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Short Communication

Simple method for preventing unsuitable solvents from entering gas chromatographic detectors

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Abstract

A simple method for preventing unsuitable solvents and other substances from entering gas chromatographic detectors is described. A split vent was constructed by connecting the outlet of the column to the unused injector and the detector with a press-tight Y-splitter and two short capillary columns. Unsuitable solvents and other substances can be discharged through the unused injector by keeping the injector open for a few minutes. When the nut on the injector is tightened, all the effluent from the analytical column enters the detector. Use of this split vent can avoid or reduce the adverse effects of unsuitable solvents on the detector performance.

1. Introduction

Many gas chromatographic (GC) detectors are used with unsuitable solvents. Electron-capture detectors are not suitable for samples that involve solvents containing halogen or nitro groups [1], and solvents containing nitrogen or phosphorus, such as acetonitrile and dimethylformamide, are not suitable for nitrogen–phosphorus detectors. Water is a very difficult solvent for GC owing to its high surface tension, the very large volume of vapour produced per unit volume of the liquid and the poor properties concerning solvent effects. In addition to the problems with the influence on injection techniques [2] and the column lifetime, water is also an unsuitable solvent for many detectors [1,3]. Water may upset electron-capture detectors. Samples containing large amount of water may also damage the rubidium salts of nitrogen–phosphorus detectors.

The most common approach to avoid the effects of unsuitable solvents on detectors is to replace them with more suitable solvents during sample preparation. For instance, in some methods that use dichloromethane to extract pesticides from water, dichloromethane is removed by evaporation and the extract residue is then dissolved in hexane before being analysed by GC with electron-capture detection (ECD). Some valve systems have also been used for this purpose [2,4,5]. Switching valves are installed either between the outlet of the column and the detector inlet or between two columns, using the first column to produce a retention gap. Unsuitable solvents can also be discharged by using a temperature-programmed injection port [6]. The retention gap between the solvent and the analytes is created by keeping the temperature relatively low at the beginning and then rapidly increasing it. Simmonds and Kerns [7] used a permselective membrane to remove water selectively prior to the sample entering the chromatographic column. The problem with this method is

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that different membranes are required for different solvents and analytes.

Most gas chromatographs are not installed with the above-mentioned valve systems when they are purchased, and it is not easy to select suitable valves and to install them in the instruments. This paper describes a simple method that can be easily adopted to avoid or minimize the adverse effects of unsuitable solvents and other substances on GC detectors. The method uses a Y-splitter and the unused injector in the instrument to construct a split vent. Unsuitable solvents and other substances can be discharged through this split vent before the sample enters the detector.

2. Experimental

2.1. Instrumentation

The construction of the split vent is shown in Fig. 1. The outlet of the analytical column is connected to the detector and injector B by a Y-splitter and two very short capillary columns. The dimensions are 10 cm × 0.53 mm I.D. for the column between the Y-splitter and injector B and 25 cm × 0.32 mm I.D. for the column between the Y-splitter and the detector. The press-tight Y-splitter was purchased from Hewlett-Packard (Avondale, PA, USA). Capillary columns with different diameters can be fitted into the splitter by gently pressing the column against the splitter. When the nut on injector B is fully loosened, all the effluent from the analytical column is discharged through injector B. When injector B is closed, all the effluent enters the detector. Unsuitable solvents can be discharged through injector B by keeping the nut on injector B fully open for several minutes. The time elapsed can be monitored using the clock installed on the instrument. When a HP-5890A gas chromatograph was used, the septum in injector B was cut smaller so that it would not stick to the mouth of the injector when the nut was loosened.

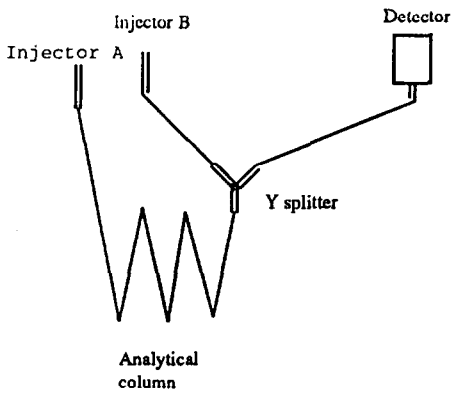

Fig. 1. Schematic diagram of the instrumental set-up.

An HP-5890 Series II gas chromatograph equipped with an electron-capture detector was used for estimating the split vent.

2.2. Gas chromatography

The pesticides lindane and methyl parathion dissolved in methanol and methanol–water (7:3) at a concentration of 1 μg ml^{-1} were determined by GC–ECD. An HP-1 capillary column (12 m × 0.2 mm I.D.) was used for isolation. The oven temperature was programmed from 130°C (held for 1.0 min) to 250°C at 15°C min^{-1}. The injection volume was 1 μl.

3. Results and discussion

When the nut on injector B was fully loosened, the effluent from the analytical column was distributed between injector B and the detector. According to the flow-rate measurement, the ratio was about 12:1 at room temperature, that is, about 92% of the effluent was discharged through injector B. When the oven temperature was increased to >60°C, no effluent entered the detector. The flat baseline at the solvent peak positions on the chromatogram (Fig. 2B) also indicates that no effluent entered the detector.

The relationship between the gas flow-rate (F) and the column dimensions can be described as

$$F = 3.14\Delta PD^4/32\eta L \quad (1)$$

Fig. 2. Chromatograms of lindane (retention time = 7.4 min) and methyl parathion (retention time = 8.1 min) dissolved in methanol–water (7:3) obtained on an HP-5890 II gas chromatograph equipped with an electron-capture detector, (A) without using the split vent and (B) with the split vent. The oven temperature was programmed from 130°C (held for 1.0 min) to 250°C at 15°C min^{-1}.

where ΔP is the difference in pressure between the inlet and outlet of the column, D and L are the inner diameter and length of the column, respectively, and η is the viscosity of the gas [8]. Therefore, the distribution ratio of the effluent between injector B and the detector can be calculated using the equation

$$F_1/F_2 = D_1^4 L_2 / L_1 D_2^4 \quad (2)$$

The result obtained is 15:1 under the conditions used. The change in the ratio when the temperature was increased was unlikely to be due to thermal expansion of the columns, as quartz has a very low thermal expansion coefficient (*ca.* $5 \cdot 10^{-7}$ $°C^{-1}$). The effect of temperature on the distribution ratio might be due to other factors.

The influence of the split vent on the accuracy and the instrument performance were studied with pesticide solutions. The results, given in Table 1, indicate that the use of the split vent did not affect the accuracy and reproducibility of the analysis when a sample using pure methanol as solvent was analysed. This is reasonable, because the carrier gas from the analytical column accounts for only 3% of the total gas flow of the detector (the rest is the make-up gas), so the interruption of the carrier gas flow should not have a noticeable effect on the detector performance. When the solvent of the sample contained 30% of water, discharging the solvent before the sample entered the detector was able to prevent the adverse effects of water on the detector response and the reproducibility. Without using the split vent, the average peak area was smaller and the relative standard deviation was larger. The chromatograms in Fig. 2 were obtained by injecting lindane and methyl parathion dissolved in methanol–water (7:3) with and without using the split vent. They suggest that the use of the split vent will not affect the retention time of the analytes.

Table 1
Effect of the split vent on the response of an electron-capture detector to lindane and reproducibility of the analysis

Sample solvent	Split	Mean response[a] (μV s)	R.S.D. (%)
Methanol	Yes	2 287 202	6.26
Methanol	No	2 340 731	5.42
Methanol–water (7:3)	Yes	2 289 558	7.23
Methanol–water (7:3)	No	1 863 029	13.5

[a] Mean of four replicates.

In addition to direct analysis of samples containing unsuitable solvents, the split vent may be used to prevent other unsuitable substances from entering detectors, provided that there is an appropriate retention gap between the substance and the analyte. The split vent is also useful in column conditioning. Column bleeding can be discharged from injector B without disconnecting the column from the detector.

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