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Note

Detection of arson accelerants using dual wide-bore bonded-phase capillary columns and static headspace sampling

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The use of gas-liquid chromatography (GLC) as an analytical tool for the detection of arson accelerants in fire debris samples has been an established technique for over 20 years^{1,2}. Heated headspace sampling followed by GLC has become one of the more common techniques for initial screening of this type of evidence³⁻¹¹. Other techniques have also been used to detect the presence of accelerants such as solvent extraction¹, steam distillation^{12,13}, and sorbent concentration followed by thermal desorption¹⁴⁻¹⁹ or elution with an organic solvent²⁰⁻²⁵. All of the techniques yield samples which are then injected into a gas chromatograph for analysis yielding chromatograms which can be compared to known standards to detect and identify the presence of an accelerant.

The ease of sample preparation, the speed with which a large number of samples can be analyzed, and the versatility of handling different types of evidence, permit heated headspace sampling followed by GLC to be a very attractive and practical technique for accelerant detection. Historically packed columns have been used for this type of analysis because of the wide concentration range and variety of accelerants encountered. The availability of wide-bore (0.75 mm I.D.) capillary columns and their increased sample capacity, as compared to the traditional narrow-bore capillary columns, has permitted their use in the analysis of accelerants by heated headspace GLC²⁶.

The most important advantage of the wide-bore capillary column is the ability to inject samples with a component mass of up to 15 μg directly onto the column and still obtain high column efficiency (*i.e.* 25 000 plates)²⁷. The wide concentration range and variety of accelerants possibly present in real samples make the increased capacity an attractive quality in column selection for arson analysis.

In a previous report we have shown that wide-bore capillary columns can be a viable alternative to packed columns when performing heated headspace analysis of arson accelerants²⁸. We now report the use of a dual wide-bore capillary column configuration with a single injection, a single chromatographic oven and dual flame-ionization detection (FID) to perform routine accelerant analysis.

EXPERIMENTAL

A Varian 3700 gas chromatograph equipped with dual flame ionization detectors was utilized throughout the investigation. SPB-1 and SPB-35 bonded phase glass capillary columns (30 m \times 0.75 mm I.D. with a 1.00- μ m film thickness) were used for the analyses. The columns (purchased from Supelco, Bellefonte, PA, U.S.A.), were glass columns mounted on protective metal cages which incorporated two capillary column butt connectors that connected each end of the glass column to lengths of flexible, deactivated 0.32 mm I.D. fused silica tubing. Deactivated glass sleeves (0.25 in. O.D. \times 0.75 mm I.D. \times 4 in.) were inserted into the detector ports and a deactivated glass tee (0.25 in. O.D. \times 0.75 mm I.D.) was inserted into the injection port with the proper connections to the capillary reducer unions. Helium carrier gas and helium make-up gas were set at 6 ml/min and 30 ml/min, respectively.

The operating conditions are given with the figures. All samples were prepared by placing known amounts of liquid accelerants on a clean Kimwipe and placing it in a clean one gallon paint can. All of the standard accelerants were purchased from common commercial sources and analyzed as received. The gallon paint cans were punctured with a nail punch and covered with filament reinforced tape. The samples were placed in an oven at 100°C for 30 min, removed and appropriate headspace samples were taken with clean disposable 1-ml syringes.

RESULTS AND DISCUSSION

The use of a single injection onto dual packed GLC columns has been reported previously²⁹. In this particular report the authors used a single all glass inlet system where the analysis mixtures were transferred onto two packed glass columns with liquid phases of different polarity. We have tried a similar approach, except we have used wide-bore (0.75 mm I.D.) capillary columns with liquid phases of differing polarities and have applied the technique to routine accelerant detection. The advantages of having two columns of different polarity is obvious. It gives the analyst two different patterns of a complex mixture to compare to a control sample. It may also make the identification of unknown accelerants much easier if the matrix to which the accelerant is adhering is giving interfering peaks. In either case it gives the analyst more information on which to base the identification with no loss in sample or increased effort.

We chose to use the SPB-1 and SPB-35 wide-bore bonded phase capillary columns. The SPB-1 was selected because it is a non-polar column similar to the SP-2100 and OV-101 phases. These phases are commonly used for the detection of accelerants²⁸. The SPB-35 column is an intermediate polarity wide-bore column similar to OV-1701, DC-710 and OV-11³⁰. We wanted a more polar column which would give a different and distinct pattern for the complex mixtures but yet would be reproducible. We have found the SPB-35 column to be satisfactory in these aspects.

Figs. 1 and 2 show the separation of a headspace sample of gasoline on both the SPB-1 and SPB-35 columns, respectively. Gasoline was chosen because it is the most frequently encountered accelerant submitted to a forensic laboratory. The different patterns for the gasoline sample are obvious. The more polar SPB-35 column shows improved resolution of the more volatile components in the gasoline mixture

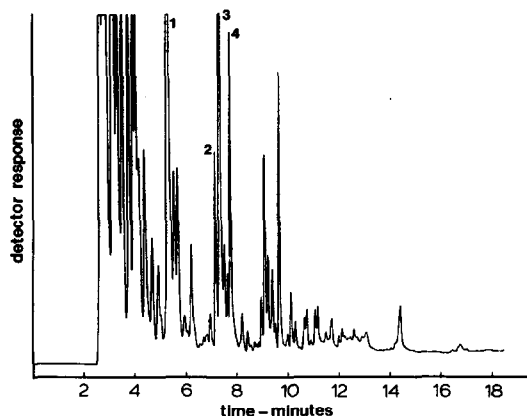


Fig. 1. Chromatogram of a 1-ml headspace sample of gasoline ($10 \mu\text{l/gallon}$) on a $30 \text{ m} \times 0.75 \text{ mm I.D.}$ SPB-1 bonded-phase glass capillary column. Column oven temperature programmed: 40°C for 3 min, 12°C/min up to 250°C ; FID temperature 280°C ; injection port temperature 250°C ; helium carrier and make-up gas. Peaks: 1 = toluene; 2 = ethylbenzene; 3 = *m*- and *p*-xylene; 4 = *o*-xylene.

as compared to the less polar SPB-1 column. However, the SPB-1 column shows improved resolution of the xylenes and ethylbenzene over the SPB-35 column. Retention times, in general, are longer on the more polar SPB-35 column. For example, toluene is eluted at approximately 10 min on the SPB-35 column, while on the SPB-1 column it is eluted at approximately 6 min. This can be seen even more dramatically in Figs. 3 and 4, which are chromatograms of headspace samples of kerosene on the SPB-1 and SPB-35 columns, respectively. The retention times of the straight chain hydrocarbons $\text{C}_9\text{--C}_{16}$ can be seen to be longer on the SPB-35 column than on the SPB-1 column. However, the resolution of the smaller peaks which fall between the straight-chain hydrocarbons is much better on the SPB-1 column. The "bell-shaped"

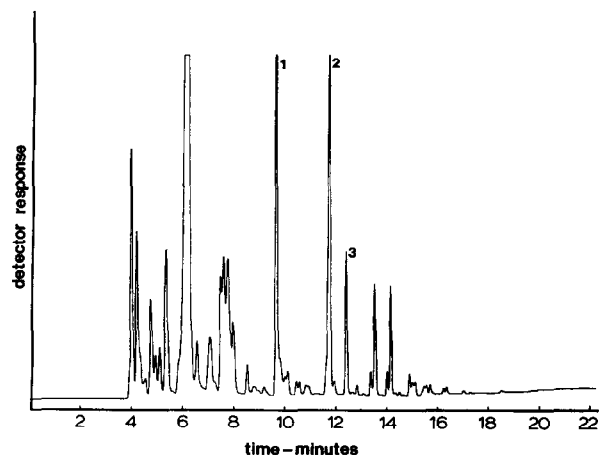


Fig. 2. Chromatogram of a 1-ml headspace sample of gasoline ($10 \mu\text{l/gallon}$) on a $30 \text{ m} \times 0.75 \text{ mm I.D.}$ SPB-35 bonded-phase glass capillary column. Column oven temperature programmed: 40°C for 3 min, 12°C/min up to 250°C ; FID temperature 280°C ; injection port temperature 250°C ; helium carrier and make-up gas. Peaks: 1 = toluene; 2 = ethylbenzene, *m*- and *p*-xylenes; 3 = *o*-xylene.

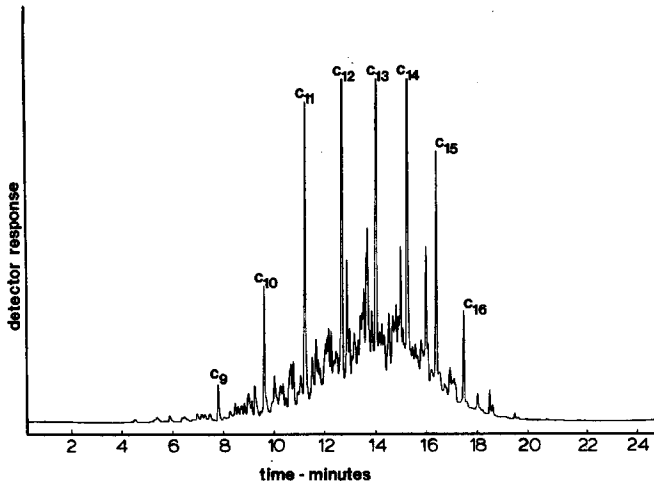


Fig. 3. Chromatogram of a 1-ml headspace sample of kerosene (10 μ l/gallon) on a 30 m \times 0.75 mm I.D. SPB-1 bonded-phase glass capillary column. Column oven temperature programmed; 40°C for 3 min, 12°C/min up to 250°C; FID temperature 280°C; injection port temperature 250°C; helium carrier and make-up gas.

curve characteristic of kerosene can readily be seen on both the SPB-1 and SPB-35 columns.

The minimum detectable levels (MDLs) of the accelerants tested were similar to the values we have previously reported for the single wide-bore column configuration²⁸. The reproducibility of the chromatograms from day to day was excellent for both columns. The retention times of the components of the common accelerants examined did not vary significantly when changing from a single column configuration to the dual column configuration. The chromatograms achieved by using a

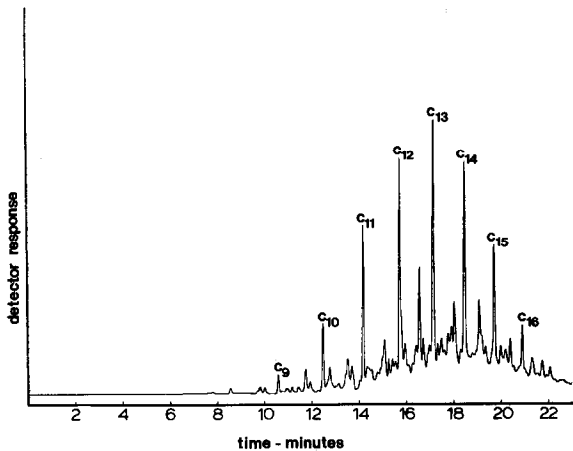


Fig. 4. Chromatogram of a 1-ml headspace sample of kerosene (10 μ l/gallon) on a 30 m \times 0.75 mm I.D. SPB-35 bonded-phase glass capillary column. Column oven temperature programmed: 40°C for 3 min, 12°C/min up to 250°C; FID temperature 280°C; injection port temperature 250°C; helium carrier and make-up gas.

single column configuration were essentially superimposable on the chromatograms achieved when using a dual column configuration.

In conclusion, the detection of arson accelerants using static headspace sampling and GLC with dual wide-bore bonded phase capillary columns can be performed routinely. This can be accomplished with one injection, dual flame ionization detection, and with the same gas chromatographic oven under the same chromatographic conditions. The extra column gives the analyst additional information with no loss in sensitivity or reproducibility.

Employing wide-bore capillary columns in other combinations of differing polarities may offer solutions to various types of separation problems. Using wide-bore capillary columns gives the analyst the advantage of solving these problems with increased sample capacity similar to packed columns while still preserving the resolution of capillary columns. The use of bonded-phase columns prolongs the life of the columns which is an important feature when sampling unknown complex mixtures of varying concentrations.

The advantage of being able to inject samples of large component masses with one injection onto two columns and still obtain capillary column efficiency with no loss in sensitivity offers the analyst an attractive alternative to the more commonly used single packed column configuration.

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