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Determination of nonylphenol ethoxylate oligomers by liquid chromatography–electrospray mass spectrometry in river water and non-ionic surfactants

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Abstract

Liquid chromatography–electrospray ionization mass spectrometry (LC–ESI-MS) for the quantitative determination of five nonylphenol ethoxylate (NPE) oligomers in river water was described. These NPE oligomers were separated on a poly(vinyl alcohol) gel column using acetonitrile–30 m*M* ammonium acetate as the mobile phase followed by ESI-MS detection without any sample concentration steps. The sample was only filtered using the disposable filter and the aliquot (100 μl) of this sample was injected into the LC–ESI-MS system. All NPE oligomers were detected using the $[M+NH_4]^+$ ion. Detection limits ranged from 160 pg/ml (NPE4) to 240 pg/ml (NPE2), repeatability and reproducibility ranged from 4.2% (NPE2) to 6.2% (NPE6) and from 7.4% (NPE5) to 9.8% (NPE6).

Keywords: Large-volume injection; Water analysis; Nonylphenol ethoxylate oligomers

1. Introduction

Polyethoxylated nonylphenols are important non-ionic surfactants which were used commercially for many years as emulsifiers and solubilizers in pharmaceutical [1] and agrochemical formulations [2], cosmetics [3] and various biotechnological processes [4] due to their favorable physicochemical characteristics. Furthermore, one of the major uses of polyethoxylated nonylphenols are as surfactants in industrial cleaners. They have the formula $R\text{-}C_6H_4\text{-}(OCH_2\text{-}CH_2)_nOH$, where $R=C_9H_{19}$ and $n=2–18$. They remain one of the largest groups of non-ionic surfactants and have attracted a great deal of attention because of their potentially adverse environmental effects [5–7]. It has been proved many times that the character of both the hydrophobic and hydrophilic parts influences the biological efficacy of non-ionic surfactants [8]. On the other hand, the highly branched nonyl group and the phenol ring of nonylphenol have been shown to have only low-to-moderate biodegradability in many studies. Increasing toxicities are found with decreasing polyethoxylate chain length. Most surfactants are discharged into municipal and industrial wastewaters. Certain surfactants used as detergents can be biotransformed to persistent and toxic metabolites shown to be a strong estrogenic compounds during their degradation in sewage treatment [9]. The alkyl phenol ethoxylates (APEs) as the non-ionic surfactants exhibit this

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metabolic behavior. Thus, in addition to knowledge of total concentrations, information about the APE oligomer distribution is essential in understanding the change in APEs, as they undergo degradation and also in assessing the environment impact of these changes. Therefore, many efforts have been devoted to the development of qualitative and quantitative analyses of these compounds [10–12]. These procedures, however, are complicated and time-consuming, lack sensitivity, specificity and are subject to interference. The use of gas chromatography for the analysis of APE oligomers is limited because these compounds contain hydroxy and ethoxy groups, thus adsorb to the surfaces of the injector and column [13].

Efficient separations of APE oligomers can be achieved by high-performance liquid chromatography (HPLC) in the normal phase on columns packed with unmodified silica gel or with amino or diol chemically bonded phases [14–16], the reversed phase [17–19] and in the gel filtration system [20–22]. In the normal phase, individual ethoxylated oligomers are eluted in the order of increasing number of oligomeric oxyethylene units, thus low ethoxylated oligomers are eluted at a short time and are subject to interference. On the other hand, in gel filtration chromatography (GFC), individual ethoxylated oligomers are eluted in the order of decreasing number of oligomeric oxyethylene units. However it is necessary to use an organic solvent in which micelles can not be formed. Furthermore, GFC has been limited in the past to polymers and ''big'' molecules. Recent technological advances have made available smaller molecules and organic solvent. For qualitative analysis of APE oligomers, many reports using mass spectrometry (MS) have been published [23–25]. But few reports have been published so far on the systematic investigation of their quantitative information. Furthermore, only recently have nonylphenol ethoxylate oligomer standards become commercially available. The aim of the present work is the determination of the amount of nonylphenol ethoxylate oligomers in environmental water and nonylphenol ethoxylate as industrial-use surfactant using HPLC with GFC gradient elution and electrospray ionization (ESI) mass spectrometry (MS). For the sample preparation of environmental water, sample was simply filtered with a 0.2-μm filter followed by a large-volume injection technique.

2. Experimental

2.1. Materials

Nonylphenol diethoxylate (NPE2), nonylphenol triethoxylate (NPE3), nonylphenol tetraethoxylate (NPE4), nonylphenol pentaethoxylate (NPE5) and nonylphenol hexaethoxylate (NPE6) were purchased from Hayashi (Osaka, Japan). Technical nonylphenol polyethoxylate surfactants containing on average two, five, seven and 10 ethyleneoxide groups per molecule were purchased from Tokyo Kasei (Tokyo, Japan). HPLC-grade acetonitrile and ammonium acetate were purchased from Wako (Osaka, Japan). All other chemicals were of reagent grade. Water was purified with a Milli-Q system (Millipore, Tokyo, Japan).

2.2. Instrumentation

A liquid chromatography–mass spectrometry (LC–MS) system consisting of an LC pump, an autosampler, a thermostated column compartment, a UV detector (Model 1100; Hewlett-Packard, Palo Alto, CA, USA), and a mass-selective detector bench top mass spectrometer (Hewlett-Packard) with ESI was used. The LC flow was introduced into the ESI interface without any splitting after detection by photodiode-array detection.

LC separation was performed on a150×2.1 mm I.D. column packed with 5 μm Shodex MSpack GF-310 2D (Showadenko, Tokyo, Japan). Gradient elution was carried out with a linear program from 10% solvent A (acetonitrile) and 90% solvent B (water containing 30 m*M* ammonium acetate) to 55% solvent A and 45% solvent B in 30 min. The column was conditioned with 10% solvent A and 90% solvent B for 15 min before injection of the next sample. The flow-rate was 0.2 ml/min. The injection volume was 100 μl.

2.2.1. Mass spectrometry

A HP 1100 series mass-selective detector single quadrupole instrument equipped with the orthogonal spray-ESI (Hewlett-Packard) interface was used for this investigation. The nebulizer gas (nitrogen, 99.5% purity), the drying gas (nitrogen, 99.5%, 350°C) and fragmentor voltage were set to 50 p.s.i., 10 l/min, and 60 V, respectively (1 p.s.i.=6894.76 Pa). The

operating parameters of the mass-selective detector were optimized by a Calibrant Delivery System using a calibration standard at 0.1 ml/min. LC–MS determinations were performed by operating the mass-selective detector in the positive ion mode. Mass spectra were acquired over the scan range m/z 100–600 using a step size of 0.1 u and a scan speed of 0.5 scan/s. Quantitative analysis was carried out using single ion monitoring (SIM) of base ion peaks at m/z 502 (NPE6), 458 (NPE5), 414 (NPE4), 370 (NPE3) and 326 (NPE2) with a dwell time of 100 ms per ion.

2.3. Preparation of standard solutions

Individual solutions of 10 mg/ml of each nonylphenol ethoxylate oligomer (NPE2, NPE3, NPE4, NPE5 and NPE6) were prepared in acetonitrile. A stock standard solution containing all nonylphenol ethoxylates (100 μg/ml of each) was prepared in acetonitrile. Working solutions with concentrations of 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200 and 500 ng/ml of each nonylphenol ethoxylate were prepared in water. For method development, solutions of 1 and 10 μg/ml were used.

2.4. Sample preparation

The solutions of four different nonylphenol polyethoxylates were prepared by dissolving 2 mg each of these surfactants in 1000 ml water for the analysis of NPE oligomers in technical surfactants. The environmental sample was collected in a 100-ml polyethylene terephthalate (PET) bottle. A 1000-μl aliquot of the sample was simply filtered through a 0.2-μm nylon filter and transfered to a 1-ml polypropylene vial.

3. Results and discussion

3.1. Retention behavior of NPE oligomers using gel filtration chromatography

The influence of the initial composition of an acetonitrile–30 m*M* ammonium acetate mobile phase for the separation of five NPE oligomers on a GF310-HQ polymer column was investigated. The elution order of the oligomers on the GFC column was reversed compared with the reversed- or normal-phase chromatography, with 30% acetonitrile all oligomers are weakly retained and cannot be separated. On the other hand, with 5 and 10% acetonitrile, the NPE oligomers were sufficiently retained but the separation selectivity was decreased (α= 1.02) with 5% acetonitrile because the peak width of all oligomers rapidly increased. The best separation of the five oligomers was obtained by using 10% acetonitrile and 90% 30 m*M* ammonium acetate as initial composition (Fig. 1). The optimized resolution on the GFC column was better than that of reversed phase, but less than that of normal-phase LC. However the quantitative analysis of the compounds is possible because the molecular mass of each NPE oligomer is different (for SIM mode, monitoring ion of each compound is different). Furthermore, all NPE oligomers have sufficient retention in GPC, which is an advantage over normal-phase LC because the broad matrix corresponding to the humic and fulvic substances of natural water is poorly retained.

3.2. Evaluation of ESI parameters

3.2.1. Effect of fragmentor voltage on the mass spectra

The fragmentor voltage is applied to the exit of the capillary and affects the transmission and fragmenta-

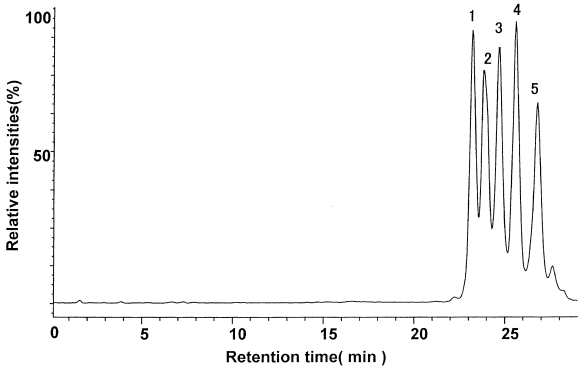

Fig. 1. Total ion chromatogram of five NPE oligomer standards each at 10 μg/ml obtained with optimized chromatographic conditions. Elution A (30 m*M* ammonium acetate) and elution B (30 m*M* ammonium acetate) was used for linear gradient from 10% B to 55% B in 30 min. 1=Nonylphenol hexaethoxylate, 2=nonylphenol pentaethoxylate, 3=nonylphenol tetraethoxylate, 4=nonylphenol triethoxylate, 5=nonylphenol diethoxylate.

tion of sample ions by the in-source collision-induced dissociation (CID) in this region [26–28]. In general, the higher the fragmentor voltage, the more fragmentation will occur. On the other hand, the compounds which do not fragment readily often have better ion transmission at the higher fragmentor voltage,because the fragmentor voltage gives the ions a push that helps them traverse the the relatively high-pressure region between the exit of the capillary and the skimmer. Thus, at higher values of voltage the maximum structural information is obtained. However, the optimum fragmentor voltage is compound dependent and, for this reason, an accurate evaluation of the fragmentor voltage on the mass spectra of each one of NPE oligomers in this work was done by varying the voltage using a 1 μg/ml standard solution. Ammonium acetate was used as the buffer of the mobile phase because NPE oligomers have more than two $-(CH_2CH_2O)-$ ethoxylate units and possess high cation affinity [29]. The results of this investigation are shown in Fig. 2. An ammonium adduct $[M+NH_4]^+$ ion was observed as the base peak in the mass spectra of all NPE oligomers at less than 60 V and the intensity of these ions decreased at the higher fragmentor voltage. On the other hand, the intensity of the quasi-molecular

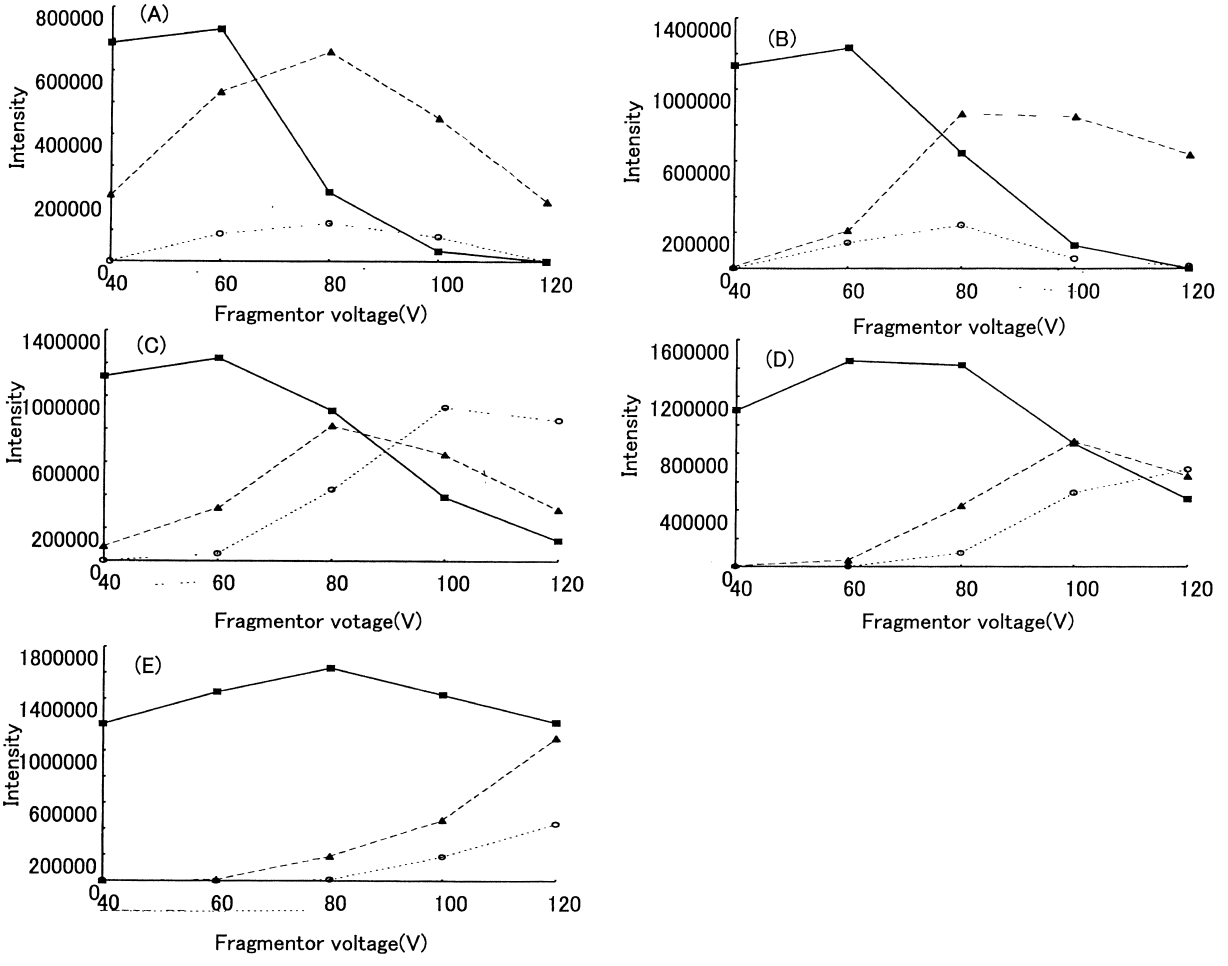

Fig. 2. The effect of fragmentor voltage on the mass spectra of NPE oligomers. Mobile phase: acetonitrile–15 m*M* ammonium acetate (1:1), for the other conditions, see Experimental. ■=$[M+NH_4]^+$, ▲=$[M+H]^+$, ○=$[HC_6H_4O(C_2H_4O)_nH+H]^+$. A=Nonylphenol diethoxlate, B=nonylphenol triethoxylate, C=nonylphenol tetraethoxylate, D=nonylphenol pentaethoxylate, E=nonylphenol hexaethoxlate.

$[M+H]^+$ ion increased by increasing the fragmentor voltage as expected [29]. The result indicates that the $[M+H]^+$ ion, which does not fragment readily has a better ion transmission at the higher fragmentor voltage. But the intensity of the $[M+NH_4]^+$ ion at 60 V was higher than that of the $[M+H]^+$ ion at 100 V. This fact indicates that the $[M+H]^+$ ion is more stable than $[M+NH_4]^+$ but NPE oligomers have a high ammonium ion affinity. The maximum response of the $[M+NH_4]^+$ ion was found at the higher fragmentor voltage for the oligomer that have the higher ethoxylate units. On the other hand, for all molecules, the loss of 126 u has been observed at more than 60 V, which indicates the loss of a nonyl group. From the above result, the fragmentor voltage for all NPE oligomers was set to 60 V. The typical mass spectra of all NPE oligomers at 60 V are shown in Table 1. The quasi-molecular and adduct ions corresponding to $[M+H]^+$, $[M+NH_4]^+$and fragment ion (m/z=M−126) in all NPE oligomers indicates the number of ethoxylate units. For the quantitation in SIM mode, the adduct $[M+NH_4]^+$ ion was set at 60 V.

3.2.2. Effect of drying gas and nebulizer gas pressure

The main operating parameters which have an impact on performance of ESI are the drying gas temperature, flow-rate and nebulizer pressure. The effects of these parameters on the MS response were investigated for all NPE oligomers. All studies were carried out under flow injection analysis in the full-scan mode at 10 μg/l.

The first step, ESI performance at different drying gas temperature (100–350°C) was compared with that at 100°C for all analytes. Higher drying gas temperature (350°C) causes as much as a fivefold increase in response for all analytes. High drying gas temperature causes an easier desolvation of the sprayed droplets without excessive heating of the dissolved analytes. In fact, from mass spectra, no decomposition was observed even at the highest temperature. Thus this parameter was maintained at 350°C.

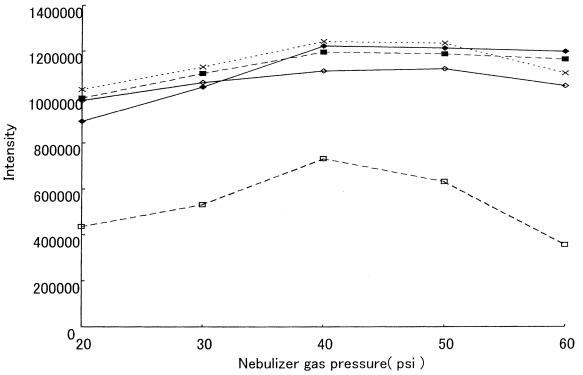

Fig. 3. The effect of nebulizer gas pressure on the signal intensities of NPE oligomers. Mobile phase: acetonitrile–15 m*M* ammonium acetate, flow-rate: 0.2 ml/min, drying gas: 10 l/min at 350°C, for the other conditions, see Experimental. ♦= Nonylphenol diethoxylate, ■=nonylphenol triethoxylate, ×= nonylphenol tetraethoxylate, ◇=nonylphenol pentaethoxylate, □=nonylphenol hexaethoxylate.

For the drying gas flow-rate, changing the flow-rate from 4 to 13 l/min at 350°C resulted in a less than 10% increase in the response of all analytes. Therefore, the drying gas flow-rate was maintained at 10 l/min. Optimization of the nebulizer pressure was done by changing pressure from 20 to 60 p.s.i.. As is shown in Fig. 3, except for NPE6, for which the maximum intensity was obtained at 40 p.s.i., less severe variation in the MS response for other NPE oligomers was observed. The optimum condition was therefore established as a nebulizer pressure of 40 p.s.i.

Table 1
m/z value and relative intensities (RIs) of the main ions formed in ESI-MS of nonylphenol ethoxylates *m/z* (RI, %); fragmentor voltage: 60 V

Nonylphenol ethoxylate	$(M+NH_4)^+$	$(M+H)^+$	$[HC_6H_4O(C_2H_4O)_nH+H]^+$
Nonylphenol diethoxylate	326 (100)	309 (75)	183 (21)
Nonylphenol triethoxylate	370 (100)	353 (17)	227 (15)
Nonylphenol tetraethoxylate	414 (100)	397 (35)	271 (12)
Nonylphenol pentaethoxylate	458 (100)	441 (8)	315 (6)
Nonylphenol hexaethoxylate	502 (100)	485 (9)	359 (2)

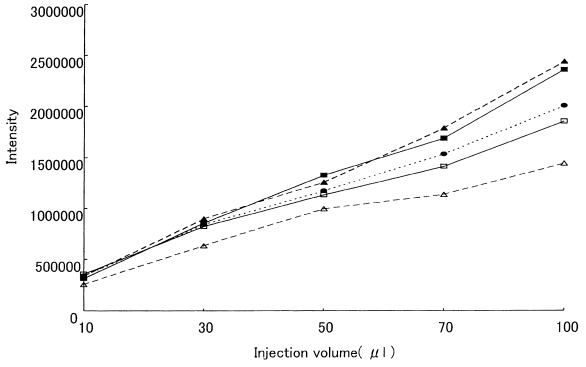

Fig. 4. The effect of injection volume on the signal intensities of NPE oligomers. ♦=Nonylphenol hexaethoxylate, ■=nonylphenol pentaethoxylate, ×=nonylphenol tetraethoxylate, ◇=nonylphenol triethoxylate, □=nonylphenol diethoxylate.

3.3. Large-volume injection with aqueous sample

In designing the sample preparation procedure, it is important to recognize that NPE oligomers are adsorbed onto various surfaces. Therefore, polypropylene and glass vials were evaluated for suitability as sample containers. As the result, in the case where the sample was preserved in the glass vial for long time, the intensity of all NPE oligomers deteriorated. On the other hand, for the polypropylene vial, the decrease in the intensity of all NPE oligomers was not observed. Therefore, the polypropylene vial was selected as a sample vial. Existing methods for the isolation of NPE oligomers from water samples include gaseous stripping of the sample into ethyl acetate [30] or a column technique described by Schmitt et al. [31]. But these methods are tedious. In this work, a large-volume injection method without any sample concentration steps was investigated. Since NPE oligomers investigated are water-soluble compounds, large-volume injection is possible by column tip concentration. A typical injection volume seems to be about 10 μl. In this study, the injection volume was varied from 10 to 100 μl. As a result, the peak areas of all NPE oligomers increased without peak broadening as the injection volume increased (Fig. 4).The optimum injection was therefore established by injecting the sample solution of 100 μl.

3.4. Linearity, detection limits and precision of the LC–MS system

In order to achieve optimum sensitivity, all experiments were carried out under SIM conditions and the ammonium adduct ions were selected as SIM ions for all NPE oligomers. The calibration curve was determined by external calibration in the concentration range from 0.2 to 100 ng/ml in injection solutions, corresponding to 0.02–10 ng on column. As shown in Table 2, the dynamic range was established about three orders of magnitude for all analytes; correlation coefficients (r^2) were higher than 0.999. The sensitivity of this analytical procedure was evaluated in terms of the minimum

Table 2
Analytical data of merit for nonylphenol oligomers

Nonylphenol oligomer	r^{2a}	Detection limit[b] (pg/ml)	Quantitative results[c] (ng/ml)	Instrument precision (RSD, %)	
				Repeatability [d]	Reproducibility[e]
Nonylphenol hexaethoxylate	0.9993	180	1.12	6.2	9.8
Nonylphenol pentaehoxylate	0.9995	180	1.05	5.2	8.8
Nonylphenol tetraethoxylate	0.9992	160	1.07	4.9	9.2
Nonylphenol triethoxylate	0.9994	190	1.15	5.0	7.4
Nonylphenol diethoxylate	0.9991	240	0.98	4.2	8.9

[a] r^2 is the correlation coefficient of calibration equation ranging from 0.2 to 50 ng/ml.
[b] Detection limit is the minimum quantitation limit defined as 10×standard deviation for five replicates of the river waters spiked with 0.2 ng/ml of each NPE oligomer.
[c] Calculated for river water spiked at the 1 ng/ml level.
[d] Repeatability was calculated on the basis of five replicates at 0.2 ng/ml within 1 day.
[e] Reproducibility was calculated on the basis of a single analysis per day for 3 days at 0.2 ng/ml.

quantitation limit (MQL) defined as 10-fold the standard deviation [32] with a spiked real sample such as river water. Since this parameter depends on the spiking concentration, The US Environmental Protection Agency (EPA) guidelines were used. These guidelines require that the ratio of spiking concentration to estimated MQL should be lower than 5:1. If the ratio is greater, the spiking concentration should be interactively reduced until the criterion is achieved. According to the above mentioned criterion, the spiking concentration selected for the river water was 0.2 ng/ml for all NPE oligomers. First of all, a blank of river water was analyzed. None of the peaks eluted at the same retention time of the analytes under the conditions studied. Afterwards, this river water was spiked with 0.2 ng/ml of each NPE oligomer and five replicates were carried out to calculate the MQL. The MQL of each NPE oligomer ranged from 160 to 240 pg/ml. The intra-day precision (repeatability) was estimated by injecting standard solutions containing all the NPE oligomers at 0.2 ng/ml five times during a working day. The inter-day precision (reproducibility) was evaluated by analyzing the same sample three times over 3 working days. The repeatability and reproducibility for all analytes ranged from 4.9 to 9.8%. The quantitative results using the spiked river water at 1 ng/ml using the external standard are also shown in Table 2 and an SIM chromatogram of this sample is shown in Fig. 5. These experimental results correlate well with the expected results and were within 20% of the expected results. Furthermore, no significant interference peaks were observed as shown in Fig. 5.

3.5. Analysis of polyethoxylated surfactants by LC–ESI-MS

Technical nonylphenol polyethoxylated surfactant contain some ethyleneoxides per molecule but only average ethyleneoxide numbers per molecule are shown. In this work, the quantitation of NPE oligomers (from NPE2 to NPE6) in four different surfactants at 2 ppm using this developed method was done. The proportion of each NPE oligomer occupied for all ethoxylates (Table 3) and the SIM chromatogram are shown in Fig. 6. The total amount

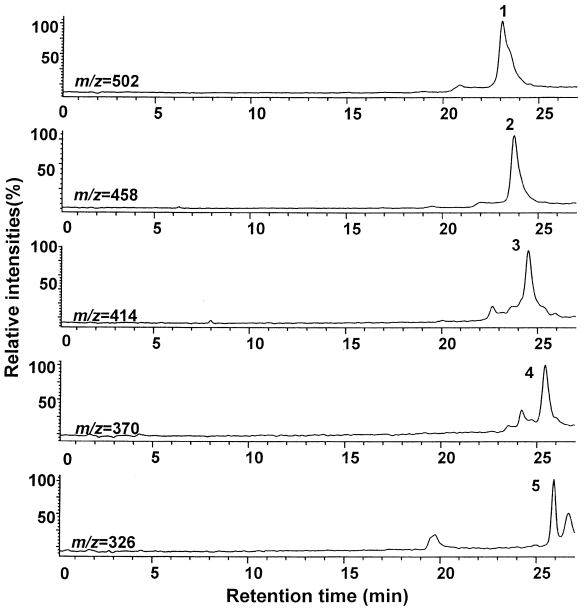

Fig. 5. Typical SIM chromatogram obtained by LC–ESI-MS of river water spiked at 0.2 ng/ml. 1=Nonylphenol hexaethoxylate, 2=nonylphenol pentaethoxylate, 3=nonylphenol tetraethoxylate, 4=nonylphenol triethoxylate, 5=nonylphenol diethoxylate.

of all NPE oligomers investigated ranged from 12.8% to 63.9% and that of the NPE oligomers in the most widely used surfactants (n=10) was 12.8%.

4. Conclusion

The present method allows the quantitation of NPE oligomers in river water and in technical surfactants by using external standards. The total

Table 3
Relative amount (%) of NPE oligomers in the surfactants at 2 μg/ml

Nonylphenol ethoxylate	n=2	n=5.5	n=7.5	n=10
Nonylphenol diethoxylate	35.2	8.5	1.1	1.1
Nonylphenol triethoxylate	19.3	15.9	4.6	0.7
Nonylphenol tetraethoxylate	6.5	16.5	7.8,	1.8
Nonylphenol pentaethoxylate	2.2	16.0	10.9	3.7
Nonylphenol hexaethoxylate	0.7	13.0	12.1	5.5
Total	64	70	37	13

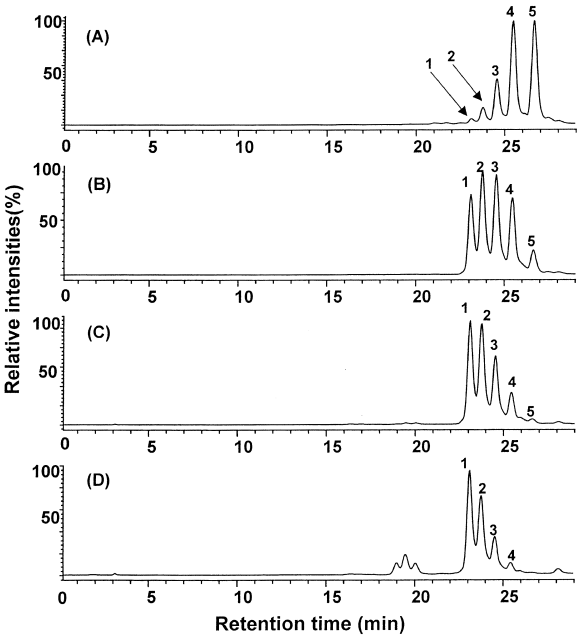

Fig. 6. SIM chromatogram obtained by LC–ESI-MS of NPE surfactants at 2 μg/ml. (A) $n=2$, (B) $n=5.5$, (C) $n=7$, (D) $n=10$. 1=Nonylphenol hexaethoxylate, 2=nonylphenol pentaethoxylate, 3=nonylphenol tetraethoxylate, 4=nonylphenol triethoxylate, 5=nonylphenol diethoxylate.

analysis time including sample preparation was only 30 min because of the direct injection of 100 μl of aqueous samples without a trace-enrichment step. GFC combined with electrospray MS detection was very useful for the analysis of environmental water because the retention times of all NPE oligomers were over 20 min and were not influenced by the sample matrix. The sensitivity of the present method seems to be sufficient for the NPE oligomers in the technical surfactants, but not for environmental water samples, Here, additional improvement of the sensitivity is required by increasing the injection volume or improving sample preparation.

References

[1] M.J. Lawrence, Eur. J. Drug Metab. Phamacokin. 19 (1994) 257.
[2] C. Reich, C.R. Robbins, J. Soc. Cosmet. Chem. 44 (1993) 263.
[3] J.J. Bolling, J.R. Seiler, S.M. Zedaker, J.W. Thompson, D. Lucero, Can. J. Forest Res. 25 (1995) 425.
[4] C.E. Forney, C.E. Glatz, Biotechnol. Prog. 11 (1995) 260.
[5] M. Ahel, W. Giger, M. Koch, Water Res. 28 (1994) 1131.
[6] M. Ahel, W. Giger, M. Koch, Water Res. 28 (1994) 1143.
[7] K.A. Evans, S.T. Dubery, L. Kravatz, I. Dzidic, J. Gumulka, R. Mueller, J.R. Stock, Anal. Chem. 66 (1994) 699.
[8] S. Kallioninen, K. Helenius, J. Yliruusi, Pharmazie 49 (1994) 750.
[9] E. Pelizzeti, C. Minero, V. Maurino, A. Sclafani, H. Hidaka, N. Serpone, Environ. Sci. Technol. 23 (1989) 1380.
[10] M. Ahel, W. Giger, Anal. Chem. 57 (1985) 1577.
[11] C.G. Naylov, J.P. Mieure, W.J. Adams, J.A. Weeks, F.J. Castadi, J. AOCS Int. 69 (1992) 695.
[12] A. Otsuki, H. Shiraishi, Anal. Chem. 51 (1979) 2329.
[13] H.T. Rasmusen, A.M. Pinto, M.W. De Mouth, P. Tourezky, B.P. McPherson, J. High Resolut. Chromatogr. 17 (1994) 593.
[14] K. Fytianos, S. Pegiadou, N. Raikos, I. Eleftheriadis, H. Tsoukali, Chemosphere 35 (7) (1997) 1423.
[15] I. Zeman, J. Chromatogr. 509 (1990) 201.
[16] N. Marquez, R.E. Anton, A. Usubilaga, J. Salager, J. Liq. Chromatogr. 17 (1994) 1147.
[17] N. Martin, J. Liq. Chromatogr. 18 (1995) 1173.
[18] P.L. Desbene, F.I. Portet, G.J. Goussot, J. Chromatogr. A 730 (1996) 209.
[19] Z. Wang, M. Fingas, J. Chromatogr. 637 (1993) 145.
[20] H. Yoshimura, T. Sugiyama, T. Nagai, JAOCS 64 (1987) 550.
[21] N. Funasaki, S. Hasa, S. Neya, J. Phys. Chem. 92 (1988) 7112.
[22] K. Noguchi, Y. Yanagihara, M. Kasai, B. Katayama, J. Chromatogr. 661 (1989) 365.
[23] A. Kosa, A. Dobo, K. Vekey, E. Forgacs, J. Chromatogr. A 819 (1998) 297.
[24] P. Jandera, M. Holcapek, G. Theodoridis, J. Chromatogr. A 813 (1998) 299.
[25] T. Yamagishi, K. Hashimoto, M. Kanai, A. Otsuki, Bunseki Kagaku. 46 (7) (1997) 537.
[26] W.M.A. Niessen, J. Chromatogr. A 794 (1998) 407.
[27] D.R. Doerge, S. Bajic, S. Lowes, Rapid Commun. Mass Spectrom. 7 (1993) 462.
[28] S. Zhou, M. Hamburg, J. Chromatogr. A 755 (1996) 189.
[29] J.B. Plomley, P.W. Crozier, V.Y. Taguchi, J. Chromatogr. A 854 (1999) 245.
[30] R. Wickbold, Tenside Detergents 9 (1972) 173.
[31] T. Schmitt, M.C. Allen, D.K. Brain, K.F. Guin, D.E. Lemmel, Q.W. Osburn, JAOCS 67 (1990) 103.
[32] R.D. Gibbons, D.E. Coleman, R.F. Maddalone, Environ. Sci. Technol. 31 (1997) 2071.