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CHLORINE-SELECTIVE MONITORING FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH A HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

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SUMMARY

Simple, inexpensive modifications have been made to a commercial Hall electrolytic conductivity gas chromatographic detector in order to utilize it for high-performance liquid chromatographic (HPLC) halogen (chlorine) selective monitoring. A portion (0.1–0.3 ml/min) of the column eluent was introduced directly together with hydrogen make-up gas into the heated quartz furnace of a Hall detector, the presence of chlorine-containing compounds in the solvent liberating hydrogen chloride, which was detected in the conventional manner by changes in electrolytic conductivity. Optimization of the detector parameters are described, important features being the length of the inlet tube protruding into the furnace, the furnace temperature and the electrolyte flow-rate. The detector was shown to be sensitive to 50 ng (1.4 ng/sec) of chlorine in chloroalkanes, eluted by reversed-phase HPLC with methanol–water solvent systems, giving a linear response over at least one order of magnitude (0.8–8.0 μg of chlorine). The choice of HPLC solvents was, however, limited to methanol and methanol–water mixtures, as with other organic solvents extensive carbon deposits accumulated in the detector furnace.

Applications of the detector are illustrated by its use for monitoring the fractionation of vinyl chloride oligomers isolated from PVC resins.

INTRODUCTION

The lack of specific sensitive detectors is often a limitation in high-performance liquid chromatography (HPLC) restricting applications to the analysis of compounds with UV absorption or fluorescence, or to compounds that can be suitably modified by derivatization. General-purpose mass response detectors, such as the refractive index detector, tend to lack adequate sensitivity for many applications and element-specific detectors in particular for halogenated compounds are not commercially available. To overcome this problem various attempts have been made to modify existing gas chromatographic (GC) detectors for use in HPLC. For halogens the electron-capture detector[1,2] has been used in combination with some system for solvent removal, *e.g.*, a moving wire transport technique, or by direct introduction of

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low flows of volatilized non-polar organic solvent eluents. Other very successful chlorine-specific HPLC detectors have been reported, for example based on flame emission[3], but unless these ideas are taken up commercially these designs, despite their potential, are restricted to laboratories with the necessary electronics and engineering facilities, and to those prepared to invest the time involved in modifications and development work.

The Hall electrolytic conductivity detector marketed as a GC detector has previously been reported in a nitrogen-specific mode for use in HPLC[4], although modifications were necessary in the form of an additional furnace and various gas splitters. In a similar fashion a Coulson electrolytic conductivity detector had earlier been employed in a chlorine-specific mode for HPLC[5], directly coupled with a minimum of modifications to the commercial detector. In this paper we substantiate these previous reports by describing the use of the Hall detector for monitoring chlorine-containing compounds by HPLC. A minimum of non-specialist work was involved in converting the detector for HPLC, and its use which is now routine in these laboratories is described for the analysis of long-chain chlorinated alkanes where detection was not possible by other available techniques.

EXPERIMENTAL

Apparatus

Detector. A schematic illustration of the Tracor Model 700 Hall electrolytic conductivity detector (Tracor Instruments, Austin, TX, U.S.A.) coupled to the HPLC splitter with a stainless steel inlet tube is shown in Fig. 1, together with specification and constructional details. The inlet tube was mounted concentrically inside the quartz furnace and protruded 45 mm past the "front" end of the furnace. The vaporized eluent was immediately swept to the hottest part of the furnace where HCl was generated from chlorinated compounds and subsequently detected by changes in electrolyte conductivity in the conventional manner.

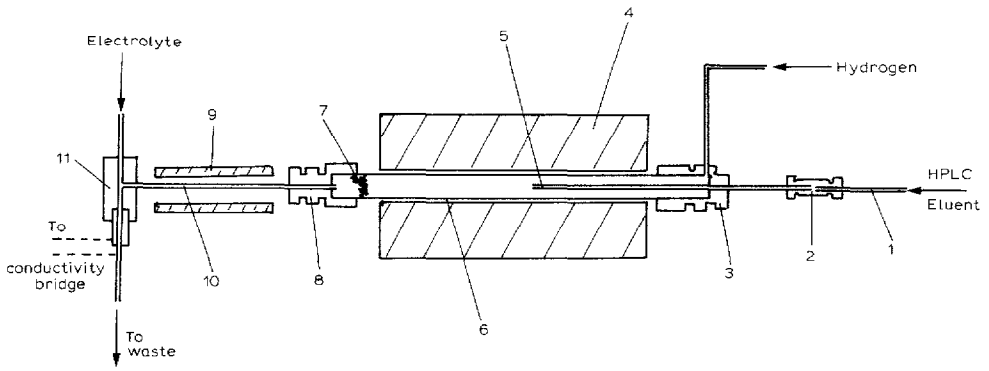

Fig. 1. Schematic illustration of Hall detector for use in HPLC mode. (1) PTFE tubing, 1.6 mm O.D. × 0.15 mm I.D.; (2) Swagelok 1.6 mm straight union; (3) 6.4 mm to 3.2 mm reducing union with inlet side tube coupled with both PTFE and vespel ferrules; (4) Hall electrolytic conductivity detector furnace; (5) stainless-steel inlet tube, 120 × 1.6 mm O.D. (0.5 mm I.D.); (6) quartz furnace tube, 180 × 6.4 mm O.D. (4 mm I.D.); (7) quartz-wool plug; (8) 6.4 mm to 1.6 mm Swagelok reducing union fitted with vespel ferrule to furnace and PTFE ferrule to outlet tubing; (9) thermostatted electric heating tape; (10) PTFE tubing, 1.6 mm O.D. × 0.8 mm I.D.; (11) conductivity cell of Hall detector.

For aqueous solvents it was necessary to heat the PTFE tubing connecting the furnace exit and the conductivity cell to prevent water condensation. A temperature of about 100°C was achieved by winding thermostatically controlled heating tape around a length of copper tubing (20 mm O.D.) through which the connecting tubing was passed. To accommodate the heater the PTFE cell of the Hall detector was detached from its mountings on the furnace block and supported on a retort stand.

Although the electrolyte (water–isopropanol, 1:1) in the conductivity cell could be operated by circulation through an ion-exchange resin as recommended by the manufacturers, in practice after operation for a few days a deterioration in sensitivity was observed. This could be overcome by avoiding recirculation and using fresh electrolyte from a supplementary reservoir discarding after use.

Solvent splitter. A precision segmented stream splitter was employed (Reeve Analytical, Glasgow, Great Britain) which operated by interchanging solvent with hydrogen (flow-rate variable from 0 to 24 ml/min) by means of a rotating four-port valve. Its operation is illustrated in Fig. 2, the valve rotating in 180° cycles sending 5 μl of solvent to the detector on each rotation. Hence in (a) the valve is admitting hydrogen to the detector whilst in (b) it is delivering a 5-μl loop of solvent. The split was thus varied by controlling the speed of rotation of the valve up to a maximum of 100 rpm, being capable of maintaining a splitting ratio of $\pm 0.1\%$ regardless of ambient temperature and mobile phase viscosity. At flow-rates of 1 ml/min the splitting ratio could be varied up to 50% directly, and higher splitting ratios attained by taking the eluent flow from the other outlet of the splitter. Higher eluent flow-rates permitted only a limited range of splitting ratios (at 2 ml/min, 0–25% and 75–100%).

HPLC system. Waters Model 6000A pumps (Waters Assoc., Milford, MA, U.S.A.) together with a Waters Model 660 solvent programmer were used. The reversed-phase column employed (250 × 4.9 mm I.D.) was packed with 5-μm Spherisorb ODS (Hichrom, Reading, Great Britain) and the system was equipped with a Rheodyne 7125 injection valve.

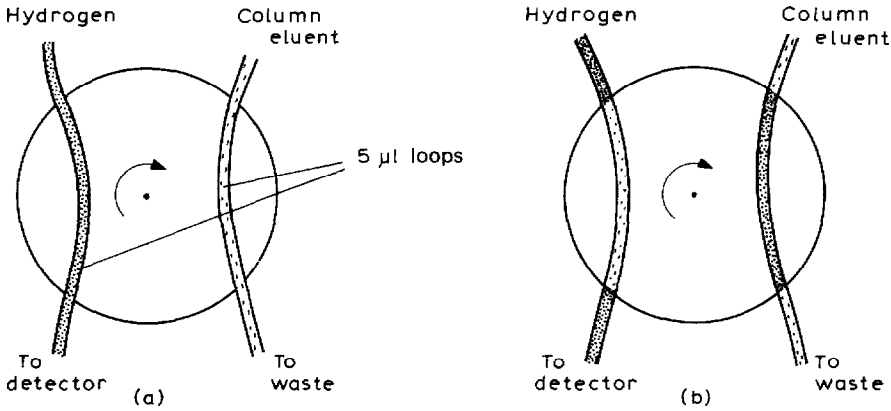

Fig. 2. Schematic illustration of HPLC segmented stream splitter. (a) Valve closed for liquid flow to the Hall detector whilst sampling solvent from the HPLC eluent; (b) valve rotated through 180° transferring 5 μl of solvent to detector.

RESULTS AND DISCUSSION

Optimization of the system was initially carried out by removal of the HPLC column and direct injection of test compounds into the solvent stream. The following detector parameters were then varied individually: (a) solvent splitting ratio, (b) hydrogen flow-rate into stream splitter, (c) length of inlet tube protruding into the furnace, (d) inner diameter of inlet tube, (e) flow-rate of hydrogen into furnace, (f) furnace temperature, (g) electrolyte flow-rate and (h) choice of electrolyte solvent. A summary of the optimum conditions for operation of the detector to achieve maximum sensitivity, with acceptable noise and minimum loss of chromatographic resolution, is given in Table I.

TABLE I

OPTIMUM CONDITIONS FOR OPERATION OF DETECTOR

Variable	*Optimum condition*
Solvent	Methanol or methanol–water
Solvent flow-rate	1 ml/min
Hydrogen flow-rate to splitter	10 ml/min
Percentage split	20% to detector
Length of inlet tube inserted in furnace	45 mm
Inner diameter of inlet tube	0.5 mm
Hydrogen flow-rate to HECD furnace	100 ml/min
HECD furnace temperature	1000°C
Temperature of post-furnace heater	100°C
Electrolyte flow-rate	0.7–1.0 ml/min

Solvent splitting ratio and solvent flow-rate to the furnace

The massive increase in the volume that occurs on converting column liquid eluent to vapour at 1000°C results in a high flow-rate in the furnace tube and a low residence time for organic compounds. Thus above a certain solvent flow-rate the residence time becomes insufficient for chlorinated compounds to be fully reduced and detector response will begin to decrease. This is illustrated in Fig. 3, which shows changes in sensitivity with flow-rate for different furnace temperatures. At 925°C the optimum flow-rate of 0.25 ml/min gave maximum response, whilst at higher temperatures (975 and 1025°C) the optimum flow-rate was 0.27 ml/min. A disadvantage of increased flow-rate was an increase in deposition of carbon in the inlet and furnace tubes resulting in increased noise levels. Peak shape was also an important criterion for optimizing splitting ratios. At very low flow-rates (0.1–0.2 ml/min) a hold-up time of around 40 sec occurred in the system, resulting in broad peaks because of increased mixing in the inlet tube. At flow-rates above 0.2 ml/min the residence time dropped to between 10 and 15 sec with improved resolution. Also at low flow-rates stream segmentation caused by the splitter was more apparent. The eluent stream interdispersed with segments of carrier gas, which could be visually observed in the PTFE tube connecting the splitter to the furnace, caused an intermittent introduction of eluent into the furnace resulting in uneven spiked peaks. This is illustrated in Fig. 4. As the flow-rate increases the solvent stream appears as a disorganized stream of

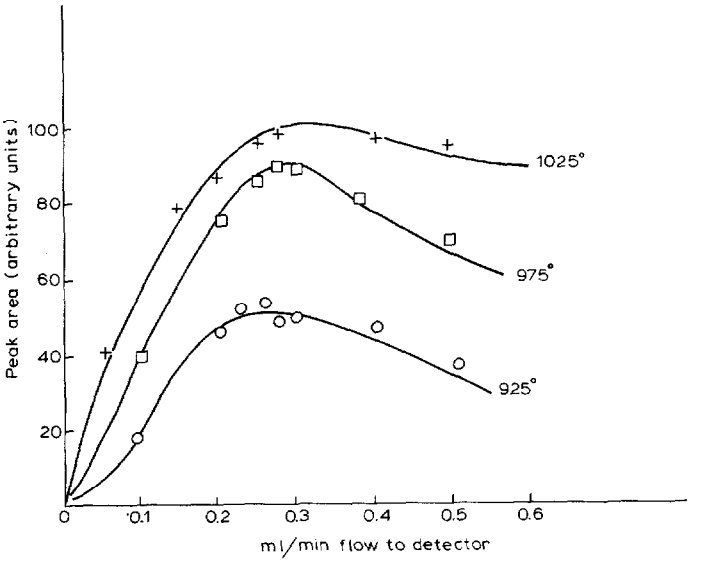

Fig. 3. Changes in detector sensitivity with solvent flow-rate (splitting ratio) at different furnace temperatures.

carrier gas bubbles and the eluent reaches the furnace as an apparent continuous stream, resulting in smoother peaks. The optimum splitting ratio appeared to be 20% at 1 ml/min when the detector was operating in the linear portion of the response curve and peak shapes were acceptable.

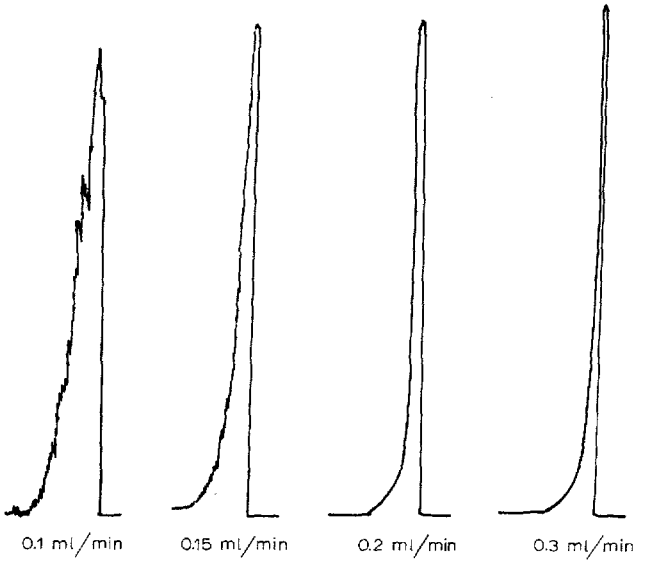

Fig. 4. Change in peak shape with splitting ratio (1 ml/min of methanol) for successive injections of dichlorobenzene.

Hydrogen flow-rate to the HPLC splitter

The role of hydrogen in the stream splitter was to act as a carrier gas for the column eluent. Varying its flow-rate between 2 and 24 ml/min produced no observable effects on sensitivity or peak shape and consequently a flow-rate of 10 ml/min was employed throughout.

Length of stainless-steel inlet tube protruding into the furnace

The position of the end of the stainless-steel inlet tube in the furnace was found to be critical. At insertion lengths of 0–30 mm relative to the "front" end of the body of the furnace, peak shapes consisted of a broad envelope of spikes and the sensitivity was very low. Maximum sensitivity and optimum peak shape were obtained with an insertion length of 55 mm, as can be seen from Fig. 5, probably because the eluent was vaporized directly into the hottest part of the furnace. However, in this position the inlet tube frequently became plugged with carbon deposits and therefore in practice a compromise of a 45-mm insertion was used, giving almost maximum sensitivity yet considerably extending the operating life time of the system (typically 1–2 days).

Stainless-steel inlet tubes were replaced as necessary and the quartz furnace tubes were cleaned every 2–3 days. Cleaning was carried out by passing oxygen through the tube heated in the furnace at 1000°C for about 2 min. After several cleanings the tube needed replacing as it appeared to be etched around the position occupied by the end of the inlet tube.

Internal diameter of stainless-steel inlet tube

Inlet tubes of 0.25 mm I.D. became plugged with carbon deposits too rapidly for practical use, whilst 0.75 mm I.D. tubes with their increased residence time and subsequent mixing resulted in poor peak shape. The best compromise was 0.5 mm I.D., producing sharp peaks with less susceptibility to blockage and this diameter tube was adopted for routine use.

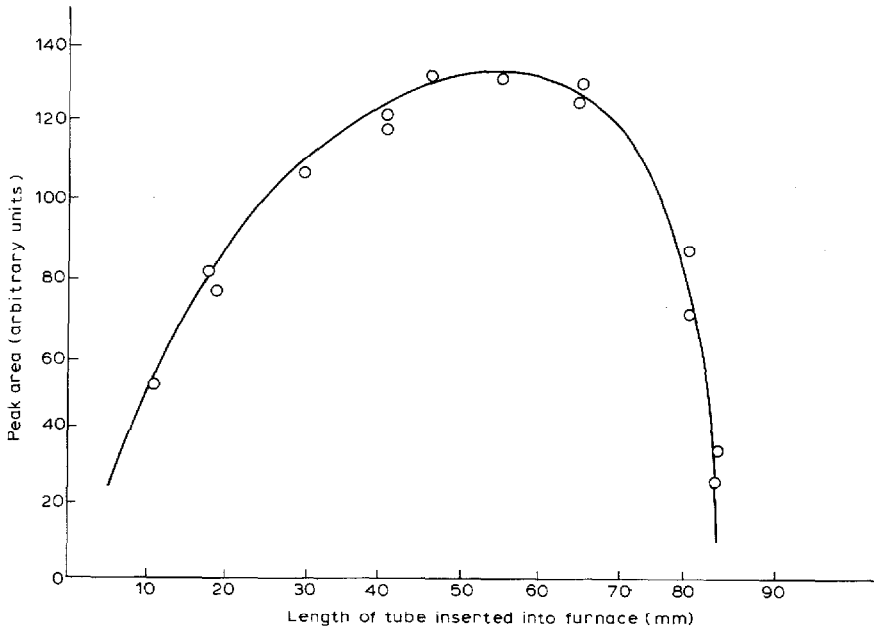

Fig. 5. Change in detector sensitivity with position of stainless-steel inlet tube inserted into the detector furnace.

Hydrogen flow-rate in furnace

The products of pyrolysis of the mobile phase have not been identified but they consisted of more than just methane and water. The effluent from the furnace tube was very acidic and required venting in a fume hood even after scrubbing with the electrolyte. It was calculated that using methanol as the eluent with a flow-rate of 0.2 ml/min, the theoretical consumption of hydrogen would be 110 ml. However, varying the hydrogen flow-rate between 40 and 500 ml/min had no observable effect on sensitivity or peak shape. A hydrogen flow-rate of 100 ml/min was routinely employed.

Furnace temperature

For a given solvent flow-rate to the furnace (at a given splitting ratio) the sensitivity increased linearly with furnace temperature up to a maximum, after which it plateaued, as shown in Fig. 6. Thus, as can be seen, maximum sensitivity at an HPLC flow-rate of 1 ml/min was obtained at 950°C for a 10% splitting ratio, 975°C for a 20% splitting and 1000°C for a 30% splitting ratio. Operation was normally at 1000°C with a 20% splitting ratio, although it should be noted that protracted operation at higher temperatures could seriously reduce the working life of the furnace.

Electrolyte flow-rate

With decreasing electrolyte flow-rate the sensitivity increases but correspondingly the noise level begins to become significant, especially below 0.5 ml/min. At high flow-rates (1.2–1.6 ml/min) the peaks were very sharp but tended to consist of an envelope of spikes. This spiking was explained by the detector responding to residual pulsing from the stream splitter, whilst at lower electrolyte flow-rates the pulses were averaged into a smooth reasonably sharp peak. In practice a flow-rate of 0.7 ml/min represented the best compromise between peak shape, noise and sensitivity.

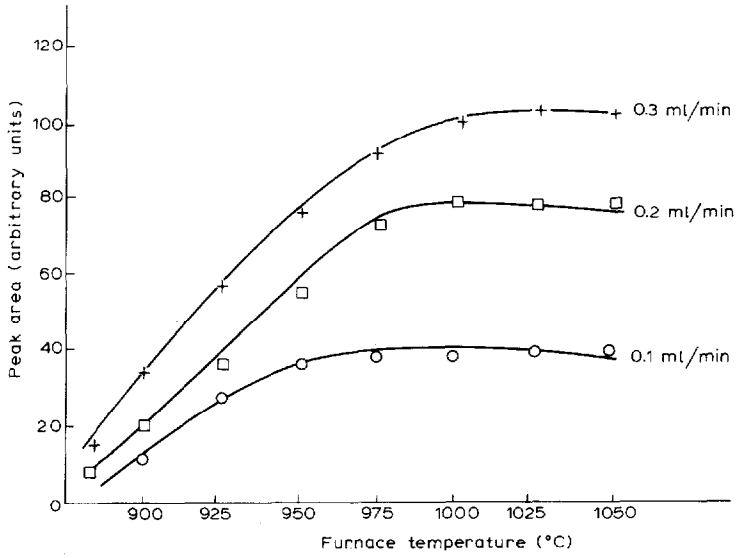

Fig. 6. Change of detector sensitivity with furnace temperature at different solvent splitting ratios (1 ml/min of methanol).

Choice of HPLC solvents

The principal limitation to the choice of solvents was the rate of carbon deposition in the furnace and inlet tube. With methanol and methanol–water mixtures the rate of contamination was acceptable, whereas with tetrahydrofuran and hexane extensive rapid deposition occurred, making these solvents impracticable. This represents perhaps the most severe limitation to the use of this detector, although methanol–water reversed-phase systems represent possibly the single most useful liquid chromatographic technique. We shall be investigating the acceptability of acetonitrile in the near future.

Even when using methanol, it was found useful to place a plug of quartz-wool in the exit end of the furnace tube to avoid depositing particles of carbon in the conductivity cell. This appeared to have no effect on resolution.

Owing to halogenated impurities in the water, which concentrated at the front of the HPLC column before each solvent-programmed run, an ODS silica pre-column was necessary in the water delivery line between the two HPLC pumps, with the plumbing of the system then inverted.

Applications of the chlorine detector

Operating the system under the established optimum conditions shown in Table I, the detector gave a linear response to the mass of chlorine injected. Calibration graphs are shown in Fig. 7 for 0–8 μg of dichlorobenzene operating with 100% methanol but without an HPLC column, and for the same concentration range but with a reversed-phase column (dichlorobenzene capacity ratio 1.9) with a methanol–water gradient. The masses refer to dichlorobenzene entering the detector, which for a 20% split with a 20-μl injection represents a sample concentration of 0.2–2.0 mg/ml. The limits of detection for the two systems were 40 ng of dichlorobenzene (*ca.* 20 ng of chlorine) without a column and 100 ng of dichlorobenzene (*ca.* 50 ng of chlorine) with an HPLC column. The detection limit, which was equivalent to about 1.4 ng/sec of chlorine, was higher in the latter instance because the peak was less sharp and the baseline noisier when using aqueous solvents.

Although the high volumes of solvent vapour restricted the sensitivity of the detector and the peaks were not as sharp as those normally associated with HPLC, the detector nevertheless has still proved very useful, especially when employed in a preparative mode. In order to improve the sensitivity more efficient conversion of the organic mobile phase to fully reduced hydrocarbons is needed, thereby reducing the standing current in the electrolysis cell. Although the Hall detector is limited in solvents which can be employed it should be noted that its use is complementary to previously described HPLC–electron capture combinations for halogen detection[1] where only relatively non-polar solvents were acceptable. A typical separation of chlorinated hydrocarbons is shown in Fig. 8, giving very similar peak shapes to those obtained when operating the HPLC splitter in conjunction with other detectors, *e.g.*, the UV detector.

Long-chain polychlorinated alkanes are of interest to these laboratories both as environmental contaminants in the food chain originating from their industrial use as plasticizers and flame retardants[6,7], and in the form of PVC oligomers as species with a potential for migration from plastic packaging into foods[8,9]. In both areas the analytical problems are identical, in that thermal instability and low volatility of these complex mixtures of chlorinated components make separation by GC impractical, whilst lack of a suitable chromophore makes detection by HPLC difficult. For the monitoring of these chlorinated compounds the Hall detector coupled to HPLC has proved to be ideal. Typical chromatograms are illustrated in Fig. 9 for

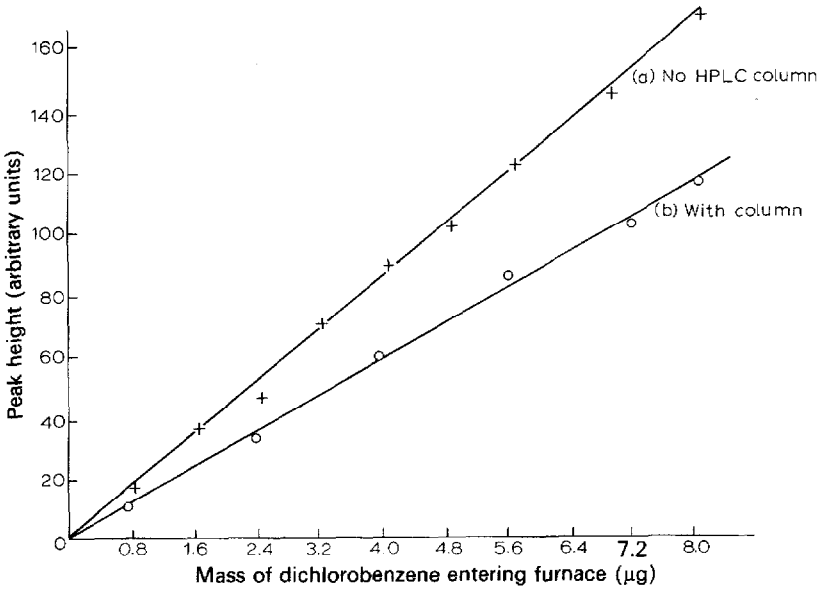

Fig. 7. Calibration graphs for dichlorobenzene. +, Omitting the HPLC column from the system; ○ including ODS reversed-phase column ($k' = 1.9$).

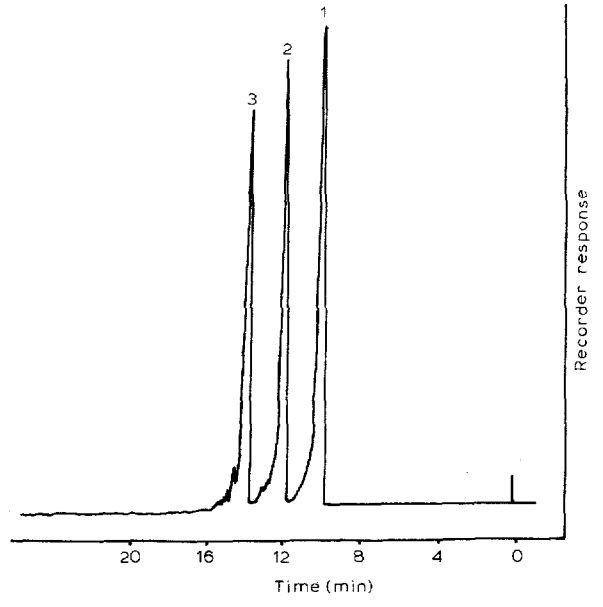

Fig. 8. HPLC trace with Hall detector showing separation of chloroalkanes. Peaks: (1) 1,4-dichlorobutane; (2) 1,6-dichlorohexane; (3) 1,9-dichlorononane. Column, 5 μm Spherisorb ODS (250 × 4.9 mm I.D.) operated at 1 ml/min eluent programmed from 80:20 methanol–water to 100% methanol in 10 min. Hall detector operated under optimum conditions given in Table I.

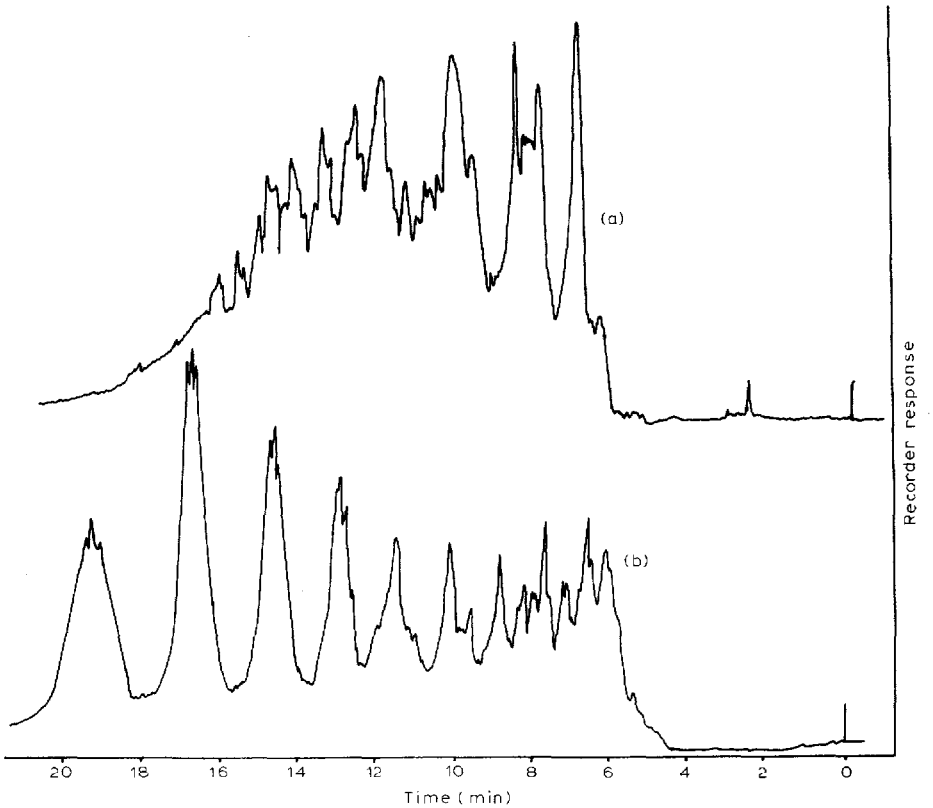

Fig. 9. HPLC traces illustrating PVC oligomers from different food contact grade PVC resins. (a) Bottle blowing: rigid foil grade PVC resin ($M_n \approx 37 \cdot 10^3$–$45 \cdot 10^3$). (b) Film grade PVC resin ($M_n \approx 65 \cdot 10^3$). Conditions as in Fig. 8.

the low-molecular-weight fractions isolated from two different food contact grade PVC resins. The selective detection of a homologous series of these oligomeric species can be clearly seen even in the presence of other non-chlorinated contaminants and the relative distribution of components can thus be determined. The use of the Hall detector in this particular application has enabled considerable progress to be made, allowing trapping of the separated species for structural elucidation by other spectroscopic techniques.

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