Electron capture detection in high-speed narrow-bore capillary gas chromatography: fast and sensitive analysis of PCBs and pesticides

Electron Capture Detection in High-Speed Narrow-Bore Capillary Gas Chromatography: Fast and Sensitive Analysis of PCBs and Pesticides

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Detection limits
PCBs
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Summary

In this work the combination of high-speed narrow-bore capillary GC with electron capture detection is evaluated. The make-up gas flow rate is a key parameter in the successful coupling of narrow-bore columns and ECD detection. The make-up flow has to be as high as possible to eliminate peak tailing caused by the large detection cell volume. The sensitivities at these elevated make-up flow rates (400 to 1000 ml/min), measured for some pesticides like HCB and dieldrin, were very good. Detection limits for these compounds of 0.1 pg were obtained, resulting in minimum detectable concentrations of approximately 0.2 ppb. The performance of the system is illustrated by several high-speed analyses of environmentally relevant samples of PCBs and pesticides.

1 Introduction

Since the introduction of capillary gas chromatography, there has been a demand for faster and more sensitive analytical systems. From the theoretical point of view, the reduction of the column inner diameter is an attractive route towards shorter analysis times [1,2]. Additionally, the minimum detectable amount is favored by the reduction of the column inner diameter [3]. Decreasing the inner diameter unfortunately also reduces the sample capacity of the capillary column [4]. To have an acceptable working range, a sensitive detection system is required.

The lack of compatible instrumentation has been the most serious drawback for the development of high-speed GC. Peak broadening due to injection and detection devices must be extremely small in order to be compatible with the small chromatographic peak width and to preserve a high column efficiency. During the last 10 years, considerable effort has been devoted to sample inlet systems compatible with high-speed GC [5–10]. Analogous to the requirements placed on the injector, also the detector has to be sufficiently fast. The combination of high-speed GC with various detection systems has been described in literature. The range of detectors studied for use in high-speed GC includes the flame ionization detector [11,12], thermal conductivity detector [13], photoionization detector [13], and various mass spectrometric detection devices [14–17]. In the past the electron capture detector (ECD) has proven to be a very sensitive, selective, and reliable detector. For this reason, the ECD is now one of the most frequently used detectors in environmental analysis. Despite the importance of the detector in environmental analysis, until now only limited attention has been paid to the coupling of high-speed GC with ECD detection. Ke *et al.* used the ECD for fast gas chromatographic air quality monitoring. The detection limits obtained were in the range from 1 to 100 pg, corresponding to a minimum detectable concentration (MDC) of 0.1 to 10 ppb [18]. Schutjes *et al.* evaluated the performance of the ECD under reduced pressures. It was found that the detector sensitivity was approximately independent of the outlet pressure applied [19]. Furthermore it was concluded that the ECD cell volume was too large to allow combination with high-speed narrow-bore capillary GC.

In the present contribution the combination of high-speed narrow-bore capillary GC with electron capture detection (ECD) is studied in detail. The influence of the ECD make-up flow on detector band broadening and sensitivity is investigated. Under optimum make-up flow conditions, the detection limits and the working range are established. Despite the very high sensitivity of the ECD detector, the MDC in high-speed GC using conventional injection techniques is too high for many practical applications because of the high split ratios used (1:500 and higher). To improve the MDC, splitless injection has to be performed. The speed and sensitivity attainable in high-speed GC with ECD detection and splitless injection are illustrated with various industrial and environmental applications including the analysis of pesticides and PCBs.

2 Instrumentation

A Carlo Erba 4160 Fractovap gas chromatograph equipped with an ECD 800 (Fisons, Milan, Italy) was used. The split injector was adapted to allow operation at high inlet pressures of the helium carrier gas. Both split and splitless injection were used. For the split injection high split flows were used in order to minimize band broadening caused by the injection. Low concentrations of a number of high boiling pesticides and PCBs were injected in the splitless mode (splitless time 3 min) in order to meet the required detection limits. Because the column flow of 50 µm columns is very low (0.4 to 0.5 ml/min), fairly long splitless times were required to ensure complete sample transfer. More-

over, a liner with a low inner diameter (1 mm) was used, again in order to speed up sample transfer. To enable high inlet pressures, a Tescom 44-1100 high pressure regulator (Tescom Inc, Minnesota, USA) was installed. The inlet pressure was 12 atm. The injector was operated at a temperature of 285 °C.

The column was a CP-Sil 5 CB Column (Chrompack, Middelburg, The Netherlands) with a length of 5 m, 50 µm inner diameter and a film thickness of 0.2 µm.

The ECD contains a ^{63}Ni beta emitting radioactive source of 379 MBq (10 mCi) and is operated in the constant current mode. The reference current was 1 nA and the pulse amplitude applied was 50 V. The ECD detector was held at 320 °C. According to the manufacturer specifications, the sensing volume of the detector is 450 µl. The pressure controller for the make-up flow in the GC was by-passed and another pressure controller was installed to allow make-up flow rates up to a few thousand ml/min. The pressure inside the ECD cell was measured using a pressure controller (Wallace & Tiernan – Chlorator GmbH, Günzburg/Do., Germany) installed just before the make-up gas (N_2) inlet of the ECD cell. The flow in the ECD cell was measured by connecting the ECD outlet to a bubble flow meter. The pressure- and temperature corrected flow in the detector was calculated according to:

$$F_{det} = \frac{p_{atm} \times F_{atm} \times T_{det}}{T_{atm} \times p_{det}} \quad (1)$$

where p_{det} is the pressure in the ECD cell, F_{det} the flow through the detector, T_{det} the temperature of the detector, p_{atm} atmospheric pressure, F_{atm} the measured flow, and T_{atm} ambient temperature (298 K). Data acquisition was performed using a VG Xchrom data acquisition system (VG Data Systems, Cheshire, England) which has the ability to acquire data using sampling frequencies up to 800 Hz.

3 Theory

Narrow-bore columns offer a large number of theoretical plates per unit time. Assuming that the only sources of band broadening are the column and the detector, the total band width σ_{tot} can be expressed as:

$$\sigma_{tot} = \sqrt{\sigma^2_{chrom} + \sigma^2_{det}} \quad (2)$$

where σ_{chrom} is the chromatographic band width and σ_{det} the peak broadening caused by the detector. Band broadening due to the detection volume can be described by:

$$\sigma_{det} = \frac{V_{det}}{K \times F_{det}} \quad (3)$$

where V_{det} is the detector cell volume, F_{det} the flow rate through the detector and K the profile factor. K equals $\sqrt{12}$ in the case of plug flow in the detector whereas K equals unity in case of exponential flow. With the use of an ECD for high-resolution chromatography, some loss of chromatographic resolution will occur owing to the significant "mixing volume" [20–22] of this detector. The magnitude of this effect will depend on the physical design of the detector. To limit peak distortion due to the detector cell volume make-up gas has to be added. Under optimal operating conditions the 5 m column used in the experimental work should yield approximately 115000 plates for a compound with a capacity factor of two. At an average linear velocity of 50 cm/s, this gives a chromatographic band width (σ_{chrom}) of 86.6 ms. If we allow a detector contribution to band broadening equal to 10% of the chromatographic band width, the detector broadening (σ_{det}) should be less than 27.7 ms. If it is further assumed that plug flow conditions prevail in the detector, the minimum make-up flow required for a detector with a volume of 450 µl is approximately 300 ml/min. Under exponential flow conditions in the detector cell, the minimum make-up flow rate required is about 1000 ml/min.

Similar to the situation for a thermal conductivity detector, the electron capture detector is generally assumed to be a concentration sensitive detector. Because higher make-up flow rates are required in order to minimize detector band broadening, one expects the minimum detectable amount (MDA) to increase drastically at higher make-up flow rates, even if the sensitivity is assumed to be constant, *i.e.* unaffected by the high make-up flow.

It was shown by Noij that the column inner diameter has a strong influence on the minimum detectable amount [3]. Depending upon the column in- and outlet pressure, a second to third power dependence on the minimum detectable amount on the column diameter exits for concentration sensitive detectors. With narrow-bore columns a concentration sensitive detector is at least in principle able to detect smaller quantities of a compound than is a mass flow sensitive detector. For this reason it is advantageous to couple narrow-bore columns to concentration sensitive detectors. This is, however, true only if the volume of the detector is very low and no make-up gas has to be used.

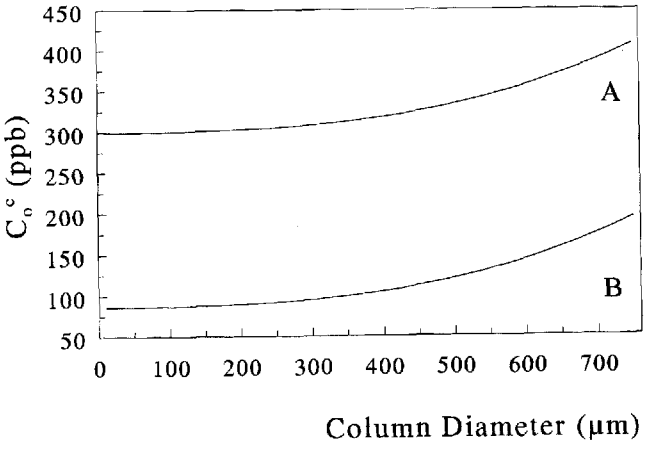

Figure 1. Detection limits for an ECD as a function of the column inner diameter allowing 10% detector band broadening under exponentional flow (A) and plug flow condition (B).

In **Figure 1**, theoretical calculations for the detection limits as a function of the column inner diameter are presented. To calculate these graphs, the chromatographic peak broadening (σ_{chrom}) under optimal separation conditions (N = 100000) was first calculated as a function of the column inner diameter. Next the maximum allowable detector band broadening was arbitrarily set to 10% of the chromatographic band broadening. The detector band broadening was than calculated according to:

$$\sigma^2_{det} = 0.1 \times \sigma^2_{chrom} \quad (4)$$

From equation (2) the required make-up gas flow rate could be calculated for different flow patterns inside the detector. An overview of the required make-up flow rate as a function of the column inner diameter is presented in **Figure 2**. For wide-bore columns the required make-up flow is very small, but it increases drastically if the inner diameter is reduced. Once the required make-up flow is known, the minimum detectable concentration can be calculated according to:

$$C_0^c = \sqrt{2\Pi} \times \frac{4R_n}{S^c} \sigma_{tot} \frac{F_{det}}{V_{inj}} \quad (5)$$

where is C_0^c the minimum detectable concentration for a concentration sensitive detector, R_n the noise level, S^C the sensitivity (concentration sensitive detector), σ_{tot} the overall band width, F_{det} the detector flow rate and V_{inj} the injected sample volume. For these calculations the sensitivity and the noise level of the ECD were assumed to be constant, *i.e.* independent of the make-up flow rate. The detection limits calculated vary from 40 ppb for 50 µm columns to 200 ppb for wide bore (530 µm) columns under plug flow conditions and increase up to 300 to 400 ppb for exponential flow conditions in the detector. It is obvious from this theoretical calculation that the MDA is favored by the reduction of the column inner diameter although high make-up flow rates are required to minimize band broadening when narrow-bore columns are used. In the calculations presented above, it was assumed that the noise level and the sensitivity were independent of the make-up flow rate. Whether this is really the case must be verified experimentally.

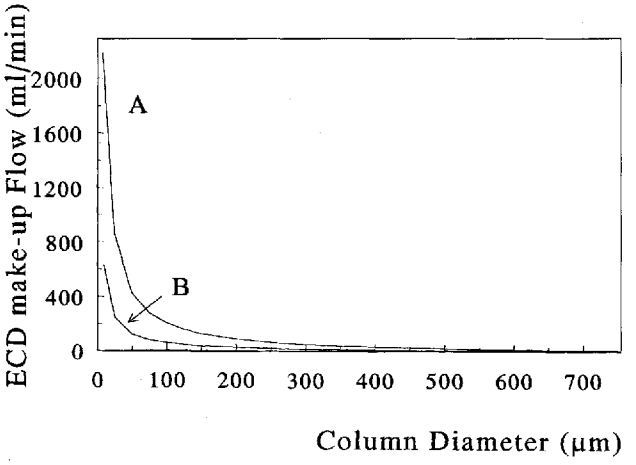

Figure 2. Make-up flow required to minimize detector band broadening to 10 % under exponentional flow (A) and plug flow (B) as a function of the column inner diameter.

4 Results and Discussion

The addition of a make-up gas flow prior to the detector is a widely used method to reduce the effective volume of the detector. For mass flow sensitive detectors, the addition of a make-up flow does not influence the detection limits of the chromatographic system. For concentration sensitive detectors, however, the detection limits are affected unfavorably by the addition of make-up gas. Therefore, the magnitude of the make-up flow rate should always be carefully optimized. Too high values should be avoided because of the adverse effects on sensitivity whereas too low values result in band broadening and loss of resolution. In ECD detectors the situation is even more complicated as here the make-up gas actively participates in the detection mechanism. The make-up gas acts as a quenching gas that converts high energy β particles emitted by the radioactive foil into electrons that are eventually responsible for the electron capturing process. Although the actual mechanism of quenching is not yet fully understood, it is known that also here there is an optimal flow rate of quenching gas. In the following paragraphs the influence of the quench gas flow rate on detector band broadening and detection limits will be addressed subsequently.

4.1 Detection Band Broadening

To avoid an excessive detector contribution to overall band width in narrow-bore GC, high make-up flow rates are required as is evident from **Figure 3**. This figure shows the tailing factors of chloroform, chlorohexane, and bromobenzene in a fast GC separation as a function of the make-up flow rate. From this figure it is evident that indeed very high make-up flow rates are required in order to minimize peak tailing. This is especially true for peaks with retention times smaller than 1 min. The tailing factor for the later eluting compounds is smaller due to the larger chromatographic band broadening. Even at very high make-up flow rates, peak tailing does not completely disappear. Most likely this residual tailing is caused by the fact that manual injection is used.

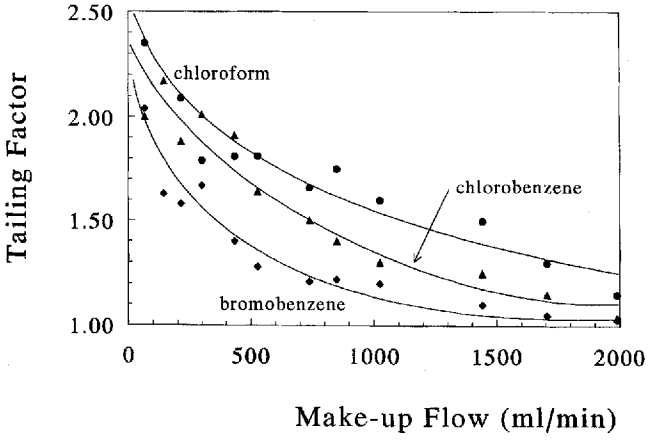

Figure 3. Tailing factor of chloroform, chlorobenzene and bromobenzene as a function of the ECD make-up flow.

Typical make-up flow rates employed when ECD detection is used in combination with normal bore columns vary from 20 to 40 ml/min. Because higher make-up flow rates are required with narrow-bore columns, the influence of this on the sensitivity and the detection limits was evaluated experimentally.

4.2 Sensitivity, Dynamic Range, and Detection Limits

In the past, the influence of the make-up flow on the detector behavior has been studied, but only for make-up flows in the range of 10 to 100 ml/min [23–27]. In most cases a maximum was observed at a make-up flow of about 30 ml/min. At higher flow rates, the response generally decreased exponentially with the flow rate. Here, the sensitivity for different compounds will be evaluated at elevated make-up flow rates.

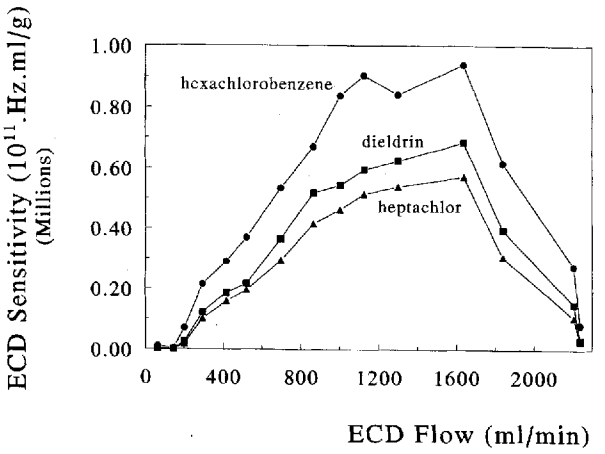

Figure 4. Sensitivity of the ECD for hexachlorobenzene, heptachlor and dieldrin as a function of the make-up flow rate (assuming concentration sensitive behavior).

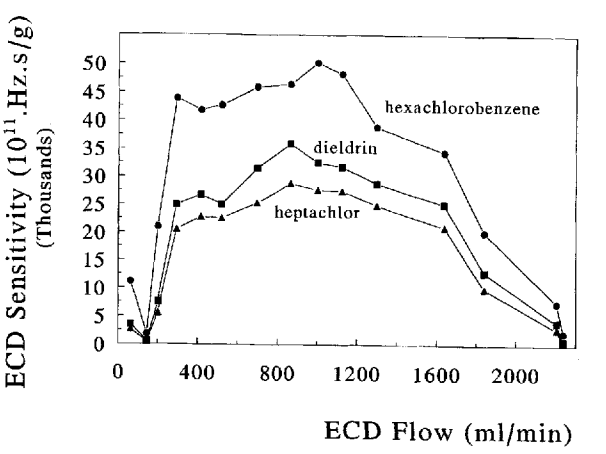

Figure 5. Sensitivity of the ECD for hexachlorobenzene, heptachlor and dieldrin as a function of the make-up flow rate (assuming mass flow sensitive behavior).

For concentration sensitive detectors, the sensitivity can be calculated according to the equation:

$$S^c = \frac{A \times F_{det}}{Q} \quad (6)$$

where S^c is the sensitivity of the concentration sensitive ECD (Hz ml/g), A the area response (mV s) and Q (g) the sample amount introduced. **Figure 4** shows a plot of the measured sensitivities of some pesticides *vs.* the make-up flow rate. At detector flows below 150 ml/min a decrease of sensitivity with increasing flow rate was observed. At higher flow rates, however, the sensitivity starts to increase drastically with increasing flow rate for all compounds tested. Increased sensitivities at higher make-up flows were also observed by Cram *et al.* [27]. At ECD make-up flow rates exceeding 1100 ml/min, sensitivity starts to decrease again. The increase of sensitivity between 150 and 1100 ml make-up per minute might be caused by the increase of the number of slower electrons that is present in the detector cell. At too high make-up flows, on the other hand, the electrons might be blown out of the detector cell which results in reduced sensitivity. For some compounds, such as 1-chloroheptane and 1,6-dibromohexane, the sensitivity already decreases at a make-up flow rate of 300 ml/min. This difference most likely is caused by the reaction times required for the electron capturing reactions. In the reaction sequence for the detection mechanism in the ECD, the resonance or dissociative electron capture by the analyte A to form negative ions A^- is described by:

$$e^- + A \xrightarrow{k} A^- \quad (7)$$

where k is the rate constant for electron capturing. The lower sensitivity for these compounds at higher flow rates is probably caused by low reaction rate constants. The residence time of the component in the detector at high flow rates is apparently not sufficiently long to obtain maximum response.

In the calculations discussed above it was assumed that the ECD is a concentration sensitive detector. For strongly electron capturing components, however, the ECD can under certain conditions also exhibit mass flow sensitive behavior [28]. Considering that the ECD detector is operating as a mass flow sensitive detector, the sensitivity can be calculated according to the equation:

$$S^m = \frac{A}{Q} \quad (8)$$

where S^m is the sensitivity for a detector with mass flow sensitive behavior (Hz s/g). If this definition was adopted, it was found that the sensitivity was almost unaffected by the make-up flow for flow rates in the range from 400 ml/min up to 1600 ml/min (**Figure 5**).

From the results shown in the Figures 4 and 5 it appears that the sensitivity depends on the make-up flow rate. Good sensitivity can be obtained at elevated flow rates. At make-up flows between 400 and 1100 ml/min, the ECD appears to exhibits mass flow sensitive behavior. The explanation for this behavior is not known until now. In addition to the make-up flow rate, other instrumental parameters, *i.e.* the detector temperature, purity of the gases, the detector regime (frequency and width of pulses) [23–24,29], *etc.*, affect the response of this detector. It is possible that these parameters become important at elevated make-up flows. For example the detector temperature can be influenced by the use of high make-up flow rates [30–33]. Also the presence of oxygen or other trace impurities in the make-up and carrier gas passing through the detector can change the detector response [28,34]. It is also known that the response depends on the flow pattern in the detector cell [33]. This could be different at higher flow rates.

The ultimate detection limits in high-speed GC-ECD are not only a function of the sensitivity, but also of the noise level. Hence it is also important to investigate the influence of the make-up flow on this parameter. A gradual decrease in the noise level and base frequency were observed when the make-up flow rate was increased to 50 ml/min. Both base frequency and noise amplitude were virtually constant in the make-up flow range of 50 to 1000 ml/min. It appears that the number of electrons available for capturing reactions is almost constant in this range. At flow rates exceeding 1000 ml/min, both noise level and base frequency increased sharply.

Although there is no exact explanation for the sensitivity behavior of the ECD detector, it is evident from the results shown in the figures 3, 4, and 5 that the ECD detector is compatible with 50 µm i.d. narrow-bore capillary GC columns. The high make-up gas flow rates required to eliminate detector band broadening have no adverse effects on the detection limits. Good detection

limits can be achieved despite the high make-up flow rates required.

For narrow-bore columns, the detection limits for some pesticides (hexachlorobenzene, heptachlor, and dieldrin) were approximately 100 fg in the range of make-up flows of 400 to 1000 ml/min. The minimum detectable concentration with high-speed GC is 0.2 ppb at an injection volume of 0.5 µl (splitless injection). The detector was found to exhibit linear behavior up to a few hundred pg.

4.3 Applications

In **Figure 6**, a fast separation of a test mixture is presented. The separation of the 8 compounds is performed in less than 20 s.

In **Figure 7** the separation of the PCB standard Arochlor 1242 is shown. The injection was performed in the split mode.

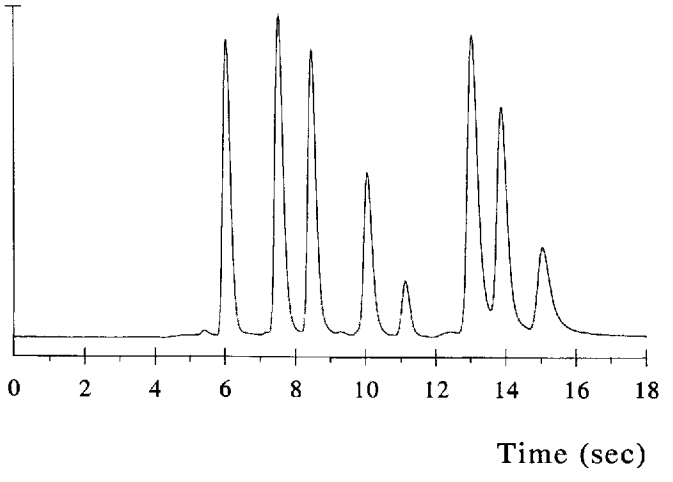

Figure 6. High-speed chromatogram of a test mixture: GC conditions: 110 °C, p_i = 20 atm, split flow is extremely high (> 1000 ml/min), sample introduction: headspace 20 µl. ECD make-up flow = 900 ml/min. Components in order of elution: chloroform, 1-iodopropane, 1,1,2-trichloroethane, 1-iodobutane, 1,1,2-trichloropropane, tribromomethane, 1,1,2,2-tetrachloroethane, diiodomethane.

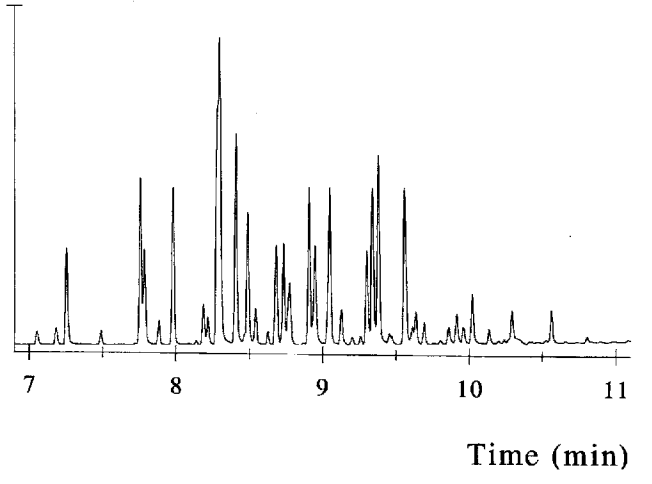

Figure 7. High-speed chromatogram of a PCB mixture (Arochlor 1242) in hexane: GC conditions: 50 °C → 20 °/min → 280 °C, p_i = 12 atm, split flow = 400 ml/min. ECD make-up flow = 400 ml/min.

Figure 8 shows the separation of PCBs extracted from transformer oil. The clean-up of the sample was performed according to the procedure published by Sandra *et al.* [35]. Here the injection mode used was splitless. The approximate concentration of the PCBs in the oil was 1 ppm. The separation of this complex mixtures was achieved in approximately 10 min. Obtaining similar resolution on a normal bore column would take approximately 45 min.

In **Figure 9**, the separation of an SFE extract of the PCB standard reference material 1939 of the N.B.S. (Gaithersburg, USA) is shown. The injection mode was splitless. Before the elution of the PCBs starts, a significant amount of co-extracted compounds were observed.

In **Figure 10** a splitless injection of some pesticides is shown. The concentration of the individual pesticides were between 10 and 100 ppb. From Figures 8 to 10 it is clear that the combination of narrow-bore columns, splitless injection, and electron capture

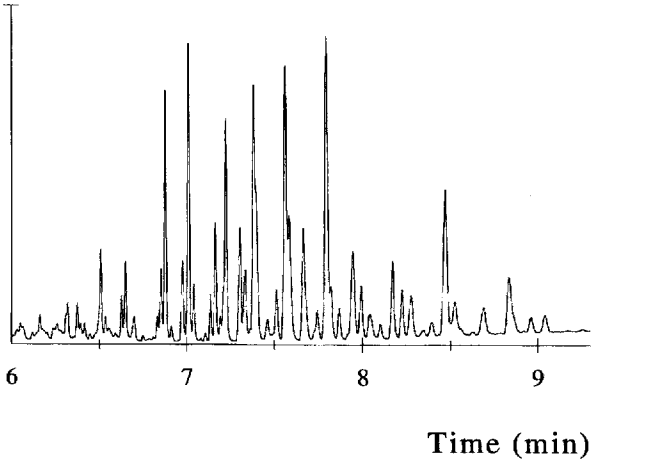

Figure 8. High-speed chromatogram of a PCB extract (Arochlor 1260) of transformer oil in hexane. GC conditions: 50 °C (3 min) ballistically heated to 280 °C, p_i = 12 atm, splitless time = 3 min, V_{inj} = 0.3 µl. ECD make-up flow = 400 ml/min.

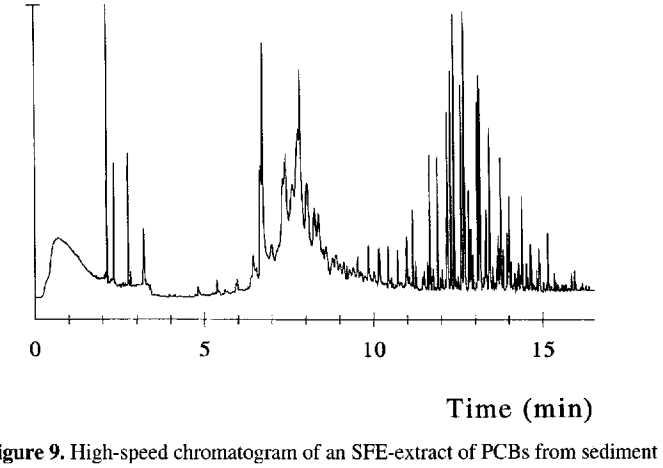

Figure 9. High-speed chromatogram of an SFE-extract of PCBs from sediment (N.B.S. Standard Reference material 1939) in acetone. GC conditions: 40 °C (4 min) → 20 °/min → 275 °C, p_i = 12 atm, splitless time = 3 min, V_{inj} = 0.3 µl. ECD make-up flow = 400 ml/min.

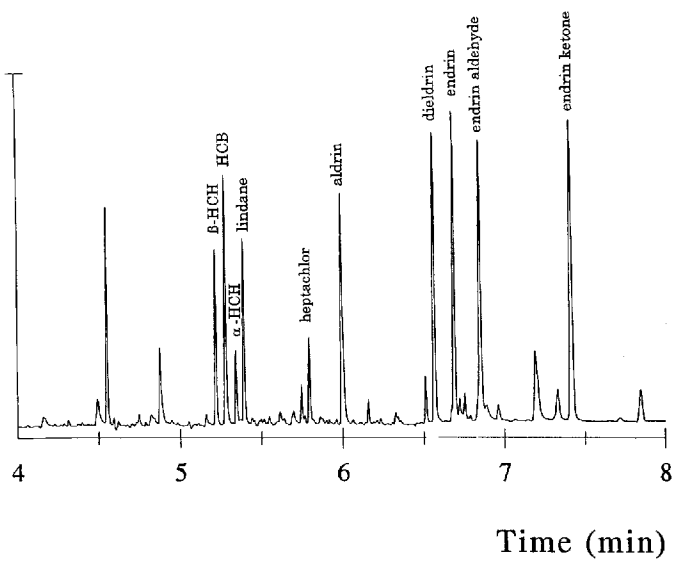

Figure 10. High-speed chromatogram of a pesticide test mixture in hexane. GC conditions: 50 °C (3 min) ballistically heated to 280 °C, p_i = 12 atm, splitless time = 3 min, V_{inj} = 0.3 µl. ECD make-up flow rate = 400 ml/min.

detection results in excellent concentration detection limits. Unfortunately, due to the fairly long residence times of the sample in the hot injector liner, splitless injection can give rise to degradation of thermally unstable components. In Figure 10, a relatively high concentration of the degradation products of endrin, endrin aldehyde, and endrin ketone, is observed.

5 Conclusions

The combination of 50 µm i.d. columns with electron capture detection enables high-speed analysis. Although high make-up flow rates are required in order to minimize peak tailing, very good sensitivity could be obtained at these elevated flow rates. Detection limits of 0.1 pg were obtained, corresponding to a minimum detectable concentration of 0.2 ppb. The detector exhibits linear behavior up to a few hundred picogram. The GC-ECD system described in this work provided reliable high-speed analysis of trace quantities for industrial and environmental applications.

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