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NOVEL APPROACHES TO THE DETERMINATION OF POLYCHLORINATED BIPHENYLS

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SUMMARY

A modified injection port is described that can be backflushed to prevent that either the solvent is introduced into the column or that high-boiling compounds can contaminate the capillary. Computer-aided recognition of chromatographic fingerprints is applied to identify samples. The performance of the system is demonstrated by analysing technical mixtures of polychlorinated biphenyls.

INTRODUCTION

In capillary gas chromatography, problems are very often caused by the large quantities of high-boiling compounds present in the sample. These compounds can contaminate the capillary, resulting in decreased resolving power of the capillary and lack of analysis precision.

To avoid such a contamination of the column, the compounds of interest must be separated from the undesired part of the sample. The usual approach for this separation would be to use a chemical method, *e.g.* solvent partition or extraction. These procedures are labour-intensive and time-consuming and also increase the danger of systematic and random errors.

MODIFIED INJECTION PORT

In the following, another approach is described for such an analysis. The usual split/splitless injection port of a Hewlett-Packard 5880A gas chromatograph was modified in such a way that it could be backflushed at a user-selectable time.

The modification was accomplished very simply[1] by using the commercially available parts of the split/splitless injection port (Hewlett-Packard 5880A-107) and replumbing the gas lines of the inlet system as shown in Fig. 1. The incoming carrier-gas flow was connected to the solenoid valve that, in the original configuration, switches the gas stream for the splitless capillary injection. The original carrier-gas supply-line was connected to the original septum-purge line via a tee, and the needle valve of the original septum purge was replaced by the pressure regulator and gauge.

The modified plumbing made it possible to reverse the direction of the gas stream in the glass-liner of the injection port, as indicated by the arrows in the flow

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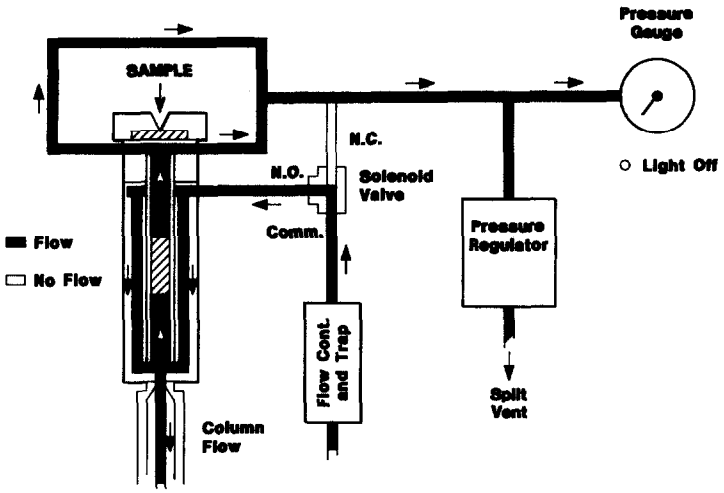

Fig. 1. Diagram of carrier gas flow before and after injection.

diagrams of Figs. 1 and 2. This glass-liner contained a small zone of 10% OV-1 on Chromosorb WHP, 100–120 mesh.

In the standby-mode, the injector is always backflushed so that contamination of the column cannot occur. In the injection mode (Fig. 2), the injector is flushed, and then the compounds that are vaporized from the packed zone according to their boiling points are introduced into the capillary. The fraction of the sample to be introduced into the column is selected by switching the solenoid to the "on-position". Thus, changing the inlet-gas-flow direction allows the user to decide whether he wants the solvent and low-boiling compounds to be purged on the column or whether he wants to backflush the high-boiling portion of the sample to prevent column contamination, or both.

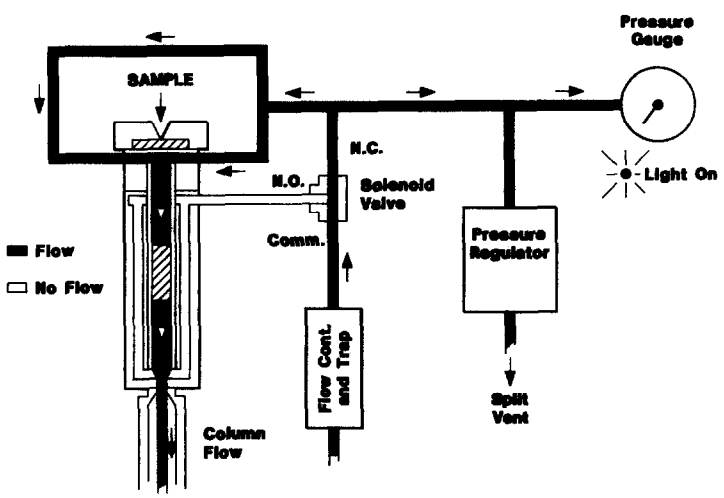

Fig. 2. Diagram of carrier gas flow during injection.

To demonstrate the feasibility of this modification to the injection port, a mixture of polychlorinated biphenyls (PCBs) was chosen as an example. This technical mixture was Clophen A60. Analysis of PCBs, in particular, is very often performed in samples such as transformer oil[2], dairy products[3,4], or food samples in general[5,6], where the high-boiling portion of the sample must, in many cases, be separated so as not to be detrimental for the capillary.

The following shows the influence of flush time on chromatograms of the Clophen A60 PCB mixture. The chromatographic conditions for these chromatograms were as follows: the instrument used was a Hewlett-Packard 5880A gas chromatograph equipped with a ^{63}Ni electron-capture detector, a dedicated cool on-column injector and a modified backflush injector; the column was a wall-coated open-tubular siloxane-deactivated fused-silica capillary, 25 m × 0.32 mm I.D.; the stationary phase was cross-linked methyl silicone with a film thickness of 0.17 μm; the carrier gas was helium with a flow-rate of 25 cm/s; the initial value for the oven temperature was 60°C (initial time 1 min), then the oven temperature was increased at a rate of 8°C/min to 100°C, when the rate was lowered to 4°C/min and the oven was heated up to 230°C (the final time at this temperature was 14 min).

For the first chromatogram no flush was applied, *i.e.* the solenoid valve was not switched on to reverse the flow. A 1-μl aliquot of *n*-hexane solution, containing 100 ppb of Clophen A60, was injected. No solvent peak occurred, demonstrating

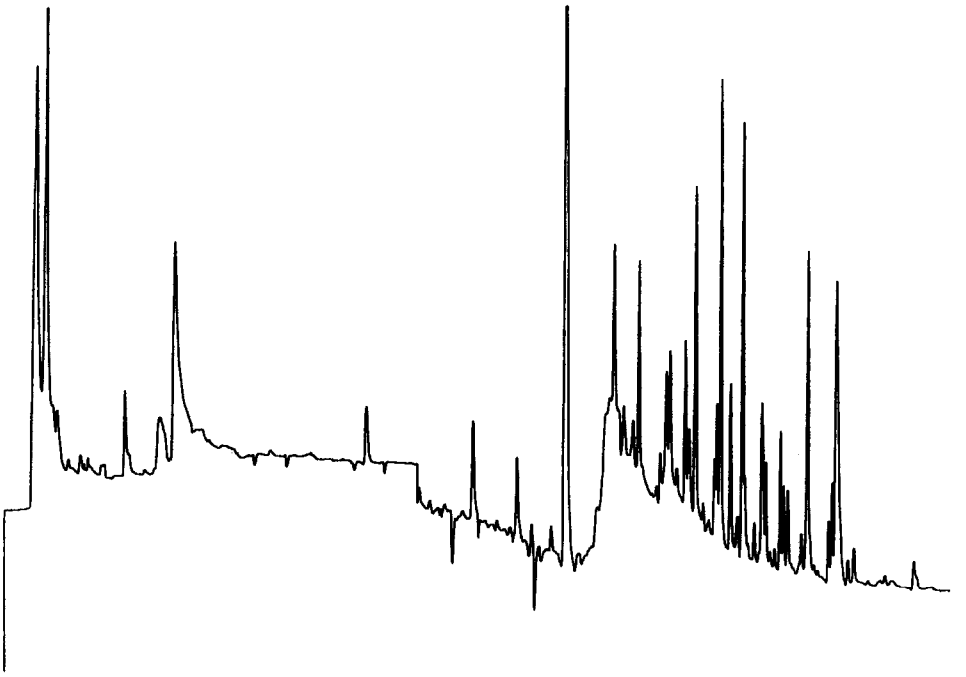

Fig. 3. Chromatogram of Clophen A60; injection via modified injection port; backflush after 1.0 min.

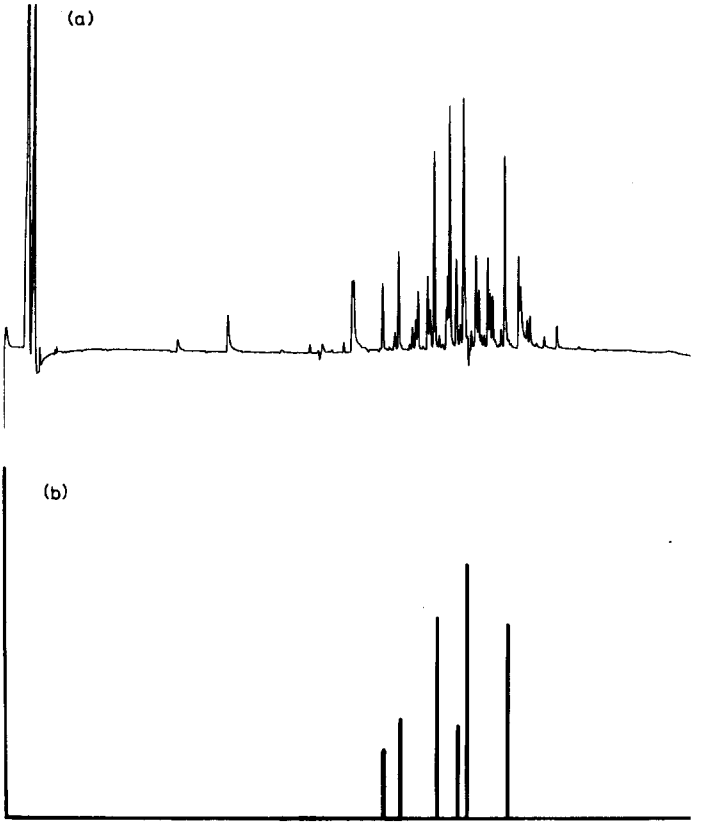

Fig. 4. (a) Chromatogram of Clophen A60; injection via dedicated cool on-column injection port. (b) Recognition templates for Clophen A60.

that no sample was purged on the column. The peaks in the chromatogram were the same as when no sample was injected and were mainly due to an improperly cleaned and unsilanized glass-liner.

For subsequent runs the flush was always turned on exactly at the beginning of the chromatogram and turned off after varied run times. When the injector was flushed for 0.1 min (6 s), the solvent peak was visible but no PCB peaks were seen. With increasing flush time, the PCB chromatograms became more and more complete and, after a flush time of 1 min (Fig. 3), all of the PCB peaks were seen and the peak ratios were the same as those obtained by cool on-column injection (Fig. 4).

AUTOMATED RECOGNITION OF CHROMATOGRAPHIC FINGERPRINTS

For computer-aided recognition of chromatographic patterns[7,8], the user chooses up to ten significant peaks of the chromatogram and defines certain limits for the retention time and peak ratios. The BASIC program for this is started after a run has been completed. It compares the actual report with calibration tables stored

on a cartridge tape unit. In this case, calibration tables for several technical mixtures of PCBs (Clophen A28, A30, A40, A50, A60) were created by running chromatograms of the pure mixtures and selecting characteristic peaks for their patterns. These calibration tables contain the recognition limits for the peaks of a pattern of interest defined by the user. If the compared peaks are within the given bounds, the identification match is confirmed. If one or more peaks are outside these bounds, the absolute deviation is determined and summed over all the peaks. If the sum is less than the specified recognition window, the match is also confirmed. The program compares the actual report with all the calibration tables stored on the cartridge tape.

Fig. 4b shows the recognition templates used to identify the Clophen A60 mixture. A typical program output (Fig. 5) contains the sample ID code and the recognition window that have to be specified by the user at the beginning of the program. The output confirms that a tentative match, which was done with the Clophen A60 calibration table, lies within the bounds given for this mixture.

Sometimes, when many samples are analysed, it may be useful to monitor the contents of the samples. Fig. 6 shows such a monitoring output obtained with a BASIC program for this gas chromatograph.

```
START PRGM

PR: 11:41  MAY 7, 1985

ENTER SAMPLE ID CODE  SAMPLE L/243/85
LIST REPORT FOR ALL TENTATIVE MATCHES (Y/N)?  N
ENTER RECOGNITION WINDOW  10

TENTATIVE MATCH WITH "CLOPHEN A 60"
CONFIRMED BY RELATIVE AREAS

IDENTIFICATION AND CALIBRATION REPORT FOR SAMPLE L/243/85

(HP) 5880A MANUAL INJECTION @ 10:54 APR 18, 1985
CLOPHEN A 60
NORM% COMPENSATED ANALYSIS

  RT      EXP RT       AREA     TYPE  WIDTH  CAL  AMOUNT   NAME

 0.00                    BASELINE @ START RUN = 755.75
 0.00                    THRESHOLD @ START RUN =  4
 0.00                    PEAK WIDTH @ START RUN = 0.04
 0.00                    RT: EXTEND RT --  ON
 0.00                    RT: INTG --  OFF
 0.00                    RP: BL MODE --  0
10.00                    RT: INTG --  ON
29.830   29.830         492.67 +  BV  0.154  1    6.323   PEAK A
31.057   31.057         759.18 +  VV  -----* 2    9.744   PEAK B
33.862   33.862        1433.31 +  VV  0.168  3   18.397   PEAK C
35.088   35.088        1861.38 +  VV  -----* 4   23.891   PEAK D
36.177   36.177        1910.32 +  VV  -----* 5   24.526   PEAK E
39.562   39.562        1333.76 +  PV  0.199  6   17.119   PEAK F
```

Fig. 5. Typical program output of the BASIC program for the recognition of chromatographic fingerprints.

```
TIME   DATE              CLOPHEN A 60
                         [  PPB  ]

07:48  APR 17             22.3
09:04  APR 17             58.9
10:07  APR 17            112.2 (*)
11:18  APR 17             81.5
12:43  APR 17             69.1
13:49  APR 17            123.0 (*)
14:56  APR 17             38.8
16:03  APR 17             50.9
17:14  APR 17             69.1

(*) AMOUNT EXCEEDS LIMIT


TIME   DATE              CLOPHEN A 60
                         1--------100
                           [  PPB  ]

07:46  APR 17            --
09:04  APR 17            -----
10:07  APR 17            --------- (*)
11:18  APR 17            -------
12:43  APR 17            ------
13:49  APR 17            --------- (*)
14:56  APR 17            ---
16:03  APR 17            -----
17:14  APR 17            ------

(*) ANALYSIS NOT IN SPECIFICATION
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Fig. 6. Typical outputs of the BASIC programs for level monitoring and trend monitoring.

CONCLUSION

The example given illustrates that the described modification of the injection port can prevent column contamination, thus lengthening the life-time of the capillary and helping to maintain the precision of the analysis. This is important, for example, in automated pattern recognition, where the reproducibility of the retention times is crucial. This automated recognition of chromatographic fingerprints can also be a valuable tool in many applications.

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