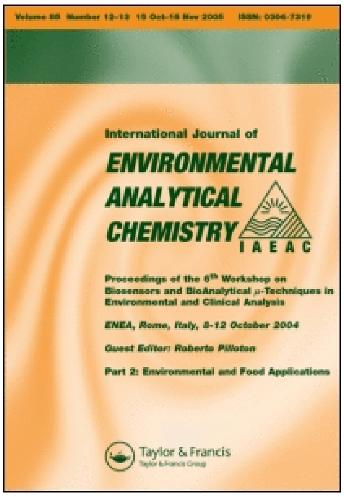

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Environmental Determination of Alkylphenol Polyethoxylate Refractory Residues Using Mass Spectrometric Techniques

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Environmental Determination of Alkylphenol Polyethoxylate Refractory Residues Using Mass Spectrometric Techniques[†]

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The use of methane chemical ionisation GC/MS gave satisfactory results when applied to environmental analysis of halogenated octylphenol polyethoxylates residues. In addition the selected ion monitoring GC/MS technique has been successfully applied for simultaneous qualitative and quantitative determination of some refractory metabolites of nonylphenol polyethoxylates in secondary sewage effluent and surface waters.

KEY WORDS: Non-ionic detergents, alkylphenol polyethoxylates, refractory metabolites, chemical ionisation GC/MS, selected ion monitoring GC/MS, environmental analysis, sewage effluents, surface waters.

INTRODUCTION

Non-ionic surfactants have enjoyed an ever-increasing market since the establishment of restrictions on the use of branched alkylbenzene sulfonates. Two particular classes of these compounds, namely the

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alkylphenol ethoxylates (APE) and the linear alcohol ethoxylates (LAE) (see Figure 1) are widely used in Europe as well as in the U.S.A.[1] Residues of the APE have been found as major refractory constituents of treated wastewater effluents[2,3,4] and river waters.[5] In addition, Giger *et al.* found that anaerobically treated sewage sludge contained extraordinarily high concentration of 4-nonylphenol (also a metabolite of NPE)[6], while in the U.S.A. it has been established[7] that the acidic and neutral metabolites of the APE react during chlorination producing brominated and chlorinated refractory products. The above findings are summarized in Scheme 1.

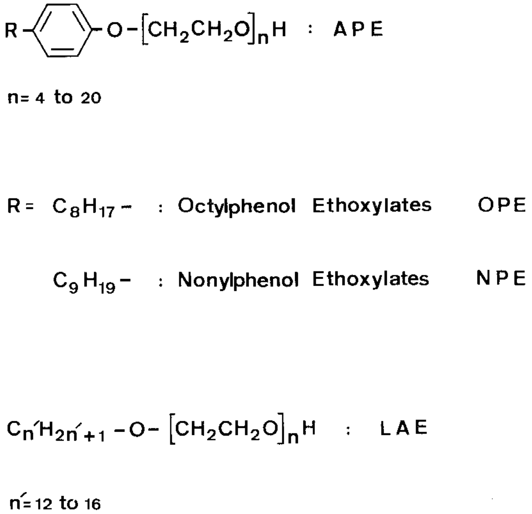
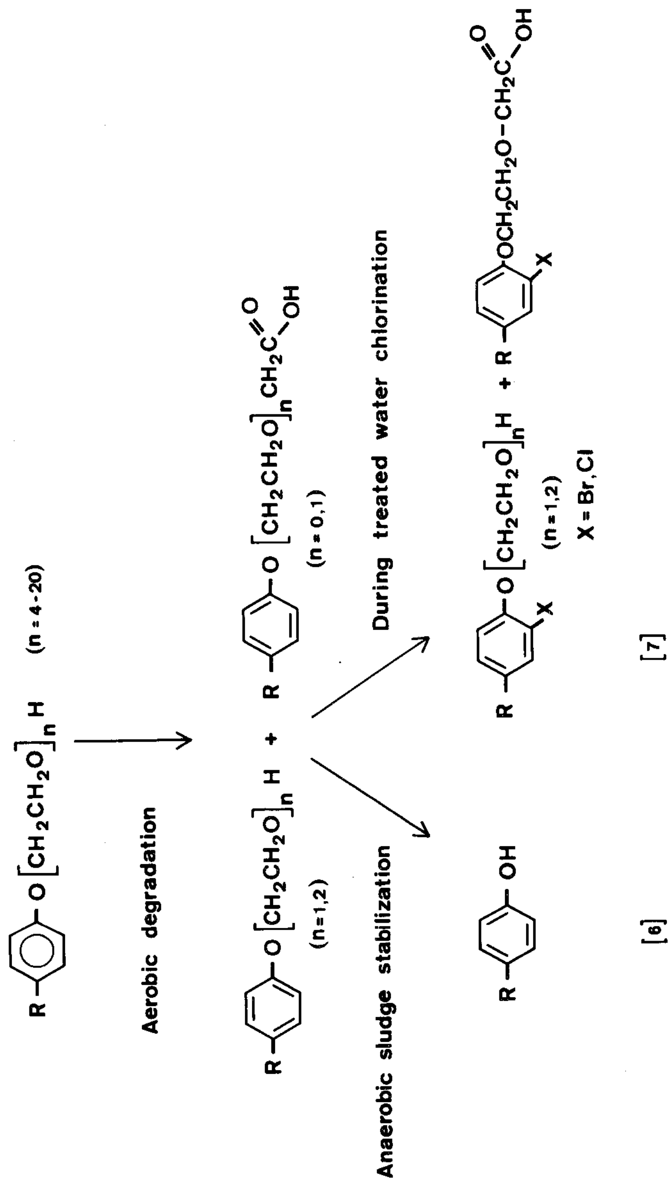


FIGURE 1 Classes of non-ionic detergents.

Considering the recalcitrance and toxicity[8] of the cited compounds, further research is needed to investigate their fate in the environment. Towards this end accurate analytical methods should be used in order to determine qualitatively and quantitatively the substances in question. Many analytical methods have been proposed[9] for measuring non-ionic surfactants. The majority of these methods suffer from lack of specificity (difficulty in the quantitative and qualitative determination of individual compounds) and other limitations (e.g. interferences by other products).



SCHEME 1 Fate of APE in the environment.[6,7]

In the present work some aspects of the capillary Gas-Chromatography/Mass Spectrometry analysis (GC/MS) of the above mentioned compounds are presented. The Chemical Ionization (CI) technique has been used for elucidation of the structure of the halogenated metabolites while the Selected Ion Monitoring (SIM) technique has been employed to yield a simultaneous qualitative and quantitative analysis of the biodegradation products of NPE in environmental matrices.

Studies required to complete this work are still on-going and will soon be reported.[10]

EXPERIMENTAL

Materials

The solvents used were freshly distilled from the "technical" grade material (Fluka, Buchs, Switzerland). The reference nonylphenol ethoxylate Marlophen 83 was provided by Chemische Werke Hüls, Marl, FRG. 2,4,6-Tribromophenol (TBP) and 4-nonylphenol were used as received from the supplier (Fluka). Sodium chloride, sodium sulfate and paper filters were pre-extracted with methylene chloride.

Extraction and sample preparation

Selective removal of neutral products was accomplished by adjustment of sample pH to 11 with KOH. The sample was then extracted with methylene chloride in a liquid-liquid extractor or in a separatory funnel as described in Reference 2. Subsequently the sample was acidified (pH 2) withe H_2SO_4 and the extraction repeated. The extracts were dried with Na_2SO_4, filtered through a pre-extracted paper filter and concentrated to 1–2 ml on a rotary evaporator under reduced pressure. Methylation of the acids was accomplished with diazomethane.[4] Prior to GC/MS analysis the internal standard (TBP) was added to the sample, which was finally reconcentrated to 0.2–0.5 ml using a nitrogen stream.

Origin of samples

The OPE halogenated residues reported here have been identified as products of a laboratory experiment simulating aerobic biodegradation and subsequent chlorination of corresponding detergents (a mixture of 4-octylphenol polyethoxylates).[7]

The NPE metabolites were found in secondary effluent samples from sewage treatment plants of Prangins, Nyon and Vidy (Switzerland) and from Geneva Lake (Lac Léman) taken in the vicinity (5–10 m from the exit of secondary effluents, at a depth of 4–5 m in Prangins and Nyon and 200 m from the exit at a depth of 6 m in Vidy) of the above plants. These are conventional mechanical-biological activated sludge plants.

INSTRUMENTATION

CI technique

A Finnigan mass spectrometer (Model 4000, upgraded with a Model 4500 EI/CI ion source) with an INCOS data system was used. The Finnigan gas chromatograph connected to the mass-spectrometer was equipped with a fused silica capillary column (J & W, Durabond-5, 30 m × 0.25 mm), coupled directly to the ion source. The CI conditions were: CH_4 pressure 0.57 torr; ion source temperature 120°C; ionization energy 62 eV; electron multiplier voltage 1700 Volts; mass range 100–500 m/z; scan time 2 sec.

SIM technique

The GC/MS system used was a Finnigan Model 4023. The original ion source was operated at 70 eV and a nominal temperature of 250°. The following mass intervals ($m/z \pm 0.5$ amu) were scanned for 0.1 sec each: 45, 89, 107, 121, 135, 179, 193, 223, 237, 251, 330. The gas-chromatograph contained a fused silica capillary column (ORION, SE-54, 25 m × 0.25 mm) connected to the ion source by another fused silica capillary.

The temperature program used in both techniques was 70°C (1 min), 70–280 (3–4°C/min) and 280°C (20 min). Helium was used in both techniques as carrier gas (back pressure 0.8 bar).

RESULTS AND DISCUSSION

CI technique

EI (top) and CI (bottom) mass spectra of the brominated 4-octylphenol diethoxylate are shown in Figure 2, while the corresponding

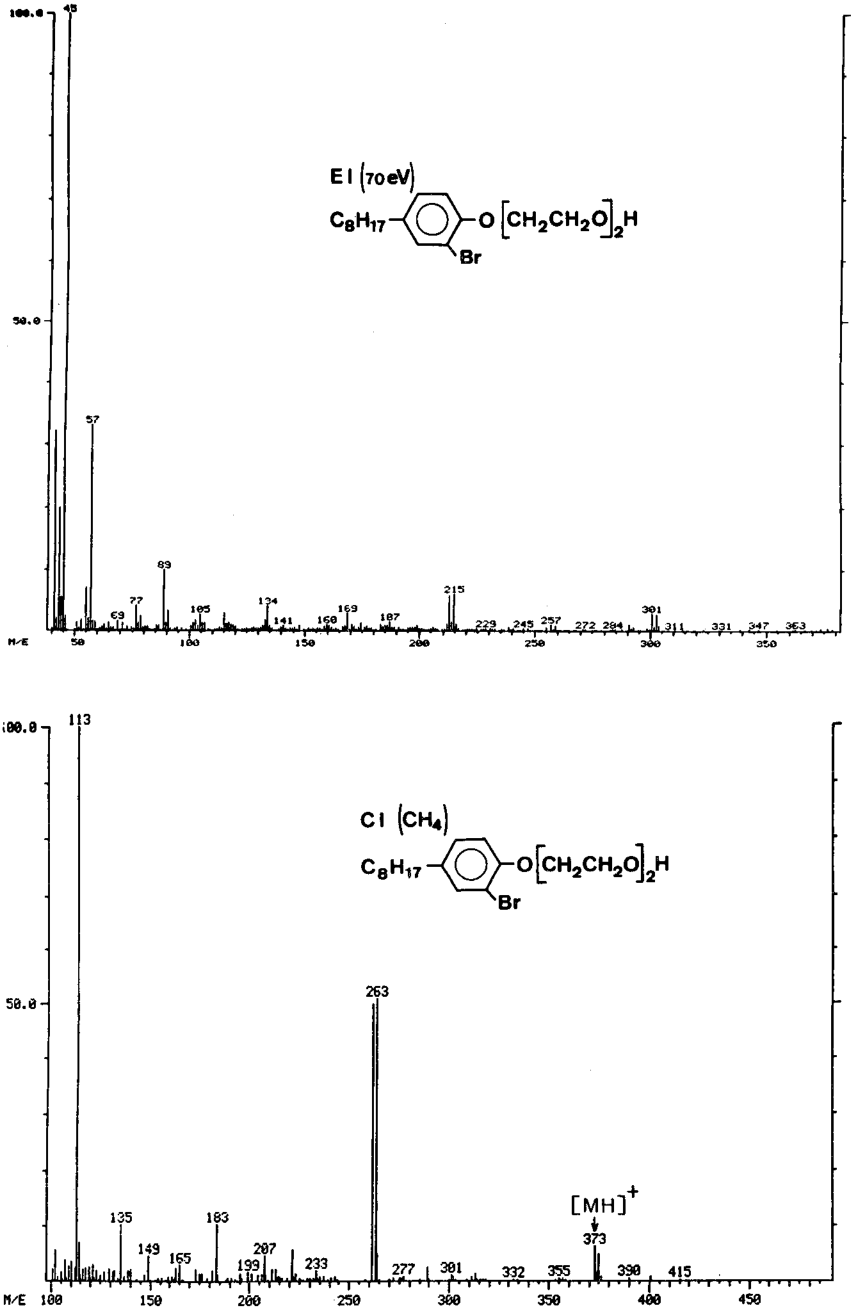


FIGURE 2 EI (top) and CI (bottom) mass spectra of 4-octylphenol diethoxylate.

spectra of the chlorinated (and for analytical purpose, methylated) 4-octylphenol-ethoxy-acetic acid are illustrated in Figure 3. The halogen atom (Br or Cl) should be ortho to the phenolic oxygen due both to it's increased reactivity and the steric hindrance present at the meta position. Both of these products have been isolated among others (see Scheme 1,)[7] during a laboratory simulation study of the biodegradation and subsequent chlorination (in presence of Br^-) of 4-octylphenol polyethoxylate surfactants. It can easily be seen that in the absence of other spectral information, the EI induced mass spectra do not allow a confident identification of the substances in question.

The most significant ions occur after benzylic cleavage (*m/z* 301 Figure 2, top and *m/z* 285 Figure 3 top) and a subsequent "onium" elimination of the oxyethylene chain providing the phenolic ions at *m/z* 213 (Figure 2, top) and *m/z* 169 (Figure 3, top). These fragmentations have already been reported.[11] The EI spectra do not provide any molecular weight information and are not conclusive as to the nature of the alkyl substituent nor the oxyethylene chain length. The CH_4–CI induced mass spectra of the non-halogenated compounds have been studied in detail.[3, 12] The fragmentation pathways of the molecular ion adducts are outlined on Scheme 2.

The adducts $|MH|^+$ and/or $|MC_2H_5|^+$, permit a confident determination of the molecular weight. After alkyl ion displacement the ion at *m/z* 113 (see on CI spectra in Figure 2 and 3) is obtained indicating the nature of the substituent. The oxyethylene chain length can be obtained from the ions produced following the olefin displacement reaction of the above adducts. The ion a *m/z* 117 on the EI spectrum of the carboxylic compound is also present in its CI mass spectrum. This ion is very useful as it allows differentiation of the acidic metabolites from the neutral components. A tentative mechanism for production of this ion is proposed in Scheme 2. Studies using high resolution techniques are on-going[10] with the aim to better elucidate this mechanism. The CI technique has been proven to be the most reliable one for determination of the LAE in the environment.[3] The results reported here show that this technique allows a confident determination of the halogenated residues of APE as well.

SIM technique

Several methods have been proposed for the determination of APE

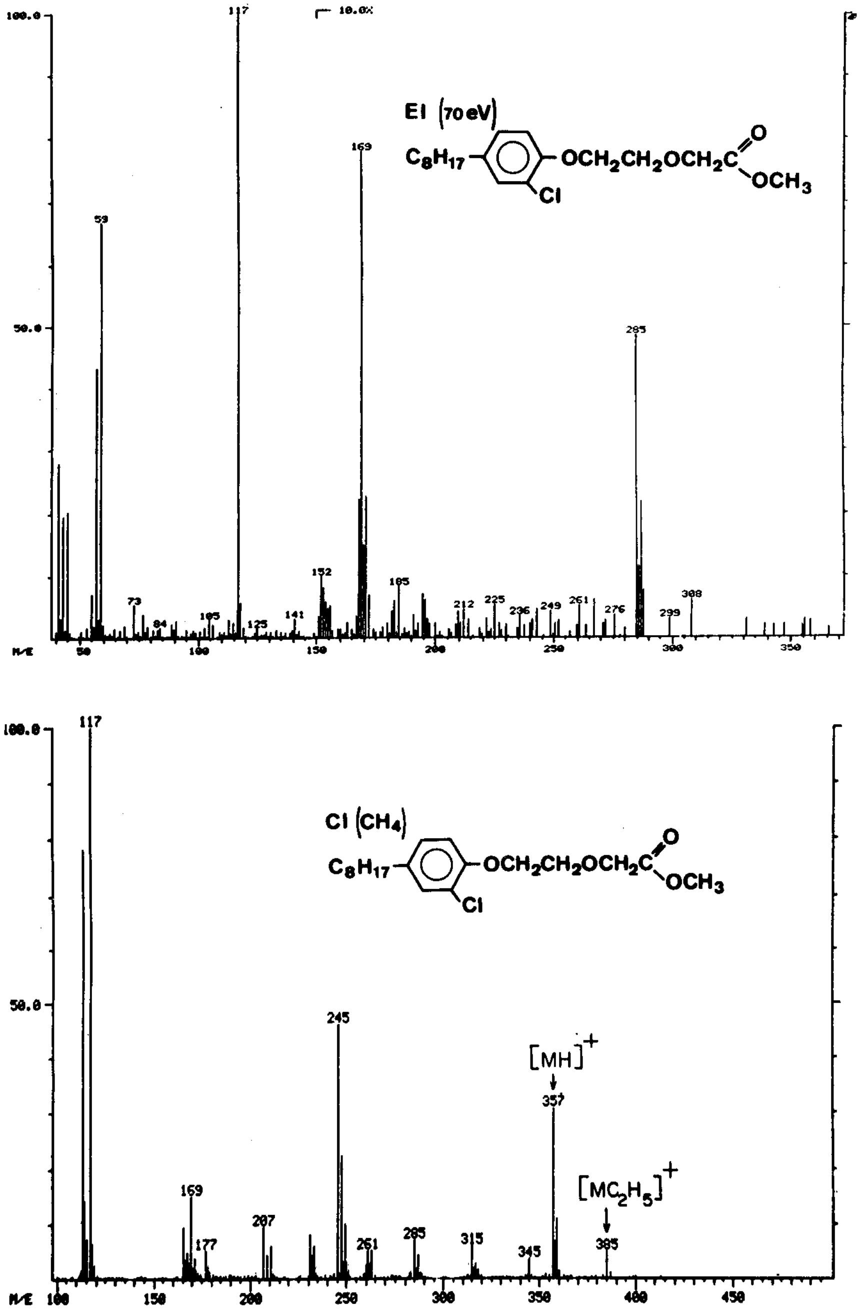
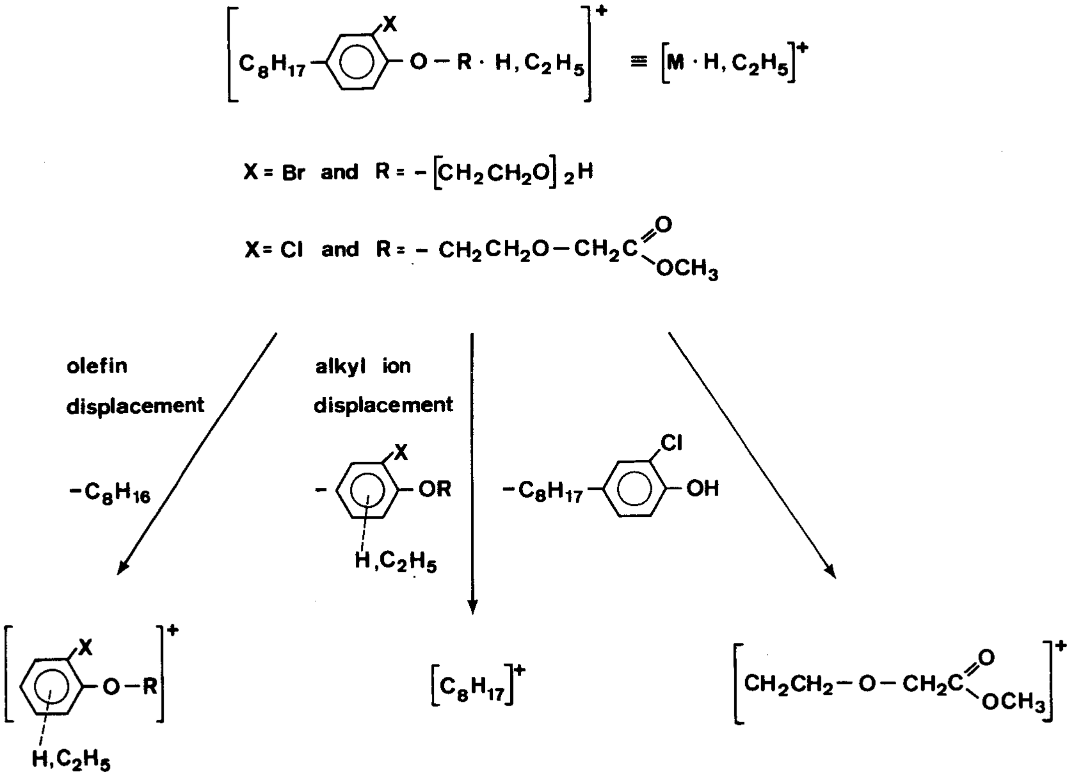


FIGURE 3 EI (top) and CI (bottom) mass spectra of chlorinated 4-octylphenol-ethoxy-acetic acid methylester.



SCHEME 2 Fragmentation of the halogenated OPE residues in the methane CI mode.

and their refractory metabolites in the environment.[2,5,9,11] The GC/MS method[11] is very useful for reliable qualitative analysis of 4-nonylphenol (NP), 4 nonylphenol mono-(NP1) and diethoxylates (NP2) while capillary GC[2] and a combination of HPLC and capillary GC[5] have given satisfactory quantitation of the same compounds. Neverthless some interferences with other substances[2,5] require prior GC/MS analyses, particularly in those instances where a complicated mixture obscures the location of the APE metabolites.

The structures of the above products have been studied through their EI mass spectra. Some ions are very typical of these compounds and can be employed for simultaneous quantitative and qualitative analysis using the SIM technique. Indeed this method has been used in our laboratory with very satisfactory results. Figure 4 shows the RIC of a secondary sewage effluent extract in the SIM mode (top) and the RIC of the same extract in the normal mode (bottom). In this extract, 4-nonylphenol, 4-nonylphenol monoethoxylate and 4-nonylphenol diethoxylate were present. In order to selectively detect these compounds, the ions A, B, C and D (Scheme 3) and the ion at m/z 330 (molecular ion of TBP; used as internal standard) were chosen. High resolution mass spectra of these compounds (allowing a complete identification of the mentioned ions) will be published shortly.[10] The above ions are characteristic of the detected substances and, as is shown in Figure 4, these substances can be selectively "picked out" and subsequently quantified. For the quantitation, the total surface area of each homologue (itself containing the chromatographic peaks of the individual isomers[2,11] due to the configuration of the benzylic carbon) is integrated and then compared with the area of the internal standard. The extraction methods used were the same as previously reported[2,5,11] and yielded identical recoveries. Table I shows the concentrations (mean values of two determinations) obtained by applying the described procedure to the determination of NPE metabolites in secondary sewage effluents and in the receiving surface waters (Lake Geneva). The relative concentration of NP was higher in Prangins and Nyon water treatment plant effluents than in Vidy. These results seem unusual when compared with other results already reported.[2,5] The primary effluents (before treatment) of these two plants have been analyzed and, in both cases, the NP has been determined. The primary effluent of Vidy did not contain any NP. This fact partially explains the higher

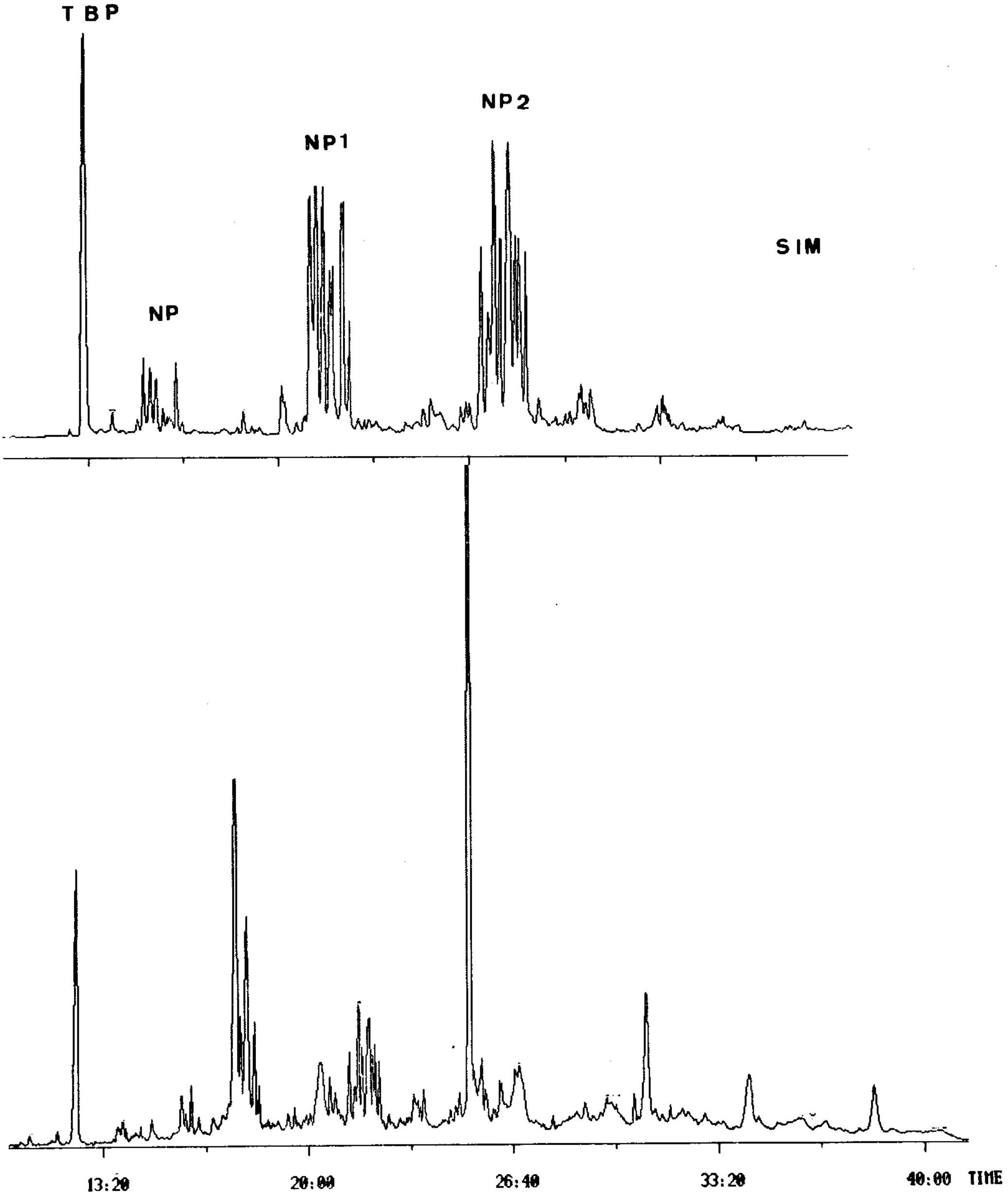
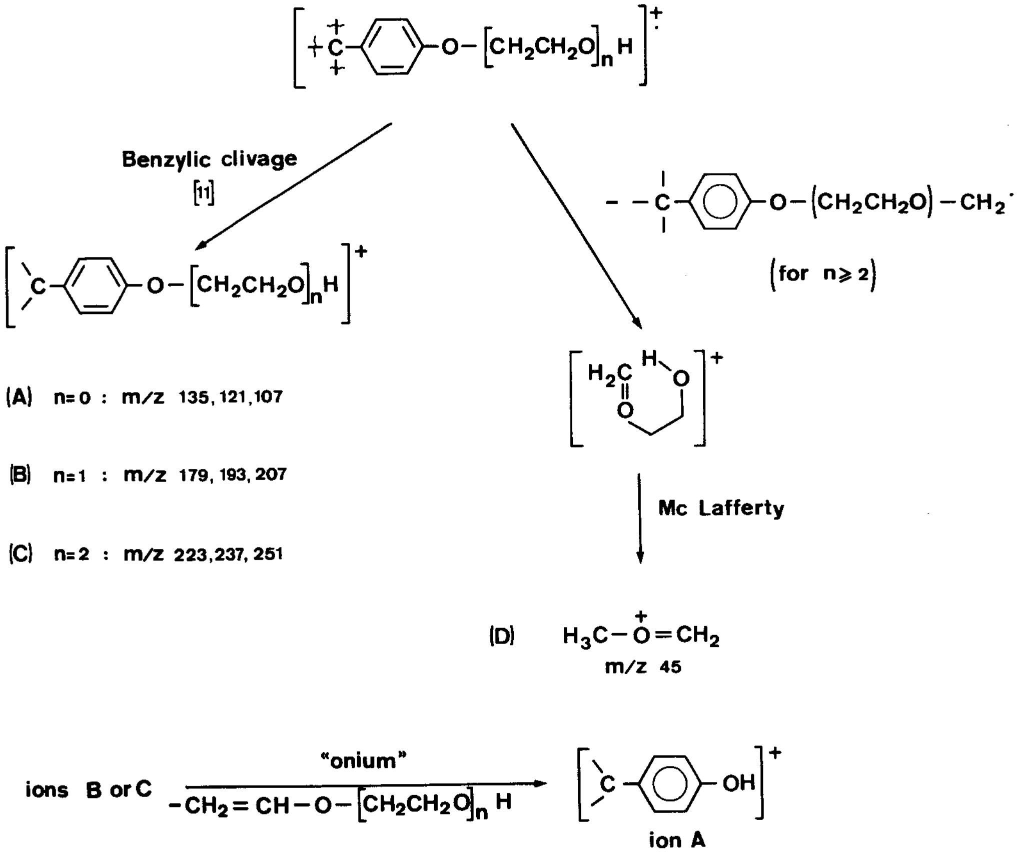


FIGURE 4 Reconstructed Ion Chromatograms (RIC) of a secondary sewage effluent extract in the SIM mode (top) and normal mode (bottom).



SCHEME 3 Partial fragmentation of the NPE in the EI (70 eV) mode.[11]

TABLE I

Concentrations of NP, NP1 and NP2 in secondary sewage effluents and receiving waters

	Concentration $|^{\mu g}/L|$					
Compound	Vidy		Nyon		Prangins	
	W.T.P.	Lake	W.T.P.	Lake	W.T.P.	Lake
NP	35.8	2.9	44.6	1.2	69.3	3.4
NP 1	189.4	3.9	24.9	1.1	43.1	4.1
NP 2	198.4	5.8	36.6	1.3	63.0	4.2

(W.T.P.: Water treatment plant).

NP concentrations in Prangins and Nyon. Systematic measures are now on-going in our laboratory with the goal of completing the study of the presence and the fate of the NPE residues in the basin of Lake Geneva.[10] These preliminary results indicate the SIM technique to be a very sensitive and reliable one; well suited for a complete determination of the APE biodegradation products. Compared with other techniques, the described method has one disadvantage: a GC/MS-system (i.e. expensive equipment) is necessary!

Acknowledgments

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