringe needle material[3], several manufacturers have followed this idea.

An important advantage of glass and fused-silica needles is their higher degree of inertness compared with steel needles, which is especially important when injecting into heated inlet systems. However, none of the available syringes, when equipped with a fused-silica needle, is suitable for use with conventional inlet systems, because the unprotected thin needle is not sufficiently rigid or stable to penetrate an injection septum. Grob *et al.*[1] pointed out a number of drawbacks regarding the use of septa, and replaced the injection membrane with a valve system. Their design involves an escape of carrier gas between the syringe needle and the annular space of the needle guide during injection, but no adverse effects were observed[4]. Several other inlet systems for syringe-based on-column injectors have been proposed, such as a duck-bill valve[5,6], a needle seal combined with a valve system[7], various constructions with needle guides[8,9], and commercially available systems (*e.g.* from S.G.E.) where an O-ring is compressed and decompressed around the syringe needle. However, with most of these systems, carrier gas also escapes when the syringe is introduced into the inlet system, or mechanical problems are encountered when very thin needles are used. Takayama[10] suggested a control device to ensure a constant gas flow through the column in order to counteract possible adverse effects of leakage around the syringe needle during injection. Other workers have designed constructions in which the chromatographic system is temporarily opened during sample loading, which necessitates an interruption of the carrier gas flow (*e.g.* refs. 11 and 12).

There are several arguments that support the use of a closed injection system and a continuous and undisturbed flow of carrier gas. First, such a gas flow is a basic requirement for obtaining reproducible retention data, particularly when isothermal conditions are employed and where precision evaluations are carried out with modern computer-based devices. Secondly, opening of the injection unit will cause air to diffuse into the flow system. At low temperatures, this has few deleterious effects, although certain detectors may show a temporary disturbance. At high temperatures (or in cases where an immediate rapid temperature programme is employed), the stationary phase can be degraded by oxidation. Moreover, an interruption of the carrier gas flow and an opening of the chromatographic system is a procedure that cannot be used for automated injection.

Although a minor escape of carrier gas from the inlet system can be accepted in well-designed systems during on-column injection, this is prohibitive with other methods, such as splitless injection. Also with high pressure gas or liquid chromatographic systems, it is necessary to have inlet systems that are permanently isolated from the environment. In this respect, the classical flexible membrane seal fulfills this requirement, and can in fact be considered as a true zero dead volume valve for a syringe needle. This led us to construct a modified syringe, equipped with a thin glass

or fused-silica needle, that allows leak-free operation with all injectors as well as vials that are closed with a silicone rubber membrane. The description and evaluation of this new sampling device is the subject of this paper.

INSTRUMENTATION

The modified syringe

In order for a very thin needle to penetrate a silicone rubber membrane, reinforcement in the form of a needle shield is necessary, which must be constructed in such a way that the actual glass needle is never subjected to a mechanical force. At the same time, the needle shield must be gas tight in respect to the glass needle,

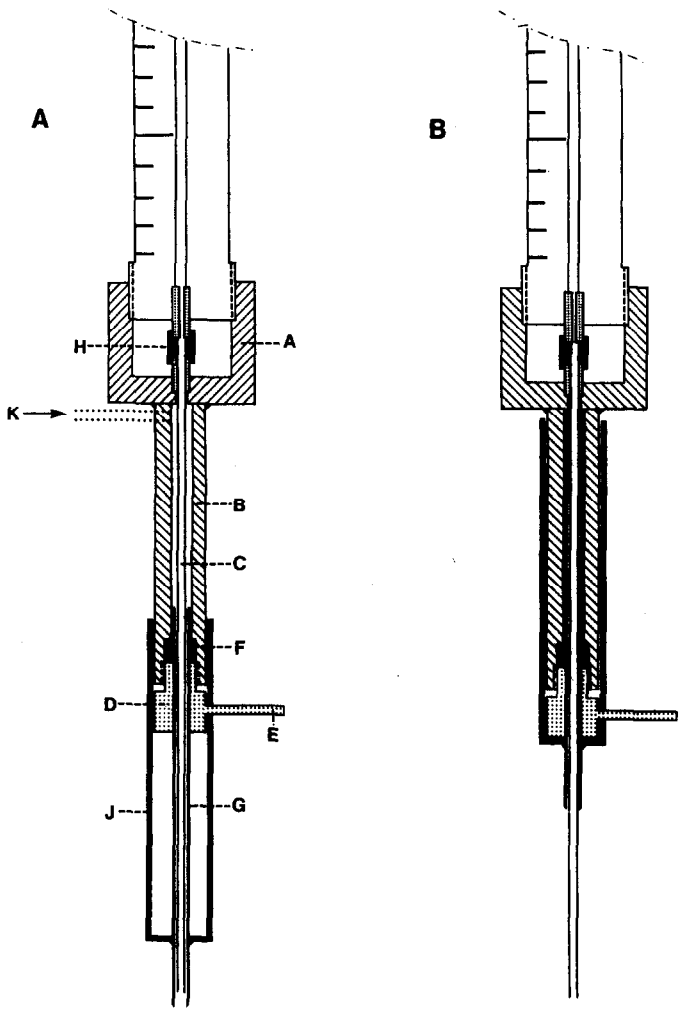

Fig. 1. Schematic drawing of the modified syringe. (A) Fused-silica needle covered with the shield. (B) Needle shield retracted. For explanation of the lettered parts, see text.

in order to avoid escape of carrier gas after insertion into a pressurised system. This was achieved with the construction shown in Fig. 1.

A commercially available syringe with a fused-silica needle (SGE 5A-SOC-75,5 μl) was modified as follows. A stainless-steel tube (B), 7 cm × 3 mm O.D. × 0.6 mm I.D., was braized on the compression nut (A), which seals the exchangeable fused-silica needle (C). The other end of the tube was drilled and threaded, so that a small PTFE gasket (F), which was compressed by a small hollow screw (D), could be fitted. This screw was equipped with a handle (E), to facilitate the compression of the gasket. A stainless-steel needle (G) (9 cm × 0.5 mm O.D. × 0.2 mm I.D.) was braized on a slotted outer tube (J) (6.5 cm × 3 mm I.D.), at a position *ca.* 2 cm from the point of the needle. As is evident from Fig. 1, the outer tube slides over the steel tube B. The handle (E), which is fixed to the screw (D), fits into the slot of this tube, and the fused-silica or glass needle is positioned in the stainless-steel needle G. Thus, the needle can either protrude or be fully protected (Fig. 1A and B, respectively). The PTFE gasket F forms a sliding seal against the needle shield. At its other end, the fused-silica needle is sealed with another PTFE gasket. Thus, a leak-free system is obtained for both the needle shield and the fused-silica needle, regardless of whether the shield is in the protecting or the retracted position. In order to lock the position of the needle shield during the insertion through the silicone membrane and to obtain a reproducible positioning of the exposed fused-silica needle during injection, two side slits were machined in the outer tube (J). The purpose of these slits is best explained by Fig. 2, which also gives a better picture of the longitudinal slit.

Septum penetration

The conventional syringe needle has a sharp, obliquely cut needle point. For single sampling operations, from vials for example, this shape can also be used for the shield. However, a sharp needle point is vulnerable and a silicone rubber membrane is destroyed after repeated injections. Frequently, the needle is also blocked by fragments of silicone rubber. Pretorius[13] eliminated this problem by using a compressed, pre-drilled membrane and a dome-shaped needle point. Rather than cutting its way through, the needle slides through the hole, and an analogue to a micro valve is obtained. We used this construction with some slight modifications. The dome-shaped point of the shield was carefully polished (micro-abrasive or electropolish) and particular care was taken to remove all inside burrs. Instead of the silicone membrane being pierced with a hot needle, the hole was made with a centre-drill. Thus, a small conical needle guide was obtained, which facilitated the correct insertion of the dome-tipped needle. Drilling with any degree of precision in a silicone membrane is cumbersome under normal conditions. However, we found this to be

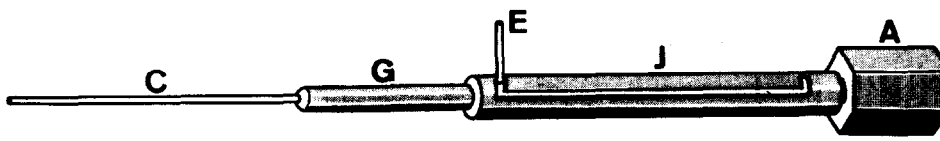

Fig. 2. Schematic perspective view of the syringe needle (needle shield retracted). A = Hexagonal nut; J = slotted stainless-steel tube; E = handle to lock the position of the needle shield; G = needle shield; C = fused-silica or glass capillary.

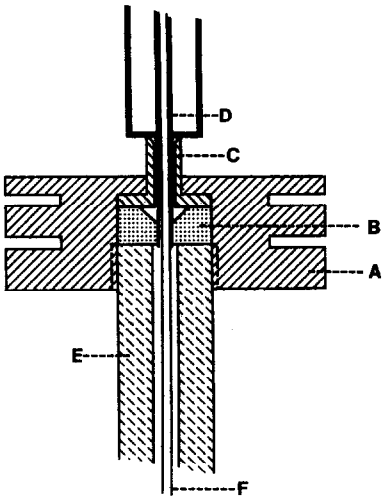

Fig. 3. Setup for injection with the new syringe through a conically predrilled septum. A = Septum holder; B = septum; C = needle guide; D = needle shield; E = injector body; F = glass or fused-silica capillary.

possible when the septum was kept in liquid nitrogen during the drilling. (We should mention that this technique allows precise shaping of most elastic materials, which will be of use for several other applications in chromatography).

To make the introduction of the syringe more convenient, a needle guide (polished stainless steel) can be installed in the septum holder. A complete setup is depicted in Fig. 3.

RESULTS AND DISCUSSION

Influence of the syringe needle material on sample decomposition

As mentioned in the introduction, the use of a syringe equipped with a glass or fused-silica needle is particularly desirable when heated inlet systems are employed. The risk of degradation of labile compounds on a hot metal needle surface has been pointed out by several workers[1,14]. In the light of the considerable efforts expended in obtaining inert chromatographic systems, it is surprising that this problem has not been given more attention. When cold on-column injection systems are employed, the choice of needle material becomes less critical, but such injection systems cannot be used for all analytical problems.

We investigated the influence of the syringe needle material on the stability of dibenzothiophene-5-oxide (DBT-O) in a heated inlet system. Oxygenated dibenzothiophenes are found in oil spill, and have been given considerable attention in view of their toxicity to marine organisms[15].

DBT-O is known to be thermolabile, and this has caused problems in its GC determination. Vignier *et al.*[16] investigated the behaviour of DBT-O in different injection systems, and reported considerable breakdown of the compound when using splitless injection at 250°C. These workers suggested that one reason for this could be contact with the hot metal needle during injection. Therefore, we considered this compound to be particularly appropriate for our comparative investigation.

DBT-O was synthesized from dibenzthiophene[17], and purified by recrystallisation from toluene. The analyses were performed on SE-54 and OV-73 capillary columns (25 m × 0.3 mm I.D.; D_f = 0.1 μm), with splitless injection at 250°C. Partial breakdown of the compound was observed. The main decomposition product proved to be dibenzthiophene, (identified by GC retention and GC–mass spectrometry), in agreement with previous work[16]. According to observations by Andersson[18], the degradation of DBT-O is not reproducible, even between consecutive injections under similar conditions. We carried out a large number of repetitive injections and also found that the degree of degradation was very dependent on the exact injection conditions. A considerable difference in the degree of breakdown between different series of analyses was not unusual, and sometimes even sudden changes within a series of consecutive injections were observed. Therefore, particular care was taken to keep all injection parameters (such as injection speed, needle position, sample size and dwell time of the needle in the injector) as constant as possible. The removable stainless-steel inlet piece from the Carlo Erba injector was replaced by a similar construction in PTFE, to eliminate possible adverse effects of this part.

Table I shows the results from comparisons between a syringe equipped alternately with a stainless-steel or a fused-silica needle. As can be observed, the least degradation occurred when the fused-silica needle was employed. Several additional series of measurements were carried out that confirmed this result. However, an overall long-term comparison of the absolute values for the degree of degradation showed large variations, which made the calculation of standard deviations rather meaningless. We attribute these variations to the difficulty of maintaining precisely the same injection conditions.

TABLE I

FORMATION OF DIBENZOTHIOPHENE FROM DIBENZOTHIOPHENE-5-OXIDE IN A CONSECUTIVE SERIES OF ANALYSES

Injection No.	*Needle material*	*Percentage conversion of dibenzothiophene-5-oxide into dibenzothiophene**
1	Steel	14.1
2	Fused silica	6.7
3	Steel	9.8
4	Fused silica	5.5
5	Steel	8.5
6	Fused silica	2.1
7	Steel	9.2
8	Fused silica	2.1
9	Steel	14.5
10	Fused silica	2.4
11	Steel	9.6
12	Fused silica with metal piece in the injector liner	83.0
13	As 12	84.8
14	Cold on-column injection	1.9**

* Calculated from peak areas.

** Probably unchanged dibenzothiophene from the syntheses.

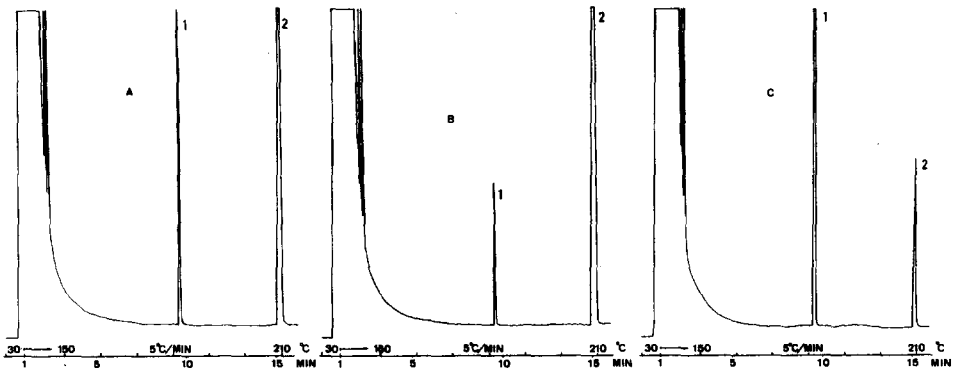

Fig. 4. Chromatograms of dibenzothiophene-5-oxide (2) and its degradation product dibenzothiophene (1). Splitless injection at 250°C. Column, SE-54 (25 m); sample size, 80 ng (in 1.5 μl of dichloromethane); GC apparatus, Carlo Erba-4160. (A) Injection with a conventional syringe with a stainless-steel needle; (B) injection with the syringe described (fused-silica needle); (C) as in B, but with a small piece of stainless-steel wire in the injector liner.

To obtain further evidence to support our conclusions, we carried out the following experiment. A small stainless-steel wire (1.5 cm × 1 mm) was inserted into the injector liner and the experiments were repeated. A large increase in breakdown of DBT-O was observed, regardless of which syringe was employed. Fig. 4 shows representative chromatograms of the different experiments.

Although our studies show that the degradation of DBT-O is influenced to a considerable extent by the catalytic activity of the metal syringe needle, a number of puzzling facts remain. Andersson[18] reported the formation of both dibenzothiophene-5,5-dioxide and dibenzothiophene when using splitless injection, whereas the French workers[16] observed only the formation of dibenzothiophene (which is similar to our observation). Gurria *et al.*[19] reported quantitative conversion of DBT-O into dibenzothiophene when the compound was heated at 250°C for several minutes. We could not confirm this. Heating DBT-O (3 mg) in a ampule at 250°C for 1 h yielded only 7% of dibenzothiophene. Heating to 270°C for 10 min, converted no more than 3% of DBT-O. It is obvious that elaborate experiments are necessary for these discrepancies to be resolved, but such studies are outside the scope of this work.

Further applications

Besides for leak-free injection under inert conditions, the syringe presented here has the particular feature that sampling with a fine needle from or into a closed vial can be performed without the sample being exposed to the atmosphere. This is particularly important with highly volatile samples or with samples under non-atmospheric pressure. An example of such an application is the sampling of head space for on-column injection. In a previous description[20], a valve system based on the principles described by Grob[1] was employed to cap the sample. This does not provide total isolation from the environment during sampling, which can lead to changes in the sample composition.

The design of the syringe permits a simple one-hand operation, without the use of platforms or fixtures.It is important to avoid contamination of the inner sur-

face of the shield with sample from the outer surface of the fused-silica needle, since this area is not flushed. Therefore, it is recommended that the needle should be left in the unprotected position during withdrawal from a sample vial. Subsequently, the needle can be dipped into a solvent before protecting it with the shield.

The most efficient way of rinsing the outer surface of the needle would be by introduction of a solvent through a side-arm in tube B (shown dashed in Fig. 1). We have not yet evaluated this procedure, but the construction offers some interesting applications that should be explored, *e.g.* dynamic dilution in a microflow of liquid or gas.

The protection of the needle allows the use of extremely thin glass needles, without risking a breakage. The rigidity of the exposed part of the needle can be controlled by the variable retraction of the shield. Thus, a stable construction suitable for high precision positioning and sample handling from and to closed microvials is obtained. There is a particular need for such a tool in spectroscopic and trace analytical work. With a few modifications, the syringe can be used to construct an automated device for direct on-column injection in capillary columns, without the need for a wide-bore injector insert or a wide-bore pre-column. The details of this work, including a further evaluation of the syringe, will appear in a separate report.

ACKNOWLEDGEMENTS

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