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SPECIATION OF ARYLOXYETHOXYETHYL BENZYL DIMETHYL AMMONIUM SALTS BY GLASS CAPILLARY GAS CHROMATOGRAPHY AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY*

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SUMMARY

Using glass capillary gas chromatography (GC) and ion-pair reversed-phase high-performance liquid chromatography (HPLC), a pair of structurally similar microbicides, benzyl diisobutylphenoxyethoxyethyl dimethyl ammonium chloride and its cresoxy-analogue, were effectively resolved and accurately quantified with a high degree of selectivity and specificity. Optimization of conditions in the chromatographic systems to attain desirable baseline separations of the components of interest is described. The minimum detectable quantities as determined are in the neighborhood of 10 ng for the quaternary ammonium salts by HPLC–UV detection, 0.1 ng for the cyanamide derivatives of the salts by GC–alkaline flame-ionization detection and 1–2 pg for the trichloroethyl carbamate derivatives of the salts by GC–electron-capture detection. In conjunction with cation-exchange chromatography for sample enrichment and purification, the glass capillary GC and ion-pair reversed-phase HPLC methods presented here are particularly suitable to separate and simultaneously analyze for the aryloxyethoxyethyl benzyl dimethyl ammonium compounds concerned in environmental samples. It appears that these chromatographic techniques possess potential applicability to the separation and quantification of other classes of quaternary ammonium compounds with closely related structures that are not separable by other methods.

INTRODUCTION

The title compounds comprise the two commonly used surfactant quaternary ammonium microbicides: benzyl diisobutylphenoxyethoxyethyl dimethyl ammonium chloride (BDPDAC) and its cresoxy analogue (BDCDAC) (Fig. 1). They find extensive use as algicides, bactericides and fungicides in dairies, farms, industries, restaurants and many other public places. The multifaceted applications have resulted in the

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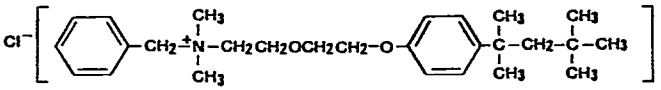
Benzyl diisobutylphenoxyethoxyethyl dimethyl ammonium chloride



Benzyl diisobutylcresoxyethoxyethyl dimethyl ammonium chloride

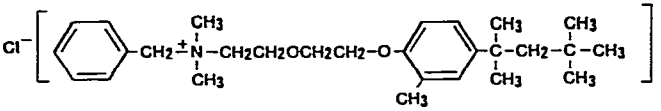


Fig. 1. Structures of the quaternary ammonium compounds investigated.

ubiquity of these germicidal substances in the environment. In the course of our continuous efforts on studying analytical methods of quaternary ammonium compounds in general, we came upon problems of separating the seemingly unresolvable pair of aryloxyethoxyethyl benzyl dimethyl ammonium analogues. It is widely recognized that gas chromatography (GC) of compounds possessing structural complexity with charged groups and thermal lability such as quaternary ammonium salts requires an appropriate chemical derivatization technique prior to quantitative measurement by GC. Our previous studies[1] revealed new methods of chemical derivatization by which the nonvolatile alkyl benzyl dimethyl ammonium chloride homologues were converted into vaporizable non-ionic substances suitable for GC. An additional advantage of these derivatization techniques was reflected in the pronounced increase in detectability of the derivatives as compared with the underivatized salts.

Extending the derivatization methods to the present situation, we have similarly prepared the cyanamide and trichloroethyl carbamate derivatives of BDPDAC and BDCDAC for GC analysis with an alkaline flame-ionization detector (AFID) and an electron-capture detector (ECD), respectively. Numerous attempts to separate either the chlorinated or nitrogenized mixture of the analogous microbicides on a variety of packed GC column under various chromatographic conditions were not fruitful. However, successful GC resolution has been achieved using a fused silica glass capillary column coated with an OV-101 stationary phase. As a viable alternative approach, we have studied the separation of mixtures of BDPDAC and BDCDAC by ion-pair reversed-phase high-performance liquid chromatography (HPLC). In this paper, details of the development of the glass capillary GC and HPLC methods for the separation and quantitative analysis of the virtually inseparable components of aryloxyethoxyethyl benzyl dimethyl ammonium compounds are presented. The usefulness of these techniques in coping with separation problems and the high degree of resolving capabilities inherent with these systems are demonstrated. To attest the applicability of the methods to environmental water samples, we also analyzed these samples treated with different levels of the title compounds.

EXPERIMENTAL

Chemicals and reagents

The reagents for derivatization and their handling have been described pre-

viously[1]. All solvents used were of chromatography grade and were obtained from Burdick & Jackson Labs. (Muskegon, MI, U.S.A.). Microbicide quality quaternary ammonium compounds were supplied as powder formulations by Onyx (Jersey City, NJ, U.S.A.) and Ruger (Hillside, NJ, U.S.A.). Pure quaternary ammonium standards, BDPDAC and BDCDAC, were prepared by repetitive recrystallization of the corresponding commercial ammonium salts. Sodium alkylsulfonates were used as received (Eastman-Kodak, Rochester, NY, U.S.A.). Sodium methanesulfonate was prepared from methanesulfonic acid (Aldrich, Milwaukee, WI, U.S.A.) and sodium methoxide in methanol. Perchloric acid (70%, w/w) was acquired from Eastman-Kodak. Carbon-14 labeled BDPDAC (2.5 mCi/mmol) was synthesized by the alkylation of the appropriate tertiary amine with benzyl chloride-7-^{14}C (California Bionuclear Corp., Sun Valley, CA, U.S.A.). The tertiary amine was prepared at this laboratory by reduction of the unlabeled quaternary ammonium compound with lithium triethylborohydride in tetrahydrofuran[1] (Aldrich). All other reagents were of analytical-reagent grade.

Chlorinated and nitrogenized derivatives

Following our recently published procedures[1], the cyanamide and trichloroethyl carbamate derivatives of both aryloxyethoxyethyl benzyl dimethyl ammonium compounds were prepared in good yield. The overall yields for the two-step derivatization reactions averaged 87 and 91%, respectively, for the former and latter derivatives.

Gas chromatography–mass spectrometry (GC–MS)

For confirmation of structural identities of all the derivatives involved, samples were analyzed on a Hewlett-Packard Model 5840A gas chromatograph with a capillary inlet system for splitless injection and a 50-m fused silica glass capillary column (OV-101) interfaced to a Hewlett-Packard Model 5985 mass spectrometer. The carrier gas (helium) head pressure was approximately 42 p.s.i. The mass spectrometer was operated at an electron energy of 70 eV with a magnetic scanning speed of 2 sec.

Glass capillary gas chromatography

A Varian Model 3700 gas chromatograph fitted with a ^{63}Ni ECD, an AFID and a splitless capillary injector was used. Two fused silica glass capillary columns (25 m × 0.21 mm I.D. and 50 m × 0.21 mm I.D.) wall-coated with an OV-101 stationary phase were purchased from Quadrex (New Haven, CT, U.S.A.). The oven temperature was held isothermally at 260°C for the shorter column (25 m) and at 290°C for the longer column (50 m). The injector and detector temperatures were set at 225 and 350°C, respectively. Nitrogen was used as the carrier gas and the inlet pressure ranged from 10 to 30 p.s.i. A Varian CDS-111C data system coupled to a Varian A-25 recorder was employed for automatic computation of peak areas.

High-performance liquid chromatography

All liquid chromatographic studies were conducted on a Varian Model LC-5000 liquid chromatograph equipped with a Valco CV-6-UHPa-N60 injection valve with a 10-μl loop (Valco Instruments, Houston, TX, U.S.A.) and a high efficiency, Ultrasphere ODS reversed-phase column (5 μm; 30 cm × 4 mm I.D.; Altex Scientific,

Berkeley, CA, U.S.A.). A guard column (5 cm × 4 mm I.D.) packed with Varian Vydac reversed-phase hydrocarbon (40 μm) was inserted between the injector and the column. Using a Varian Varichrom multiple-wavelength UV detector, a wavelength of 215 nm was chosen for detection of absorption. Peak areas and retention times were determined on a Varian Model 9176 strip chart recorder connected to a Varian Model CDS-111L data system.

Mobile phases consisting of varied concentrations of the ion-pairing reagents in acetonitrile–water were freshly prepared before use. The pH values were measured in aqueous solutions. The dead time for the reversed-phase column used was obtained by noting the time where the unretained peak emerged after injection of a solution of sodium nitrate in water into the column. The flow-rates were adjusted to suit particular experiments and to maintain retention times within proper limits.

Sample enrichment and recovery studies

Natural water samples (10–1000 ml) collected from local lakes and streams were treated with various levels of aryloxyethoxyethyl benzyl dimethyl ammonium chlorides. To each of these samples, 50 nCi of [^{14}C]BDPDAC (internal standard) in 80 ml of methanol was added. The resultant solution was passed through a glass column (25 × 2 cm I.D.) filled with 20 g of cation-exchange resin (Bio-Rad AG 50W-X4), which had been preconditioned and washed several times with methanol. Adsorption of the quaternary amine salts on the resin was complete as indicated by the absence of radioactivity in all the 10-ml fractions of column eluates. The resin was then eluted in sequence with 200 ml of methanol, 100 ml of 0.1 *M* aqueous hydrochloric acid, 100 ml of water, 150 ml of 5% diethylamine in methanol–water (1:1), 150 ml of water and 100 ml of methanol. There was no detectable radioactivity in each of the eluates collected. Final elution of the resin column with 100 ml of 50% 12 *M* methanolic hydrochloric acid effectively desorbed the quaternary amine salts from the resin. The recovery at this point based on the radioactivity measurement was 97–100%. The methanolic hydrochloric acid solution was evaporated under a reduced pressure to remove excess methanol. The remaining aqueous solution was neutralized to pH 6–7 by the dropwise addition of 20% sodium hydroxide in water at 0–5°C. Extraction of this mixture with three 50-ml portions of chloroform followed by evaporation of the combined organic extracts gave a residue which was dissolved in acetonitrile and diluted to exact volume for direct analysis by HPLC. The recovery of the solvent partitioning step was quantitative (92–97%). For GC analysis, the combined organic (chloroform) phase was dried over anhydrous sodium sulfate and filtered. The residue obtained after evaporation of the dry chloroform solution was derivatized to the cyanamides and trichloroethyl carbamates before aliquots of desired concentration were injected into the glass capillary GC column for detection by the AFID and the ECD, respectively.

RESULTS AND DISCUSSION

Some spectral data for the structural characterization of the derivatives of BDPDAC and BDCDAC by glass capillary GC–MS are presented in Table I. The appearance of nearly identical mass fragments notwithstanding the appreciable variation in intensity in the spectra within the same type of derivatives is indicative of

TABLE I

GC–MS DATA FOR THE CYANAMIDE AND TRICHLOROETHYLCARBAMATE DERIVATIVES OF THE ARYLOXYETHOXYETHYL BENZYL DIMETHYL AMMONIUM SALTS STUDIED

Compound	*Observed molecular ion* $(M)^+$	*Abundant ion (m/e)**
Cyanamide derivatives of		
BDPDAC	332	41, 42, 43, 57, 69, 83, 101, *134*, 261
BDCDAC	346	41, 42, 43, 57, 69, 83, 101, *148*, 275
Trichloroethylcarbamate derivatives of		
BDPDAC	482	44, 55, *57*, 58, 102, 131, 133, 134, 161, 276
BDCDAC	496	44, 55, *57*, 58, 102, 131, 148, 276

* Base peaks italicized.

similar molecular structures between the two analogous compounds. Molecular ions (relative intensity, 4–6%) emerging at *m/e* $(M)^+$ in accord with the molecular weights of relevant compounds were detected for all derivatives under consideration. It appears that for both cyanamide and carbamate derivatives the major fragmentation pathway proceeds via the initial cleavage of the bonds at the diisobutyl and ethoxy groups linked to the aromatic moiety producing presumably an isopropylidene phenoxonium ion at *m/e* 134 (or an isopropylidene cresoxonium ion at *m/e* 148) in high abundance. The observed mass ions listed in Table I are by no means the most abundant mass ions. Some of these represent the structurally significant mass fragments. A comparison of each of the above spectra with that obtained by direct probe MS shows matchable spectral features. This fact obviates the possibility of thermal decomposition during GC of the derivatized compounds.

The values of minimum detection limit for the two types of derivatives investigated are reported in Table II along with retention times relative to the phenoxy compounds. At a signal-to-noise ratio of 2:1, the minimum detectable quantities for the trichloroethyl carbamates are in the range of 1–2 pg with GC–ECD. Using GC–AFID, the limit for the cyanamides is around 0.1 ng. In each of all the three detecting systems that include a FID, the detector response was found to be linear over four orders of magnitude. A representative chromatogram of a sample of a mixture of cyanamide standards is shown in Fig. 2. It is clearly demonstrated that an excellent baseline resolution of the components has been achieved, although the two component peaks are separated by only 0.2 min. Fig. 3 shows a chromatogram of a sample of natural water treated with 50 μg/l of a commercial powder formulation of the supposedly homogeneous BDCDAC according to the information provided on the product label. Obviously this formulated product of practical microbicide quality contains at least 5% of the phenoxy analogue as impurity (the early eluting minor component A in Fig. 3) whose structural identity has been verified by glass capillary GC–MS and by co-chromatography with an authentic sample of the cyanamide

TABLE II

VALUES OF RELATIVE RETENTION TIME AND MINIMUM DETECTION LIMIT (GC)

RRT = relative retention time.

Compound	*RRT*	*Minimum detection limit (g)*		
		ECD	*AFID*	*FID*
Cyanamide derivatives of				
BDPDAC	1.00	$1.0 \cdot 10^{-8}$	$0.8 \cdot 10^{-10}$	$2.6 \cdot 10^{-7}$
BDCDAC	1.05	$1.2 \cdot 10^{-8}$	$1.1 \cdot 10^{-10}$	$3.2 \cdot 10^{-7}$
Trichloroethylcarbamate derivatives of				
BDPDAC	1.00	$1.1 \cdot 10^{-12}$	–	$3.4 \cdot 10^{-7}$
BDCDAC	1.05	$2.0 \cdot 10^{-12}$	–	$3.9 \cdot 10^{-7}$

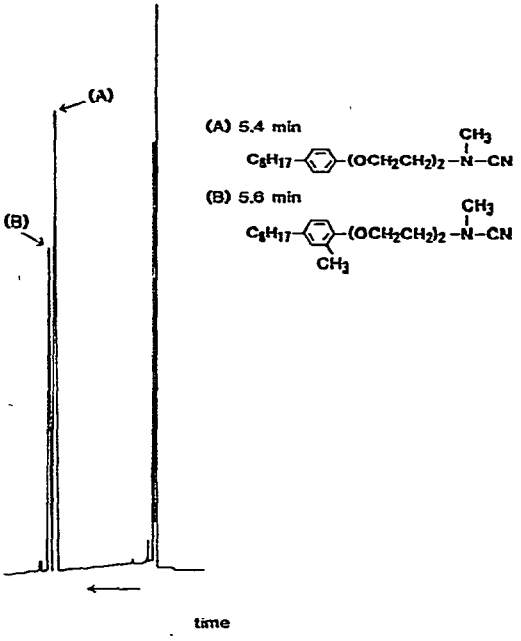


Fig. 2. Gas chromatogram of the cyanamide derivatives of a mixture of standard BDPDAC and BDCDAC (on a 50-m fused silica column at 290°C).

derivative of BDPDAC. The possible source of contamination could probably be originated from incomplete alkylation during the industrial manufacturing process. The disclosure of the occurrence of a mixture of analogous quaternary ammonium compounds in a commercial microbicide product further accentuates the environmental significance of the present study. Under the same glass capillary column conditions as in Fig. 3 except using an ECD, a mixture of pure BDPDAC and

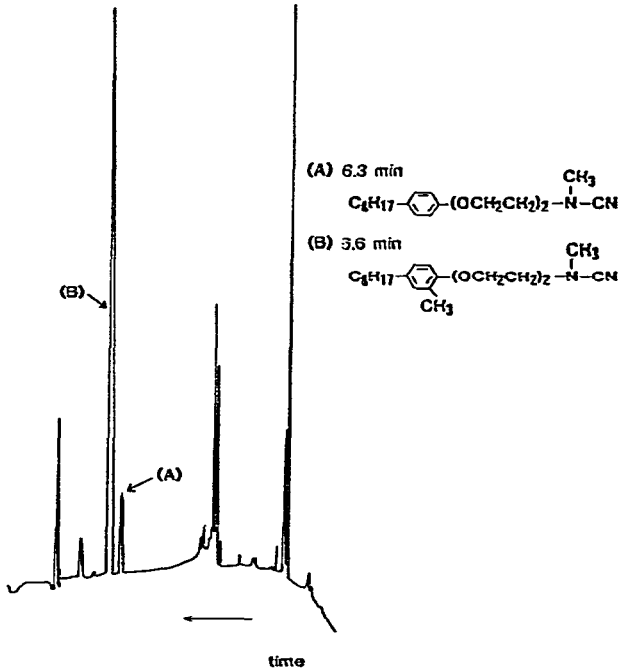


Fig. 3. Gas chromatogram of the cyanamide derivatives of BDPDAC and BDCDAC recovered from a sample of natural water treated with a commercial formulation of BDCDAC (on a 25-m fused silica column at 260°C).

BDCDAC as their trichloroethyl carbamate derivatives were well separated. A chromatogram showing the detector response of a sample of natural water treated with the above mixture of quaternary amine salts (BDPDAC–BDCDAC, 80:20 μg/l) is shown in Fig. 4.

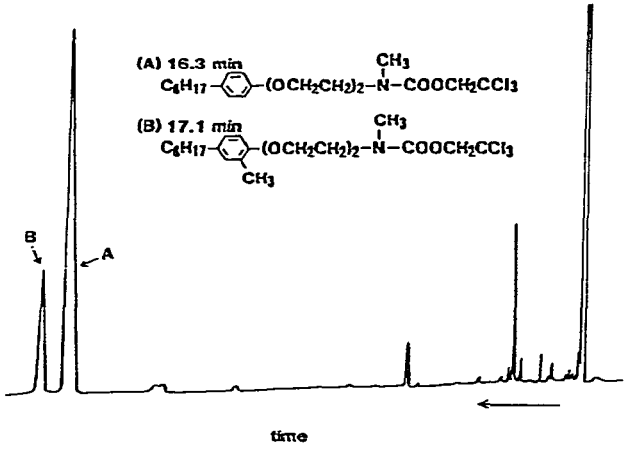


Fig. 4. Gas chromatogram of the trichloroethylcarbamate derivatives of BDPDAC and BDCDAC recovered from a sample of natural water treated with a mixture of pure BDPDAC and BDCDAC, 80:20 (μg/l) (GC conditions are the same as in Fig. 3).

As part of initial futile HPLC investigation, intensive efforts were made for the resolution of the mixture of aryloxyethoxyethyl benzyl dimethyl ammonium chlorides on several commercially available normal-phase polar columns and also on a reversed-phase octadecylsilane bonded column using various combinations of solvent systems as mobile phases. In spite of the broad range of solubility of these quaternary ammonium compounds in many organic solvents owing to the long chain lipophilic groups in the molecules, the negative results were not unexpected because of the strong affinity of the highly polar ionic solutes for each of the stationary phases tested. It was observed, however, that the addition of certain ion-pairing reagents including some organic and inorganic salts to the mobile phase (acetonitrile–water) of a reversed-phase HPLC system not only greatly improved the sensitivity for detection but also gave sufficient selectivity for separation of the two quaternary ammonium components of merely infinitesimal difference in structure. The effects of a few selected ion-pairing reagents with and without added buffer salts on retention characteristics of the analyte analogues, BDPDAC and BDCDAC, are shown in Table III.

TABLE III

EFFECTS OF SOME ION-PAIRING REAGENTS WITH AND WITHOUT ADDED BUFFER SALTS ON HPLC RETENTION CHARACTERISTICS (k')

No.	*Mobile phase reagent*	*pH*	*Capacity factor (k')*	
			BDPDAC	*BDCDAC*
1	0.01 *M* $HClO_4$ + 0.01 *M* $NaClO_4$	2.26	5.0	6.1
2	0.01 *M* $HClO_4$ + 0.01 *M* $NaCH_3SO_3$	2.30	5.2	6.5
3	0.01 *M* $HClO_4$ + 0.01 *M* $NaC_5H_{11}SO_3$	2.22	5.6	6.8
4	0.01 *M* $HClO_4$ + 0.01 *M* $NaC_8H_{17}SO_3$	2.17	6.4	7.9
5	0.01 *M* $HClO_4$ + 0.005 *M* $NaC_5H_{11}SO_3$	2.19	8.0	9.8
6	0.01 *M* $HClO_4$ + 0.005 *M* $NaC_5H_{11}SO_3$ + Na_2HPO_4	3.00	9.1	11.1
7	0.01 *M* $HClO_4$ + 0.005 *M* $NaC_5H_{11}SO_3$ + Na_2HPO_4	4.00	10.8	13.1
8	0.01 *M* $HClO_4$ + 0.005 *M* $NaC_5H_{11}SO_3$ + Na_2HPO_4	5.00	11.5	13.9
9	0.01 *M* $HClO_4$ + 0.1 *M* $NaC_5H_{11}SO_3$	2.25	5.0	6.1
10	0.05 *M* $HClO_4$ + 0.05 *M* $NaCH_3SO_3$	1.60	7.6	9.4
11	0.1 *M* $HClO_4$ + 0.005 *M* $NaC_5H_{11}SO_3$	1.30	3.5	4.7
12	0.01 *M* $HClO_4$*	2.16	9.7	12.3
13	0.01 *M* $NaC_5H_{11}SO_3$*	7.25	10.0	12.3

* Peak tailing occurred.

The capacity factors (k') were determined with reference to the column dead time as measured by the time needed for the unretained sodium nitrate to elute through the column. In earlier exploratory experiments on a few reversed-phase columns of low efficiency, baseline resolutions could be propitously obtained only in limited cases where it was possible to optimize the chromatographic conditions to achieve separation. The difficulties were overcome by switching to a high efficiency Ultrasphere reversed-phase column. Using this column under isocratic conditions with a mobile phase of acetonitrile–water (70:30) containing some ion-pairing reagents (Table III), good baseline separations were achieved in all cases given. Comprehensive accounts on ion-pair separation techniques have been well documented in the literature[2–7]. The primary function of the ion-pairing anionic counterions in the presence of the quaternary ammonium solutes can be envisioned as to impart differential retentivity to the analyte cations of interest by way of forming ion pairs during the chromatographic separation process. The retention data in Table III are in close conformity with the conventional generalities of ion-pair reversed-phase HPLC that a more hydrophobic anionic counterion tends to yield a longer retention time of the cation on the hydrophobic column. For the aryloxyethoxyethyl benzyl dimethyl ammonium compounds studied, the retention times increased as the pH values and polarity of mobile phases increased. When an ion-pairing reagent was used alone in the absence of buffering salts in the mobile phase, adsorption of the quaternary ammonium solutes on the column seemed to occur during the chromatographic differentiation process, since the components were chromatographed with some degrees of tailing. The effects of variation in the solvent composition (acetonitrile–water) on the capacity factor are visualized in Fig. 5. Increasing the solvent polarity as going from low to high water content increased the k' values to such an extent favorable for the separation of BDPDAC and BDCDAC. There exists a non-linear relationship between the solvent parameters and capacity factors. Fig. 6 illustrates a typical separation obtained from the HPLC analysis of a mixture containing the aryloxyethoxyethyl benzyl dimethyl ammonium standards and benzyl dimethyl tetradecyl ammonium chloride (an inter-

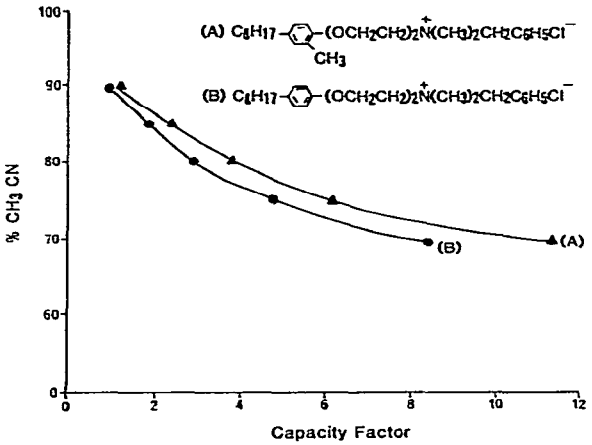


Fig. 5. Effects of the composition of acetonitrile and water on capacity factors (HPLC mobile phase: acetonitrile–water, 0.01 M $HClO_4$, 0.01 M $NaClO_4$, pH 2.3; isocratic elution).

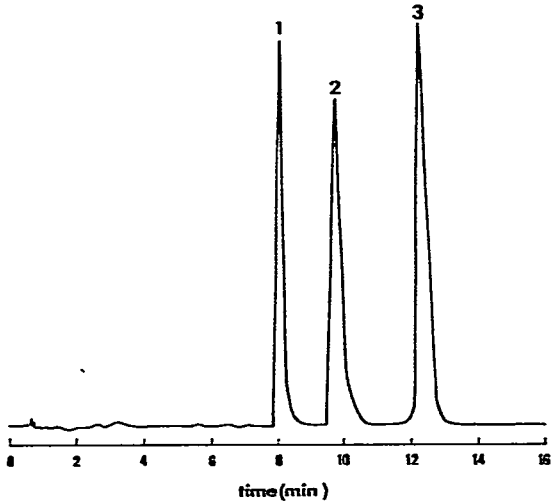


Fig. 6. Typical HPLC separation of a mixture of standard salts. (1) BDPDAC, (2) BDCDAC and (3) benzyl dimethyl tetradecyl ammonium chloride (internal standard). Mobile phase: acetonitrile–water (70:30), 0.01 *M* $HClO_4$, 0.01 *M* $NaC_5H_{11}SO_3$, pH adjusted to 3 with Na_2HPO_4: isocratic elution.

nal standard). Adapting the conventional procedure for the construction of standard curves, the area ratio of each analyte peak to that of the internal standard was calculated for each chromatogram. The pertinent calibration data to demonstrate linearity of detector (UV) response are tabulated in Table IV. The lowest limit of detection is 10 ng with a signal-to-noise ratio of 2:1. The coefficient of variation for five successive injections of 10 μl of standard samples in various concentrations varied from 2.1 to 4.8%.

TABLE IV

REPRESENTATIVE CALIBRATION DATA FOR STANDARD MICROBICIDE SOLUTIONS (HPLC–UV)

Microbicide	*Concentration (μg/10 μl)*	A_x/A_I*	*Slope*	*Intercept*	*r***
BDPDAC	1.25	0.890			
	1.00	0.699			
	0.75	0.513	0.7629	−0.0603	0.999
	0.50	0.318			
	0.20	0.091			
BDCDAC	1.25	0.824			
	1.00	0.645			
	0.75	0.491	0.6967	−0.0415	0.999
	0.50	0.310			
	0.20	0.098			

* A_x is the peak area of the microbicide; A_I is the peak area of the internal standard (benzyl dimethyl tetradecyl ammonium chloride) at a concentration of 2.5 μg/10 μl.

** r = correlation coefficient obtained from regression analysis.

Both glass capillary GC and ion-pair reversed-phase HPLC systems proved to be applicable to the separation and quantification of mixtures of BDPDAC and BDCDAC in environmental water samples. Results of the GC and HPLC analyses of natural water samples fortified with known levels of the quaternary ammonium compounds are summarized in Table V. The numerical figures as given are the mean values of three determinations. The average recoveries for respective GC and HPLC methods were 80.4 and 85.2% with corresponding averaged coefficient of variation of 7.1 and 6.7%. Incorporation of a radiolabeled tracer technique into the sample cleanup procedure permits accurate assessment of recoveries at each individual stages throughout the ion-exchange and solvent partition operations. HPLC quantification of BDPDAC at lower concentrations (trace levels) was performed by the isotope

TABLE V

RECOVERY OF ARYLOXYETHOXYETHYL BENZYL DIMETHYL AMMONIUM CHLORIDES ADDED AT VARIOUS LEVELS TO NATURAL WATER

Level added (μg/l)	*Recovery (%)*			
	GC		*HPLC*	
	BDPDAC	*BDCDAC*	*BDPDAC*	*BDCDAC*
1	73	75	83	77
3	75	76	82	78
5	74	73	79	81
10	76	74	85	83
50	79	79	85	88
100	83	85	89	87
500	85	84	90	86
700	86	86	90	85
1000	88	86	89	88
2000	86	85	91	88

dilution method in order to take into consideration the slight but not negligible contribution to the composite peak area caused by the peak overlaps of the labeled and unlabeled compounds. In dealing with dilute aqueous solutions that contain trace levels of the quaternary ammonium analytes, it required relatively large volume of water samples (500–1000 ml) for adsorption on the resin to compensate for the sensitivity limitation associated with the low UV absorptivity of the compounds under analysis. Adequately enriched samples usually generated more reliable and reproducible analytical data as generally observed. For glass capillary GC quantification of BDPDAC and BDCDAC in natural water samples, normally 10–500 ml of the aqueous solutions were sufficient to yield dependable analytical results. The ion-exchange resin employed in this study is the strongly acidic cation exchanger of low cross-linking polymer. It served two purposes in the development of the analytical method. In addition to its major function as a medium for preconcentration of water samples via sorption of the quaternary ammonium cations, the use of the cation-exchange resin provided a convenient means to remove interferences from other organic and inorganic compounds possibly present in the environmental water. The

latter was effected by eluting the resin with dilute acidic and weakly basic methanol prior to the desorption of the quaternary ammonium analyte ions from the resin[8]. In view of the total miscibility of aryloxyethoxyethyl benzyl dimethyl ammonium chlorides and water, the conditions for the solvent partition step following cation-exchange chromatography were optimized so that a maximum recovery of the ammonium compounds into the organic phase (chloroform) could be obtained. Initial diagnostic attempts at using excessive volume of the aqueous phase as obtained by neutralization of the hydrochloric acid eluate from the resin with a dilute sodium hydroxide solution resulted in poor recoveries of the two analogous quaternary ammonium compounds after extraction with chloroform.

CONCLUSIONS

Glass capillary GC and ion-pair reversed-phase HPLC can be utilized for the efficient separation of the closely related aryloxyethoxyethyl benzyl dimethyl ammonium microbicides, BDPDAC and BDCDAC. The HPLC–UV method allows direct quantitative analyses of these compounds as their original salts, whereas the GC–ECD and GC–AFID methods necessitate chemical derivatization of the salts to form respective trichloroethyl carbamates and cyanamides before GC quantification with increased sensitivity. The cation-exchange chromatographic technique has the desirable advantages of concentrating dilute aqueous solutions of the quaternary ammonium salts and effectively removing interferences from environmental contaminants in natural water. The methods may be applicable to the analysis of other quaternary ammonium microbicides with similar structures in environmental water. These general procedures would appear to offer logical approaches to the investigation, which is now under way, of analytical methods involving the title compounds and other related quaternary ammonium compounds in organic tissue samples of biological as well as environmental interest.

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