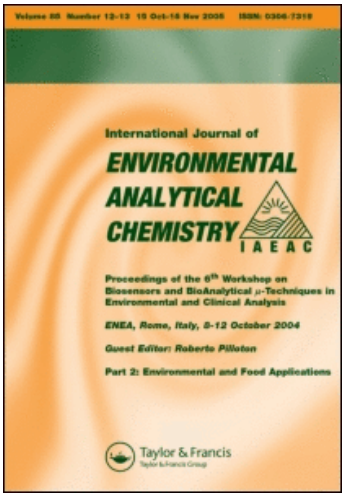

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DETERMINATION OF ALKYLPHENOL ETHOXYLATES AND THEIR ACETIC ACID DERIVATIVES IN DRINKING WATER BY PARTICLE BEAM LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY

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Particle beam liquid chromatography/mass spectrometry (PB/LC/MS) was used to analyze finished drinking water for non-volatile organic compounds. 500 liters of finished water were extracted with an on-line continuous liquid/liquid extractor with dichloromethane at pH 7.4. PB/LC/MS was an excellent tool to detect and identify ng/L concentrations of alkylphenol polyethoxylates ($n = 3 - 8$), materials which went undetected by on-column gas chromatography/mass spectrometry. In addition, alkylphenol polyethoxylate carboxylates with 2–7 degrees of ethoxylation could be detected without chemical derivatization.

KEY WORDS: Particle beam liquid chromatography/mass spectrometry, alkylphenol ethoxylates, alkylphenol ethoxylate carboxylates, drinking water.

INTRODUCTION

Alkylphenol polyethoxylates are non-ionic surfactants which are used as wetting, scouring, dye leveling and emulsifying agents in tanning and textile processing. In 1988, the production of non-ionic surface-active agents in the United States was

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over 2 billion pounds, with octylphenol polyethoxylates (OPEO) and nonylphenol polyethoxylates (NPEO) accounting for 20% of the total production[1]. Structurally, the alkylphenol polyethoxylates consist of branched tertiary alkylphenols attached to a hydrophilic polyethylene glycol resin having 1–30 ethoxy units. The structures of the nonylphenol and octylphenol polyethoxylates and their acetic acid derivatives are shown in Figure 1.

We have used both on-column gas chromatography/mass spectrometry (GC/MS)[2,3,4], thermospray liquid chromatography/mass spectrometry (TSP/LC/MS)[3] and particle beam liquid chromatography/mass spectrometry (PB/LC/MS)[4] as the final determinative steps in an on-going study to determine the nature and amounts of chemicals in New Jersey surface and drinking water. It was observed that PB/LC/MS was an excellent tool to detect and identify low concentrations of alkylphenol polyethoxylate surfactants and their acetic acid derivatives, materials which were undetected by on-column GC/MS analysis. Because of the widespread use of these surfactants and the apparent inability of water treatment plants to effectively remove them[5], we report on the use of PB/LC/MS for their detection in drinking water.

EXPERIMENTAL

Sample preparation

500 liters of finished drinking water were extracted with an on-line continuous liquid–liquid extractor (CLLE)[6] which had been redesigned to extract at a rate of 10 L/h instead of 2 L/hr.[7] The extraction solvent, dichloromethane, was stabilized with pentene instead of cyclohexene (EM Science, Gibbstown, NJ, USA) to eliminate

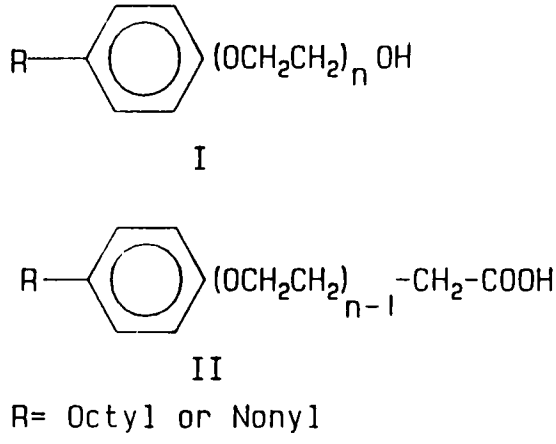

Figure 1 Structure of alkylphenol polyethoxylates (I) and their acetic acid derivatives (II).

the interferences from chlorinated cyclohexenes and chlorinated cyclohexanes formed by chlorination of the cyclohexene preservative[8]. The solvent-to-water ratio was 1:10 and the water was extracted at its natural pH value of 7.4. Any free chlorine present in the finished water was removed, before the extraction, by injecting a 300 ppm, ammonium chloride solution into the water at a flow rate of 2 mL/min. The solvent extract was dried on a Na_2SO_4 column and concentrated to 5 mL on an automated evaporative concentration system (EVACS)[9], modified with an infrared sensor beam to control the volatilization rate. A 3-mL aliquot was used for MS analyses. Prior to each sample extraction, the CLLE apparatus was sequentially cleaned with 1:1 HCl:H_2O, Milli-Q water and dichloromethane. In addition, solvent and water sampler blanks were analyzed prior to each CLLE extraction. A 'trip blank' of (pure solvent) was also completed for each sample location. Each 3 mL aliquot was concentrated to 1 mL under a gentle stream of nitrogen gas. The samples were then spiked, prior to analysis, with both 100 μg d_{10}-anthracene (Chem Services, West Chester, PA, USA) and 4-fluoro-4'-hydroxybenzophenone (Aldrich, Milwaukee, WI, USA), respectively. The former material served as a GC/MS internal standard while the latter was the LC/MS internal standard. Prior to PB/LC/MS analysis, the samples were further concentrated to 0.5 mL under a gentle stream of nitrogen.

Nonylphenol ethoxylate standard solutions

A 100-μg/mL stock solution consisting of 100 μg/mL each of four different (1 to 2 EO, 4 EO, 6 EO and 8 EO) nonylphenol ethoxylates standards (Chem Services) was used for the determination of mass spectra.

Instrumentation conditions

GC/MS analyses were performed on a Finnigan MAT 8230 High Resolution Mass Spectrometer (Finnigan MAT, San Jose, CA, USA) directly interfaced to a Varian 3400 capillary gas chromatograph (Varian, Sunnyvale, CA, USA). The samples were analyzed in the electron ionization (EI) mode. Library searches were made with the National Bureau of Standards (NBS) and Environmental Protection Agency-National Institute of Health (EPA-NIH) data bases. A 30 m, 0.25 μm film thickness, 0.32 mm i.d. DB-1 fused silica capillary column (J&W Scientific, Folsom, CA, USA) was temperature-programmed from 50°C to 320°C at a rate of 4°C/min with a final hold time of 10 min. The mass spectrometer was operated at injector temperature, 260°C; source temperature, 250°C; electron energy, 70 eV; filament current, 1 mA; scan rate, 1 sec/decade; interscan time, 0.8 sec; masses scanned, 35–550 amu. The GC injection volume was 1 μL and the samples were injected by an on-column injection technique[10]. Data were acquired and processed using a Finnigan MAT SS300 data system.

PB-LC/MS analyses were performed in the EI mode on a Vestec Model 201 LC/MS (Vestec, Houston, TX, USA), equipped with a Universal Interface. The chromatographic system used was a Kratos Spectroflow 400 Ternary Pumping System (Kratos Analytical, Ramsey, NJ, USA) equipped with a 254 nm UV detector.

A 25 cm × 4.6 mm i.d. reversed-phase LC column (Brownlee Labs, Santa Clara, CA, USA) and guard column were used for the LC separations. The Teknivent Vector/One Mass Spectrometry Data System (Teknivent, St. Louis, MO, USA) was used for acquiring and processing data. Mass spectra were searched on a Wiley/NBS library data base. The ion source, probe tip and momentum separator temperatures were 265°C, 140°C and 130°C, respectively. The solvent gradient began with 70% 0.01% ammonium acetate and 30% methanol and ended with 99% methanol and 1% 0.01% ammonium acetate in 80 min. The aqueous component of the LC mobile phase contains 0.01% ammonium acetate to improve signal sensitivity by improving the transport efficiency of the analyte through the interface[11]. The flow rate was 0.8 mL/min, and the scan range was 45–450 amu. The LC injection volume was 50 μL.

Quantitation

Semi-quantitative estimates for the concentration of individual pollutants were obtained by peak area comparisons of the internal standard to those of the analytes.

RESULTS AND DISCUSSION

A total of 36 different compounds (ranging in concentration from 7 ppt to 878 ppt) were detected in the finished drinking water by GC/MS and 34 of these compounds were identified (Table 1). The three main classes of compounds identified were sugar derivatives, non-ionic surfactants and plasticizers. In the surfactant group, ten isomers of NPEO (n = 1–2) and one isomer of OPEO (n = 1) were identified. PB/LC/MS analysis also indicated the presence of diisononyl phthalate and hydroxy-7H-benzopyranone. Four compounds could not be identified. The use of PB/LC/MS resulted in a dramatic increase in the number of detected alkylphenol polyethoxylates and their derivatives. Six NPEOs (n = 2–7) eluted between 64–67 min while seven OPEOs (n = 2–8) eluted between 60–65 min. (Monoethoxylated NPEO and OPEO were not observed in PB/LC/MS because they are too volatile to pass through the Universal Interface and into the mass spectrometer). We also identified six nonylphenol polyethoxylate acetic acid derivatives (n = 2–7) eluting between 46–53 min and three octylphenol polyethoxylate acetic acid derivatives (n = 2–4) eluting between 41–45 min. Acetic acid derivatives have previously[12,13] been observed by GC/MS only after derivatization to the methyl esters and by FAB analysis. The semi-quantitative concentration values of non-ionic surfactants detected are listed in Table 2.

Each nonylphenol ethoxylate analogue has several diagnostic ions which can be used for identification purposes. The significant ion fragments and their relative intensities for NPEO (n = 1–8) standards are listed in Table 3. The fragmentation patterns of some of the smaller NPEO analogs (n = 1,2) have been reported elsewhere[14]. A typical NPEO spectrum is shown in Figure 2. Typical ions observed in each analogue are due to $(M\text{-}C_2H_5)^+$, $(M\text{-}C_3H_7)^+$, $(M\text{-}C_4H_9)^+$, $(M\text{-}C_5H_{11})^+$, and $(M\text{-}C_6H_{13})^+$. The latter ion is the most intense of the diagnostic ions while the $(M\text{-}C_3H_7)^+$ ion is of very low intensity and is, therefore, not listed.

Table 1 Chemicals identified in drinking water by on-column GC/MS

Compound name	*CAS No.*	*Conc. (ng/L)*
Sugar derivatives		
aminodeoxy bis(methylethylidene) glucofuranose	34322935	86
bis(methylethylidene) fructopyranose	20880926	28
bis(methylethylidene) xylofuranose	20881043	161
di-o-isopropylidene talofuranose	23262784	27
tris(methylethylidene) mannitol	3969593	263
bis(methylethylidene) talofuranose	23262795	878
tris(methylethylidene) mannitol	3969593	539
unknown sugar derivative		94
Non-ionic surfactants[a]		
nonylphenol monoethoxylate (isomer b)		29
nonylphenol monoethoxylate (isomer a)		18
nonylphenol monoethoxylate (isomer d)		15
nonylphenol monoethoxylate(isomer h)		15
nonylphenol diethoxylate (isomer d)		34
nonylphenol diethoxylate (isomer e)		21
nonylphenol diethoxylate (isomer f)		23
nonylphenol diethoxylate isomer		15
nonylphenol diethoxylate isomer		26
nonylphenol diethoxylate isomer		28
tetramethyl butyl phenoxy ethoxy ethanol	2315619	32
dimethyl ethyl phenoxy ethanol	713462	37
Plasticizers		
butyl-methyl-propyl phthalate	18699484	45
diethyl phthalate	84662	52
di-2-ethylexyl phthalate	117817	97
tris(2-butoxy ethyl) phosphate	78513	179
phosphoric acid triphenyl ester		8
phosphoric acid tributyl ester	126	105
Other compounds		
propenyl octadecanoate	6289312	24
ethyl benzene	620144	23
tetramethyl benzene	527537	7
octahydro-2H-indenone	20379991	7
tetrahydrotrimethyl benzofuranone	15356748	13
tetradecanoic acid	544638	17
caffeine	58082	30
tetramethyl decyndiol		28
hexahydromethoxy phenanthrenone	55255511	13
unknown		22

[a] Isomers reported by Giger *et al.*[14]

Ions common to all NPEOs arise from two homologous series starting at HO—C_6H_6-nonyl (e.g., m/z 107 and 121) and C_6H_5-nonyl (e.g., m/z 133, 147, 161 and 175)[14]; M/z 133 may also be due to $[(CH_2CH_2O)_3H]^+$ while the base peak, m/z 89, is most probably $[(CH_2CH_2O)_2H]^+$. The actual base peak is almost certainly m/z 45, but we did not scan below 65 amu because ammonium acetate was a component of the LC mobile phase.

Table 2 Alkylphenol polyethoxylates and derivatives identified in drinking water

Compound name	*Mol. wt.*	*Concentration (ppt) with*	
		PB/LC/MS	*GC/MS*
Octylphenol diethoxy carboxylate	308	40	—
Octylphenol triethoxy carboxylate	353	11	—
Octylphenol tetraethoxy carboxylate	396	1	—
Nonylphenol diethoxy carboxylate	322	164	—
Nonylphenol triethoxy carboxylate	366	16	—
Nonylphenol tetraethoxy carboxylate	410	14	—
Nonylphenol pentaethoxy carboxylate	454	4	—
Nonylphenol hexaethoxy carboxylate	498	5	—
Nonylphenol heptaethoxy carboxylate	542	24	—
Octylphenol diethoxylate	294	2[a]	32
Octylphenol triethoxylate	338	35	—
Octylphenol tetraethoxylate	382	8	—
Octylphenol pentaethoxylate	426	7	—
Octylphenol hexaethoxylate	470	23	—
Octylphenol heptaethoxylate	514	8	—
Octylphenol octaethoxylate	558	43	—
Nonylphenol monoethoxylate	294	—[a]	111
Nonylphenol diethoxylate	308	—[a]	113
Nonylphenol triethoxylate	352	62	—
Nonylphenol tetraethoxylate	396	75	—
Nonylphenol pentaethoxylate	440	123	—
Nonylphenol hexaethoxylate	484	112	—
Nonylphenol heptaethoxylate	528	129	—

[a] No detection or low values due to volatility.

Characteristic m/z ions of OPEO (n = 1–3) have been published previously[15]. The ion corresponding to $(M\text{-}C_5H_{11})^+$ is either the base peak or a significant peak in the mass spectrum of OPEOs. Therefore, m/z 267, 311, 355, 399, 443 and 487 and the molecular ions were used as the major diagnostic ions for OPEOs (n = 2–8). The OPEO analogue also have the same common ions (m/z = 89, 133, 161 and 175) as the NPEO analogues.

The mass chromatograms of the $(M\text{-}C_6H_{13})^+$ ions of NPEO (n = 3–8) and the $(M\text{-}C_5H_{11})^+$ ions of OPEO (n = 3–8) in the finished drinking water sample are shown in Figure 3.

The diagnostic ions can also be used to confirm NPEOs in environmental samples. Figure 4 shows the mass chromatograms of the diagnostic ions of nonylphenol hexaethoxylate. The OPEOs give only one intense diagnostic ion and confirmation has to be made from that ion and the molecular ion as shown in Figure 5 for octylphenol pentaethoxylate.

The EI mass spectra of the nonylphenol and octylphenol carboxylates have, to the best of our knowledge, not been published before because the compounds could only be separated as methyl esters. The mass spectrum of nonylphenol triethoxycarboxylate (Figure 6) shows a molecular ion at m/z 366 and alkyl losses at m/z 337, 323, 309, 295, 281 and 267. Alkyl losses from the phenol are also observed at m/z 149,

Table 3 Per cent relative intensities of ions in nonylphenol polyethoxylate series

NPEO	*Mol. wt.*	*Diagnostic ions (m/z)*				*Common ions (m/z)*						
	M^+	$(M\text{-}C_2H_5)^+$	$(M\text{-}C_4H_9)^+$	$(M\text{-}C_5H_{11})^+$	$(M\text{-}C_6H_{13})^+$							
$n = 3$	352	323	295	281	267	175	161	147	133	121	107	89
	2	4	11	17	30	10	16	18	53	25	40	100
$n = 4$	396	367	339	325	311							
	1	3	4	12	15	6	15	21	34	21	38	100
$n = 5$	440	411	383	369	355							
	0.7	2	1	4	6	8	12	12	44	14	18	100
$n = 6$	484	455	427	413	399							
	0.2	1	0.5	2	5	7	18	12	43	12	16	100
$n = 7$	528	499	471	457	443							
	0.2	0.4	0.1	0.6	1.3	11	17	9	39	10	10	100
$n = 8$	572	543	515	501	487							
	a	0.2	0.3	0.6	1	13	24	17	80	17	19	100

[a] Did not scan above m/z 550.

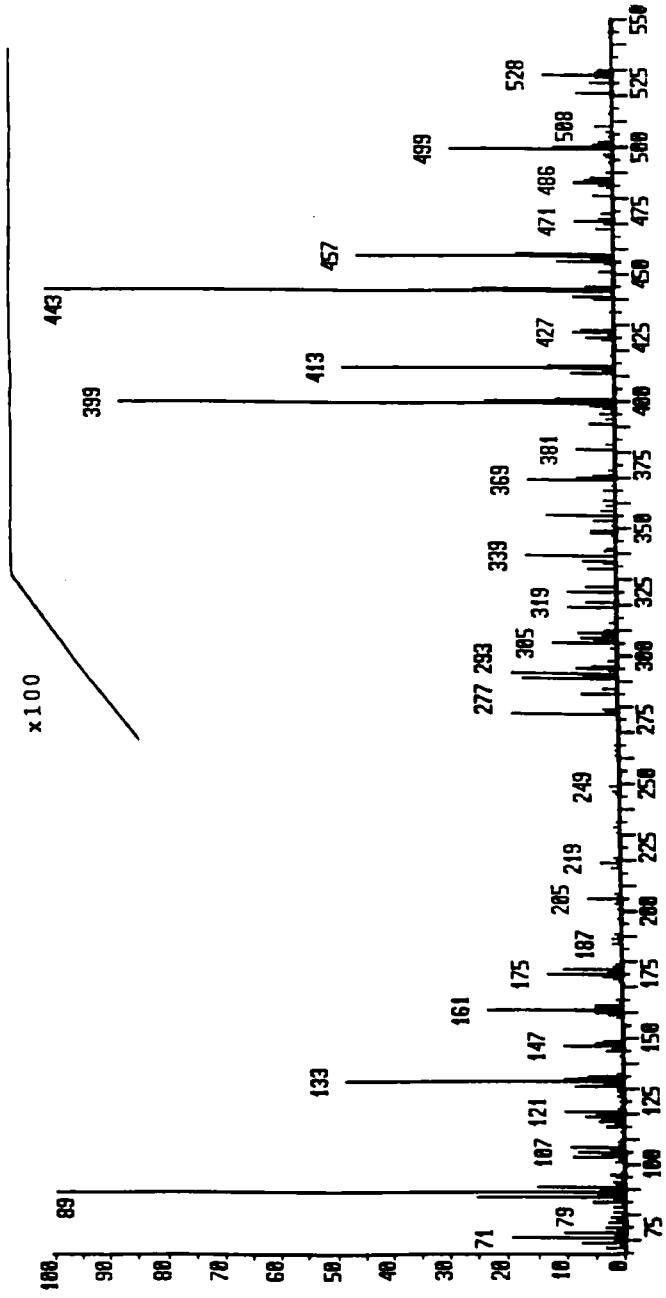

Figure 2 Mass spectrum of nonylphenol heptaethoxylate by PB/LC/MS.

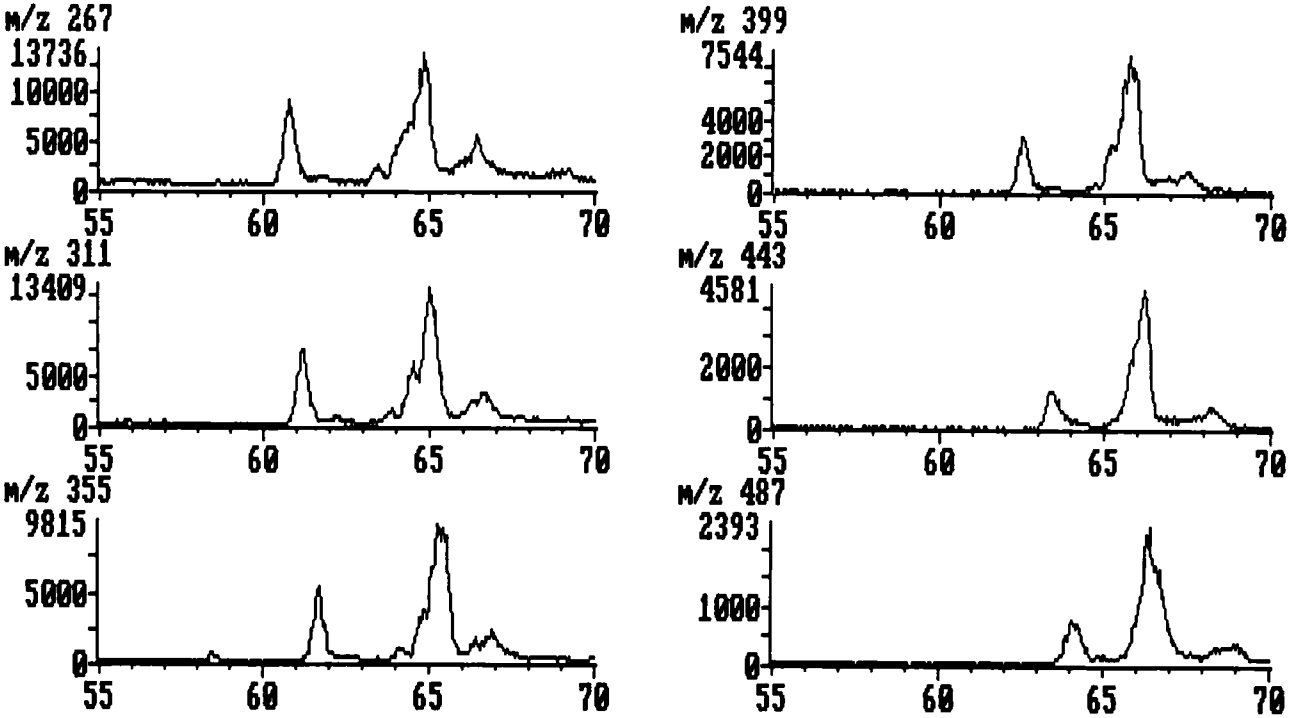

Figure 3 Mass chromatograms of the $(M\text{-}C_5H_{11})^+$ ions of OPEOs (earlier elating peak) and $(M\text{-}C_6H_{13})^+$ ions of NPEOs (later elating peak). m/z 267, triethoxylate; m/z 311, tetraethoxylate; m/z 355, pentaethoxylate; m/z 399, hexaethoxylate; m/z 443, heptaethoxylate; m/z 487, octaethoxylate.

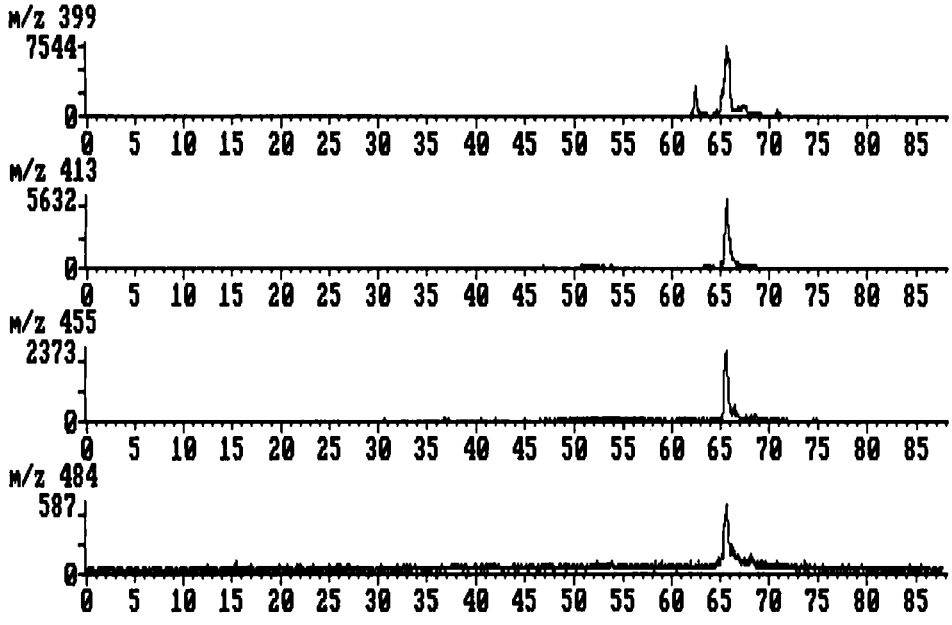

Figure 4 Mass chromatograms of the major diagnostic ions of nonylphenol hexaethoxylate. The m/z 399 peak at 62.5 min is from octylphenol hexaethoxylate.

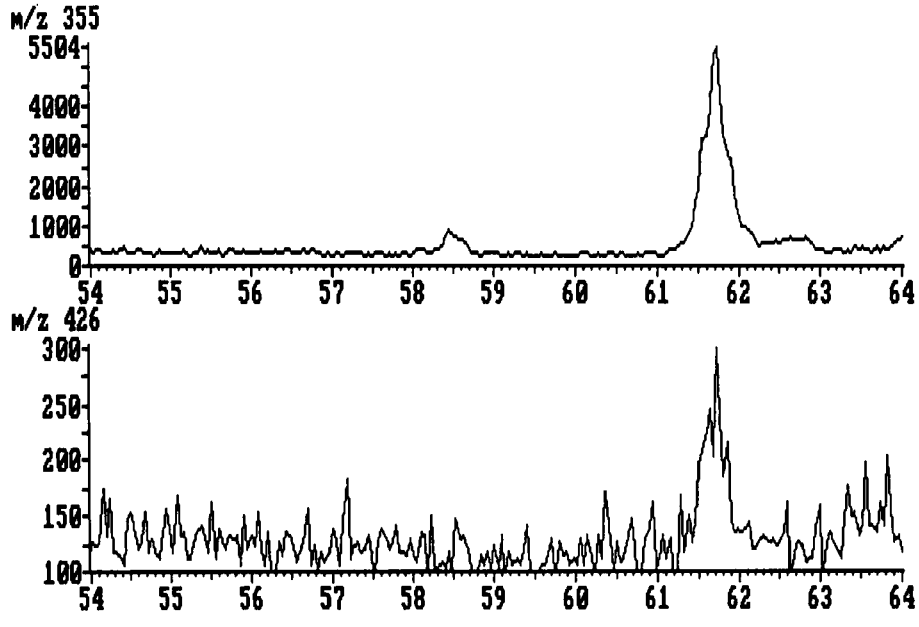

Figure 5 Mass chromatograms of the major diagnostic ion (m/z 355) and the molecular ion (m/z 426) of octylphenol pentaethoxylate.

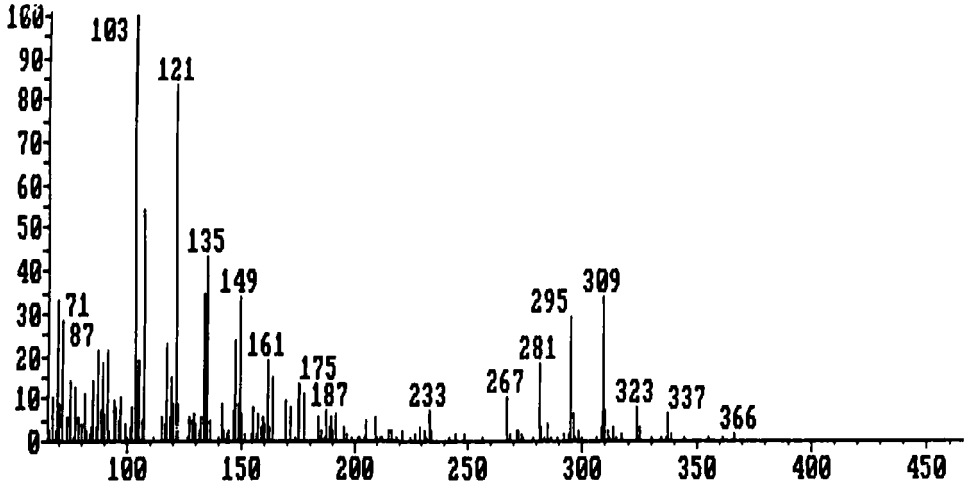

Figure 6 Mass spectrum of nonylphenol triethoxycarboxylate by PB/LC/MS.

135, 121 and 107. In general, the fragmentation patterns of the carboxylates are similar to those of their alcohol analogues, i.e. loss of alkyl groups from the molecular ion as well as loss of alkyl groups from the phenol. The ion that distinguishes the carboxylates in m/z 103, which is due to $(CH_2CH_2—O—CH_2—COOH)^+$.

Mass chromatograms of the diagnostic ion, $(M\text{-}C_5H_{11})^+$, were used to detect the presence of nonylphenol and octylphenol polyethoxylate carboxylates (Figures 7 and 8) in finished drinking water.

CONCLUSIONS

In previous investigations, GC/MS has been used to identify non-ionic surfactants in water. Octylphenol polyethoxylates (n = 1–5) have been detected in the primary effluent of a Palo Alto wastewater treatment plant by using GC/MS in the EI and chemical ionization (CI) modes[16]. Sheldon and Hites identified octylphenol and octylphenol polyethoxylates (n = 1–5 and n = 1–3) in a Delaware River industrial effluent and in drinking water, respectively[17,18]. Stephanou and Giger[19] (with a reported limit of detection of 10 μg/L) found nonylphenol and NPEOs (n = 1–3) at levels of 36–202 μg/mL in the effluents of three activated slude sewage treatment plants. NPEOs, with degrees of ethoxylation from 1 to 7, were detected in river water near the sites of surfactant and textile manufacturing plants. When the surfactants were present at much lower levels, such as in drinking water, materials with degrees of ethoxylation above 3 could not be detected, although fast atom bombardment MS indicated that NPEOs (n = 0–10) were present[5,20].

These results, together with ours, indicate that alkylphenol polyethoxylates with low to moderate degrees of ethoxylation may be determined by GC/MS at high

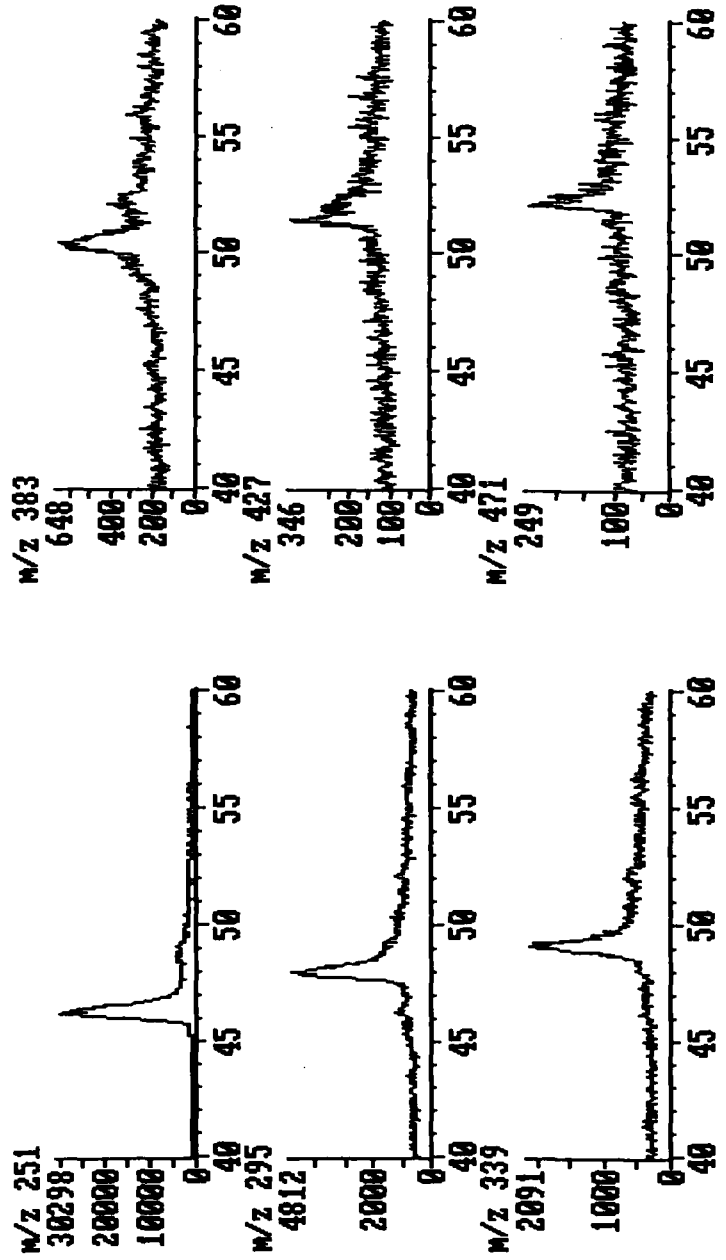

Figure 7 Mass chromatograms of nonylphenol polyethoxylate carboxylate $(M\text{-}C_5H_{11})^+$ diagnostic ions for $n = 2$–7.

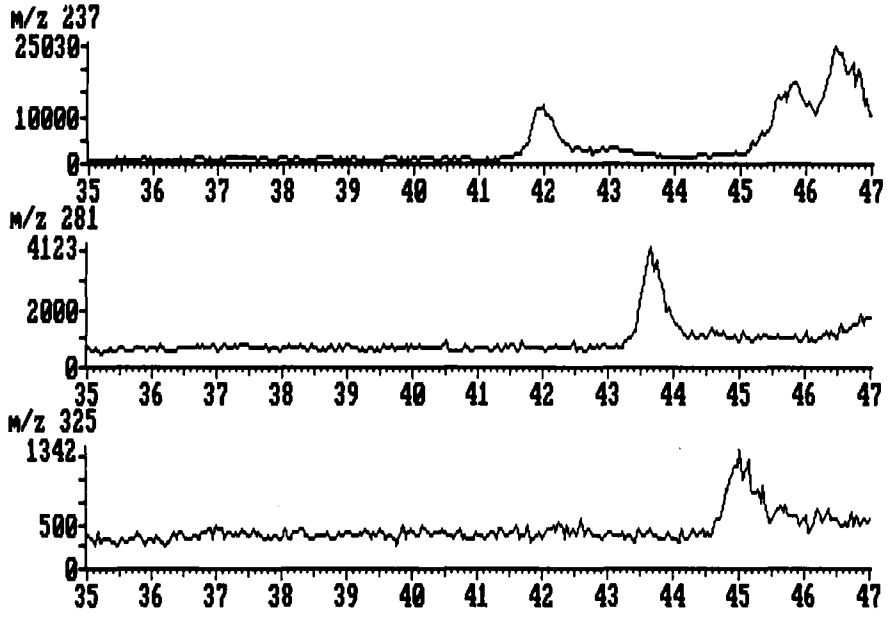

Figure 8 Mass chromatograms of octylphenol polyethoxylate carboxylate $(M\text{-}C_5H_{11})^+$ diagnostic ions for $n = 2$–4. The peaks at approx. 45–47 min are from nonylphenol diethoxycarboxylate.

concentrations but not at the concentrations at which these materials are normally found in drinking water. PB/LC/MS can detect alkylphenol polyethoxylates with degrees of ethoxylation of 3–8 at the parts per trillion level and is also capable of determining their acetic acid derivatives without chemical derivatization.

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