Note

Should the septum part of vaporizing injectors be kept at lower temperatures?

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Using a classical vaporizing injector in quantitative gas chromatography (GC), a severe problem associated with the syringe needle arises. As the needle is inevitably warmed as soon as it passes through the septum, it can seldom be avoided that a portion of the needle content passes into the injector. On withdrawing the plunger, the proportion of the liquid that left the needle can be measured. Obviously, however, the sample components usually do not leave in the same proportion as the solvent, and it cannot be assumed that the different components reach the column in equal proportions. High-boiling substances are more likely than volatile substances to remain inside the needle, and they are therefore discriminated in the chromatogram. Such effects are already known[1–3]. They were shown to be the prevailing cause of discrimination for a sample with a wide range of alkanes[4] and (for splitless injections) of triglycerides[5]. It has also been shown that the extent of the discrimination and its reproducibility can be greatly influenced by the syringe technique used during the injection[4,6].

Under apparently identical conditions we found great differences in the discrimination of high-boiling sample components when a sample was injected into different instruments. The main cause was found to be the different heating, *i.e.*, the different temperature gradient along the axis of the injector from the heating block towards the septum cap. In the work reported in this paper, the temperature gradient was varied on purpose and correlated with the discrimination as observed for a mixture of alkanes. The question that arose was, therefore, whether the septum cap should be kept at a lower temperature to avoid problems with the septum, or whether this would have too strong a negative effect on quantitative analyses?

EXPERIMENTAL

An old, modified gas chromatograph (Carlo Erba, Milan, Italy; Model GI) was used, equipped with a vaporizing split/splitless injector as described earlier[7]. The injector body was seated in a heated aluminium block only 3 cm high, positioned such that the space between the exit of the fully introduced syringe needle and the capillary entrance was optimally heated, but leaving the upper part of the injector (about 7 cm) without active heating. The temperature of the aluminium block was kept at 300°C throughout this experiment. In order to create a different temperature gradient between the heated zone and the septum, the following configurations were used:

(A) The injector body above the heating block and the septum cap were exposed to ambient air.

(B) The injector body was insulated with a PTFE ring 4 cm high and 8 mm thick, reaching to the top of the glass liner inside the injector. The area of the septum flush and the septum cap were still exposed to ambient air.

(C) The whole injector was packed into glass-wool, which covered even the septum cap, leaving only a small hole to enter the syringe.

(D) The upper part of the injector was actively heated by means of a heating belt, adjusting so as to obtain 300°C at the septum cap.

The temperature profiles for the four configurations are given in Fig. 1 (measured by means of a thermocouple). For situations C and D the temperature inside the injector could not be measured without disturbing the configuration and these measurements were therefore omitted. Only the temperature of the septum cap was determined in these two instances.
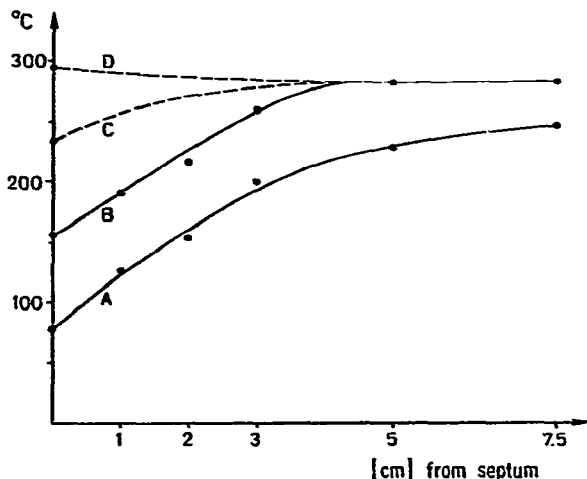

Fig. 1. Temperature gradient in a vaporizing injector measured from the septum cap down towards the column entrance as far as the syringe needle (7.5 cm) reaches. The experimental arrangements for obtaining gradients A–D are described in the text.

All four configurations were tested with a mixture containing equal amounts of alkanes from C_{10} to C_{44} (1:5000 dissolved in n-hexane), using a splitting ratio of 1:30. Injections were made by the "cold needle" and the "hot needle" techniques as described earlier[4] (the sample is withdrawn from the needle into the barrel of the syringe; for the "cold needle" technique the sample is injected immediately upon insertion, whereas in the "hot needle" technique the empty needle is pre-heated in the injector for 3–5 sec). The sample volume was 1 μl, corresponding to the needle volume of the syringe (10-μl Hamilton syringe, 3-in. needle). Parts of the sample not leaving the needle during the injection were analysed by re-injection. A 1-μl volume of pure n-hexane was picked up and moved forwards and backwards to wash the inside of the needle. The resulting solution was injected using the "hot needle" technique and the peak areas were corrected according to the discrimination deter-

mined by the corresponding type of injection for the original sample. The corrected peak areas of the re-injection were compared with the missing area of the first injection.

Peak areas were normalized on the C_{10} peak (set at 100%). It can be assumed that C_{10} eluted completely out of the needle (with the exception of the equivalent that remained in the volume of about 0.05 μl of the whole solution which usually "hangs" on the plunger). Hence the percentage determined for the higher alkanes also indicates
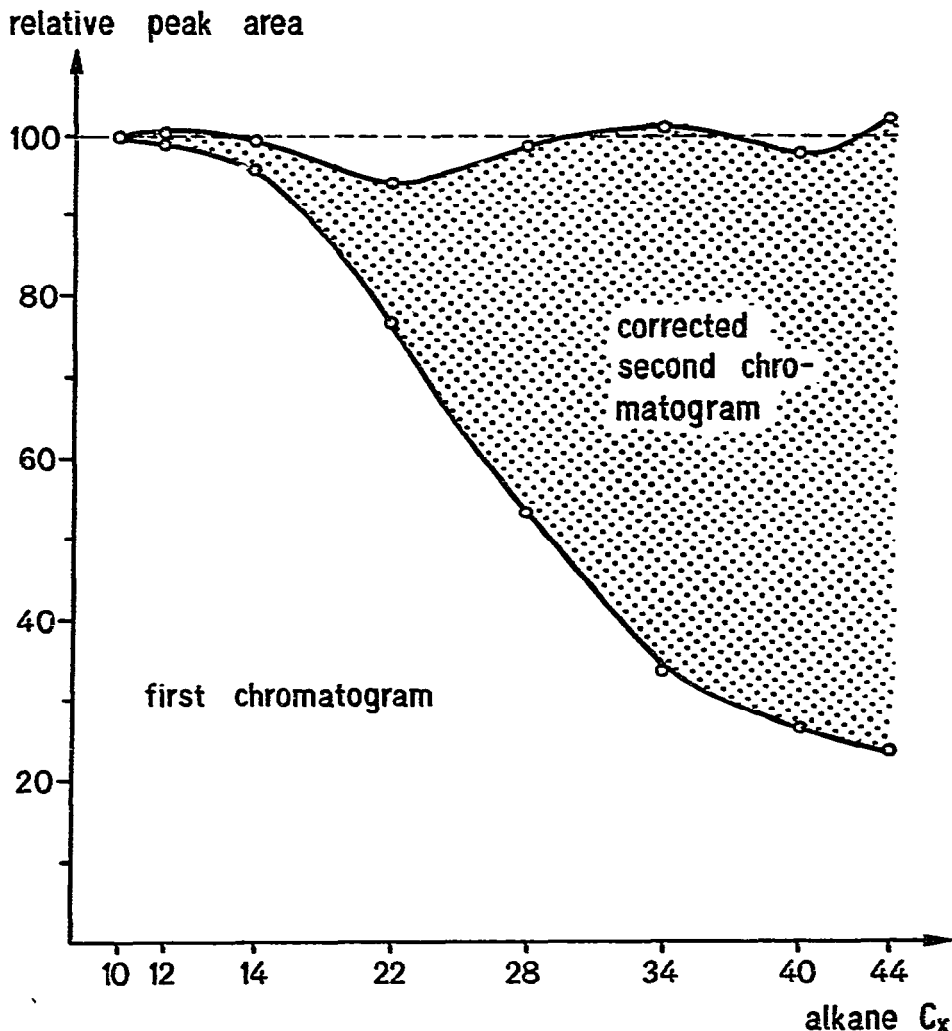

Fig. 2. Lower curve: peak areas as obtained by "cold needle" injections into an injector with temperature gradient B (Fig. 1). Sample: mixture of equal amounts of alkanes, 1:5000 in n-hexane; peak areas normalized on C_{10} (set at 100%). The sample material left in the syringe needle was re-injected and the peak areas were corrected by the corresponding discrimination factors and added on top of the curve of the first injection. The total of the two curves is approximately 100%, demonstrating that the losses inside the syringe needle accounted for virtually all of the discrimination shown by the lower curve.

the proportion of the component eluted. The peak areas of the re-injections were also normalized on the C_{10} of the first injection. A 10 cm × 0.30 mm glass capillary, coated with 0.15-μm OV-73 was used with 0.3 atm inlet pressure (hydrogen). The temperature was programmed from 40 to 300°C at 10°C/min.

RESULTS

Fig. 2 confirms for "cold needle" injections using situation B that the discrimination of the high-boiling alkanes in the test sample was due nearly exclusively
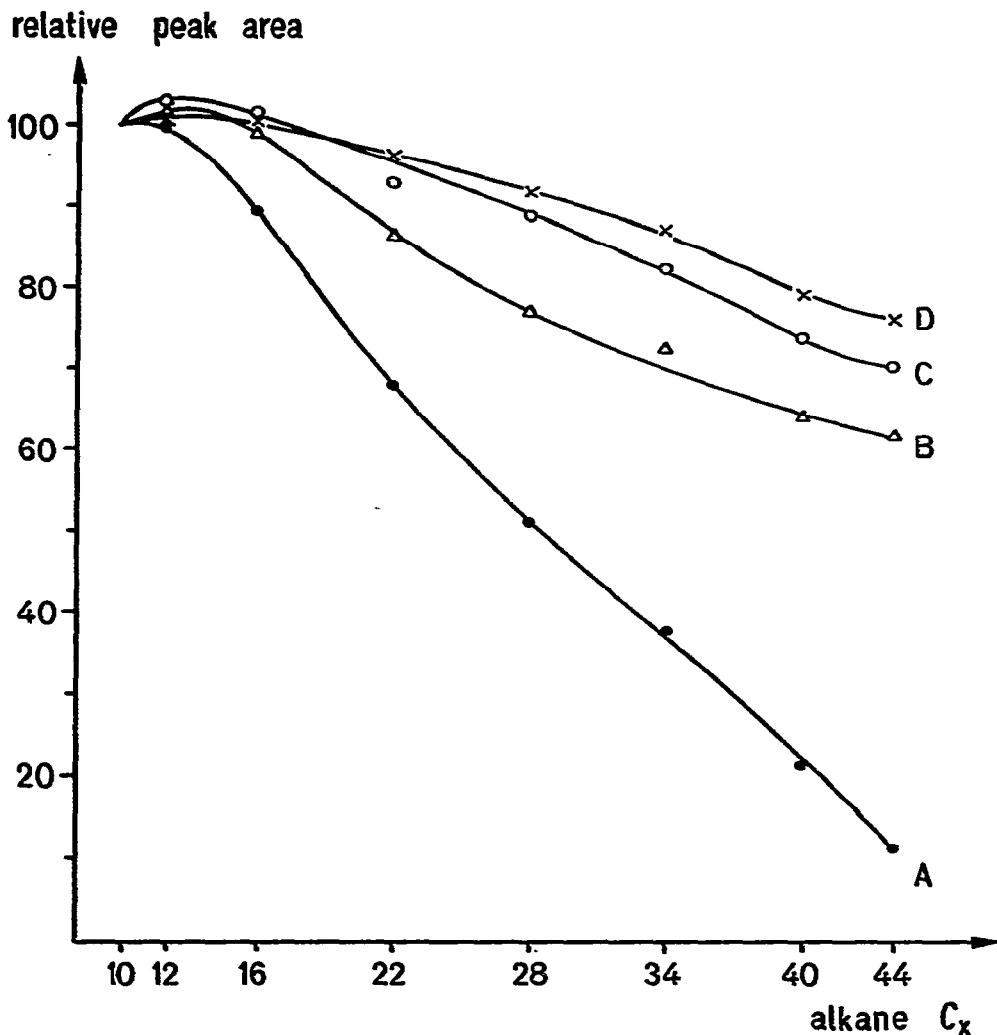

Fig. 3. Peak areas (normalized on C_{10}) obtained by "hot needle" injections depending on the temperature gradient in the upper part of the injector (Fig. 1). Sample as in Fig. 2. It is concluded that the losses of high-boiling sample components inside the syringe needle increase strongly when the parts near the septum are kept at lower temperatures than the heated centre of the injector. Nevertheless, a fully heated injector (situation D) does not prevent such losses completely.

to the losses inside the needle (and not caused for example, by non-linear splitting or losses in the injector). The values given are based on four injections and re-injections; similar results were obtained for the "hot needle" technique and the other configurations.

Fig. 3 shows the discrimination of the higher alkanes obtained with the different configurations, *i.e.*, dependent on the temperature drop towards the septum cap (mean values of at least five determinations). The graph for configuration A (with the septum cap at a temperature below 100°C) deviates dramatically from horizontal (about half of C_{28} and 85% of C_{44} are lost in the needle). Configurations B and D produced much better, but still strongly discriminated chromatograms, tending to the values of situation D, where the entire injector was homogeneously heated to 300°C. In the last instance the losses of the higher alkanes were still about 10% for C_{28} and 20% for C_{44}.

From Fig. 3 it can be concluded that (a) the losses inside the syringe depend strongly on the temperature gradient in the upper part of the injector, *i.e.*, the needle temperature achieved by the pre-heating as used for the "hot needle" technique, and (b) the losses cannot be avoided completely even when the entire needle is heated to a high temperature.

Table I compares results obtained by the "cold needle" and "hot needle" injection techniques for configurations A, B and C.

TABLE I

COMPARISON OF NORMALIZED PEAK AREAS AS OBTAINED BY "COLD NEEDLE" AND "HOT NEEDLE" INJECTIONS FOR TEMPERATURE GRADIENTS A, B ANP C (FIG. 1)

Sample as in Fig. 2.

Alkane, C_x	Configuration					
	A		B		C	
	Cold	Hot	Cold	Hot	Cold	Hot
10	100	100	100	100	100	100
16	80	90	96	98	102	100
22	39	67	77	87	94	98
28	25	52	53	77	88	92
34	15	37	37	74	76	89
40	10	21	27	64	65	79
44	8	14	25	62	63	76

DISCUSSION

The expression "vaporizing chamber" is usually used synonymously with the glass liner in the injector, assuming that this would be the space where most of the liquid sample is evaporated. More precisely, it is understood to be the area between the needle exit and the column entrance. Consequently, this is usually the part of the injector which is truly temperature controlled, where great care is taken to keep surfaces clean and possibly even to deactivate them. However, our experiments have shown that for most of the samples (depending on the volatility of the solvent at the injector temperature) the most important vaporizing chamber is the syringe needle. In the needle the liquid is in direct contact with hot surfaces and picks up a relatively large amount of heat in a very short time.

The syringe needle, acting as a vaporizing chamber, bears just about all the undesirable characteristics that may be associated with injectors. (1) The walls are metallic, and therefore catalytically active. (2) It is very difficult to inspect the inside of the needle to establish its condition. However, extrapolating from the experiences with the glass liner in the injector, it can be assumed that the needle walls are covered with a brown, lacquer-like material that is difficult to wash out with the usual cleaning solvents. (3) The needle is a dead volume. Hence the transfer of high-boiling substances out of the needle requires a much higher vapour pressure than is required to move these compounds in an injector cavity that is steadily flushed. At the moment the solvent has left the needle, nothing remains that can serve as a carrier, so that even a fully evaporated compound has lost the last opportunity to reach the column. (4) The temperature control of this vaporizing chamber is poor. The temperature of the "injector" (which often means only its centre part) is commonly indicated in publications, but not the temperature of the possibly more important "vaporizing chamber", the needle! This very important temperature depends on the temperature gradient towards the septum and on the technique used for handling the syringe needle. The indication of the needle technique seems to us to be at least as important as the "injector temperature".

An important aspect of a revised concept of the "vaporizing chamber" including the needle is to reconsider the arguments for selecting the injector temperature. The evaporation of the fraction of the sample that leaves the needle as a liquid and the prevention of adsorption on the injector surfaces may be even less important than the temperature of the syringe needle. The needle temperature should probably be even higher than the injector temperature, because the needle is a dead volume and may be dirty.

Let us consider the septum. The classical opinion was that the septum should be kept out of the hot zone of the injector in order to minimize bleeding. As this has a negative effect on the accuracy of the analyses, another solution should be found. In the short term, a compromise may be achieved by using high-temperature septa combined with a septum flushing device that steadily sweeps away materials evaporating from this plastic membrane[8]. This should allow the upper part of the injector to be heated to higher temperatures than are often used today. The time to design the septum cap as a cooling shell is gone. However, in the long term it would be greatly preferable to find a device to replace the septum of vaporizing injectors. It seems, at least for thermostable compounds, that accuracy and precision increase with increasing injector temperature, the realization of which is usually hindered by the septum. On the other hand, for capillary GC cold on-column sampling looks very promising for replacing vaporizing injections for most samples.

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