ELSEVIER

Journal of Chromatography A, 824 (1998) 79–90

JOURNAL OF CHROMATOGRAPHY A

Analysis of nonylphenol polyethoxylates and their degradation products in river water and sewage effluent by gas chromatography–ion trap (tandem) mass spectrometry with electron impact and chemical ionization

Wang-Hsien Ding*, Shin-Haw Tzing

Department of Chemistry, National Central University, Chung-Li 32054, Taiwan

Received 6 May 1998; received in revised form 13 July 1998; accepted 13 July 1998

Abstract

A method is presented for the analysis of nonylphenol polyethoxylate (NPEO) residues and their degradation products, nonylphenol polyethoxy carboxylates and carboxyalkylphenol ethoxy carboxylates, in the samples of river water and sewage effluent. The method involves extraction of the samples by graphitized carbon black (GCB) cartridge, propylation by a propanol/acetyl chloride derivatization procedure, and separation, identification and quantitation by ion-trap GC–MS with electron impact ionization (EI), liquid-chemical ionization (CI) and CI-MS–MS modes. The large-volume injection technique provides high precision and sensitivity for both NPEO residues and their degradation products, to quantitation at ≥0.01 μg/l in 100 ml of water samples. Dicarboxylic acids of NPEO residues were identified by the CI-MS–MS technique with relatively high concentrations in the samples of river water and sewage effluent. Recovery of nonylphenol and octylphenoxyacetic acid in spiked water samples ranged from 81 to 107%. Relative standard deviations of replicate analyses ranged from 2 to 12%. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Sewage effluent; Environmental analysis; Nonylphenol polyethoxylates; Polyethoxylates; Surfactants

1. Introduction

It is only in recent years that society has put great interest in the impact of alkylphenol polyethoxylate (APEO) residues and their degradation products on the environment due to their estrogen-mimicking activity and wide usage. These residues have been detected in wastewater effluents [1–5], sewage effluents [6–8], surface waters [8–11] and paper mill effluents [8]. The biodegradation pathway of APEOs has been studied elsewhere [12,13]. These compounds may be transformed by two primary biodegradation processes: (a) shortening of the polyethoxy chain, resulting in the formation of alkylphenols (APs) and shorter ethoxy chain APEO residues (such as AP1EO, AP2EO and AP3EO), and (b) carboxylation of the terminal ethoxy unit, resulting in the formation of alkylphenol polyethoxycarboxylates (APECs). The general structures of these compounds are presented in Fig. 1.

Gas chromatography (GC) combined with chemical ionization mass spectrometry (CI-MS) has

*Corresponding author.

0021-9673/98/$ – see front matter © 1998 Elsevier Science B.V. All rights reserved.
PII: S0021-9673(98)00593-7

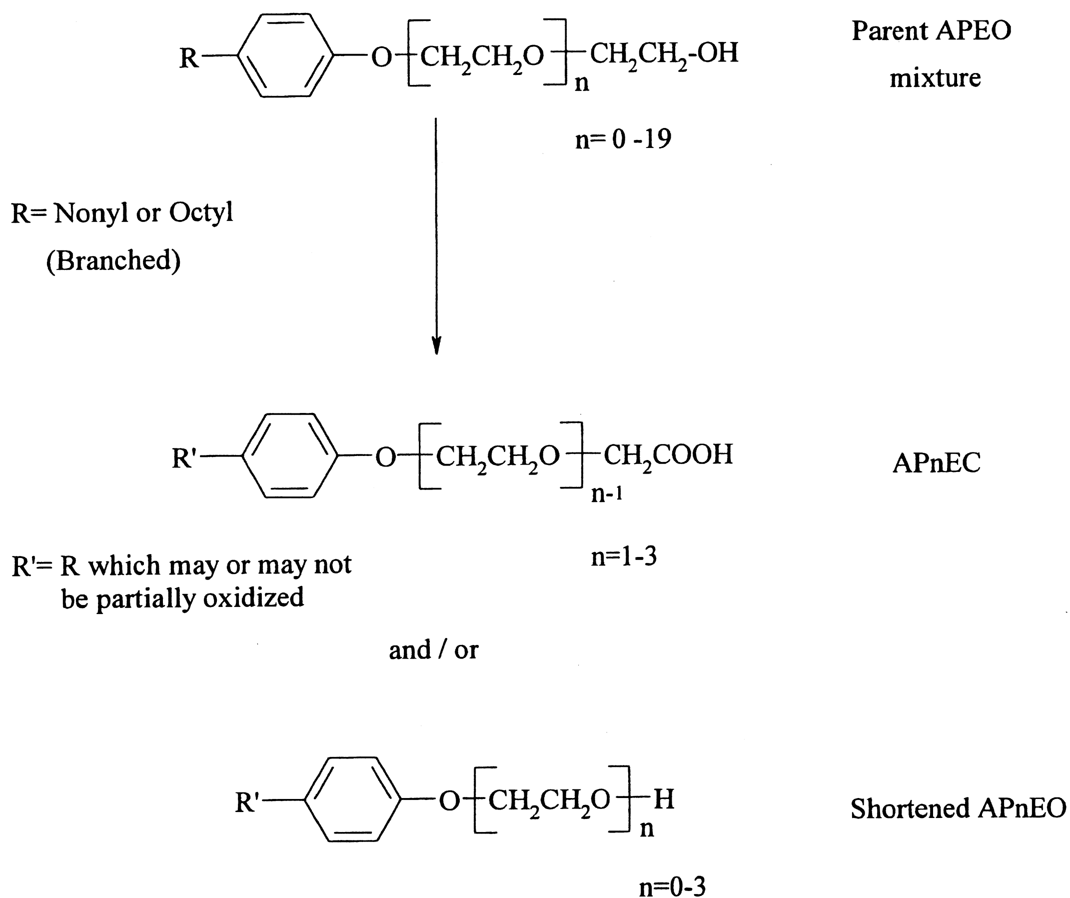

Fig. 1. Structures of APEOs and their degradation products detected in the samples of river water and sewage effluent. The index *n* indicates the number of ethoxy units for AP*n*EO, and the number of ethoxy units plus a terminal acetic acid for AP*n*EC.

proved to be a simple and useful technique for the characterization of non-ionic surfactant residues and their degradation products in the environmental samples [5,8,14–16]. It is highly complementary to the electron impact ionization (EI) MS technique for compounds with a weak or absent molecular ion. Recently, an inexpensive benchtop ion-trap GC–mass spectrometry (MS) system with low-pressure CI and MS–MS capabilities was developed for quick switching between EI and CI scans, as well as MS–MS mode without compromises in spectral quality. In this system, a variety of organic solvents can also be introduced into the ion-trap as CI reagents to improve the CI mass spectra for structural elucidation. The general requirements for the solvents are a moderate vapor pressure and fairly low molecular mass. A tandem-in-time mass spectrometer for the ion-trap MS system could be operated simply by using a well-defined time-programmed radio frequency (RF) scan on the ring electrode with additional waveforms applied to the end cap electrodes. This MS–MS technique has been applied routinely for many environmental analyses in various matrices [17–20].

The aim of this study was to develop an improved method for the routine determination of nonylphenol polyethoxylate (NPEO) residues and their degradation products in water samples by using a graphitized carbon black (GCB) solid-phase extraction (SPE) technique [7] and an ion-trap GC–MS system

with a variety of MS techniques. In addition to the EI and methane-CI-MS studies, we report for the first time the employment of acetone as chemical ionization reagent to facilitate molecular mass determination of propylated NPEC derivatives in water samples. We also demonstrate the power of the ion-trap CI-MS–MS technique by confirming the carboxylation of the alkyl side chain in NPECs detected in the samples of river water and sewage effluent.

2. Experimental

2.1. Chemicals and reagents

Unless noted otherwise all high purity chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA), Tedia (Fairfield, OH, USA) and Merck (Darmstadt, Germany), and were used without further purification. Nonylphenol (technical grade) was purchased from Aldrich. The surrogate *tert*.-octylphenoxyacetic acid (OP1EC) was synthesized as described by Fujita [21].

2.2. Sample collection

Sewage effluent samples (specific conductance 400 μS/cm) were collected from a municipal wastewater treatment plant in metropolitan Taipei, Taiwan. Surfactant polluted river water samples (specific conductance 850 μS/cm) were collected from Lao-Jie River in Chung-Li city, which receives untreated municipal wastewater directly from the city. Blank surface water samples (specific conductance 250 μS/cm) were collected from an unpolluted river in the mountains of Tao-Yuan County, upstream of a drinking water reservoir.

2.3. Sample extraction and preparation

The procedures used for sample extraction of NPEOs and their degradation products by graphitized carbon black (GCB or ENVI-Carb, trade name from Supelco, USA) and derivatization have been reported elsewhere [5,7], and were used with minor modifications. For recovery studies, 10 μg/l each of nonylphenol (NP) and OP1EC standard solutions were added to 100-ml water samples, and allowed to equilibrate for 2 h. Then the spiked water samples were acidified to pH 3 with concentrated HCl. The NPEO residues and their degradation products were extracted by passing the water sample through the ENVI-Carb cartridge at a flow-rate of about 10–20 ml/min with the aid of a vacuum. After the extraction, the cartridge was dried completely by drawing air through it for 2 min. The NPEO residues and their degradation products were eluted from the cartridge with 7 ml of methylene chloride–methanol (9:1, v/v) eluent amended with 25 m*M* of formic acid.

After completion of the elution process, the extract in the reaction vial was completely evaporated to dryness by a stream of nitrogen. The residue was redissolved in 400 μl of chloroform. This was divided into two portions of 200 μl each. The first aliquot was again evaporated to dryness by a stream of N_2. The residue was redissolved in 100 μl of chloroform containing 20 ng/μl of $[^2H_{12}]$chrysene (chrysene-d_{12}) as internal standard. This part of the extract was used for NP, NP1EO, NP2EO and NP3EO analysis by GC–MS directly. The second 200 μl aliquot of extract was completely evaporated to dryness, and then 2 ml of *n*-propanol–acetyl chloride (9:1, v/v) reagent was added to the flask. The flask was heated to 80°C for 1 h. This procedure converts the carboxylic acids into propyl esters. After cooling, the solution was evaporated to dryness, and the residue was redissolved in 100 μl of chloroform containing 20 ng/μl of chrysene-d_{12} as internal standard. The esterified NPECs were then determined by GC–MS. Acidified 100-ml samples of river water and sewage effluent were prepared with the same extraction and derivatization procedures described above.

2.4. GC–MS analysis

Analyses were performed on a Varian 3400CX gas chromatograph directly connected to a Saturn 2000 ion-trap mass spectrometry (Varian, USA). Sample introduction was performed with a ChromatoProbe device (or direct sample introduction, DSI, from Varian) and a temperature-programmed injector (Varian 1078 injector port) with 3.4 mm I.D. liner, as described by Jing and Amirav [22]. Sample solution (10 μl) was introduced into a DSI micro sample vial,

the vial was placed into a DSI vial holder, and then placed into the injector. The injector temperature was held at 80°C for 4 min for solvent vaporization, then the injector was heated to 280°C at a rate 300°C/min, and held for another 30 min. A DB-5MS capillary column (30 m×0.25 mm I.D., 0.25 μm film, J & W Scientific, USA) was used. After 2 min of holding the injector temperature at 280°C, the GC temperature program began as follows: 100°C for 5 min, followed by a temperature ramp at 8.5°C/min to 280°C, and hold for 15 min. At the end of the analysis, the sample vial was removed from the DSI vial holder and disposed of.

The transfer line was set at 280°C. Full scan EI data was acquired under the following conditions: mass range 50–500 *m/z*, scan time 1 s, solvent delay 12 min, manifold temperature 120°C, emission current 10 μA, automatic gain control (AGC) target 25 000. For CI-MS analysis, methane was used as CI reagent gas in the selected ejection chemical ionization mode (SECI). Reagent ions were ionized for a variable duration set by automatic reaction control (ARC) of the instrument. The CI full scan data were acquired under the following conditions: mass range 100–500 *m/z*, scan time 1 s, solvent delay 12 min, manifold temperature 100°C and ion trap temperature 110°C. ARC parameters for methane were set as follows: 0.1-ms ARC ionization time, 2.0-ms CI maximum ionization time, 40-μs CI maximum reaction time, 5-u CI ionization storage level, 13-u CI reaction storage level, 45-u CI background mass, and 9-V reagent ion eject amplitude.

For liquid–CI-MS analysis, acetone was used as CI reagent gas in the SECI mode. ARC parameters for acetone were the same as described using methane as CI reagent gas, except for the following: 25 u for CI ionization storage level, 25 u for CI reaction storage level, 65 u for CI background mass and 9 V for reagent ion eject amplitude. The autotune program was used to set most instrument parameters with target 10 000. The pressures of reagent gases in the ion trap were approximately $2 \cdot 10^{-5}$ Torr (1 Torr=133.322 Pa). For tandem-in-time MS–MS operation, non-resonant collision induced dissociation (CID) waveform amplitudes from 45 to 70 V were evaluated, with 20 ms residence time.

3. Results and discussion

3.1. Large volume injection

Large-volume sample introduction is an attractive method to improve detection limits and to prevent discrimination inside the syringe needle and injector liner associated with injection of a small volume of sample. The technique of inserting glass wool in the large dimensions of injector liners has been evaluated and reviewed by Mol et al. [23]; they referred to this sample introduction method as ''solvent-split injection''. In this study, we used the temperature-programmed injector with the DSI device for large-volume injection in capillary GC. The sample was introduced with the split exit open at a temperature of 80°C. After evaporation of the solvent, the split valve was closed, and the analytes retained in the micro vial were transferred to the analytical column in splitless mode by rapidly increasing the injector temperature. The quantitation limit of the total NP mixture and propylated OP1EC by EI-MS was at 0.01 ng/μl. The precision of the method for 0.05 ng/μl to 10 ng/μl of the total NP was approximately 3.2% R.S.D. The calibration curve for five concentrations of the total NP standard mixture was linear between 0.05 ng/μl to 50 ng/μl with a correlation coefficient of 1.00, based on the total peak areas of the quantitation ions at *m/z* 135.

3.2. EI and CI-MS of NPEOs and NPECs

Fig. 2 shows the selected EI characteristic ion chromatograms of NP, NP1EO, NP2EO and NP3EO, and their corresponding mass spectra detected in a river water sample. The most significant ions are produced by benzylic cleavages of $[M-71]^+$ and $[M-85]^+$, corresponding to the ions of *m/z* 149 and 135 for NP isomers, ions of *m/z* 193 and 179 for NP1EO isomers, ions of *m/z* 237 and 223 for NP2EO isomers, and ions of *m/z* 281 and 267 for NP3EO isomers. These ions are very common for most EI mass spectra of NP and NPEOs. The ions at *m/z* 149 and 135 in NP1EO and NP2EO (Fig. 2b Fig. 2c) were attributed to a loss of the polyethoxy chain with H transfers from the $[M-71]^+$ and $[M-85]^+$ ions, respectively. The NP and NPEOs in water

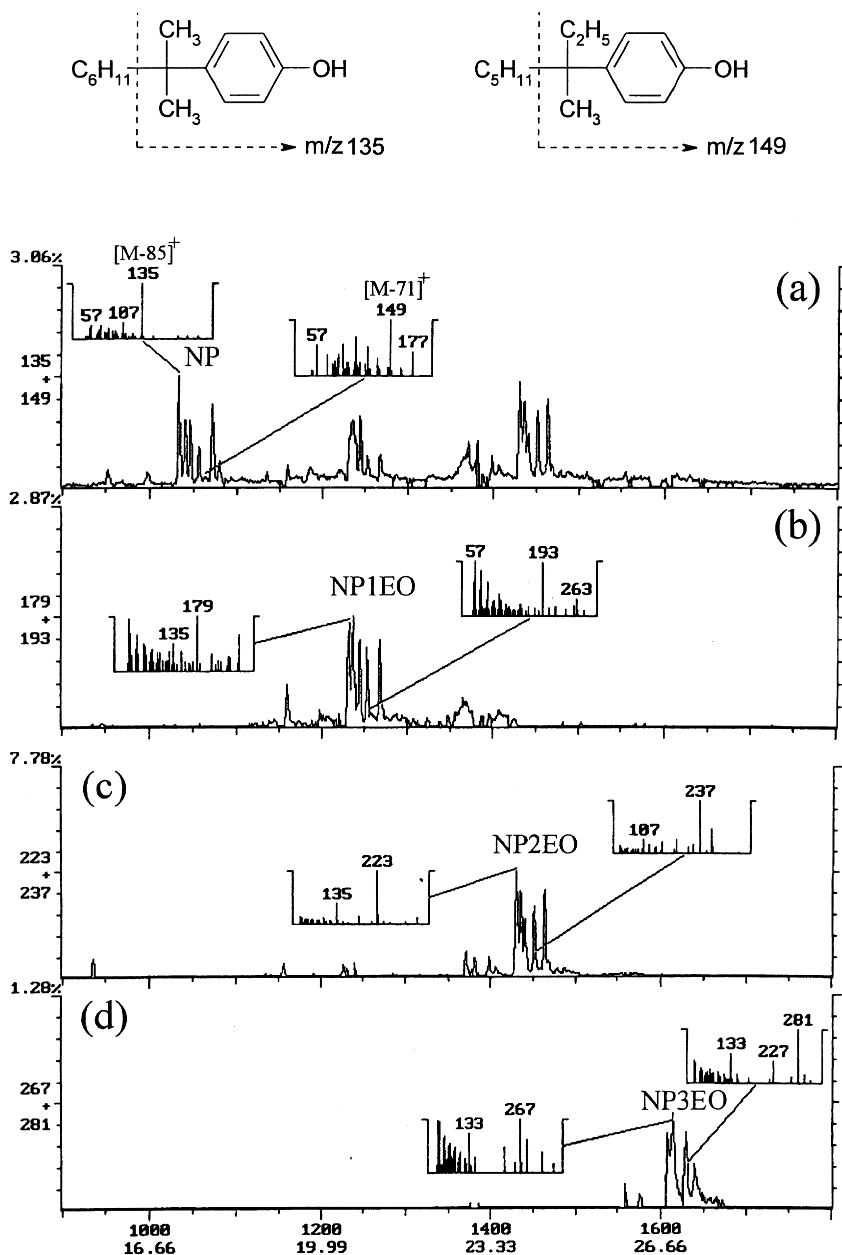

Fig. 2. The selected EI characteristic ion chromatograms of (a) NP, (b) NP1EO, (c) NP2EO and (d) NP3EO, and their corresponding mass spectra detected in a river water sample.

samples were semi-quantified by comparison with the internal standard peak area to the sum of the total peak areas of selected characteristic ion chromatograms at *m*/*z* 135/149, 179/193, 223/237 and 267/281 for NP, NP1EO, NP2EO and NP3EO, respectively.

Fig. 3 shows the EI, CH_4-CI and acetone-CI ion trap mass spectra of one isomer of propylated

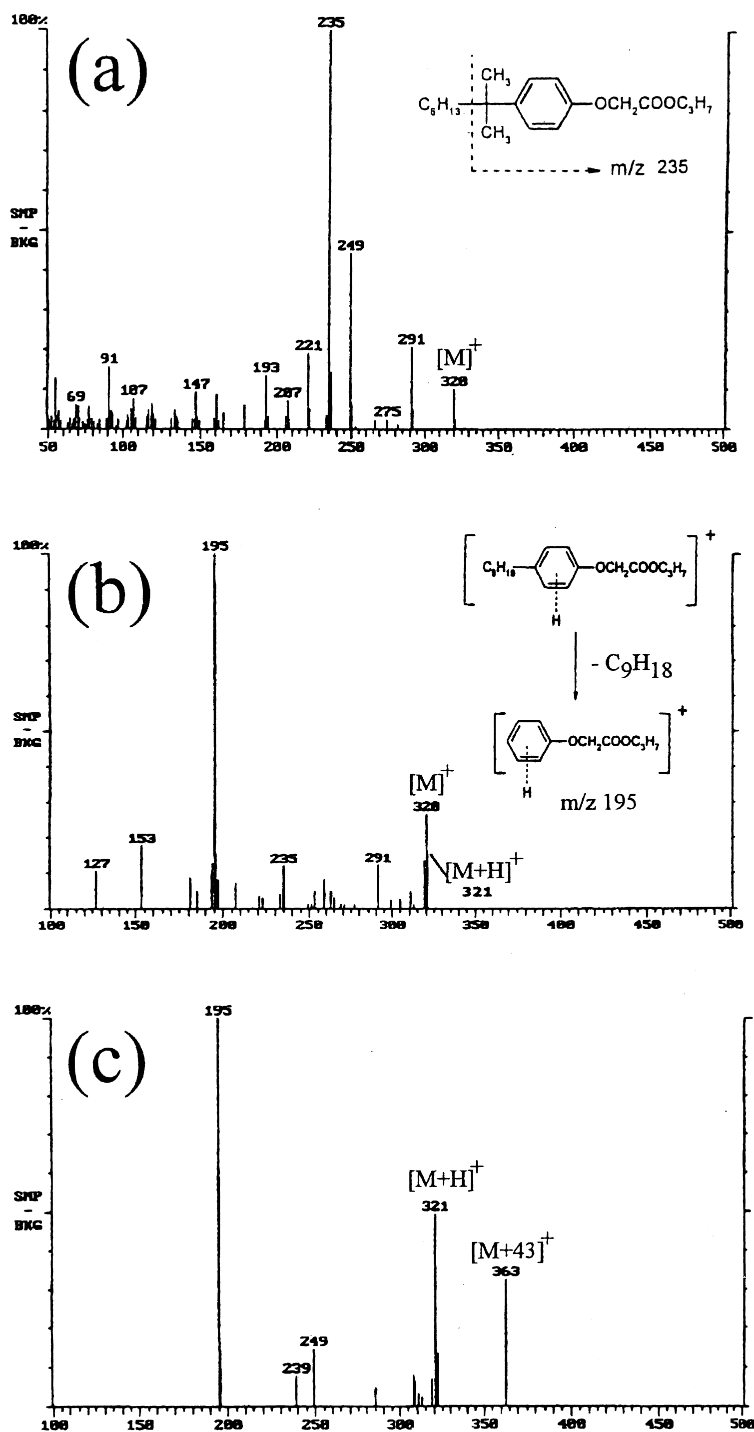

Fig. 3. The (a) EI, (b) CH_4-CI and (c) acetone-CI ion-trap mass spectra of one isomer of propylated NP1EC detected in a river water sample.

NP1EC detected in a river water sample. In this example, the predominant ion of *m/z* 235 is observed in the EI spectrum. The benzylic cleavage of $[M-85]^+$ is very common for most propylated NPEC compounds in EI mass spectra. Although the determination of the molecular mass of the analyte could be successfully conducted by interpreting the CH_4-CI mass spectrum (Fig. 3b), use of acetone as CI reagent (Fig. 3c), a relatively high abundance of protonated molecular signal (*m/z* 321) with $[M+43]^+$ adduct ion make it easy to determine the molecular mass of propylated NP1EC isomer. The $[M+43]^+$ ion located at *m/z* 363 is typical of an acetyl cation attachment as described by Eberlin et al. [24]. The CH_4-CI and acetone-CI mass spectra are predominated by the ions of $[MH\text{-}126]^+$, for example the ion at *m/z* 195 in Fig. 3b and c, which are due to the loss of the entire alkyl group from the protonated molecule.

Fig. 4 shows the EI and acetone-CI selected characteristic ion chromatograms of NP1EC, NP2EC and NP3EC and their corresponding mass spectra detected in a river water sample. As seen with the NP and NPEOs mass spectra, the most significant ions in EI for propylated NPECs are also produced by benzylic cleavages of $[M-71]^+$ and $[M-85]^+$, corresponding to the ions of *m/z* 249 and 235 for NP1EC isomers, ions of *m/z* 293 and 279 for NP2EC isomers, and ions of *m/z* 337 and 323 for NP3EC isomers. Although these ions are not very informative in respect to structural elucidation or molecular mass determination, they provide an indication of the presence of NPEC residues in water samples. The significant ions in acetone-CI mass spectra are the ions of $[MH-126]^+$, $[M+H]^+$ and $[M+43]^+$. The NP1EC, NP2EC and NP3EC isomers in water samples were semi-quantified by comparison with the internal standard peak area to the sum of total peak areas of two EI selected characteristic ion chromatograms for each isomer group as described previously.

3.3. EI, CI and CI-MS–MS product-ion MS of CNPECs

In addition to the detection of NPECs, dicarboxylic acids of NPEO residues, carboxylated on both side chains (the ethoxy and the alkyl chains), were also detected in the samples of river water and sewage effluent. The dicarboxylic acids are referred to here as carboxyalkylphenol ethoxy carboxylates (CNPECs, Ref. [5]). Degradation of the hydrophobic part of non-ionic surfactants has been reported by carrying out with ^{14}C-labelled stearyl alcohol ethoxylates [25]. The study indicated that the terminal carbon atom was firstly oxidized to an alcohol by an oxygenase enzyme and then subsequently oxidized to the aldehyde and carboxylic acid; the pathway is known as ‘‘ω-oxidation’’. The biodegradation on linear alkyl chains can then proceed by oxidative cleavage of two carbon-units, called ‘‘β-oxidation’’.

Fig. 5 shows the EI and CH_4-CI selected ion chromatograms and mass spectra of propylated CNP1EC and CNP2EC, tentatively assigned as C_9 (eight carbon-unit plus one carboxylic group) and C_7 (six carbon-unit plus one carboxylic group) of CNPECs, in a river water sample. The most significant ions in EI-MS are also produced by benzylic cleavages of $[M-71]^+$ and $[M-85]^+$, corresponding to the ions of *m/z* 249 and 235 for CNP1EC isomers, ions of *m/z* 293 and 279 for CNP2EC isomers. From the CI mass spectra and retention times, we can distinguish between the NPEC and CNPEC species of the same benzylic cleavages of $[M-71]^+$ and $[M-85]^+$. The C_7-CNP1EC and C_7-CNP2EC isomers were determined with the protonated molecular signals at *m/z* 365 and 409, respectively. The strong $[MH-60]^+$ ions were observed, attributed to the loss of propanol [5]. The benzylic cleavage was also observed but less prominently than in the EI mass spectra. The C_9-CNP1EC and C_9-CNP2EC isomers were detected with the protonated molecular signals at *m/z* 393 and 437, respectively.

The carboxylation of the alkyl side chain of the NPECs was also determined by comparing methylated and propylated extracts of the same sample as described by Ding et al. [5]. From the molecular masses and characteristic base ions of methyl and propyl esters of CNPECs, we suggested that there are two carboxylic acid groups on the NPE residues. The second carboxylic acid group should be attached to the alkyl side chain of the molecule. The ions at *m/z* 171 in C_7-CNPEC were tentatively assigned as the displacement of a carboxylated alkyl side chain $[C_3H_7OOC\text{-}C_3H_6\text{-}C_3H_6]^+$ from the phenoxy ring [5]. The ions at *m/z* 199 in C_9-CNPEC

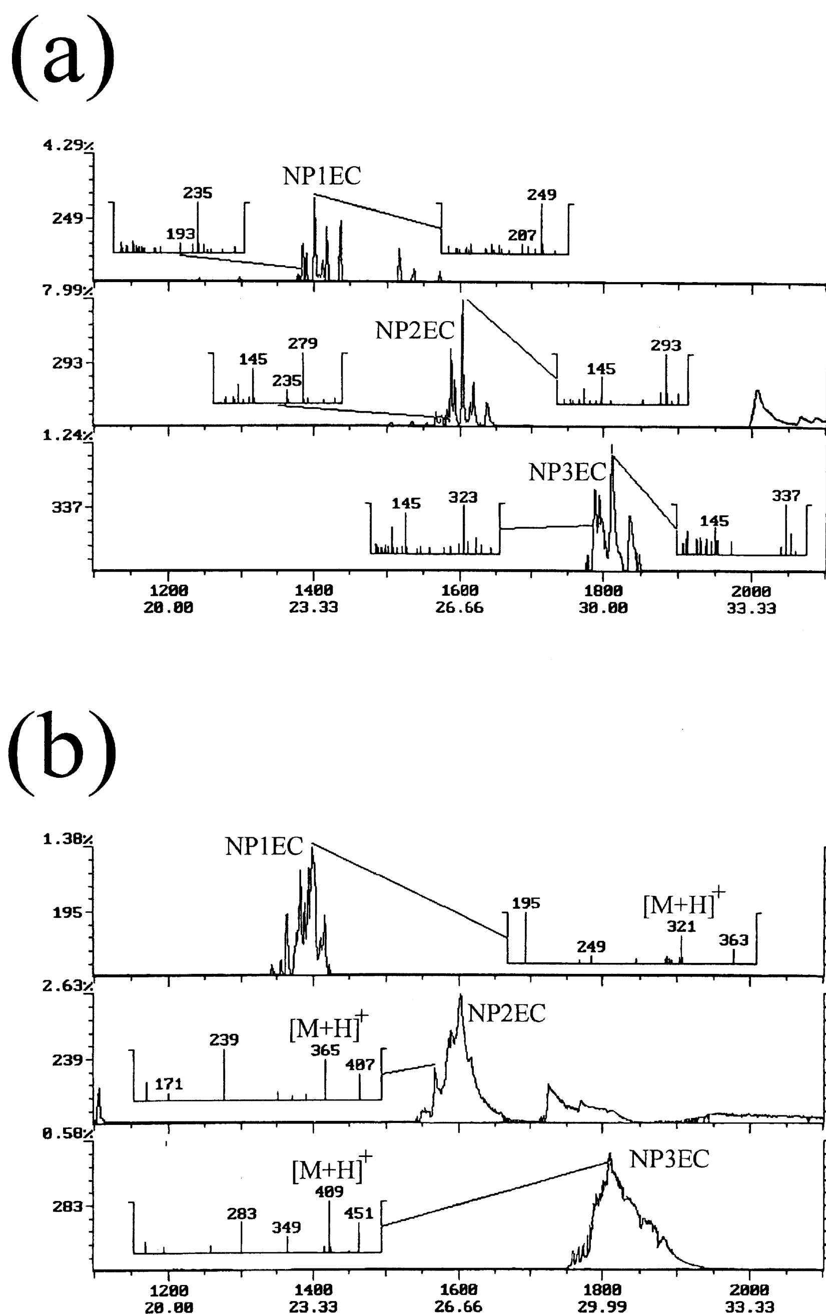

Fig. 4. The (a) EI and (b) acetone-CI selected characteristic ion chromatograms of propylated NP1EC, NP2EC and NP3EC, and their corresponding mass spectra detected in a river water sample.

were tentatively assigned as the displacement of a carboxylated alkyl side chain with an additional two carbon-units $[C_3H_7OOC\text{-}C_5H_{10}\text{-}C_3H_6]^+$ from the phenoxy ring. The CNP1EC and CNP2EC isomers in water samples were semi-quantified as described previously by using the sum of total peak areas of

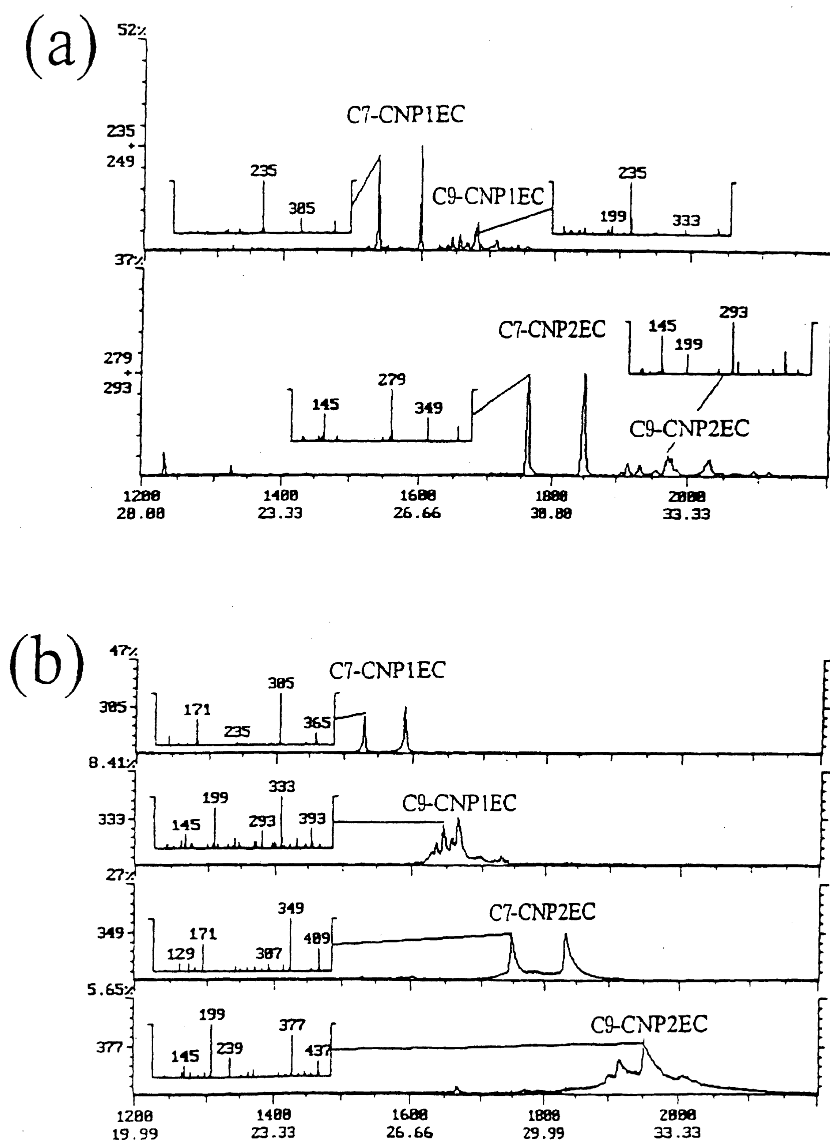

Fig. 5. The (a) EI and (b) CH_4-CI selected ion chromatograms and mass spectra of propylated CNP1EC and CNP2EC in a river water sample.

two selected characteristic ion chromatograms for each isomer group in the EI mode.

For confirmation of the proposed fragmentation mechanism, the CI-MS–MS product-ion mass spectra of these two ions was studied. Fig. 6 depicts the product-ion mass spectra of (a) ion at *m/z* 171 and (b) ion at *m/z* 199. In Fig. 6a, the ion at *m/z* 129 may be produced by proton rearrangement and loss of propene (CH_2=CH-CH_3, 42 u), and the relatively intense ion at *m/z* 111 results from the loss of propanol (C_3H_7OH, 60 u) from the parent ion. These two types of fragmentations are common in CI mass spectra of fatty acid alkyl esters as described by Munson and Field [26], and Tsang and Harrison [27]. In Fig. 6b, the product-ion mass spectrum of the *m/z* 199 ion shows the same fragmentation patterns of the losses of propene and propanol, with product ions at *m/z* 157 and *m/z* 139, respectively.

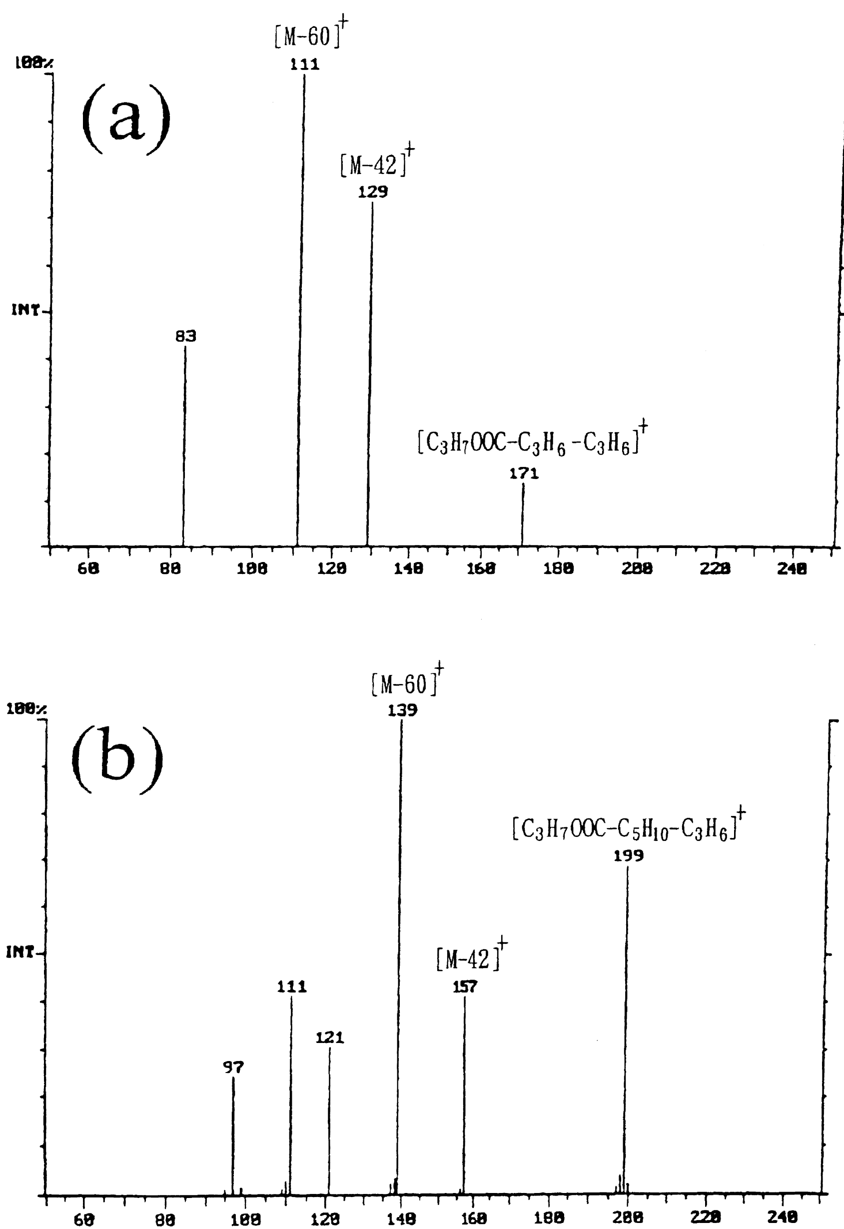

Fig. 6. The product-ion mass spectra of (a) ion at m/z 171 and (b) ion at m/z 199, at non-resonant CID amplitude 50 V.

The CI-MS–MS product-ion mass spectra of methylated CNP1EC and CNP2EC displayed similar fragmentation, except that the loss of the alkene from the methylation esters was not observed because the elimination of alkene from CI-MS spectra is only observed for propyl or higher esters [26].

3.4. Recovery study and application to environmental samples

The recovery from GCB SPE was evaluated by spiking known amounts of commercial NP standard mixture and OP1EC into deionized water. Three

Table 1
Estimated average concentration of NPEOs and NPECs, and recovery results of NP and OPIEC spiked into different water samples

Sample	NP	NP1EO	NP2EO	NP3EO	Surrogate OP1EC	NP1EC	NP2EC	NP3EC
Blank surface water								
Average concentration (μg/l)	0.6	0.4 (12%)	0.9 (7%)	n.d.		n.d.	n.d.	n.d.
Spiked recovery (%)	81 (2%)				107 (6%)			
Polluted river water								
Average concentration (μg/l)	3.0	10.3 (2%)	10.1 (5%)	0.9 (12%)		35.6 (3%)	105 (1%)	17.6 (4%)
Spiked recovery (%)	90 (6%)				93 (12%)			
Sewage effluent								
Average concentration (μg/l)	1.6	9.6 (12%)	15.3 (5%)	5.4 (4%)		19.2 (3%)	99.2 (2%)	26.3 (3%)
Spiked recovery (%)	88 (7%)				84 (5%)			

The relative standard deviation (R.S.D.) is given in parentheses, $n=3$.
n.d.=Not detected.

replicate 100-ml deionized water samples were each spiked to obtain the final concentrations of 10 μg/l of NP and 10 μg/l of OP1EC. The recovery was 82% (R.S.D.=7%) for NP and 85% (R.S.D.=4%) for OP1EC. The recoveries of NP and OP1EC from environmental samples were evaluated by means of standard addition experiments. Three replicate 100-ml samples of blank surface water, surfactant polluted river water and sewage effluent were used to perform the studies. Concentrations of NP, and NPEO residues and their degradation products in environmental samples were determined semi-quantitatively by relating the EI characteristic ion in each isomer group to the internal standard (chrysene-d_{12}). Because the authentic standards were not available, the concentrations given were estimated assuming that the response factors for the internal standard and the analyte were the same. The recoveries of NP and OP1EC were estimated by comparing the response factors of the standard mixture and the samples.

Table 1 summarizes the average percent recoveries of NP and OP1EC in the samples of river water and sewage effluent, as well as their estimated average background concentrations. Recoveries of NP in environmental samples ranged from 81% to 90% with R.S.D.s ranging from 2 to 7%. Average recovery of the OP1EC surrogate was 95±12%. The results indicated that the method performed satisfactorily despite the variable compositions of environmental samples. Table 2 summarizes the estimated average concentrations of CNPEC compounds in the samples of river water and sewage effluent. The R.S.D.s of three replicate sample analyses ranged from 2 to 5%. Relatively high concentrations of

Table 2
Estimated average concentration of CNPEC residues in different water samples

Sample	C_7-CNP1EC	C_9-CNP1EC	C_7-CNP2EC	C_9-CNP2EC
Blank surface water				
Average concentration (μg/l)	n.d.	n.d.	n.d.	n.d.
Polluted river water				
Average concentration (μg/l)	138 (5%)	100 (2%)	113 (3%)	66.5 (3%)
Sewage effluent				
Average concentration (μg/l)	26.7 (2%)	14.7 (4%)	67.2 (2%)	50.0 (3%)

The relative standard deviation (R.S.D.) is given in parentheses, $n=3$.
n.d.=Not detected.

CNPEC residues were detected in surfactant polluted river water as compared to the sewage effluent; this may be due to the directly discharge of untreated wastewater into the river. The limit of quantitation for NPEO residues and their degradation products was estimated at a signal-to-noise ratio (S/N) of 10. The quantitation limit was calculated to be 0.01 μg/l in 100 ml of water samples.

4. Conclusions

In this work we have demonstrated procedures for positive identification and quantitation of NPEO residues and their degradation products, NPECs and CNPECs, in the samples of sewage effluent and river water using ion-trap GC–MS with EI, CI and CI-MS–MS modes. The results suggest that the ion-trap GC–MS system in variety of ionization modes is reliable, and offering a convenient analytical technique for trace level determination of target compounds in complex environmental samples. Although the detailed biodegradation pathways of the alkyl side chain of NPECs are not understood, evidence of the carboxylation of the alkyl side chain of NPECs is provided by product-ion mass spectra in this study and in a previous report [5] by comparison of methylated and propylated CNPEC derivatives. It is difficult to assess the impact of CNPEC residues in effluents and river water on aquatic organisms due to the lack of the data regarding to their toxicity and potential bioaccumulation. Further research is necessary in order to understand the fate and effects of NPEO residues and their degradation products in untreated wastewater directly discharged into the aquatic environment.

Acknowledgements

Funding for this study was provided by the NSC of Taiwan, contract No. NSC 87-2113-N-008-004. We are grateful to Professor Martin Reinhard, Drs. Yoshiko Fujita and Jian Zhou for review of the manuscript, and Mr. Allen Huang from Varian-Taiwan for technical support.

References

[1] M. Reinhard, N. Goodman, K.E. Mortelmans, Environ. Sci. Technol. 16 (1982) 351.
[2] E. Stephanou, W. Giger, Environ. Sci. Technol. 16 (1982) 800.
[3] H.A. Ball, M. Reinhard, in: R.L. Jolley, et al. (Eds.), Water Chlorination, Vol. 5, Lewis, Chelsea, MI, 1985.
[4] M. Ahel, W. Giger, Anal. Chem. 57 (1985) 2584.
[5] W.H. Ding, Y. Fujita, R. Aeschimann, M. Reinhard, Fresenius J. Anal. Chem. 354 (1996) 48.
[6] M. Ahel, W. Giger, M. Koch, Water Res. 28 (1994) 1131.
[7] A. Di Corcia, R. Samperi, A. Marcomini, Environ. Sci. Technol. 28 (1994) 850.
[8] J.A. Field, R.L. Reed, Environ. Sci. Technol. 30 (1996) 3544.
[9] M. Ahel, W. Giger, C. Schaffner, Water Res. 28 (1994) 1143.
[10] M.A. Blackburn, M.J. Waldock, Water Res. 29 (1995) 1623.
[11] W.H. Ding, J. Wu, M. Semadeni, M. Reinhard, in preparation.
[12] R.D. Swisher, Surfactant Biodegradation, Marcel Dekker, New York, 2nd ed., 1987.
[13] M. Ahel, D. Hrsak, W. Giger, Arch. Environ. Contam. Toxicol. 26 (1994) 540.
[14] E. Stephanou, Organic Mass Spectrom. 19 (1984) 510.
[15] E. Stephanou, M. Reinhard, H.A. Ball, Biomed. Environ. Mass Spectrom. 15 (1988) 275.
[16] W.H. Ding, Y. Fujita, M. Reinhard, Rapid Commun. Mass Spectrom. 8 (1994) 1016.
[17] P. Sandra, J. Beltran, F. David, J. High Resolut. Chromatogr. 18 (1995) 545.
[18] J.B. Plomleg, R.E. March, R.S. Mercer, Anal. Chem. 68 (1996) 2345.
[19] T. Turnes, I. Rodriguez, C.M. Garcia, R. Cela, J. Chromatogr. A 743 (1996) 283.
[20] S.M. Pyle, L.D. Betowski, A.B. Marcus, W. Winnik, R.D. Brittain, J. Am. Soc. Mass Spectrom. 8 (1997) 183.
[21] Y. Fujita, Ph.D. Dissertation, Stanford University, 1997.
[22] H. Jing, A. Amirav, Anal. Chem. 69 (1997) 1426.
[23] H.G.J. Mol, H.G. Janssen, C.A. Cramers, U.A.T. Brinkman, J. High Resolut. Chromatogr. 18 (1995) 19.
[24] M.N. Eberlin, T.K. Majumdar, R.G. Cooks, J. Am. Chem. Soc. 114 (1992) 2884.
[25] J.R. Nooi, M.C. Testa, S. Willemse, Tenside 7 (1970) 61.
[26] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 88 (1966) 4337.
[27] C.W. Tsang, A.G. Harrison, J. Chem. Soc. Perkin Trans. 2 (1975) 1718.