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Reversed-phase liquid chromatographic column switching for the trace-level determination of polar compounds

Application to chloroallyl alcohol in ground water

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ABSTRACT

Reversed-phase liquid chromatographic (LC) column-switching employing two C_{18} columns was used for the trace-level determination of the polar compound chloroallyl alcohol (CAAL), a key metabolite of the soil sterilant dichloropropene, in ground water. The selectivity of the LC procedure is crucial as CAAL does not possess a chromophoric group and must be detected by UV absorbance at 205 nm. It is shown that the selectivity can be enhanced considerably by the use of a column-switching technique.

A completely automated procedure was developed for the determination of CAAL with a limit of detection (LOD) of 1 ppb (10^9) (signal-to-noise ratio = 3). Recoveries at the 20 ppb level were 103% for *cis*-CAAL [relative standard deviation (R.S.D.) = 3.4%] and 102% for *trans*-CAAL (R.S.D. = 2.5%). Response was linear over more than two decades. The sample throughput is high, as the total time required for the analysis is less than 10 min. If necessary, LODs can be lowered to 0.1 ppb by means of a liquid–liquid extraction combined with a concentration step, resulting in recoveries of 88% (R.S.D. = 4.1%) at a level of 2 ppb.

Confirmation of CAAL and a second metabolite of dichloropropene, chloroacrylic acid (CAAC), was performed by gas chromatography–negative ionization chemical mass spectrometry (GC–NCI-MS), using derivatization procedures to convert CAAL and CAAC into their pentafluorobenzoyl and pentafluorobenzyl derivatives, respectively.

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INTRODUCTION

In a recent review[1], it was stated that precolumn technology is a powerful means for selective sample handling in liquid chromatography (LC). A major advantage of on-line techniques is that sample preparation and clean-up are fully integrated in the chromatographic procedure. Short precolumns (2 × 4.6 mm I.D.) packed with C_{18} material have been used successfully for the trace enrichment of apolar and moderately polar pesticides in water[2–5]. A disadvantage of this method is the poor selectivity, especially in combination with UV detection. The selectivity can be improved by applying more selective electrochemical[2,4] or fluorescence[3] detection. However, the inherent selectivity of these detection techniques restricts them to only a limited number of compounds.

In our previous studies longer C_{18} precolumns (15 × 3.2 mm I.D.) were used, in order to perform an efficient clean-up, with a precise cutting of the relevant fraction to the analytical column for the determination of some fungicides[6] and herbicides[7,8] in extracts of contaminated water. These procedures have a more selective clean-up performance than methods involving preconcentration of large volumes of water on a precolumn, followed by desorption.

When dealing with medium to highly polar compounds, other types of adsorbents are often preferred which possess higher affinities than the C_{18} material for such compounds. For example, polymer PRP-1 precolumns were used for the preconcentration of phenoxyacetic acids in industrial effluents[9,10] and ion-exchange precolumns have been used for trace enrichment of anilines and phenols in surface water[11,12]. The very strong sorbent properties of polymer phases with respect to almost all polar and non-polar organic compounds makes this type of phase less selective than C_{18} materials. The use of ion-exchange precolumns is limited to ionic species.

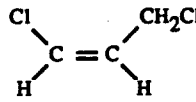
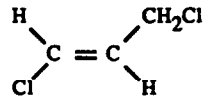
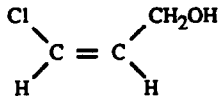
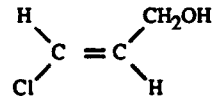
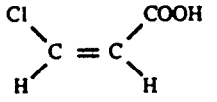
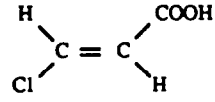
In this work, we developed a column-switching procedure for the determination of a polar compound in ground water using two C_{18} columns with high separation power, increasing the selectivity by applying the cutting technique and the sensitivity by using large volume injections. It was applied to chloroallyl alcohol (CAAL), which is expected to occur in ground and surface waters as a metabolite of the soil fumigant 1,3-dichloropropene (DPE). DPE is frequently used in certain areas of The Netherlands for the control of nematodes in agriculture, horticulture and ornamental culture. As is known[13–18], *cis*- and *trans*-DPE hydrolyse rapidly to the corresponding CAALs in the presence of water, which in turn may undergo microbial conversion to the acrylic acids. The latter conversion is thought to take place much more slowly. The proliferation of these metabolites depends strongly on their mobility in soil, of which little is still known. However, based on the polarity of these compounds, a high mobility can be expected.

Several gas chromatographic (GC) methods for the determination of CAAL have been described[12–17], but most of them lack sensitivity and/or selectivity and, moreover, most of them are laborious. Reversed-phase LC (UV detection, 210 nm) has been used for the determination of DPE and CAAL at relatively high levels (sub-ppm) in water[19]. This paper describes the development of an automated, sensitive (sub-ppb[a]

[a] Throughout this article, the American billion (10^9) is meant.

TABLE I

STRUCTURAL FORMULAE AND UV CHARACTERISTICS OF DICHLOROPROPENE (DPE), CHLOROALLY ALCOHOL (CAAL) AND CHLOROACRYLIC ACID (CAAC)

Compound	*Structural formula*		λ_{max} *(nm)*	ε_{205} *(l/mol · cm)*
	cis	*trans*		
DPE			200	15000
CAAL			190	10000
CAAC			232	12000

level) and selective LC method involving column switching for the determination of CAAL in ground water. GC–mass spectrometric (MS) confirmation techniques were developed for CAAL and chloroacrylic acid (CAAC) in order to confirm the data produced by field studies. The latter methods were based on electron-capture negative chemical ionization (ECNCI) of the pentafluorobenzoyl derivative of CAAL and the pentafluorobenzyl derivative of CAAC, respectively.

The structural formulae of the various compounds and relevant UV characteristics are given in Table I. In this paper, the abbreviations of DPE, CAAL and CAAC indicate the *cis*- and *trans*-isomers, unless stated otherwise.

EXPERIMENTAL

Reagents

1,3-Dichloropropene [a mixture of 49.9% (w/w) *trans*- and 45.8% (w/w) *cis*-DPE], *cis*-chloroallyl alcohol (98.7%, w/w) and *trans*-chloroallyl alcohol (97.5%, w/w) were obtained from Shell (Sittingbourne, Kent, U.K.). *trans*-3-Chloroacrylic acid (99%), *cis*-3-chloroacrylic acid (98%) and triethylamine (99%) were purchased from Janssen Chimica (Beerse, Belgium) and pentafluorobenzoyl chloride, pentafluorobenzyl bromide and dimethylaminopyridine from Pierce (Rockford, IL, U.S.A.). Analytical-reagent grade toluene, hexane, dichloromethane, ethyl acetate and diethyl ether were obtained from Merck (Darmstadt, F.R.G.) and methanol and acetonitrile, both of HPLC grade, from Baker (Deventer, The Netherlands). Analytical reagent grade sodium chloride (NaCl), anhydrous sodium sulphate (Na_2SO_4) and hydrochloric acid (0.1 *M* HCl) were obtained from Merck. De-

mineralized water was purified in a Milli-Q (Millipore, Bedford, MD, U.S.A.) system to obtain LC-grade water for use in eluents and standard solutions.

Equipment

LC instrumentation. The automated LC column-switching system, shown schematically in Fig. 1, consisted of the following components: an ASPI 232-401 autosampler (Gilson, Villiers-le-Bel, France) equipped with two programmable six-port valves and a 200-μl injection loop. The first separation column (SC-1) was a 50 × 3.0 mm I.D. column packed with ChromSpher C_{18}, 5 μm (Chrompack, Middelburg, The Netherlands). An LC-250 binary gradient pump (Perkin-Elmer, Norwalk, CT, U.S.A.) with a helium degassing system was used for solvent delivery (100% water or 100% methanol) to the first LC column. A Model 301 pump (Gilson) was used for delivering methanol–water (5:95, v/v) to the second separation column (SC-2) (100 × 4.6 mm I.D., packed with MicroSpher C_{18}, 3 μm; Chrompack). All flow-rates were set at 1 ml/min. UV detection (205 nm) was performed with an LC-95 (Perking Elmer) detector equipped with a CI-10 integrator (LDC/Milton Roy, Co. Clare, Ireland).

GC–MS instrumentation. GC–MS analyses were performed on a Model 4500 instrument (Finnigan MAT, Sunnyvale, CA, U.S.A.). Ionization of samples was achieved with ECNCI with methane as the moderator gas (0.3 Torr) and 70-eV electrons with a filament emission current of 0.3 mA. The temperature of the source was set at 170°C and the GC–MS interface at 250°C. Multiple-ion detection (MID) was used with a dwell time of 50 ms per ion.

The GC separation was carried out on a 25 m × 0.25 mm I.D. CP Sil-19 CB fused-silica capillary column (d_f = 0.12 μm) obtained from Chrompack. After a splitless injection of 1 μl at an injection temperature of 250°C, the column temperature was programmed from 70°C (held for 2 min) at 8°C/min to a final temperature of 200°C, which was held for 10 min.

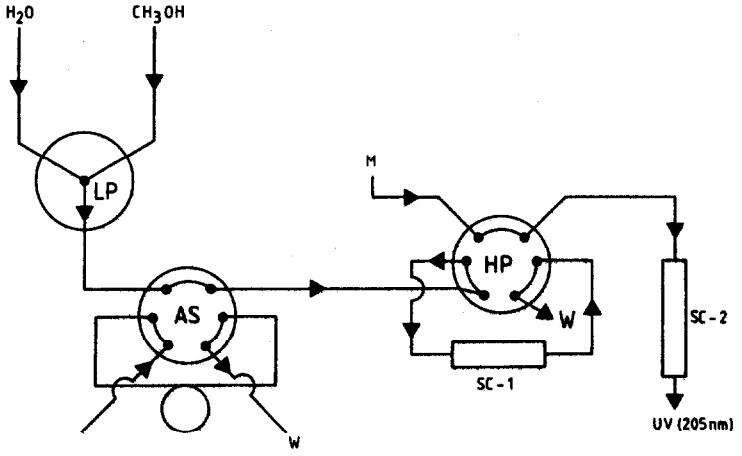


Fig. 1. Scheme of the experimental set-up. AS = Autosampler with a 200-μl loop; LP = low-pressure three-way selection valve; HP = high-pressure six-port valve; SC-1 = 50 × 3 mm I.D. C_{18} precolumn; SC-2 = 100 × 4.6 mm I.D. C_{18} separation column; M = mobile phase, methanol–water (5:95, v/v); flow-rates, 1 ml/min. For the timing of the eluent streams, see Fig. 2 and Results and Discussion.

LC analysis

Direct LC determination of CAAL in water samples (LOD, 1 μg/l). A 200-μl volume of sample was injected onto the first column (SC-1) employing water as the mobile phase (1 ml/min). After clean-up (1.0 min), SC-1 was switched on-line with the second column (SC-2), and the fraction containing CAAL was transferred to SC-2 in 0.8 min with methanol–water (5:95, v/v), the mobile phase for SC-2. Then SC-1 was switched off-line from SC-2 and reconditioned prior to the next injection with 3 ml of methanol followed by 10 ml of water. Depending on the occurrence of interfering peaks, the reconditioning step can be postponed until after about ten samples in order to increase the sample throughput.

LC determination of CAAL in water samples (LOD, 0.1 μg/l). A 100-ml volume of water was transferred to a 250-ml separating funnel. After the addition of 10 g of NaCl, extraction of CAAL was performed twice with 25 ml of diethyl ether by shaking the funnel for 2 min. The combined organic layers were placed in a 250 ml round-bottomed flask together with 2 ml of LC-grade water. The diethyl ether was removed in a rotating film evaporator at ambient temperature. The aqueous residue was transferred to a calibrated tube and the final volume was brought to 2.5 ml with LC-grade water. A 200-μl volume of this solution was injected as described in the previous section.

GC–MS confirmation of CAAL and CAAC

Extraction The same extraction procedure was used for CAAL and CAAC. A 5-ml volume of a water sample was pipetted into a test-tube and, after the addition of 1 ml of 0.1*M* HCl, 200 mg of NaCl and 5 ml of diethyl ether, the tube was shaken vigorously for 5 min. The organic layer was transferred into another tube and carefully evaporated to dryness under a gentle stream of nitrogen at ambient temperature.

Derivatization of CAAL. Toluene (0.5 ml), 10 μl of pentafluorobenzoyl chloride and 50 μl of a dichloromethane solution of dimethylaminopyridine (20 mg/ml) were added to the residue. The tube was closed with a glass stopper and heated for 30 min at 70°C. After cooling to room temperature, 0.5 ml of hexane and 0.5 ml of 0.1 *M* HCl were added and the derivative formed (CAAL–PFBCO) was extracted into the hexane–toluene layer. In this step, the excess of dimethylaminopyridine is largely removed from the sample as its hydrochloride salt. A 1-μl aliquot of the organic phase was injected into the GC–MS system.

Derivatization of CAAC. The residue obtained after extraction was dissolved in 50 μl of acetonitrile, and 10 μl of pentafluorobenzyl bromide and 10 μl of triethylamine were added. The mixture was heated for 10 min at 40°C. The ester formed (CAAP–PFB) was isolated from the reaction mixture by shaking with ethyl acetate (1.0 ml) and 0.1 *M* HCl (0.5 ml). The tube was then centrifuged (1500 *g*) for 1 min and 1 μl of the organic layer was used for GC–MS analysis.

RESULTS AND DISCUSSION

Choice of the method of analysis for CAAL and related compounds

Many polar compounds are difficult to detect in LC because they do not contain a chromophoric group. In this event UV detection at low wavelengths (200–215 nm) sometimes still provides sufficient sensitivity. If this non-selective detection mode has

to provide detection limits in the low-ppb range, a highly selective sample clean-up is required. In low-wavelength UV detection, background absorption plays an important role, especially if the chromatographic procedure involves changes in mobile phase composition. In this study, 205 nm turned out to be a suitable detection wavelength with respect to both sensitivity and low fluctuation of the background absorption on switching of the mobile phases.

In order to investigate the feasibility of a reversed-phase LC (RP-LC) determination of dichloropropene-related compounds, with emphasis on CAAL, the chromatographic behaviour of this compound and CAAC and DPE was studied on 5-μm C_{18} bonded silica material with methanol–water mixtures as eluent. The capacity factors (k') of CAAL and DPE are given in Table II. As expected, even with pure water as eluent, CAAC elutes shortly after t_0 (dead time) from a C_{18} bonded phase. Retention was obtained by using a 0.03 *M* phosphate buffer (pH 2.5); the results are given in Table II. The acrylic acids, however, gave tailing peaks with asymmetry factors at 10% peak height (A_s) of 2.0 (*cis*-CAAC) and 2.5 (*trans*-CAAC), which makes this buffered C_{18} system unsuitable for the trace-level determination of these compounds. The use of a phophate buffer did not influence the chromatographic behaviour of CAAL and DPE in comparison with unbuffered water–methanol systems.

Direct assay of CAAL in ground water

From the data in Table II, it can be seen that some trace enrichment of, *e.g.*, DPE will be possible on C_{18} precolumns, but problems will occur with CAAL as it shows insufficient retention even in a completely aqueous mobile phase. This results in an early breakthrough and excessive band broadening on transfer to the analytical column. In previous applications of column-switching techniques[6–8], limited volumes (100–1000 μl) were injected onto longer C_{18} precolumns (15 × 3.2 mm I.D.). For the present application, it can be estimated that, for example, with 200-μl injections of water samples containing CAAL onto such a large precolumns with a mobile phase of 100% water, only *ca.* 300 μl of mobile phase are available for clean-up before CAAL starts to break through. Moreover, ground-water samples contain relatively high

TABLE II

CAPACITY FACTORS ON A 50 × 3 mm I.D. COLUMN PACKED WITH 5-μm CHROMSPHER C_{18}[a] FOR CAAL AND DPE IN METHANOL–WATER AND FOR CAAC IN METHANOL–PHOSPHATE BUFFER (pH 2.5) MIXTURES

Methanol(%)	*k'*					
	cis-CAAL	*trans-CAAL*	*cis-DPE*	*trans-DPE*	*cis-CAAC*	*trans-CAAC*
0	7.2	7.3	59	55	7.3	17.6
10	3.8	3.9	44	41	3.4	9.9
20	2.4	2.5	23	22	1.7	4.9
30	1.8	1.9	16	15	1.3	3.3
40	1.3	1.4	9.4	8.9	1.0	2.4
50	1.0	1.1	4.7	4.7	–	–

[a] t_0 (Br^-) = 0.16 min.

concentrations of ionic species, which will produce a high UV response at 205 nm in the early part of the chromatogram (solvent peak), so causing interferences in the same part of the chromatogram where the components of interest are eluting.

Obviously, an even larger precolumn has to be selected in order to improve the clean-up performance of the system and, thus, to develop a successful RP-LC column-switching operation for compounds in the polarity range of CAAL. As an alternative, 50 × 3 mm I.D. guard columns packed with 5-μm ChromSphere C_{18} were studied. Such columns, which lie between a precolumn and a full separation column, were used as a first separation column (SC-1) in our further experiments. Because CAAL starts to migrate immediately on SC-1 after injection, the volume of sample introduction was set arbitrarily at 200 μl, in order to have a sufficient clean-up possibility.

To illustrate the problem of the separation of CAAL in ground water, chromatograms (recorded at a high attenuation) from 200-μl injections on SC-1 of a concentrated CAAL standard (200 ng) and a blank ground-water sample are shown in Fig. 2. The chromatograms show that after the 200-μl injection, a clean-up with about 1 ml of solvent can be used before CAAL starts to break through. In experiments with ground-water samples using the column-switching technique described below, it appeared that a flush with 1.0 ml of water after the injection provides a sufficient

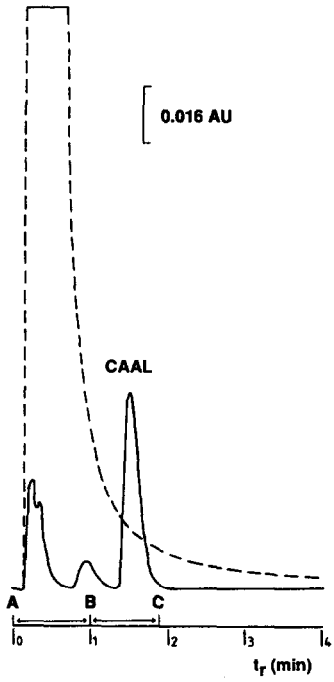


Fig. 2. Chromatograms of 200-μl sample injections on the SC-1 column (conditions as in Fig. 1) illustrating the selection of the column-switching conditions. Solid line, injection of sample containing 1000 ppb *cis*-CAAL in LC-grade water; dashed line, blank ground water sample. A to B, injection (0.2 ml) + clean-up with 0.8 ml of pure water; B to C, desorption of CAAL with 0.8 ml of methanol–water (5:95, v/v) to SC-2 column.

clean-up. With water, CAAL elutes completely from SC-1 within 1.8 ml and therefore after the clean-up a desorption volume of 0.8 ml was selected to transfer the CAAL fraction from the first to the second column.

In order to obtain peak compression and hence an increased sensitivity for CAAL, the mobile phase for the second separation column, *i.e.*, the real separation column, has to contain an organic modifier; 5% methanol in water was selected for use as the mobile phase for the second separation column. Considering the small retention of CAAL on C_{18} bonded silica, a highly efficient second column (SC-2; Fig. 1) should be used to obtain sufficient resolution between CAAL and either early eluting interferences or the baseline disturbance caused by the eluent switch. Several columns with C_{18} bonded phases were tested for their efficiency (expressed as N and A_s) and usefulness (expressed as k') as a second separation column; the results are given in Table III. From these data it can be concluded that the tested 4.6 mm I.D. columns were more efficient than the 3.0 mm I.D. columns. Possibly the larger I.D. of the second column enhances the peak compression caused by the step gradient from 0 to 5% methanol. Because of the shorter time of analysis and the slightly higher k' values, the 100 × 4.6 mm I.D. MicroSpher C_{18} column was preferred as a second separation column. The use of methanol–water (5:95, v/v) instead of pure water results in an enhancement of the peak shape. Compared with pure water, N increases from 3800 to 4800 and A_s decreases from 1.6 to 1.2 with the addition of 5% methanol.

Unfortunately, *cis*- and *trans*-CAAL cannot be separated on any of the four C_{18} bonded phases tested. McCall[19] separated *cis*- and *trans*-CAAL on the polymeric PRP-1 phase. However, his study indicated that the CAAL isomers elute as broad peaks (σ = 1.1 min) with a resolution of only 0.5, which leads to a much lower sensitivity. From an ecotoxicological point of view, separation of *cis*- and *trans*-CAAL is not too important, as the half-life of the conversion of *cis*-DPE into *cis*-CAAL is equal to that of *trans*-DPE into *trans*-CAAL.

The final set-up of the column-switching procedure for the determination of CAAL in water involves the injection of a 200-µl sample, clean-up on a 50 × 3 mm I.D. C_{18} column using water as the mobile phase, followed by desorption of the CAAL

TABLE III

COMPARISON OF C_{18} BONDED PHASE COLUMNS TO BE USED AS A SECOND SEPARATION COLUMN FOR THE DETERMINATION OF CAAL

For conditions, see Fig. 2.

Column dimensions length × I.D. (mm)	*Packing material*	*k'*		*N*[a]	*A*[s][b]
		cis-CAAL	*trans-CAAL*		
100 × 3	ChromSpher C_{18}, 5 µm	4.1	4.2	525	2.6
100 × 3	Hypersil ODS, 5 µm	2.5	2.5	440	2.3
150 × 4.6	Hypersil ODS, 5 µm	7.3	7.3	6380	1.4
100 × 4.6	MicroSpher C_{18}, 3 µm	8.2	8.3	4820	1.2

[a] Plate number calculated as $(t_r/\sigma)^2$, where t_r is retention time and σ is standard deviation, for *trans*-CAAL.

[b] Asymmetry calculated at 10% of the peak height, for *trans*-CAAL.

fraction to a second 100 × 4.6 mm I.D. C_{18} column with methanol–water (5:95, v/v) and UV detection at 205 nm.

Determination of CAAL in ground water. With a 200-μl injection of aqueous sample and UV detection at 205 nm (80% of the maximum UV absorbance at 195 nm), an absolute limit of detection (LOD; signal-to-noise ratio = 3:1) of 0.2 ng of CAAL was obtained, corresponding to an LOD of 1 ppb for the direct assay of CAAL in water. The response for CAAL was linear from 10 to 200 ppb ($r = 0.9996$, $n = 6$). The relative standard deviation (R.S.D.) of the peak height at a level of 40 ppb was 2.3% for *cis*-CAAL ($n = 6$) and 1.7% for *trans*-CAAL ($n = 10$). The R.S.D. of the retention times was 0.45% for both *cis*-CAAL and *trans*-CAAL ($n = 6$). The mean recoveries at a level of 20 ppb of *cis*-CAAL ($n = 5$) and 22 ppb of *trans*-CAAL ($n = 5$) were 103%

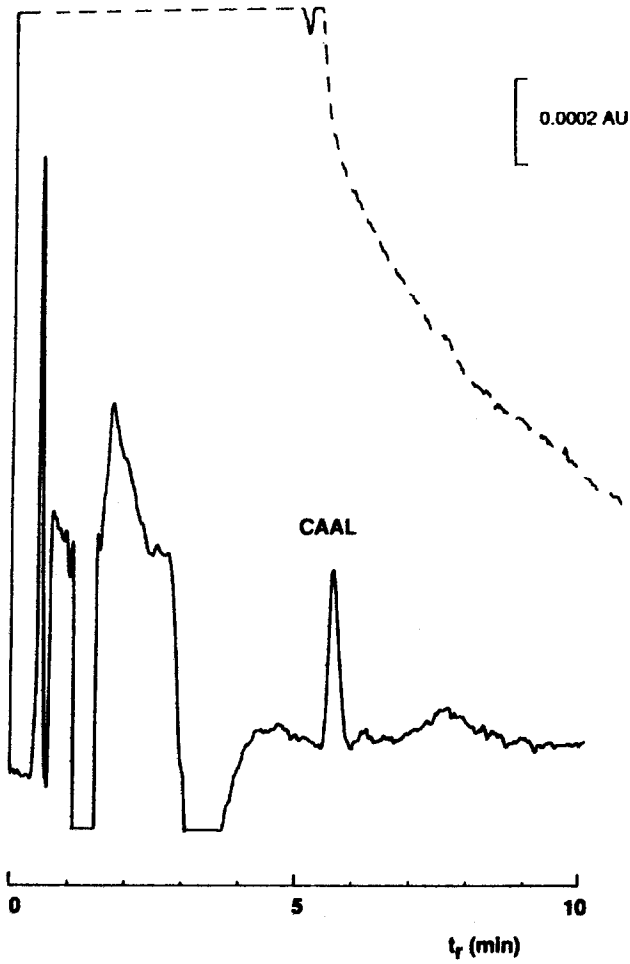


Fig. 3. RP-LC of 200-μl injections of a ground-water sample spiked with 10 ppb of *trans*-CAAL. Solid line, chromatogram obtained using the column-switching procedure; dashed line, chromatogram obtained with the same two columns coupled on-line, but without the column-switching procedure. Mobile phase: methanol–water (5:95, v/v) at 1 ml/min.

(R.S.D. = 3.4%) for *cis*-CAAL and 102% (R.S.D. = 2.5%) for *trans*-CAAL (n = 5). The sample throughput is high; each sample can be analysed within 10 min and for the ground-water samples investigated the washing step of the first column with methanol can be left until after ten injections.

The remarkable gain in selectivity obtained with the present procedure is illustrated in Fig. 3, showing the analysis of ground water spiked with 10 ppb of CAAL with and without column switching. In the latter instance, the same two columns (SC-1 and SC-2) were used but coupled on-line. As stated above, the high UV absorbance in the first part of the chromatogram obtained without column switching is caused mainly by the presence of inorganic ions. A typical conductivity value of this type of ground-water samples is 570 μS/cm, corresponding with a total ion strength of about 7 mmol/l. The anion composition of ground water typically is *ca.* 80% chloride and 20% nitrate. From this it can be estimated that a sample of 200 μl of ground water will contain about 40 μg of Cl^- and 15 μg of NO_3^-. According to Ayers and Gillett[20], the UV detection limit at 205 nm is 30 ng for Cl^- and 0.5 ng for NO_3^-. Consequently, at the wavelength of 205 nm used to detect CAAL, a water sample containing μg/ml levels of these anions will indeed produce a large UV response in the early part of the chromatogram. Multi-dimensional LC obviously is an efficient means of separating large amounts of anions from CAAL, which is not possible with single-column LC.

In a field experiment, according to the set-up of Boumans *et al.*[21], the mobility of CAAL and some pesticides were investigated. With the developed direct assay method, 22 ground-water samples were analysed and residues of CAAL were found in the range from 1 to 118 ppb.

Assay of CAAL in water after diethyl ether extraction and concentration

In order to decrease the LOD for CAAL to 0.1 μg/l, which is the EC tolerance level for pesticides in drinking water, a concentration step is necessary. According to Maddy *et al.*[18], CAAL can be concentrated by liquid–liquid extraction with diethyl ether followed by partial evaporation of the organic extract. For the LC analysis the final solution must consist of pure water. However, it is not possible to remove all of the traces diethyl ether (necessary for the LC analysis) without considerable losses of CAAL. This problem can largely be eliminated by adding a small volume of water to the diethyl ether extract to retain CAAL before the rotating film evaporation takes place. An additional advantage is that the final aqueous solution, after it has been adjusted to the volume required, can be injected directly into the RP-LC system. During the diethyl ether extraction most of the anionic interferences are eliminated and column switching as a clean-up step therefore becomes less urgent. However, the column-switching procedure will prevent the occurrence of later eluting peaks, and so reduce the total time of analysis.

An illustration of the LC analysis after extraction with diethyl ether is shown in Fig. 4, which is a chromatogram of a blank ground water spiked with 1 ppb of CAAL. The recovery of CAAL was tested by adding *cis*- and *trans*-CAAL to ground water at levels of 2 and 20 ppb, respectively. This resulted in mean recoveries of 88% (n = 10; R.S.D. = 4.1%) for *cis*-CAAL and of 87% (n = 10: R.S.D. = 2.7%) for *trans*-CAAL. No significant differences in the recovery at the two levels were found.

Seven ground-water samples were taken from suspected locations and analysed using the present method. None of the samples contained more than 0.1 ppb of CAAL, which is the limit of detection.

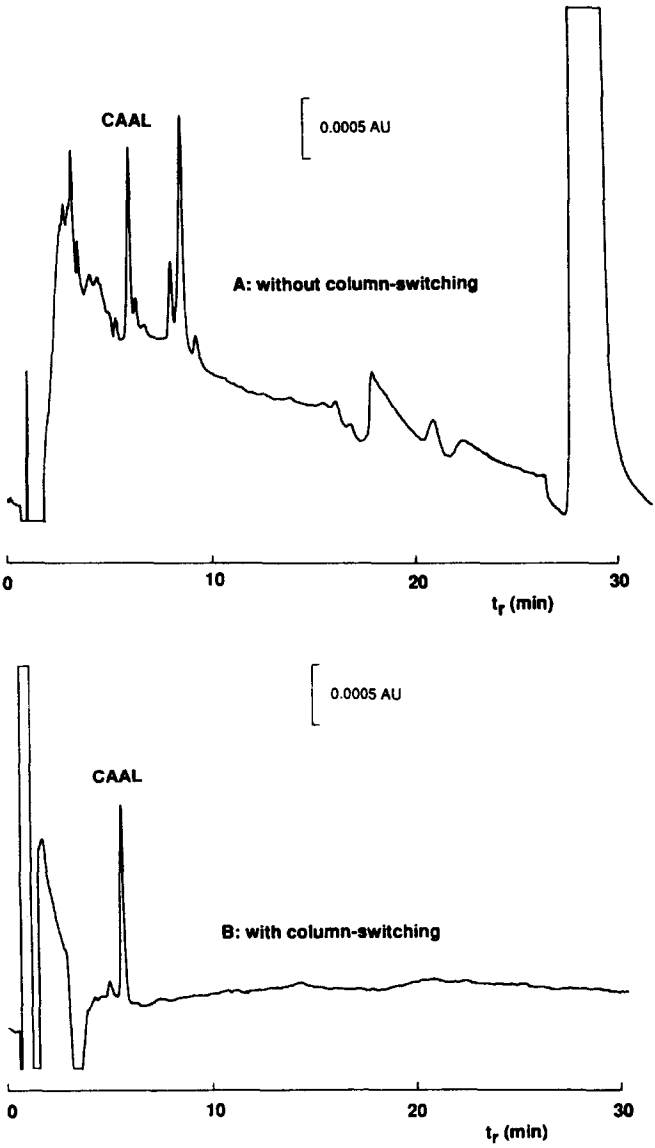


Fig. 4. RP-LC of a blank ground-water sample spiked with 1 ppb of *trans*-CAAL after extraction and concentration with diethyl ether, (A) without and (B) with column switching.

GC–MS confirmation of CAAL and CAAC

If CAAL is found in a drinking-water source, an independent alternative analytical method should be available for confirmation purposes. GC–MS is a very sensitive and selective technique, especially when performed in the ECNCI mode Therefore, a derivatization procedure was developed for CAAL with pentafluorobenzoyl chloride. The use of the strong base dimethylaminopyridine markedly

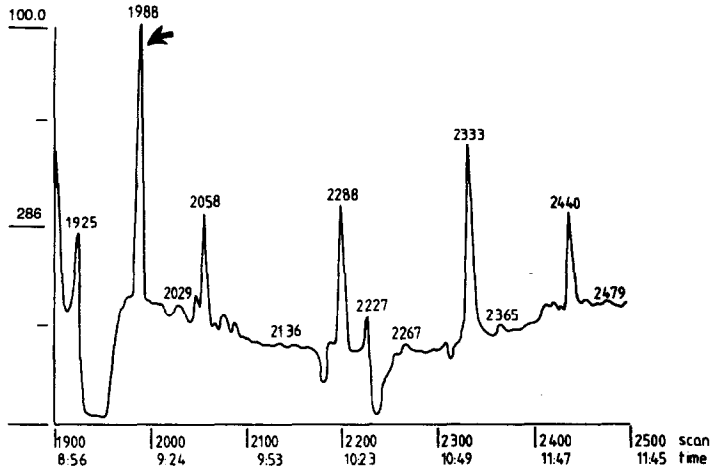


Fig. 5. GC–ECNCI-MS with selected ion detection at *m/z* 286 of a drinking-water sample spiked with 1 ppb of *trans*-CAAL, after extraction and derivatization with pentafluorobenzoyl chloride. Time in min:s.

increases the rate of the reaction, resulting in quantitative (>95%) yields. This was confirmed by residual analysis for free (unreacted) CAAL in the reaction medium by the LC method described here. The derivatives are very stable for several weeks in the organic phase solution when it is stored cool (5°C) and in the dark.

For the confirmation of CAAL, the molecular ion (*m/z* 286) of the pentafluorobenzoyl derivative, its ^{37}Cl isotope (*m/z* 288) and the fragment ions at *m/z* 211 ($PFCOO^-$) and *m/z* 167 (PFB^-) were monitored in the multiple-ion mode. The last two ions are not compound-specific. For positive identification of a peak at the proper retention time, the intensity ratio of the peaks at *m/z* 286 and 288 should be between 0.30 and 0.36, which represents the natural isotope ratio for $^{35}Cl/^{37}Cl$ of 0.33 (±10%).

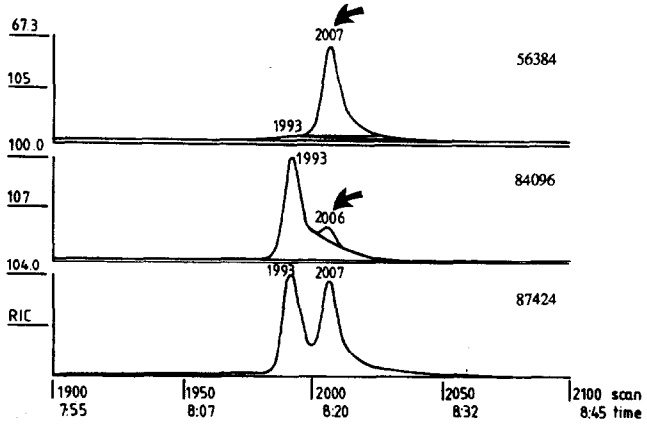


Fig. 6. GC–ECNCI-MS (*m/z* 105 and 107) of the analysis of drinking water spiked with 1 ppb of *trans*-CAAC after extraction and derivatization with pentafluorobenzyl bromide. Time in min:s.

Fig. 5 shows the GC–ECNCI-MS of CAAL in drinking water spiked at the 1 ppb level and indicates that an LOD at this level can easily be obtained.

It is interesting that preliminary experiments with CAAC, for which no proper LC procedure has yet been developed, show that a GC–MS method similar to that for CAAL can serve for identification purposes. In this instance, derivatization is effected with pentafluorobenzyl bromide, yielding the PFB ester[22]. The NCI mass spectrum of the CAAC–PFB derivative shows an intense compound-specific carboxylate anion at *m/z* 105 and 107 (chlorine isotope). The anion is formed by the loss of the PFB moiety from the molecular ion, a well known fragmentation pattern for PFB esters under ECNCI conditions[23]. The intensity ratio of the *m/z* 105 and 107 peaks should, as for CAAL, also be in the range 0.30–0.36. Fig. 6 shows the GC–ECNCI-MS of drinking water spiked with 1 ppb of CAAC, and indicates that the limit of detection of at least 1 ppb was restricted by an interference close to the *m/z* 107 trace and might be considerably improved if a better GC separation could be achieved.

CONCLUSIONS

A sensitive and selective multi-dimensional RP-LC method was developed for the trace-level determination of chloroallyl alcohol, the main metabolite of the pesticide dichloropropene, in drinking and ground waters. Sensitivity was obtained by non-selective UV detection at 205 nm but the selectivity was regained by using a column-switching procedure. The method has a high sample throughput, which makes it useful for screening purposes at a level of 1 ppb. The limit of detection can be reduced to 0.1 ppb by a liquid–liquid extraction with a subsequent evaporation step. The method has been applied to several types of ground- and drinking-water samples. The approach of using a relatively large column with a greater separation power than conventional precolumns for clean-up purposes in determining polar compounds such as CAAL was successful with respect to the overall selectivity of the procedure. The technique has previously been applied to improve the clean-up in the determination of organochlorine pesticides and polychlorinated biphenyls by normal-phase LC[24]. We are currently investigating the applicability of the technique to the trace-level determination of moderately polar and non-polar pesticides. For confirmation purposes a new GC–ECNCI-MS procedure has been developed for both chloroallyl alcohol and chloroacrylic acid, involving extraction and derivatization with fluorine-containing reagents of the analytes. Identification can be achieved down to at least 1 ppb.

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