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CONCEPT FOR THE SAMPLING AND DERIVATIZATION OF PENTACHLOROPHENOL FROM AIR IN A CAPILLARY PRE-COLUMN, FOLLOWED BY GAS CHROMATOGRAPHIC DETERMINATION

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SUMMARY

Several litres of sample air are sucked through a capillary column a few metres long, coated with an apolar, immobilized stationary phase of optimized film thickness. The loaded column is attached as a pre-column in front of a separation column already hanging in the oven of the gaschromatograph. The separation column is coated with a thicker film of stationary phase than the pre-column in order to achieve a retention gap effect. The derivatization of pentachlorophenol is carried out in the pre-column by on-column injection of a derivatization reagent.

INTRODUCTION

Pentachlorophenol (PCP) is widely used to preserve wood and to kill woodworms. There is some concern about the concentration of PCP in the air of treated rooms.

Air samples are often analysed using traps containing Tenax or charcoal, with subsequent liquid or thermal desorption. The liquid desorption must occur off-line, and with PCP derivatization is desirable, which usually involves some 'wet chemistry'.

The thermal desorption of packed pre-columns is problematic because of the low carrier gas flow-rate through the trap if a splitless transfer is applied, as discussed, *e.g.*, by Adlard and Davenport[1].

Traps containing a packing material have an excessively high retention power for PCP during the sampling process. For thermal desorption this must be overcome by strong heating. We sought a more elegant method, using a length of capillary column as a trap to solve the problem of the flow-rates and adjusting the retention power (film thickness) of the trap such that cooling is not necessary during the sampling process and heating above the temperature of the separation column during the description (analysis) is not needed. As PCP is spread throughout the pre-column, a retention gap effect is required in order to reconcentrate PCP at the beginning of the separation column[2,3].

The pre-column (trap) is loaded on-site by sucking an air sample through it. After it has been brought back to the laboratory, the exit is attached, *e.g.*, with

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shrinkable PTFE tubing, to the separation column in the oven of the gas chromatograph and the inlet is connected with an on-column injector.

PCP was derivatized in the pre-column at the beginning of the gas chromatographic (GC) analysis. Street[4] introduced 'on-column' derivatisation in packed column GC. Christophersen *et al.*[5] used 'flash-heater' trimethylsilylation to form derivatives inside a vaporizing injector during splitless injection. The procedure proposed here for derivatizing PCP differs from these methods in that it allows a reaction in the coated, oven thermostated pre-column.

The key points of the proposed method are discussed separately first, then the resulting experimental setup is considered. This enables to point out the variable parameters, which may be optimized depending on the required sample volume, the columns available and some aspects of the analytical procedure to be specified.

DISCUSSION OF EXPERIMENTAL CONDITIONS

Pre-column

The pre-column used to sample PCP in air may be regarded as a GC column, run at ambient temperature with air as the carrier gas. Its sampling capacity is limited by the volume of air that is sucked through, rather than by the amount of PCP retained. The capacity is given by the migration speed of PCP; the pre-column is 'full' when the first PCP material arrives at the exit.

The pre-columns consisted of lengths of glass capillaries with an I.D. of 0.3 mm, coated with an apolar stationary phase (OV-1, SE-54, OV-73 or similar), which was immobilized (cross-linked) to facilitate the derivatization of PCP.

The retention power for PCP of a 1-m pre-column coated with a 0.15-μm thickness of OC-1 was determined with the help of a second pre-column in series, coupled with shrinkable PTFE tubing. Air that had passed through a flask containing a few crystals of PCP was sucked through the columns. The vacuum applied to the second pre-column by a water aspirator yielded a flow rate 0.9 l/h (15 ml/min). A series of experiments with different sampling times indicated that the first PCP material entered the second section of capillary column after 1.7 l of sampled air had passed.

Separation column

In the sampling procedure the pre-column is loaded with PCP throughout its length. During the derivatization some of the PCP is flushed forwards, but it does not change the fact that the initial band of the PCP is strongly broadened in space[2], resulting in broadened and distorted peaks if not reconcentrated before the start of the chromatographic process.

The retention gap was proposed for reconcentrating bands broadened in space as produced by on-column and splitless injection[3]. The band is reconcentrated because the retention power is reduced in the flooded column inlet compared with the main separating part of the column. For on-column and splitless injection it was proposed to remove the stationary phase completely from the inlet, which is flooded by the sample. However, the pre-column serving to sample PCP from air must have a certain minimum retention power which allows the PCP to be retained from a sufficient volume of air. Hence a reconcentration by the retention gap effect can only

be obtained by increasing the retention power of the separating column above that of the pre-column. This increase may be achieved by the use of a more polar stationary phase. However, for simplicity we shall restrict further discussions to the use of apolar stationary phases with an increased film thickness (the retention power of a column is proportional to the film thickness of the stationary phase). If a slight broadening of the PCP peak is accepted and if the separating column is at least 15 m long, an increase in the film thickness by a factor of five (and the corresponding reconcentration) is considered to represent an acceptable minimum.

Joint between the pre- and separation columns

It should be easy to join and disconnect the pre- and separation columns. At least for glass capillary columns a joint made with shrinkable PTFE is the method of choice. The two butts to be connected were fire-polished to round off the edges, then PTFE tubing about 20 mm long was shrunk on to them with a small burner. The pre-column was slipped out of the joint or moved within the joint before the PTFE was fully cooled to prevent the PTFE sticking to the glass.

The two columns should not be pulled apart because the plastic tubing is streched and forced more tightly on to the glass on pulling. It is preferable to strip the PTFE tubing off. The pre-column is held with two fingers of one hand near the joint and the edge of the PTFE tubing is pushed off the butt of the pre-column with the thumbnail of the other hand. To avoid uncontrolled moves by the hands, the force should not come from the arms, but from pushing the two thumbs apart from each other. It is easy to insert the pre-column back into the joint, as long as the sharp edges of the butt are rounded off.

The PTFE joints are thermostable up to about 235°C (depending on the column inlet pressure). At excessively high temperature the joint parts and the carrier gas blows into the GC oven. If hydrogen is used as the carrier gas, a hydrogen sensor, which checks the oven atmosphere for hydrogen, eliminates the risk of oven explosions (available, *e.g.*, from Brechbühler, Schlieren, Switzerland, or Carlo Erba, Milan, Italy).

Butt connectors (*e.g.*, Supelco or Carlo Erba) give a safe and technically perfect joint. However, their installation requires the column to be taken out of the GC oven.

Derivatization of PCP

PCP may be analysed as the free phenol, but it is strongly acidic and tends to be adsorbed also by forces other than acid–base interactions. Even if perfect PCP peaks are initially eluted from a column, there is some doubt about the duration of this performance. Especially if small amounts of PCP are detected by highly sensitive detectors, adsorption becomes a serious problem.

Two derivatives of PCP were found to be readily formed inside the column inlet (at ambient temperature): the acetate by injection of aceticanhydride–pyridine (1:1) and the methyl ether using diazomethane in diethyl ether.

Reagent was injected on-column in a volume that was adjusted to flow nearly as far into the pre-column as the PCP was distributed, ensuring reaction in the liquid phase, which is faster than that in the gas phase. The reaction time corresponds to the time required to evaporate the reactive material[6]. This time is relatively short in

the rear part of the flooded zone, but in this zone almost no PCP is left because the flowing reagent carries the PCP further into the pre-column.

If injected by the on-column technique, liquids of low viscosity as the reagents flow on a fully wettable surface of the column to a distance between 20 and 30 cm per microlitre of liquid[7]. The PCP beyond the flooded zone was found to be derivatised also, presumably owing to retention of the reagent in the stationary phase, which also dissolved the PCP (a process similar to phase soaking[6]). Therefore, it was not critical to find the volume of reagent which just fully flooded the pre-column.

To ensure complete methylation by the very volatile diazomethane, a solution of this reagent was injected three times at intervals of 1 min. The volume of reagent injected was increased by 0.3 μl each time to ensure that the second and third injections slightly exceeded the length of the flooded zone of the former injection. This improved the derivatization of the PCP that accumulated towards the front of the flooded zone.

To test the efficiency of the derivatization, a solution of 100 ppm of PCP in diethyl ether was prepared and 5 μl of this solution were diluted in 10 ml of diethyl ether or in the same volume of reagent. For the acylation the solution was heated for 1 h. The solution of the derivatized PCP served to indicate the peak area to be achieved by (on-column) injection of the free PCP in diethyl ether followed by injection(s) of the derivatization reagent. Recoveries exceed 95% for single injections of the aceticanhydride–pyridine mixture and triple injections of diazomethane.

If no on-column injector is available, the reagent is introduced into the pre-column on the laboratory bench or when connected to the separation column but before it is mounted in an injector (then just serving to supply the carrier gas). This is effected with an ordinary 10-μl syringe fitted to the pre-column with a piece of plastic tubing. If carried out on the laboratory bench, a vacuum should be applied to the exit of the pre-column to suck the reagent plug through it. The flow-rate due to the vacuum must be reduced by a restriction, *e.g.*, a capillary of dimensions around 30 m × 0.3 mm.

RESULTING EXPERIMENTAL SETUP

Design of the method

The parts of the method discussed above are interrelated and must fit together. However, as the needs of the analyst may vary, just as the columns and detection systems he has available, we shall point out the principles rather than giving a specific solution.

If a PTFE joint is used to connect the pre-column to the separation column, the maximum acceptable elution temperature of the derivatized PCP is 230–235°C, which limits the film thickness of the (apolar) separation column to 3 μm. If butt connectors are used (probably preferable for connecting fused silica to fused silica) thicker films and/or more polar stationary phases may be used to increase the sensitivity of the method further.

A number of parameters may be optimized to increase the sensitivity of the method by increasing the sample size (air volume). For this discussion, the separation column is assumed to be coated with an apolar stationary phase of 3 μm film thickness (as used in our experiments). The film thickness of the pre-column must be five

times lower than that of the separation column (0.6 μm). As the GC retention power is proportional to the film thickness of the stationary phase (assuming a constant inner diameter of the columns), this pre-column allows four times more air to be sampled than the pre-column tested, *i.e.*, 6.8 l per metre length of the pre-column.

The pre-column may be lengthened with a proportional increase in sample capacity. A 4 m × 0.3 mm I.D. pre-column (0.6 μm film thickness) is able to retain PCP completely from more than 20 l of air. However, the increased length of the pre-column reduces the flow-rate of the air and inncreases the sampling time for a 20-l volume to between 20 and 30 h.

The sampling time may be reduced by the use of wide-bore pre-columns, which allow a higher flow-rate. However, the retention power at a constant film thickness decreases by the same factor as the inner diameter of the pre-column increases. This may be balanced by increasing the film thickness.

There is no need to use main columns with an inner diameter identical with that of the pre-column. However, in order to retain a five-fold higher retention power (phase ratio β to include the influence of the inner diameter of the column) in the main column than in the pre-column, the film thickness of the separation column must be further increased by the same factor as its inner diameter is reduced compared with the pre-column.

It should be remembered that excessively high flow-rates through the pre-column during the sampling process reduce the sample capacity. Hence the reduction in the sampling time by using wide-bore pre-columns is limited.

Finally, the retention power of the pre-column may be increased by cooling. The retention power (sample capacity) doubles for each 15°C the temperature is lowered below 25°C, until the temperature is reached at which the stationary phase starts to behave as a solid rather than a liquid.

This discussion shows the limitations of the method. However, it is not usually of interest to exploit the maximum possible sample capacity. In the air of rooms containing freshly PCP-treated boards, several nanograms of PCP per litre were found (ref. 8 and our own determinations). This allows the method to be made easier to use, *e.g.*, by reducing the sampling time, using more readily available columns or using a lower elution temperature.

The detection of PCP derivatives was more difficult than expected. Flame ionization detection (FID) is neither very sensitive nor sufficiently specific to allow positive identification of PCP in all samples. Electron-capture detection (ECD) is more selective and far more sensitive. However, impurities, probably mainly from the derivatization reagents, and column bleeding caused considerable problems. Mass spectrometry might be detection method of choice for difficult samples, whereas FID is sufficient for other cases (see below).

Practical example

PCP was determined in the air of a room containing a few square metres of boards that had been treated with PCP nearly 2 years earlier.

A 2-m lenth of glass capillary column coated with 0.6 μm of SE-54 was used as a trap, through which 10 l of air were drawn at 20 ml/min (20°C). The separation column (20 m × 0.33 mm I.D., coated with 3 μm of SE-54) was first equipped with a short inlet piece (attached with shrinkable PTFE tubing) to be cleaned by heating,

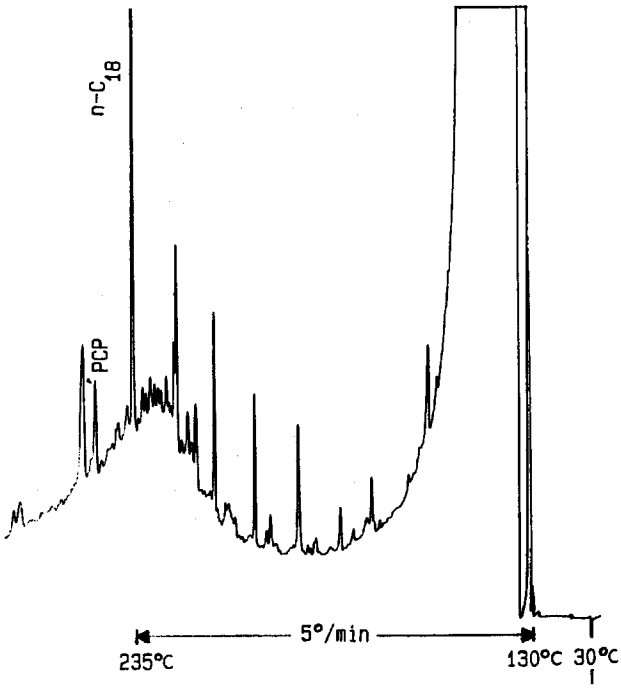

Fig. 1. Chromatogram of an air sample (10 l) from a room containing boards that had been treated with PCP nearly 2 years earlier. *n*-Octadecane (n-C_{18}) was injected as an internal standard. Flame-ionization detector. The PCP concentration was calculated to be 0.6 ng/l.

then the trap was connected to the separation column. A 1.μl volume of *n*-octadecane (10 ppm in *n*-hexane) was injected to serve as an internal standard for quantitation and peak identification. After 1 min, 1 μl of aceticanhydride–pyridine (1:1) was injected on-column into the pre-column (25°C). The oven temperature was increased 4 min after the injection to start the temperature programme (see Fig. 1). FID was used.

The concentration of PCP in the sampled air was found to be 0.6 ng/l.

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