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ISOTHERMAL GAS CHROMATOGRAPHY WITH WALL-COATED GLASS CAPILLARY COLUMNS, ELECTRON-CAPTURE DETECTION AND A SOLID INJECTOR

I*. AVOIDANCE OF GHOST PEAKS

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SUMMARY

The ease of operation of a glass solid injector (SI) of the moving needle type, with wall-coated glass capillary columns and electron-capture detection, was tested under isothermal conditions. Ghost peaks arising from the SI were completely suppressed by combining carrier gas pre-filtration with a method of open sampling.

INTRODUCTION

Recently, we became interested in exploring the ease of application of a system consisting of a glass solid injector (SI) of the moving needle type, a wall-coated glass capillary (WCOT) column and a macro-size electron-capture detector (ECD) to current problems of enzyme kinetics involving the assay of ECD-sensitive derivatives. We constructed an instrumental configuration very similar to that adopted by Franken *et al.*[1] for their study of the behaviour of chlorinated pesticides on WCOT columns.

The moving needle injector has a considerable tendency to produce ghost peaks owing to the adsorption of certain contaminants on the surface of the glass plunger. These contaminants emanate from inadequately pre-filtered carrier gas but, in our application, crude derivatized samples obviously released a very volatile fraction causing additional ECD-sensitive ghosts.

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When we started our work, two methods were known for suppressing artefact peaks due to the SI: (1) the housing of the lifted glass plunger is heated above room temperature, which can reduce or suppress the initial adsorption of contaminants[2]; and (2) carrier gas is supplied at a lower point of the SI, so that the longest possible segment of the plunger is back-flushed in the injection mode[3].

This paper describes a third, alternative mode of operation of the moving needle injector: (a) an activated charcoal pre-filter efficiently traps the adsorbable ECD-sensitive contaminants present in the carrier gas; (b) the loading port is open to the atmosphere during sample deposition and concentration; in this way, sweeping gas leaves the loading bulb of the SI via the short path of the introduction port. Thus, the flow of vapour released from the sample has virtually no contact with the plunger at the concentration step.

EXPERIMENTAL

Gas chromatograph

The instrument is shown in Fig. 1. The oven is a Pye 104 with a rebuilt top plate. The oven safety limit is lowered to 260°. The electron-capture detector is a Pye Unicam Model 795012 connected to a Pye Unicam Model 795022 pulse-

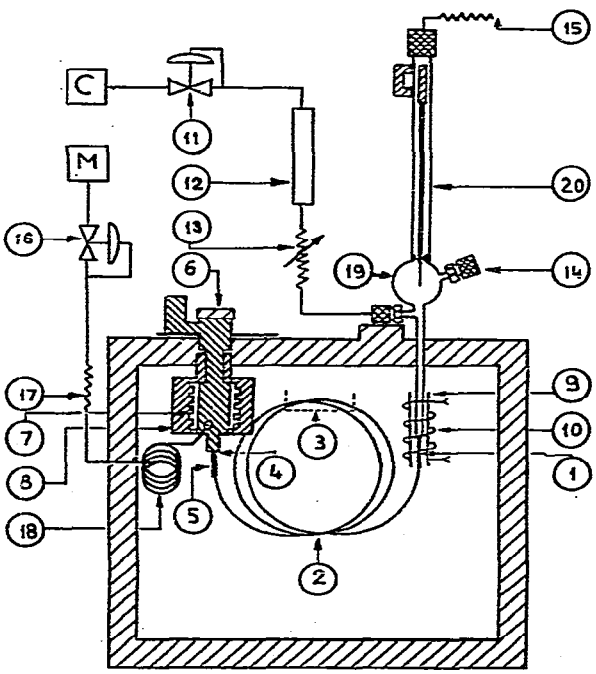

Fig. 1. Schematic representation of the chromatograph. 1 = Injector base and shrinking PTFE column inlet junction; 2 = capillary column; 3 = column seat; 4 = detector inlet nut; 5 = column outlet junction; 6 = detector electrode holder; 7 = detector overheater; 8 = insulation; 9 = 6.5-mm I.D. glass tube; 10 = inlet overheating coil; C = carrier gas cylinder; 11 = pressure controller; 12 = charcoal filter; 13 = flow restrictor; 14 = injector port; 15 = purge restrictor; M = make-up gas cylinder; 16 = pressure controller; 17 = make-up restrictor; 18 = pre-heating coil; 19 = injector loading bulb; 20 = plunger housing.

modulated amplifier. The ECD cell is equipped with an overheater (Nichrome strip) located inside the isothermal oven. The cell temperature is read by means of a contact thermocouple. The vaporization area, at the injector base, is mantled with an overheater consisting of a Nichrome coil wound around a 6.5-mm I.D. glass tube. The latter overheater is freely exposed to stirred air, which minimizes the risk of hot spots. Shrinking PTFE is used for the connection of WCOT columns at both ends. A low-volume passage across the detector inlet fitting consists of a short length of 0.8-mm O.D., 0.3-mm I.D. platinum–10% iridium capillary. Pressure regulators are of the metal-diaphragm type and all the gas lines are made of baked metal tubing. The carrier gas line features a charcoal filter and a downstream flow restrictor (Brooks needle No. 1) with the shortest possible connection to the solid injector. Flow-rates are read on a soap-bubble flow meter and injector and column inlet pressures are read on a low-volume differential mercury manometer occasionally connected to the loading port.

Columns, test samples and gases

Pyrex-glass WCOT columns (0.5 mm I.D.), coated by the static method[4] with SE-52 on untreated glass (film thickness about 0.3 μm) were gifts from Dr. Johan Bouche. Soft-glass WCOT columns (0.5 mm I.D.; 0.3 μm SE-30) were also used.

Quantitative mixtures of organochlorine pesticides in isooctane were gifts from Professor Edgard Delvaux. Further dilutions were made in Nanograde *n*-hexane.

Argon–methane (95:5) (50 ml/min) was used for detector make-up. Helium and occasionally argon or argon–methane (laboratory grade, Air Liquide, Liège, Belgium) were used as carrier gases.

Operating conditions

The carrier gas inlet pressures ranged from 10 to 35 cmHg. The ECD ionization current ($1.5 \cdot 10^{-9}$ A) was about half of the runaway value. The oven temperature ranged from 180 to 220°. The flash heater and detector temperatures were usually 30° above the oven temperature. Occasionally the detector temperature was increased to $300 \pm 1°$. The length of the WCOT columns varied from 5 to 25 m.

Samples of 1 μl were applied to the moving needle across the open loading port, after unscrewing the septum holder. Normally the loading port was kept open until only a dry residue of the sample was left at the tip of the needle. As a result of the open sampling procedure, the vapour released from the liquid sample remained confined to the volume of the loading bulb of the SI.

RESULTS

With unfiltered carrier gas, the SI produced several ghost peaks on the ECD record, and a molecular sieve filter did not improve the situation. However, a charcoal filter completely suppressed the spurious responses at all attenuations down to $\times 8$. At this attenuation, a few tenths of a picogram of lindane yielded a full-scale response without any undue additional signals.

We noted no detrimental effect from possibly increasing the amount of oxygen reaching the system (through back-diffusion of atmospheric air) after open

sampling. When conventional closed sampling and open sampling were compared with identical samples, no noticeable difference in the ECD responses was observed across the chromatograms.

Using a standard mixture of organochlorine pesticides, an excessive duration of the concentration step, on the moving needle, caused losses by evaporation for the monocyclic compounds (HCHs) and the chlordane derivatives (aldrin, etc.). Fig. 2 demonstrates the mechanism of ghost peak production when such losses are promoted with the SI closed. Thus in Fig. 2A, the moving needle was dipped into the oven for 2 sec and then immediately withdrawn: only constituents at the needle tip could vaporize and the chromatogram was normal. In Fig. 2B, the whole mass of the plunger was allowed to warm up; the black areas after the regular peaks originate from a lost fraction that recondensed onto the glass rod at a higher level in the SI.

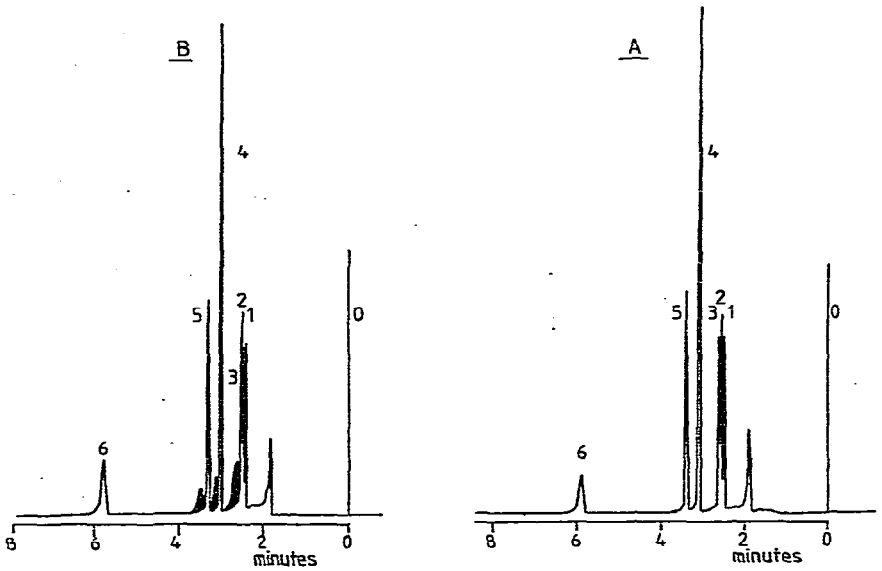

Fig. 2. Duplicate chromatogram demonstrating the origin of ghosts due to sample volatiles. (A) Plunger inserted for only 2 sec; (B) plunger left inside the oven. Peaks: 0 = injection; 1 = α-HCH; 2 = γ-HCH preceded by hexachlorobenzene; 3 = β-HCH; 4 = heptachlor; 5 = aldrin; 6 = p,p'-DDT (50 pg). Conditions: Soft-glass WCOT column, 19 m, SE-30 at 220°; argon carrier gas (inlet pressure 28 cmHg); injector purge flow-rate, 85 ml/min; amplifier attenuation, ×128.

A rugged commercial version of the SI, operated with open sampling, yielded the following overall performance data: column, 17 m SE-52 at 221° with helium carrier gas (inlet pressure 31 cmHg); efficiency for lindane (n_{theor}), 35,000 plates; sampling quality factor according to Kaiser[5], $Q_s = 0.81$.

Fig. 3 shows a rapid analysis of pesticides on a 6.5-m SE-52 column at 212° with helium carrier gas (inlet pressure 32 cmHg). These conditions have been adopted in our laboratory for the routine assay of N-hydroxy-2-fluorenylacetamide after two-step derivatization into N-chloro-2-fluorenylmonochloroacetamide[6].

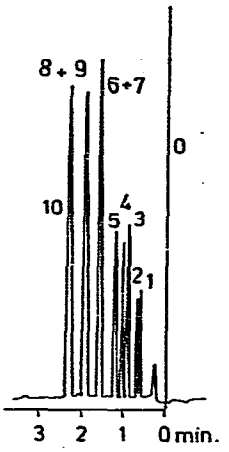

Fig. 3. Chromatogram of pesticides obtained on a 6.5-m SE-52 column at 212° with helium carrier gas (inlet pressure 32 cmHg); attenuation × 1024. Peaks: 0 = injection; 1 = α-HCH (33 pg); 2= lindane; 3 = heptachlor; 4 = aldrin; 5 = heptachlor epoxide; 6+7 = DDE + dieldrin; 8+9 = *p,p'*-DDD + *p,p'*-DDT; 10 = *p,p*-DDT.

Some overheating of the vaporization area, at the base of the SI, was found beneficial with biological extracts, leading to improved returns to the baseline. In contrast, inlet overheating was found to be unnecessary with model mixtures. To date, our routine analyses were carried out with a minimum of detector overheating (30° above the oven temperature), which yielded slightly sluggish but undistorted records. At 300° the chemical response of the ECD cell is perhaps more accurate as regards the fingerprinting of trace peaks.

We compared the present system with conventional packed columns connected to similar ECD cells. For practical purposes the sensivity limits are of the same order. During prolonged use with the open sampling method, the capillary system showed a high degree of baseline stability which considerably exceeded that of packed columns with an ECD operated with on-column injection of liquid samples. Interestingly, with argon–methane as the make-up gas we could not detect a change of ECD response after replacement of the capillary carrier gas (argon or argon–methane for helium).

DISCUSSION

The results support the view that the successful operation of the moving needle injector, with an ECD, requires more then mere extrapolation of the results obtained with the same injector and flame-ionization detection. It is perhaps safe to assume that all of the common carrier gas sources and delivery systems necessitate the use of an active pre-filter close to the SI inlet. It appears that active charcoal offers a simple means of trapping ECD-sensitive carrier contaminants at room temperature. For ECD work, especially with biological extracts, it seems essential to improve the cycle of the original solid injector by some means. Open sampling appears to represent an interesting addition to the choice of such means.

REFERENCES

1 J. J. Franken, R. C. M. de Nijs and F. L. Schulting, *J. Chromatogr.*, 144 (1977) 253.
2 J. J. Franken and J. A. Rijks, personal communication.
3 Publication No. 1206, Packard Becker, Delft, 1977.
4 J. Bouche and M. Verzele, *J. Gas Chromatogr.*, 6 (1968) 501.
5 R. E. Kaiser, *Chromatographia*, 9 (1976) 337.
6 C. Razzouk, E. Evrard, G. Lhoest, M. Roberfroid and M. Mercier, *J. Chromatogr.*, 161 (1978) 103.