CHROMSYMP. 662

DETERMINATION OF TRACE CHLORINATED BENZENES IN FUEL OIL BY ON-LINE MULTIDIMENSIONAL CHROMATOGRAPHY USING PACKED-CAPILLARY LIQUID CHROMATOGRAPHY AND CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The application of a multidimensional chromatography system with a packed-capillary liquid chromatographic (LC) column, coupled on-line with a capillary gas chromatograph, for the determination of trace chlorinated benzenes in fuel oil is described.

The liquid chromatograph is utilized as a highly efficient clean-up step prior to introduction of the sample into the gas chromatograph. This significantly reduces sample preparation times and demonstrates that an on-line high-resolution LC–gas chromatography (GC) system is superior to either LC or GC alone, since the analyses described could not be accomplished by either of the two techniques used independently. The detection limits obtained ranged from 8.0 to 17 μg/g for the various chlorinated benzenes.

INTRODUCTION

The determination of minor components in complex hydrocarbon matrices can be accomplished by techniques that involve extensive preseparation procedures, such as liquid–liquid extraction[1], derivatization prior to gas chromatographic (GC) separation, and mass spectrometric detection[2], or by the use of element-selective detectors, such as the nitrogen–phosphorus detector[3] or Hall conductivity detector[4] if the components of interest contain detectable functional groups.

Multidimensional open tubular GC systems, in which a selected cut, eluted from one column is switched into a second column of different selectivity (heart cutting) have already been described[5,6]. More recently, the use of a multidimensional process, consisting of liquid chromatography (LC) and GC was reported for the characterization of gasoline[7]. However, using conventional LC columns, only small fractions of a peak could be introduced into the gas chromatograph. The present work describes the use of an on-line multidimensional system, consisting of highly efficient, packed-capillary LC columns, coupled with a capillary gas chromatograph[8] and its application to the determination of trace chlorinated benzenes in fuel oil. The use of this system allows complete fractions of the LC effluent to be introduced

reproducibly into the capillary gas chromatograph without loss in resolution or detrimental effects on peak shape.

EXPERIMENTAL*

The system used is essentially the same as that described previously[8], where the liquid chromatograph consisted of a Jasco Uvidec II detector with a modified cell with an illuminated volume of 6 nl. Injections were made with a Valco Model N14W injection valve (Valco, Houston, TX, U.S.A.). Injection volumes were 60 nl. The solvent delivery system consisted of a Waters Model M-45 pump, equipped with a micro-flow module (Waters Assoc., Milford, MA, U.S.A.); the flow-rate was 10.6 μl/min. The columns were constructed of fused-silica capillaries with an internal diameter of 250 μm (Spectran, Sturbridge, MA, U.S.A.), 105 cm long. Columns were packed with Zorbax (DuPont, Wilmington, DE, U.S.A.) silica (particle diameter, 7 μm) at 6000 p.s.i. in a 20% (w/v) slurry in methyl iodide–pentane (1:1). The LC mobile phase used through this work was heptane (distilled-in-glass, Burdick & Jackson, Muskegon, MI, U.S.A.).

The GC system consisted of a Hewlett-Packard Model 5790 chromatograph, equipped with a flame-ionization detector. Connection of the micro liquid chromatograph to the gas chromatograph was made with a ten-port valve (Valco Model 4NI10WT) to keep the dead-volume to a minimum. The valve was installed outside of the oven cabinet. An inlet section of the fused-silica capillary column, free of stationary phase, was connected between the switching valve and the analytical column. This retention gap, as previously described[9], effectively focused the components of interest at the head of the column and allowed the introduction of large volumes into the capillary GC column without detrimental effects on the peak shape of the components. A glass-lined stainless-steel butt connector (Scientific Glass Engineering, Austin, TX, U.S.A.) was used to couple the retention gap to the analytical column with essentially no dead-volume.

The analytical column used was a 30 m × 0.25 mm I.D. column, coated with Supelcowax 10 of 0.25 μm thickness (Supelco, Bellefonte, PA, U.S.A.). The carrier gas was helium at a linear velocity of 70 cm/s. Nitrogen at 30 ml/min was used as the make-up gas for the flame-ionization detector, operated at 275°C. The oven temperature was 105°C for 7 min, with a temperature programme to 245°C at 5°C/min.

The resolution obtained with packed-capillary LC was compared to that obtained with a conventional system, which consisted of a Altex Model 110A pump, a Rheodyne Model 7125 injection valve, equipped with a 20-μl loop, a Perkin-Elmer LC-75 variable-wavelength ultraviolet detector, a Hewlett-Packard Model 3380 integrator, and a 250 × 4.6 mm I.D. Partisil-10 silica column (Whatman, Hillsboro, OR, U.S.A.). The eluent consisted of heptane, at a flow-rate of 2.0 ml/min. The detector was set at 214 nm.

DISCUSSION

A standard, containing the chlorinated benzenes of interest (chlorobenzene,

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* The method and apparatus described in this publication are the subjects of pending patent applications.

1,2-dichlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, pen-
tachlorobenzene, and hexachlorobenzene) at concentrations of 50–100 μg/10 ml, was
prepared and injected into the conventional LC system described in the Experimental
section. A sample of the fuel oil, prepared by dissolving 1.00 g in 10.0 ml of heptane,
was analyzed in the same manner. Fig. 1 shows the chromatograms obtained. As can
be observed, only hexachlorobenzene could be marginally separated from the sample
matrix. A standard solution of the chlorobenzenes (500–1000 μg/10 ml) and the so-
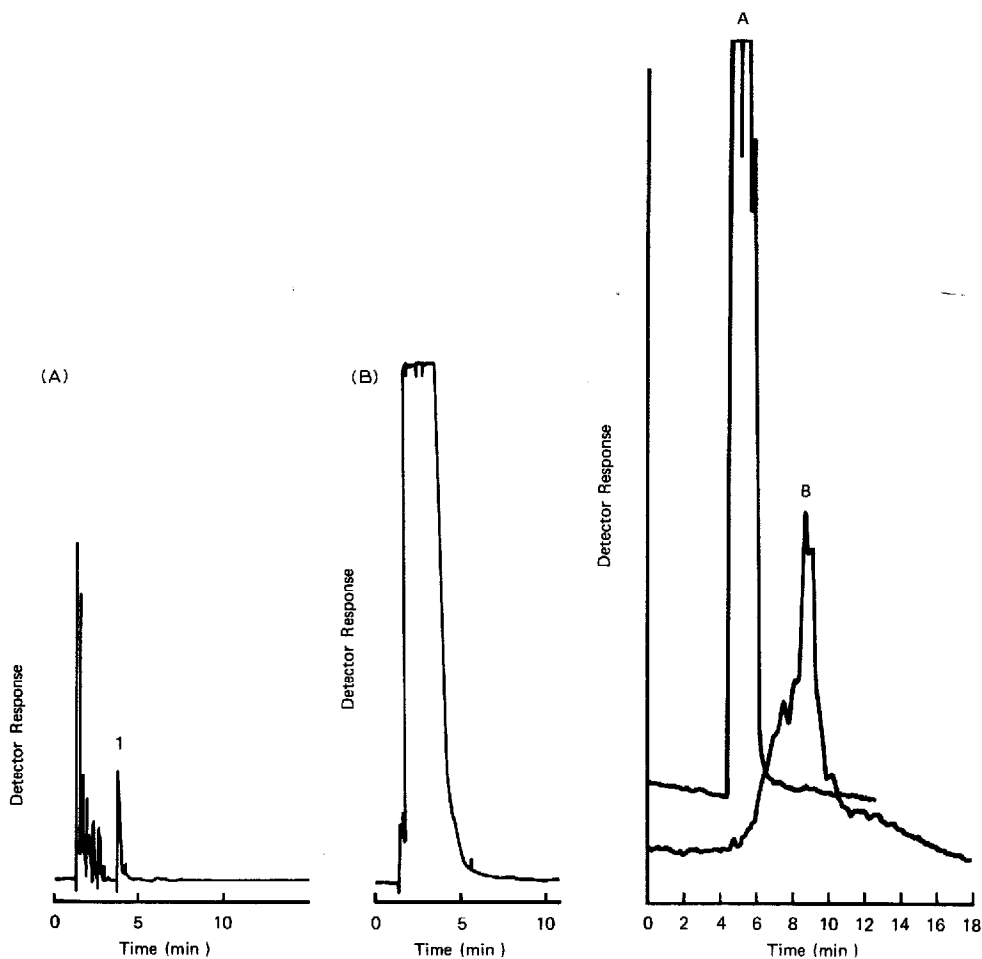lution of fuel oil were then injected into the packed-capillary LC system. Fig. 2 shows

Fig. 1. Chromatograms of chlorinated benzenes (A) and fuel oil sample (B) on conventional system. 1
= Hexachlorobenzene. Column, Whatman Partisil-10 (250 × 4.6 mm I.D.); mobile phase, heptane; flow-
rate, 2.0 ml/min; UV at 214 nm; pressure, 1000 p.s.i.; standard, 50–100 μg/10 ml; sample, 1.00 g/10 ml
heptane.

Fig. 2. Chromatograms of chlorinated benzenes (A) and fuel oil sample (B) on a packed-capillary column.
Column, 105 cm × 250 μm I.D., packed with Zorbax silica (particle diameter, 7 μm); mobile phase,
heptane; flow-rate, 10.6 μl/min; detector, Jasco Uvidec II at 214 mm; pressure, 3800 p.s.i.; standard,
500–1000 μg/10 ml.
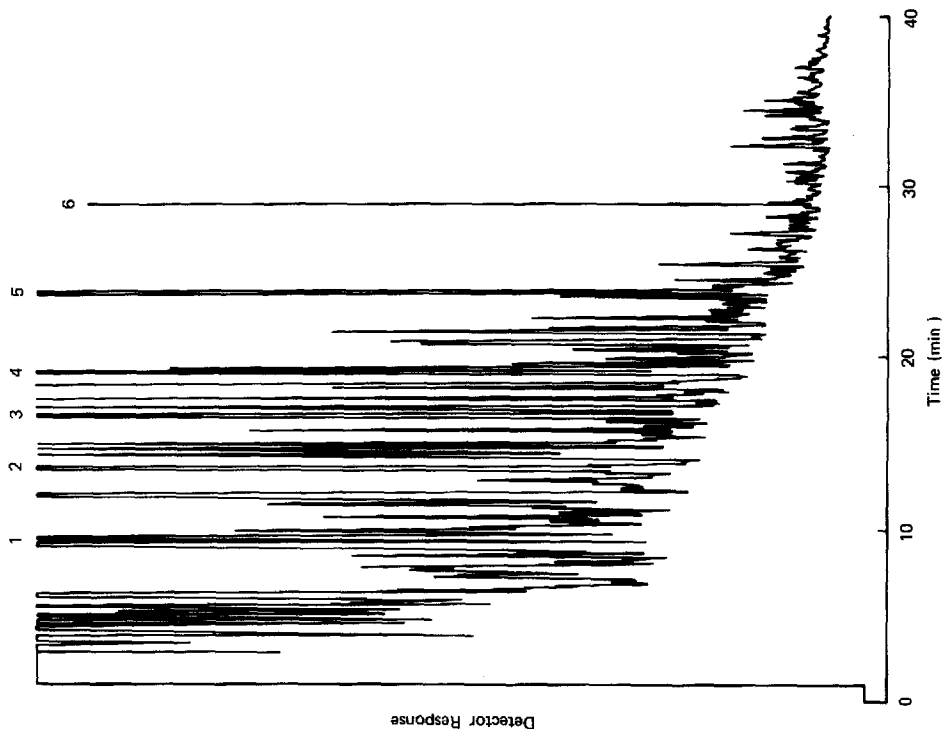
Fig. 3. Capillary gas chromatogram of fuel oil. Column, 30 m × 0.25 mm I.D. Supelcowax 10 ($d_f = 0.25$ μm); retention gap, 15 m × 250 μm I.D. fused silica; oven temperature, 105°C for 9 min, programmed to 245°C at 5°C/min; carrier, helium at 70 cm/s; make-up gas, nitrogen at 30 ml/min; detector, flame-ionization detector at 275°C; sample size, 10 μl.
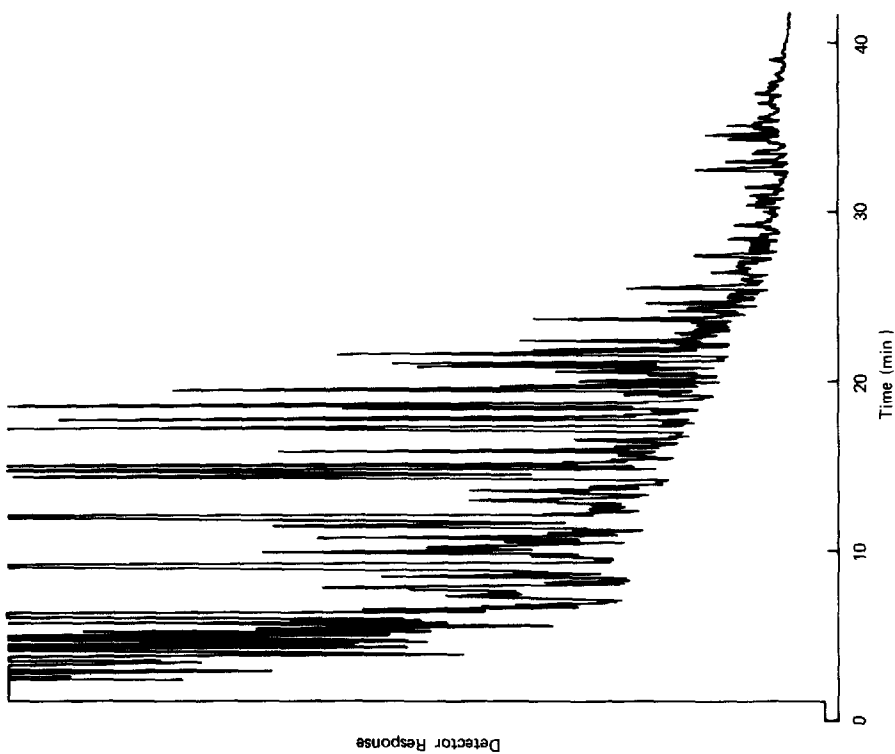
Fig. 4. Capillary gas chromatogram of fuel oil, spiked with chlorobenzenes. Conditions as in Fig. 3. Peaks: 1 = chlorobenzene; 2 = 1,2-dichlorobenzene; 3 = 1,2,4,5-tetrachlorobenzene; 4 = 1,2,3,4-tetrachlorobenzene; 5 = pentachlorobenzene; 6 = hexachlorobenzene.

the chromatograms obtained. The chlorobenzenes were separated from the majority of the components in the fuel oil matrix.

A 10-μl injection of the fuel oil solution was made into the gas chromatograph, using the switching valve described above. The resulting chromatogram is presented in Fig. 3. The fuel oil was then spiked with the chlorobenzene standard, and the resulting solution was chromatographed in the same manner. As can be observed in Fig. 4, the chlorobenzenes of interest are eluted together with various components in the sample matrix when analyzed by capillary GC alone. The liquid chromatograph was then connected to the switching valve, and the selected fraction of the effluent was introduced into the gas chromatograph.

Fig. 5A represents the chromatogram obtained when the chlorobenzene standard was analyzed by packed-capillary LC and indicates the fraction introduced in the gas chromatograph. Fig. 5B is the resulting capillary gas chromatogram, obtained from this LC effluent fraction.

Fig. 6A represents the chromatogram of the fuel oil solution obtained with the LC system. The indicated fraction was introduced into the gas chromatograph, and Fig. 6B shows the resulting chromatogram. The retention times for the chlorinated
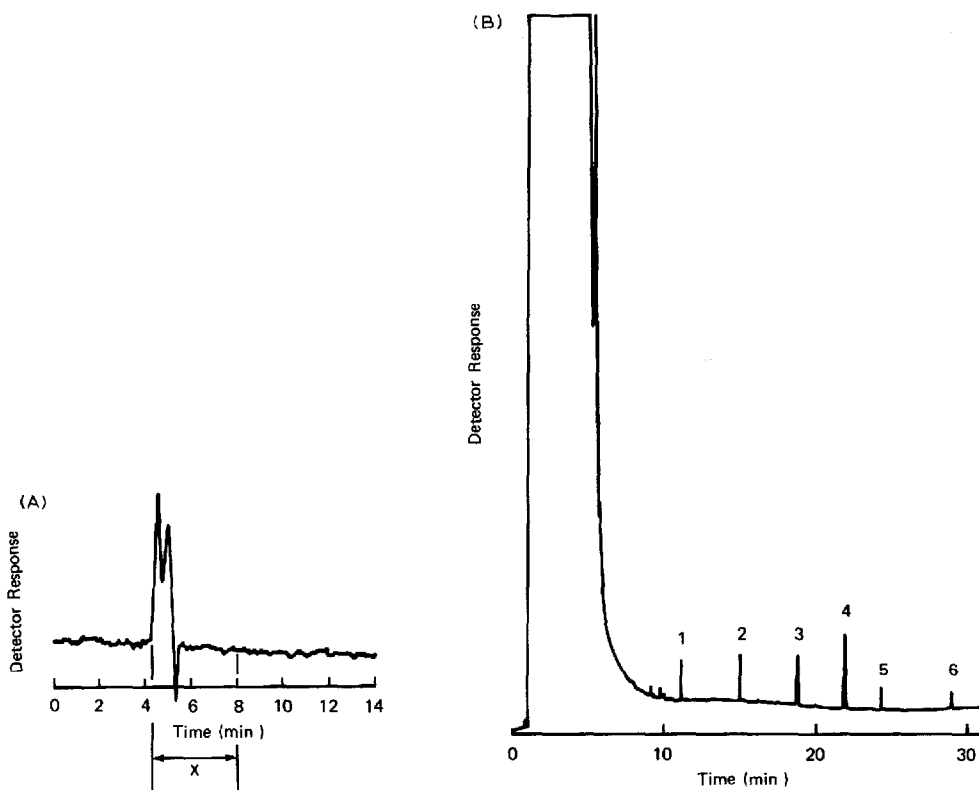

Fig. 5. Chromatograms of chlorobenzene standard. (A) Packed-capillary liquid chromatogram. Conditions as in Fig. 2. Sample, 100 mg/10 ml in heptane. X = Cut introduced into the gas chromatograph. (B) Capillary gas chromatogram. Conditions as in Fig. 3. Sample volume, 22 μl. Retention times of chlorobenzenes of interest are indicated. Peak identification as in Fig. 4.
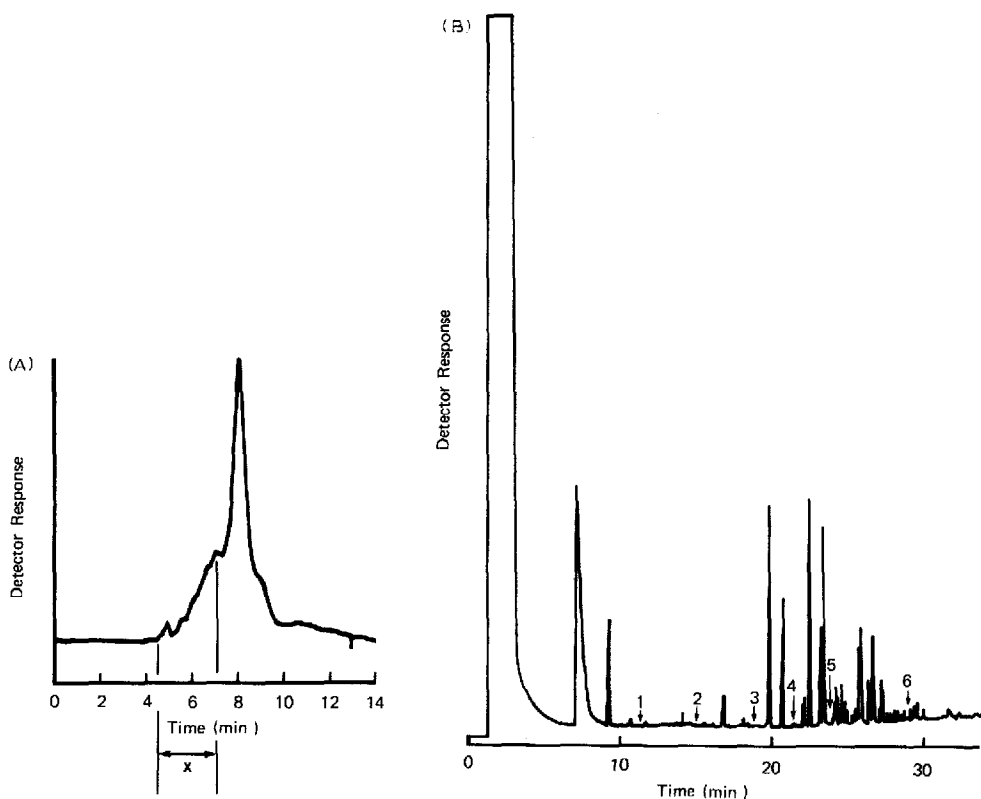
Fig. 6. Chromatograms of fuel oil sample. (A) Packed-capillary liquid chromatogram. Conditions as in Fig. 2. Sample, 1.00 g/10 ml in heptane. X = Cut introduced into the gas chromatograph. (B) Capillary gas chromatogram. Conditions as in Fig. 3. Sample volume, 22 μl. Retention times of chlorobenzenes of interest are indicated. Peak identification as in Fig. 4.

benzenes of interest are also shown. The volume injected into the gas chromatograph was 22 μl, and the chlorinated benzenes were resolved from the interferences in the fuel oil matrix without detrimental effects on peak shape.

CONCLUSIONS

A multidimensional chromatographic system, in which highly efficient packed-capillary LC columns are coupled with a capillary GC column, has been utilized to determine minor components in a complex hydrocarbon matrix without prior sample clean-up or preconcentration steps.

The chlorinated benzenes of interest were found to be absent in the sample analyzed at detection limits of 8.0 to 17 μg/g, calculated as three times baseline random noise level. On-line coupling of packed-capillary LC and capillary GC offers the advantages of a highly efficient clean-up or chemical class fractionation without prior separation steps, and thus significantly reduces sample preparation time in many applications. The speed of analysis and high degree of resolution obtained demonstrates the superiority on the on-line multidimensional LC–GC system over the use of LC or GC alone.

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