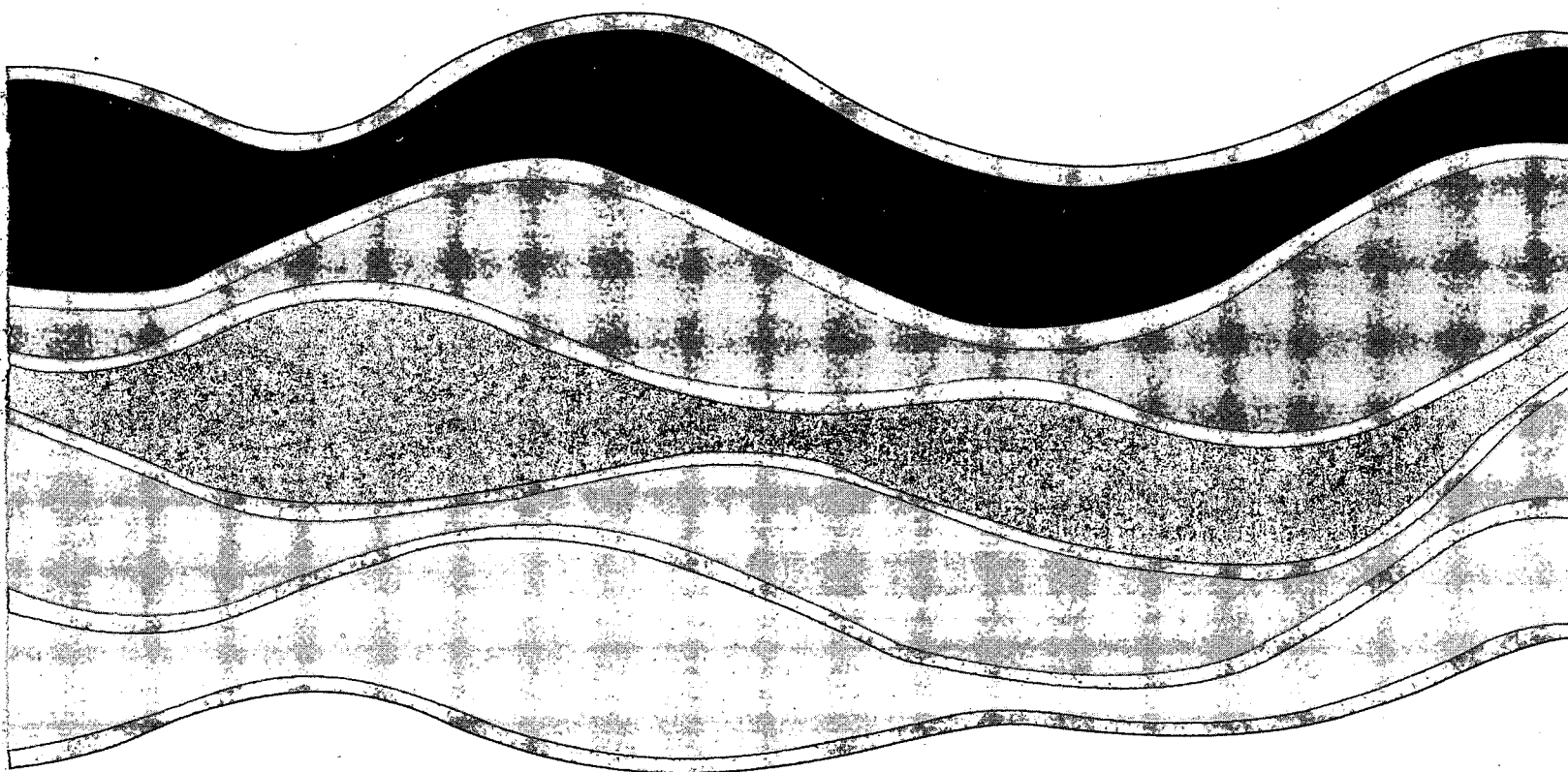
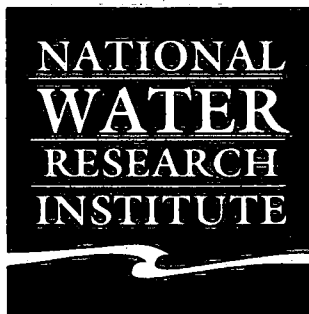


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**A REVIEW OF ANALYTICAL METHODS FOR THE
DETERMINATION OF NONYLPHENOL AND
RELATED COMPOUNDS IN ENVIRONMENTAL
SAMPLES**

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NWRI Contribution No. 98-008

**A review of analytical methods for the
determination of nonylphenol
and related compounds in environmental samples**

by

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MANAGEMENT PERSPECTIVE

Nonylphenol ethoxylates (NPEO) are a major type of non-ionic surfactant used in the production of detergents. They are on the PSL2 of CEPA. Although NPEO degrade extensively under sewage treatment conditions, their degradation products, which are discharged into the environment, are persistent as well as toxic and estrogenic to fish. Chemical data are needed to monitor the occurrence of NPEO and their metabolites so that their impact to the Canadian aquatic environment can be assessed. This manuscript reviews the major analytical methods available for the determination of NPEO and related compounds in environmental samples.

SOMMAIRE A L'INTENTION DE LA DIRECTION

Les éthoxylates de nonylphénol sont un type important de surfactants non ioniques utilisés pour la production des détergents. Ils figurent sur la LSIP2 de la LCPE. Bien que ces composés se dégradent fortement dans les conditions de l'épuration des eaux usées, leurs produits de dégradation, qui sont rejetés dans l'environnement, sont persistants et toxiques pour les poissons, en plus d'avoir une action oestrogène sur ces derniers. Des données chimiques sont nécessaires pour la surveillance de l'occurrence des éthoxylates de nonylphénol et de leurs métabolites afin qu'on puisse évaluer leur impact sur l'environnement aquatique canadien. Dans ce manuscrit, on examine les principales méthodes d'analyse disponibles pour le dosage de ces composés, ainsi que de composés connexes dans des échantillons du milieu.

ABSTRACT

Analytical methods published in the last 20 years for the extraction, chromatographic separation, and quantification of alkylphenol ethoxylates (APEO) and related compounds in environmental samples are reviewed. Examples of various isolation and preconcentration techniques for water, effluent, sediment, and sludge are presented. This includes procedures from the classical liquid-liquid and Soxhlet extraction to the up-to-date solid phase and supercritical fluid extraction. Chromatographic separation of APEO by normal and reversed phase liquid chromatography (LC) and capillary column gas chromatography (GC) is compared. A variety of quantification methods involving the common LC and GC detectors as well as various mass spectrometric techniques are also discussed.

RÉSUMÉ

On a examiné les méthodes analytiques publiées au cours des vingt dernières années pour l'extraction, la séparation chromatographique et le dosage des éthoxylates d'alkylphénol et de composés connexes dans des échantillons du milieu. On présente des exemples de diverses techniques d'isolation et de préconcentration pour l'eau, les effluents, les sédiments et les boues, notamment une gamme de méthodes allant des techniques d'extraction classiques comme l'extraction liquide-liquide et Soxhlet à des méthodes de pointe d'extraction en phase solide et à fluide supercritique. On compare la séparation chromatographique de ces composés par chromatographie liquide (CL) normale et inversée et par chromatographie gazeuse sur colonne capillaire (CG). On examine aussi diverses méthodes de dosage utilisant des détecteurs communs de CL et de CG, ainsi que diverses techniques de spectrométrie de masse.

I. INTRODUCTION

Alkylphenol ethoxylates (APEO) are a major product type in non-ionic surfactants used in the manufacture of domestic and industrial detergents (Aboul-Kassim and Simoneit, 1993). The most common APEO are derived from the ethylene oxide adducts of alkylphenols such as 4-nonylphenol (NP) and 4-*tert*-octylphenol (OP). Under different reaction conditions, ethoxylation of these phenols results in the formation of a series of oligomers with one to up to 100 ethoxy units. Each APEO product usually consists of a mixture of these oligomers. Their relative abundance follows a Poisson distribution and the product is characterized by the average number of ethoxy units. Table 1 lists a few examples of some commercial preparations of APEO and their approximate compositions. Chemical structures of the alkylphenolics are shown in Figure 1.

The major users of nonylphenol ethoxylates (NPEO) are the pulp and paper and the textile industries as well as the manufacturers of household and industrial detergents based on NPEO, with an estimated total use of 7,000 tonnes annually in Canada (Metcalf et al., 1996). In sewage treatment processes, NPEO readily degrade to NP and the lower ethoxylates such as the mono- (NP1EO) and di- ethoxylates (NP2EO) under anaerobic conditions, and to nonylphenoxyacetic acid (NP1EC) and nonylphenoxy-ethoxyacetic acid (NP2EC) under aerobic conditions (Ahel et al., 1994a). Because of the estrogenic properties as well as the toxicity and persistence of their degradation products (Soto et al., 1991, Jobling and Sumpter, 1993, White et al., 1994), the use of APEO in some European countries has gradually been phased out and replaced by the fatty acid and alcohol ethoxylates as well as other ionic surfactants.

Fewer studies have been focused on octylphenol ethoxylates (OPEO), although they are known to undergo degradation similar to NPEO under aerobic and anaerobic conditions (Ball et al. 1989). Very little information is available on the toxicity and estrogenicity of the degradation products of OPEO; however, OP has been estimated to be over 40 times higher in estrogenic potency than NP or NP1EC using rainbow trout *in vitro* hepatocyte bioassay data (Nimrod and Benson, 1996).

The occurrence of NPEO and their metabolites in sewage treatment plant and environmental samples is well documented in Europe (Stephanou and Giger, 1982, Ahel and Giger, 1985a and b, Ahel et al., 1987, 1994a and b, 1996) and the United States (Kubeck and Naylor, 1990, Naylor et al., 1992, Field and Reed, 1996). In Canada, these contaminants are readily detected in sewage treatment plant samples such as untreated influent, treated effluent and sludge (Lee and Peart, 1995, Bennie et al., 1997b, Lee et al. 1997, 1998). Albeit at much lower concentrations, they have also been found in lake and river waters and sediments (Bennie et al., 1997a). Their occurrence in Canadian textile and pulp and paper mill effluents is currently under investigation.

In the last 20 years, many analytical methods have been developed for the extraction, chromatographic separation, and detection of NP and related compounds. This paper reviews the major methods available for the determination of these compounds in environmental samples.

II. SAMPLE COLLECTION AND STORAGE

Water samples, collected in brown glass bottles, are preserved with formaldehyde (1%, v/v) and kept at 4°C in the dark. For better representation, 24-hr composite samples are collected instead of grab samples of sewage and industrial effluents. Few stability data are available for the nonylphenolics. In one study, the levels of NP, NP1EO, and NP2EO in a formaldehyde-preserved, biologically treated municipal wastewater remained constant over a storage period of 12 days at 4°C (Ahel and Giger, 1985a). Chloroform, formaldehyde, copper (II) and mercury (II) salts have been tested as preservatives of water samples for the determination of non-ionic surfactants including Triton X-100 (Szymanski et al., 1995). Indirect tensammetric measurements (a polarographic technique) were applied to the analysis of surfactants in the samples. Formaldehyde was found to be most effective preservative and a concentration of 1% was sufficient to maintain a stable surfactant concentration for at least 20 days. Refrigeration at 4°C alone was ineffective.

Sediment and sludge samples, collected in wide-mouth glass bottles, are stored frozen. Alternatively, they can be stored at room temperature after air- or freeze-drying.

III. EXTRACTION TECHNIQUES

A. Wastewater/water

1. Solvent sublation

A standardized procedure based on the original work of Wickbold has been developed for the extraction of APEO in water including unfiltered samples such as raw sewage and industrial effluent (Ahel and Giger, 1985b, Scarlett et al., 1994, Ibrahim and

Wheals, 1996a). Typically, a one litre sample adjusted to a pH of 7 to 8 was overlaid by 60 to 100 mL of ethyl acetate in a sublation apparatus and nitrogen was purged through the liquids for 5 to 10 min. The ethoxylates enriched in the gas-liquid phase boundary were carried by the gas stream into the ethyl acetate layer. This procedure was repeated one to three more times with fresh solvent for better recovery. Sodium chloride could be added to the sample to improve the extraction recovery.

2. *Steam distillation*

The classical steam distillation procedure for hydrophobic, semi-volatile organics developed by Veith and Kiwus (1977) has been applied to the concentration of NP and NPEO in water (Giger et al. 1981). After the pH was adjusted to 7.0-7.5 and 20 g of sodium chloride was added, a 2 L sample was refluxed for 3 hr by using cyclohexane (1-2 mL) to concentrate the distillates. While this technique produced near quantitative results for NP, NP1EO and NP2EO, the recovery for NP3EO was poor (15%) (Ahel and Giger, 1985a). This procedure is unlikely to be applicable to the extraction of the higher ethoxylates in water samples due to their lower volatility and higher solubility (Ahel and Giger, 1993a and b).

3. *Liquid-liquid extraction*

Because of the polarity of the higher ethoxylates, solvent extraction, either continuous or non-continuous liquid-liquid extraction of an aqueous sample, is usually limited to the less polar components such as NP/OP and the ethoxylates and carboxylates with a few ethoxy units. The extraction recoveries of the nonylphenolics in effluent using dichloromethane (DCM) were 87-98% for NP and 79-100% for NP1EO, NP2EO, and NP3EO (Stephanou and Giger, 1982, Wahlberg et al., 1990). The addition of salt to a

sample tends to improve the extraction recovery and reduce the formation of emulsion. NP1EC, NP2EC, and NP3EC were successfully extracted from effluents by DCM (Stephanou, 1985) or chloroform (Ahel et al., 1987) after acidification of the samples to pH 2. Similarly, OPEC and halogenated OPEC in sewage were extracted by diethyl ether after the sample was acidified to pH 1.5 (Ball et al., 1989). The extraction of NP and NPnEO (n=1 to 3) was also demonstrated by means of a continuous extraction apparatus and a solvent heavier than water such as DCM. In that case, the recoveries were 101% for NP and 87-93% for the ethoxylates (Stephanou and Giger, 1982).

A unique example of liquid-liquid extraction of NP and OP was achieved by an *in situ* acetylation of the phenols with acetic anhydride in the presence of a base followed by the extraction of the acetyl derivatives with petroleum ether. In this case, quantitative recoveries of the phenols in sewage effluent were obtained as the non-polar derivatives were readily extracted into the organic phase (Lee and Peart, 1995).

4. *Solid phase extraction (SPE)*

In comparison to liquid-liquid extraction, SPE has the advantages of lower solvent consumption, automated operation. It also has the ability to extract polar and ionic species and to handle large sample volumes. Since the extraction time is directly proportional to the sample size, SPE can be very fast if the sample volume is small. It also avoids the formation of emulsions which often occurs in the solvent extraction of many sewage and wastewater samples. In order to avoid plugging of the adsorption medium (either a disk, a cartridge, or a column), the sample is usually filtered through a glass fibre filter of pore size 1.2 μm , or smaller, prior to extraction.

a. XAD

Amberlite XAD-2, -4, and -8 resins have been applied to the extraction of ethoxylates in water with recoveries over 80%. Before extraction, these resins were prepurified by washing them with organic solvent. Depending on the size of the column, sample size could vary from 1 to as much as 2000 L of water. Elution of the APEO was done with acetone/water (9:1) or sequentially with diethyl ether and methanol.

Desorption of the ethoxylates could also be effected by Soxhlet extraction of the resin with methanol (Jones and Nickless, 1978a and b).

b. Carbon

In some earlier work, granular activated carbon has been used for the extraction of water samples with large volumes (e.g. 2000 L). When the extraction was completed, the NPEO adsorbed on carbon was removed by Soxhlet extraction with DCM (Ventura et al. 1988, 1989). However, the recently developed graphitized carbon black (GCB, 120-400 mesh) cartridges are more efficient as they provide the simultaneous preconcentration of several classes of ionic as well as non-ionic surfactants including NP, NPEO, and NPEC in water samples (Di Corsia et al., 1994, Crescenzi et al., 1995). At the same time, various groups of surfactants can be sequentially eluted from the cartridge with different solvent systems. For example, NP and NPEO were eluted in fraction 1 (DCM/methanol, 70:30, v/v), NPEC were eluted in fraction 2 (DCM/methanol 90:10, v/v, in the presence of formic acid), and linear alkylbenzene sulfonates (LAS) were eluted in fraction 3 (DCM/methanol, 90:10, v/v, in the presence of tetramethylammonium hydroxide) (Di Corsia et al., 1994).

c. Octadecylsilane (C₁₈) or ODS

ODS cartridges have been used for the preconcentration of NP, OP, NPEO, as well as NPEC in effluent and water samples (Marcomini et al., 1987, 1989, 1990, and 1993, Kubeck and Naylor, 1990, Blackburn and Waldock, 1995, Lee et al. 1998). Prior to extraction, a 1 g ODS cartridge is preconditioned with 5 mL of acetonitrile, 5 mL of methanol, and 10 mL of water. The filtered sample (from 10 mL to 1 L) is then passed through the cartridge at a flow rate between 10 and 30 mL/min. If the extraction of the carboxylates is required, the pH of the sample is adjusted to 2. Elution of the organics is achieved with 5 mL of methanol.

d. Ion exchange resins

Strong anion exchange (SAX) solid phase extraction disks (25 mm diameter) have been used for the extraction of nonylphenol polyethoxy carboxylates, namely, NP1EC to NP4EC, in paper mill effluents, sewage effluents and river waters. The disks were first conditioned by 5 mL of acetonitrile, followed by 5 mL of water. After the sample (up to 500 mL) was applied to the disk, the acids were desorbed by 1 mL of acetonitrile and methylated at 80°C in a vial for GC/MS analysis (Field and Reed, 1996).

Kubeck and Naylor (1990) described a dual-column procedure for the extraction of APEO (n=1 to 17) in environmental water. The first column containing a mixed-bed ion-exchange resin (Biorad 501 x 8 (D), 20-50 mesh) was used to remove the ionic species in the sample. The ethoxylates adsorbed on the second column (0.7 g of ODS) were removed by warm (55°C) methanol.

e. Solid-phase microextraction (SPME)

Solid-phase microextraction using fibres coated with Carbowax/template resin and Carbowax/divinylbenzene coatings allowed successful extraction of Triton X-100 and other alkylphenol ethoxylates in water samples. In this example, the fibre was exposed to the sample (4 mL) for 60 min with stirring at room temperature. After extraction, the fibre was exposed to the LC mobile phase for 1 min in a desorption chamber before the ethoxylates were analyzed by the LC. The addition of salt also improved the recoveries of longer chain ethoxylates. Extraction of the ethoxylates by other coated phases was unsuccessful (Boyd-Boland and Pawliszyn, 1996).

B. Sludge, sediment and solid samples

Relatively few methods are available for the extraction of AP, APEO, and APEC in solid matrices. Samples are usually air- or freeze-dried and pulverized prior to extraction. The earlier reports mostly involved Soxhlet extraction and steam distillation and their application was limited to the more volatile and less polar components such as NP, NP1EO and NP2EO. More recently, supercritical fluid extraction using modified carbon dioxide has been applied to sediment and sewage sludge samples. This modern technique is a better alternative to Soxhlet extraction and steam distillation because of its higher efficiency as well as its applicability to a wider range of surfactants, including LAS (Field et al., 1992), NP (Lee and Peart, 1995), NPEO and NPEC (Lee et al., 1997).

1. *Soxhlet*

Soxhlet extraction of NP, NP1EO and NP2EO from solid samples such as river and lake sediments, sewage sludge, and detergent powder has been successfully demonstrated. Although various solvents or mixtures of solvents such as hexane

(Marcomini et al., 1988, 1990, 1991), methanol (Marcomini and Giger, 1987, Marcomini et al., 1988, 1991), 2-propanol (Jungclaus et al., 1978), DCM (Lee et al., 1997), methanol/DCM (1:2, v/v) (Valls et al., 1988), and acetone/hexane (59:41, v/v) (Lee et al., 1997) have been applied, the use of more polar solvents is necessary for the better recoveries of higher ethoxylates. In a study by Marcomini et al. (1991) on the extraction of LAS, NP and NP1EO from dated sludge, the recoveries of these surfactants by Soxhlet extraction with methanol were much higher if sodium hydroxide (20%, w/w) was added to the dry sludge.

2. *Steam distillation*

Extraction of NP, NP1EO and NP2EO from solid samples by steam distillation has been demonstrated (Giger et al., 1981, 1984, Ahel and Giger, 1985a, Ahel et al., 1994a and b). A sediment or sludge sample of 10 to 50 g suspended in 1.5 L of water is extracted for 3 hr with a steam distillation column in a procedure similar to an effluent sample described above. The organics, concentrated in a small volume of cyclohexane, are ready for GC or LC analysis.

3. *Supercritical fluid extraction (SFE)*

While there were few examples in the literature, SFE of NP, NPEO, and NPEC from sewage sludge and sediment has been reported. In one study, a homogenized, air- or freeze-dried sediment or sewage sludge (1 g) was extracted at 80°C with pure carbon dioxide at ca. 345 atm. The native NP and OP were extracted by a combined static and dynamic extraction and converted into their acetyl derivatives *in situ* in the presence of acetic anhydride and triethylamine (Lee and Peart, 1995). For the SFE of NPEO, two mL of water was added to a 1 g sample prior to extraction. The addition of water as a

modifier of supercritical carbon dioxide was critical in obtaining good recoveries for the polar, long chain ethoxylates (up to NP17EO). Extraction of NPEO from sludge was achieved at 80°C and 345 atm in 25 min (10 min static and 15 min dynamic). The ethoxylates adsorbed on an ODS sorbent trap were eluted with methanol at 60°C (Lee et al., 1997). The carboxylates (NP1EC and NP2EC), extracted and eluted under similar conditions, were methylated off-line for later GC/MS analysis.

Another SFE method for NP, OPEO (Triton X-100), and NPEO (with an average 13 ethoxy units) in spiked sediment samples has also been described. In this case, methanol was added to the sample prior to a 4-step, 45-min SFE (100°C, 150 and 450 atm) with CO₂ modified with methanol. Recoveries were 85% for NP and NPEO and 65% for OPEO. These recoveries were substantially reduced after the samples were aged for 4 months (Kreisselmeier and Dürbeck, 1997).

IV. CHROMATOGRAPHIC SEPARATION AND DETECTION METHODS

A. Liquid chromatography (LC)

In spite of its lower resolution and some coelution problems described below, LC is a very versatile analytical technique suitable for compounds with a wide range of polarity, volatility, and molecular weights such as the APEO. It has also been applied to the analysis of AP and APEC without derivatization. While standard (4.6 mm i.d.) and narrow bore (2.1 mm) columns with 10 and 5 (or 3) µm packings have been used, those with a smaller packing and a narrower bore have higher efficiency and use less solvent. LC

analysis of non-ionic surfactants with polyethoxy chains has recently been reviewed (Miszkiwicz and Szymanowski, 1996). Another related review on the chromatographic determination of non-ionic aliphatic surfactants of the alcohol polyethoxylate type in the environment has also been published (Marcomini and Zanette, 1996).

1. *Normal phase separation*

An APEO molecule consists of a hydrophobic alkylphenyl moiety as well as a hydrophilic polyethoxylate chain. Since APEO oligomers differ from each other by the length of the polyethoxylate chain, they are best separated by a normal phase LC column due to the different interaction (partition and/or adsorption) of the ethoxy chain and the polar stationary phase. The order of elution in a normal phase separation is according to the number of ethoxy units: the retention time of an oligomer increases with the length of its ethoxy chain. As the polarity of APEO oligomers varies widely, a solvent gradient is required for the separation of a multi-component mixture. Isocratic runs are only useful for the analysis of a few oligomers of similar polarity.

Among the various packing materials available for normal phase work, silica of 3 to 5 μm particle size modified by chemically bonded amino (Ahel and Giger, 1985b, Marcomini and Giger, 1987, Ahel et al. 1994a and b, 1996) and cyano (Pilc and Sermon, 1987, Kubeck and Naylor, 1990, Scarlett et al., 1994) groups are most popular for the separation of APEO mixtures. Mobile phases for such columns are usually mixtures of hexane, 2-propanol, and water. In a comparison of various stationary phases for the normal phase LC separation of APEO, Jandera et al. (1990) observed that the amino-bonded phase offered better separation for the individual oligomers than the diol (Zhou et al., 1990) and cyano bonded phases. A *p*-nitrophenyl-bonded silica phase has been used in

association with a ternary elution gradient (*n*-heptane/DCM/methanol) for the resolution of long chain NPEO such as Igepal CO 720, CO 890, and CO 990 (Desbène and Desmazieres 1994). The separation of NP_nEO (*n*=1 to 17) oligomers in a standard and a sludge extract on a Hypersil APS column is shown in Figures 2 and 3, respectively.

Several studies have also been reported on the separation of APEO with bare silica. In one example, baseline separation of APEO oligomers with average ethoxy units as high as 40 was accomplished by a silica column (Si-100, 5 μm) (Anghel et al., 1994). These authors also claimed that the presence of a bulky alkyl group in the *ortho* position hinders the interaction between the hydroxyl group of silica and the polyethoxy chain of the surfactant. Consequently, for each oligomer, the *ortho*-isomer elutes ahead of the *para*-isomer. In another study, a combination of a reversed phase precolumn (Hypersil ODS, 7.5 mm length) and a 3 μm silica column (150 mm length) was used for the separation of NP_nEO (*n*=3 to 50) in Tergitol surfactants. This LC method utilized a gradient with acetonitrile and water (normally used in reversed phase separations) so that direct injections of aqueous samples were possible (Kibbey et al., 1996). Oligomers in Triton X-100 and Synperonic NP10/NP20 were separated on Spherisorb silica with eluents containing 20-50% acetonitrile in aqueous pH 3 phosphate buffer (Ibrahim and Wheals, 1996b).

Depending on the column and the mobile phase used, NP is either eluted as the first peak (Kubeck and Naylor, 1990), between NP1EO and NP2EO, or between NP2EO and NP3EO (Ahel and Giger, 1985a). OP coelutes with NP on aminosilica columns, and, at each level of ethoxylation, OPEO and NPEO are either coeluting or they have very

similar retention times. Only one literature example is available for the normal phase LC (with a Lichrosorb-NH₂ column) determination of NPEC (Ahel et al., 1987).

2. *Reversed phase separation*

As all NPEO oligomers have the same hydrophobic moiety, they elute as a single peak with columns using non-polar C₁₈ and C₈ packing materials. Due to their weaker hydrophobic nature, OPEO elute, also as a single peak, ahead of NPEO with reversed phase columns. An exception to this rule was observed with the C₁ (trimethylsilyl) column. Although classified as a reversed phase column, C₁ is appreciably hydrophilic and behaves like a normal phase column (Wang and Fingas, 1993b). Separation of individual oligomers of OPEO with up to 40 ethoxy units in various Triton mixtures has been demonstrated with this column under isocratic conditions using a mixture of methanol and water as mobile phase. The determination of APEO as well as linear alkylbenzene sulfonates in river water using a C₁ column has also been reported (Scullion et al. 1996).

With a RP-C₈ column, coelution of OP and OPEO as well as NP and NPEO was reported in one work (Ahel and Giger, 1985a) yet separation of NP and NPEO was demonstrated in another (Di Corcia et al., 1994). Resolution of NP_nEC (n=1 to >3) in a sewage effluent extract by the same column has also been cited (Di Corcia et al., 1994).

3. *UV and fluorescence detection*

Due to the presence of a chromophore (i.e. the phenyl group) in APEO, the latter can be readily detected by the UV or photodiode array (DAD) detector. For better selectivity, the wavelength of the detector was usually set at about 277 nm. At one time the UV molar absorptivity was assumed to be the same for all oligomers, however, it was later found that the absorptivity decreased with increasing length of the ethoxy chain (Ahel

and Giger, 1985, Zhou et al., 1990). A more sensitive and selective method for the analysis of APEO can be provided by a fluorescence detector. As OPEO and NPEO have the maxima in their excitation and emission spectra at ca. 230 and 300 nm, respectively, these wavelengths have been commonly used by most workers for the analysis of the ethoxylates (Kudoh et al., 1984, Holt et al., 1986). The wavelengths mentioned above in the UV and fluorescence detection are also applicable to the analysis of OP, NP, and their carboxylates. Although chemical derivatization is rarely needed for the LC analysis of APEO, acetylation of APEO followed by fluorescence detection of the derivatives has also been reported (Mackay et al., 1997).

4. *Liquid chromatography/mass spectrometry (LC/MS)*

a. Particle beam (PB) LC/MS

The determination of NPEO, OPEO, and their carboxylate metabolites in drinking water by continuous liquid/liquid extraction and PB/LC/MS has been investigated (Clark et al., 1992). In this case, a reversed phase column and a solvent gradient using methanol and 0.01% ammonium acetate were used. Since PB/LC/MS was performed under electron impact conditions, the molecular ions of the ethoxylates were very weak. While many fragmentation ions were observed, the ions $[M-C_6H_{13}]^+$ and $[M-C_5H_{11}]^+$ were most intense for NPEO and OPEO, respectively, and were therefore used as the diagnostic ions. Again, the ion $[M-C_5H_{11}]^+$ was used to detect the presence of NPEC and OPEC in a sample. Based on a concentration factor of 1,000,000 and a sample size of 500 L, APnEO (n=3-8) and APnEC (n=2-7) at ng/L levels have been detected in finished drinking water by this technique.

b. Electrospray (ES) LC/MS

The atmospheric pressure ionization (API) electrospray mass spectrometry has become very popular recently because of its wide application to large and small, polar and non-polar, as well as singly and multiply charged species. With minimal fragmentation of the molecular ion, it also represents a true soft ionization technique. In the API-ES process, ions are formed from the liquid phase by ejection from shrinking charged droplets. ES/MS has been used to identify the photocatalytic degradation products of non-ionic surfactants such as the primary and secondary alcohol ethoxylates and NPEO used in wool scouring (Sherrard et al., 1994). Each surfactant, diluted in a solution of water, methanol, and acetic acid, was injected directly into the spectrometer and nitrogen was used as both the drying gas and as the nebulizer. The spectrum of NPEO showed a series of peaks which clearly indicated the presence of the $[M+H]^+$ ions (e.g. m/z 397 for $[NP4EO+H]^+$). Each main peak was separated from its neighbor by 44 mass units corresponding to one ethoxy unit.

Methods have also been developed for the determination of non-ionic surfactants in environmental waters and sewage effluents by ES/LC/MS (Crescenzi et al., 1995, Mackay et al., 1997). In these cases, major peaks of the Na^+ , and to a much smaller extent, the H^+ , K^+ , and NH_4^+ adducts of the molecular ions were observed. For example, m/z 639 or $[NP9EO+Na]^+$ is the base peak for NP9EO (molecular weight 616). Even though all the oligomers were lumped together as a single chromatographic peak as a reversed phase column was used, quantitative information on the oligomeric distribution in an environmental sample could readily be obtained by extracting chromatograms of selected ions (corresponding to each Na^+ adduct) from the total ion chromatogram (TIC).

c. Atmospheric pressure chemical ionization (APCI) LC/MS

APCI is another soft ionization technique where ions are formed in the gaseous phase instead of the liquid phase as in the case of ES/MS. Pattanaargson et al. (1995) have used APCI/MS to determine the oligomer distribution of Tergitol NP-4, NP-6, NP-10, NP-13, and NP-40. In their work, no chromatographic separation was employed as the surfactant, prepared in an acetonitrile-water mixture, was directly introduced into the spectrometer. A series of protonated molecular ions, MH^+ , of NPEO (corresponding to $m/z 221 + 44n$ where n is the degree of ethoxylation) were observed in the mass spectrum. A preliminary investigation by Scullion et al. (1996) indicated that the mobile phase used with a C_1 column was compatible with APCI LC/MS analysis of OPEO. Only positive ions arising from OPEO were observed in that study and the dominant ones are $[M+Na]^+$ (e.g. $[OP8EO+Na]^+$ at $m/z 581$) and $[M+2Na]^+$ (e.g. $[OP8EO+2Na]^+$ at $m/z 604$).

B. Gas Chromatography (GC)

GC has been applied to the analysis of free and derivatized APEO, NP and OP as well as derivatized APEC. Because of the low volatility of the higher molecular weight APEO and APEC, so far this technique has only been applied to the analysis of oligomers with six or less ethoxy units. Although packed columns have been used, nearly all GC separations of AP and APEO have been done by capillary columns with low polarity stationary phases, such as OV-1 (Giger et al., 1981), DB-5 (Stephanou, 1984), and SE-54 (Ahel et al., 1987). In contrast to HPLC, a group of peaks, attributed to the presence of isomers on the alkyl side chain, are observed for NP by GC due to the higher resolution of a capillary column. Similarly, at each level of ethoxylation, a group of peaks are observed

for the free or derivatized NPEO and derivatized NPEC. Only one peak is observed for OP since it is a single isomer, i.e., 4-(1,1,3,3-tetramethylbutyl)phenol.

1. *Flame ionization detector (FID)*

A mixture of NP and Marlophen 83 (NPnEO with an average n of 3.15) were separated by a 15 m OV-73 column and detected by a FID (Stephanou and Giger, 1982). The gas chromatogram showed five groups of peaks, namely, NP and NPnEO (n=1 to 4), with an elution order of increasing molecular weight. Separation and characterization of a technical mixture of NP has been attempted by using a cross-linked methyl silicone capillary column (PONA) (Bhatt et al., 1992). Tentative structures of 14 isomers of NP have been assigned by virtue of GC/MS, GC/FTIR, and ¹³C NMR results (see later discussion). Isomers of 2-NP, octadecene, OP, and dinonylphenol were also identified in this mixture. The optimization of GC determination of NP using an orthogonal array design and electronic pressure programming using a 25 m HP-1 column has also been described (Chee et al., 1996).

2. *Electron capture detector (ECD)*

APEO and their metabolites AP and APEC do not possess electron-capturing groups and therefore attachment of a halogen-containing group by chemical derivatization is required for their analysis by ECD. For example, detection of the pentafluorobenzyl (PFB) ether derivatives of NP by an ECD using 30 m DB-5 column was reported (Chaloux et al., 1994). Nine major peaks were observed and the limit of detection for this procedure was estimated to be 20 pg. Heptafluorobutyl and pentafluorobenzoyl derivatives have been prepared for the determination of NP and NPnEO (n=1 to 6) in water, sludge, and biota samples. The pentafluorobenzoyl derivatives were shown to have

longer retention times and better responses by electron capture detection (Wahlberg et al., 1990).

3. *Gas chromatography/mass spectrometry (GC/MS)*

a. Electron impact ionization (EI)

This classical GC/MS method has been most widely used by workers in the analysis of free or derivatized AP, APEO, and APEC. Mass spectra of the different isomers for the free NP were first reported by Giger et al. (1981) and were later described in detail by Bhatt et al. (1992) and Wheeler et al. (1997). In these studies, major fragmentation ions were observed at m/z 107, 121, 135, 149, 163, and 177 due to the loss of various fragments of the alkyl chain. It was also noted that, in the above three studies, nearly all major NP isomers have at least one alkyl substituent (e.g. methyl, ethyl, dimethyl, etc.) on the α carbon of the side chain. The molecular ion for NP (m/z 220) was weak for all isomers.

The mass spectra of acetylated NP have also been shown to produce the same fragmentation ions except that the M^+ , also very weak, occurred at m/z 262 (Lee and Peart, 1995). With a base peak at m/z 135 and M^+ at m/z 248, the mass spectrum of the acetylated OP was consistent with its α,α -dimethyl structure (Lee and Peart, 1995). Total ion chromatograms (TIC) of an acetylated NP/OP standard as well as the extract of a primary sewage effluent depicting the occurrence of NP and OP are shown in Figures 4 and 5, respectively.

The M^+ for the PFB derivative of NP was also weak, however, two major fragments were observed at m/z 315 and 181 (Chaloux et al., 1994).

While EI GC/MS of NPEO has been reported, this technique has only been applied to the analysis of the more volatile oligomers, i.e. ethoxylates with four or less ethoxy units (Giger et al., 1981, Stephanou and Giger, 1982). The major fragmentation ions observed were m/z 179, 193, and 235 for NP1EO, and m/z 223, 237, and 279 for NP2EO. The M^+ for both ethoxylates (m/z 264 and 308) were weak. Due to the presence of longer chain oligomers in environmental samples, GC/MS is not suitable for the analysis of total APEO. The identification of halogenated and non-halogenated OPEO residues by EI GC/MS has also been reported (Stephanou et al., 1988). In the cases of OP n EO ($n=1$ to 3), the base peaks were invariably the $[M-71]^+$ or $[M-C_3H_{11}]^+$ fragment. APEC are usually converted into methyl esters for enhanced chromatographic properties (Figure 6). A TIC of a sewage extract indicating the occurrence of OP1EC/NP1EC and OP2EC/NP2EC in the final effluent is shown in Figure 7. Owing to the presence of different isomers of the nonyl group, the methyl esters of NP1EC and NP2EC again exhibited a group of peaks in the chromatogram. Although volatility of these derivatives is again a limitation of this GC/MS procedure, it is not considered as much a handicap as in the case of the NPEO since the major alkylphenol carboxylates in environmental samples have only a few ethoxy units. Under EI conditions, the molecular ions for the methyl esters of AP1EC and AP2EC are weak and thus are not suitable for selected ion monitoring work. Detailed descriptions of the mass spectra of these derivatives have been reported by Ahel et al.(1987) and Stephanou et al. (1988).

b. Positive ion chemical ionization (PCI)

This less commonly used technique has been applied to the analysis of OP n EO ($n=1$ to 5) (Stephanou, 1984a and b, Stephanou et al., 1988) as well as NP n EC in their

methyl ester form ($n=1$ to 4) (Stephanou et al., 1988) in surfactants and effluent samples. When methane was used as reagent gas in the work of OPnEO, the resulting spectra were very rich in ions. The characteristic ions, of varying intensities, were derived from the proton and ethyl adducts ($[M+H]^+$, $[M+C_2H_5]^+$) of the substrate. In contrast, when ammonia was the reagent gas, the most important ions for OPnEO were the $[M+NH_4]^+$ species and they were invariably the base peaks for the ethoxylates (Stephanou, 1984b).

Although PCI GC/MS with methane as reagent gas has also been documented for the detection of the methyl esters of halogenated and non-halogenated OPnEC ($n=1$ to 3) (Stephanou et al., 1988), ammonia as reagent gas again gave intense $[M+NH_4]^+$ adduct for the NPnEC ($n=1$ to 4) derivatives with little or no secondary fragmentation (Field and Reed, 1996). Therefore, multiple ion monitoring at m/z 310, 354, 398, and 442 has been successfully applied to the selective detection of NP1EC, NP2EC, NP3EC, and NP4EC, respectively, in paper mill and sewage effluents as well as river waters (Field and Reed, 1996).

c. Negative ion chemical ionization (NCI)

There are only a few reports for the analysis of alkylphenolics by NCI GC/MS. The pentafluorobenzoyl derivatives of NP and NPnEO have been demonstrated to produce intense molecular ions under NCI conditions using methane as reagent gas (Wahlberg et al., 1990). Therefore, ions at m/z 414, 458, 502, and 546 were used for the selective detection of NP, NP1EO, NP2EO, and NP3EO, respectively, in sewage effluents. The detection limit of NP (2 pg absolute) as pentafluorobenzyl (PFB) ether derivatives by methane-NCI was reported to be five times lower than that by the EI/GC/MS procedure (Chaloux et al., 1994). The higher sensitivity under NCI conditions

was attributed to the absence of further fragmentation for the characteristic ion $[M-PFB]^+$ (m/z 219) used for quantitative work.

C. Other techniques

1. *Miscellaneous mass spectrometric methods*

In some earlier studies, field desorption mass spectrometry (FDMS) was used in the confirmation of OPEO and NPEO in wastewater extracts (Otsuki and Shiraishi, 1979, Yasuhara et al., 1981, Crathorne et al., 1984). While major ions corresponding to the molecular masses of all APEO oligomers were observed in one case (Otsuki and Shiraishi, 1979), quasi-molecular ions such as $[M+Na]^+$, $[M+K]^+$, and $[M+H]^+$ were more commonly found in a FD mass spectrum (Yasuhara et al., 1981, Crathorne et al., 1984). The latter phenomenon often occurred in surface water extracts where there were sufficient amounts of coextracted alkali salts to form these ions.

Fast atom bombardment (FAB) mass spectrometry and FABMS/MS have been applied for the identification of NPnEO and NPnEC in raw and drinking water extracts (Rivera et al., 1987, Ventura et al., 1988, 1989, 1991, and 1992). Thioglycerol saturated with NaCl was used as a matrix for FABMS of the surfactants. NPnEO and NPnEC (as methyl esters) oligomers can readily be distinguished in the FAB mass spectra by their $[M+Na]^+$ ions separated by 44 mass units. For example, the presence of NP3EC and NP4EC in the sample is evidenced by the observation of ions at m/z 447 and 491, respectively (Ventura et al., 1991). The formation of $[M+Na]^+$ ions instead of $[M+H]^+$ ions is enhanced by salt added to the matrix. Since the intensity of the quasimolecular ions decreases with molecular weight, this technique, however, is not suitable for quantitative

analysis unless isotopically labeled internal standards are used. In contrast, field desorption MS and desorption chemical ionization MS methods generate abundant quasimolecular ions $[M+H]^+$; therefore they are well suited for molecular weight determinations of APEO.

2. *Supercritical fluid chromatography (SFC)*

The use of SFC for the quantitative analysis of non-ionic surfactants has been investigated (Wang and Fingas, 1993a and c). Separation of Triton (OPEO) and Igepal (NPEO) mixtures was achieved by a 5 m x 50 μ m i.d. SB-Phenyl-30 (30% biphenyl, 70% methylpolysiloxane) capillary column and detection was accomplished by a flame ionization detector. A linear pressure program of the mobile phase, supercritical carbon dioxide, from 2000 to 5500 psi, and column oven temperatures of 100, 150, and 180°C were used. The retention times of APEO oligomers are a function of their polarity or molecular masses. The less polar, shorter chain oligomers were eluted first by carbon dioxide of lower solvating power (or pressure and density). Under optimized conditions, APEO oligomers of up to 25 ethoxy units were satisfactorily separated. While SFC and C1 reversed phase HPLC produced similar quantitative results for the oligomeric distribution of Triton and Igepal mixtures, SFC offered a better resolution of the oligomers. Since SFC is not available in many laboratories, there has been no reported method for its application in environmental analysis involving APEO.

3. *Capillary electrophoresis (CE)*

An interesting example of the electrophoretic separation of APEO was given by Heinig et al. (1996). For the analysis of non-ionic surfactants, the addition of sodium dodecyl sulfate (SDS) to provide a charged pseudophase and high contents of organic

modifier (20 % of acetonitrile or more) are needed. Separation was achieved by using a 50 cm x 75 μ m i.d. fused-silica capillary and uv detection was set at 200 or 214 nm. The migration order for the ethoxylates in CE is opposite to the elution order in HPLC, i.e. NPEO and OPEO are detected in the order of decreasing number of ethoxy units. In another study by He and Lee (1996), the addition of cyclodextrin to the SDS buffer was shown to improve the separation of NP isomers by micellar electrokinetic chromatography. While CE provides a faster and higher resolution separation than LC for many ionic and non-ionic surfactants, this emerging technique has not yet been utilized in environmental analysis of APEO.

V. SUMMARY

In the last 20 years, a wealth of analytical methods have been developed for the identification and quantification of AP, APEO, and APEC in water and sludge samples. Over this period of time, the extraction technique for water samples has gradually changed from solvent sublation, steam distillation, and liquid-liquid extraction to solid phase extraction. Among the few methods available for solid samples, Soxhlet extraction is a viable technique for most laboratories although supercritical fluid extraction is a more efficient alternative.

Due to the presence of isomers and oligomers in APEO, quantitative analysis of these complex mixtures always presents a challenge to analytical chemists. LC is a popular technique for the comprehensive analysis of APEO and their metabolites. In the absence of a mass spectrometer, a fluorescence detector coupled to a normal phase

column with solvent programming is very useful for the determination of oligomer distribution in an environmental sample. In contrast, an isocratic run with a reversed phase column gives a quick separation of the octyl and nonyl homologues and it is particularly suitable for LC/MS work. High resolution capillary column GC is an excellent complementary method. It is actually more convenient for the analysis of the volatile components such as NP and OP as well as AP1EC and AP2EC in their methyl ester form. A mass spectrometer interfaced to LC or GC has become a very versatile and powerful tool for the analysis of nonylphenolics because of its sensitivity and positive identification. It can also be used in the absence of chromatographic separation if the characteristic quasimolecular ions are formed.

Analytical methods and reported detection limits for the determination of APEO, AP, and APEC in environmental samples are summarized in Tables 2, 3, and 4, respectively.

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Table 1. Examples of a few commercial APEO preparations.

Product name	Type	Average no. of ethoxy units	Manufacturer
Igepal CA-210	OPEO*	2	GAF Corp.
Igepal CA-520	OPEO	5	
Igepal CA-720	OPEO	12	
Igepal CO-210	NPEO	2	
Igepal CO-520	NPEO	5	
Igepal CO-720	NPEO	12	
Igepal CO-890	NPEO	40	
Igepal CO-990	NPEO	100	
Imbentin-N/7A	NPEO	5	W. Kolb, AG
Imbentin-N/200	NPEO	20	
Imbentin-O/050	OPEO	5	
Imbentin-O/200	OPEO	20	
Lissapol TN 450	NPEO	8-9	ICI Chemicals
Lissapol TN XP	NPEO	8-9	
Marlophen 810	NPEO	11	Chemisch Werke Hüls
Marlophen 83	NPEO	3.15	
Surfonic N-40	NPEO	4	Texaco
Surfonic N-95	NPEO	9	
Synperonic OP10	OPEO	10	ICI Chemicals
Tergitol NP15	NPEO	15	Union Carbide
Tergitol NP40	NPEO	40	
Terric N2	NPEO	2	ICI Chemicals
Terric N4	NPEO	4	
Triton N-101	NPEO	9.5	Rohm and Haas
Triton X-15	OPEO	1.2	
Triton X-35	OPEO	3.0	
Triton X-45	OPEO	4.3	
Triton X-114	OPEO	7.4	
Triton X-100	OPEO	9.4	
Triton X-102	OPEO	11.6	
Triton X-165	OPEO	14.7	

* OPEO=octylphenol ethoxylates, NPEO=nonylphenol ethoxylates

Table 2. Methodologies for the determination of APEO in water/wastewater and sediment/sludge samples.

Matrix	Parameter	Extraction	Analysis	Detection limit	Reference
wastewater	NPnEO	SPE (ODS)	LC/UV, Bondapak C-18 FD/MS	low µg/L	Otsuki and Shiraishi (1979)
sewage	NPnEO (n=1 to 3)	steam distillation	GC/EI/MS, OV-1		Giger et al. (1981)
sewage	NPnEO (n=1 to 3)	continuous liquid-liquid extraction (DCM)	GC/FID, OV-73 GC/EI/MS, OV-73	10 µg/L	Stephanou and Giger (1982)
wastewater	OPnEO (n=1 to 5)	DCM	GC/PCI/MS, DB-5	qualitative	Stephanou (1984a)
wastewater sludge	NP1EO, NP2EO	steam distillation	LC/UV, Lichrosorb-NH ₂	0.5 µg/L, water low µg/g, sludge	Ahel and Giger (1985a)
wastewater	NPnEO/OPnEO (n=1 to 18)	solvent sublation	LC/UV, Lichrosorb-NH ₂ , Hypersil APS	1-3 µg/L	Ahel and Giger (1985b)
sewage	APnEO (n=1 to 16)	solvent sublation	LC/FL, Zorbax-NH ₂ , Partisil 5 PAC	0.2 ng of each APEO oligomer	Holt et al. (1986)
sewage wastewater	NPnEO	SPE (ODS)	LC/FL, Lichrosorb RP-8	4 µg/L	Marcomini et al. (1987), Brunner et al. (1988)
sediment sludge	NPnEO	Soxhlet (MeOH), sediment steam distillation, sludge	LC/UV, Lichrosorb RP-8 LC/FL, Hypersil APS	95 ng	Marcomini and Giger (1987), Brunner et al. (1988)
raw and tap water	NPnEO and halogenated derivatives	SPE (granular activated carbon) then Soxhlet (DCM)	GC/EI/MS, BP-5, FAB/MS LC, Lichrosorb RP-18, FAB/MS	qualitative	Ventura et al. (1988, 1989)
sewage	OPnEO (n=1 to 5) and Br derivatives	diethyl ether	GC/EI/MS, DB-5	0.005 µM	Ball et al. (1989)
wastewater	NPnEO (n=1 to 6)	DCM	GC/ECD, GC/EI/NCI/MS of PFB		Wahlberg et al. (1990)

sludge		acetone/water/ether	and HFB derivatives		
wastewater	NPnEO (n=1 to 18)	SPE (ODS and ion exchange resins)	LC/FL, Microsorb CN		Kubeck and Naylor (1990)
sludge	NP1EO	Soxhlet (hexane)	LC/FL, Hypersil APS		Marcomini et al. (1991)
river water sediment	NPnEO (n=1 to 17)	steam distillation (NP1EO) SPE (NP2EO to NP17EO)	LC/FL, Microsorb CN	0.067-1.58 µg/L (water), 2.26 µg/g (sediment)	Naylor et al. (1992)
drinking water	NPnEO/OPnEO (n=2 to 8)	continuous liquid-liquid extraction (DCM)	LC/PB/MS, C18	1 ng/L	Clark et al. (1992)
wastewater	NPnEO	centrifugal partition chrom.	UV and FL detection	0.5-3 mg/L	Menges et al. (1992)
sewage	NPnEO	SPE (ODS)	LC/FL, Lichrosorb RP-18		Marcomini et al. (1993)
wastewater	NPnEO (n=1 to 13)	ethyl acetate sublation	LC/UV, Resolve CN		Scarlet et al. (1994)
sewage	NPnEO	SPE (graphitized carbon black)	LC/FL, C8		Di Corcia et al. (1994)
sewage river water	NP1EO, NP2EO NPnEO (n=3 to 20)	steam distillation (lower NPnEO) solvent sublation (higher NPnEO)	LC/UV, Hypersil APS	10 ng/L	Ahel et al. (1994a and b, 1996)
wastewater	NPnEO	SPE (graphitized carbon black)	LC/API/ES/MS		Crescenzi et al. (1995)
water	Triton X-100	SPME (Carbowax/template resin coating)	LC/UV, Supelcosil LC-NH ₂	low µg/L	Boyd-Boland and Pawliszyn (1996)
river water	APEO	SPE (ODS and SAX)	LC/FL, TMS LC/APCI/MS, TMS	0.05 µg/L	Scullion et al. (1996)
wastewater	APEO	solvent sublation	LC/FL, Spherisorb silica	100 µg/L	Ibrahim and Wheals (1996a)
wastewater	OP1EO/OP2EO NP1EO/NP2EO	SPE (ODS)	GC/EI/MS, DB-5	0.5 µg/L	Paxéus (1996)
sewage	OPnEO/NPnEO (n=1	SPE (graphitized carbon black)	LC/FL and LC/API/ES/MS, C18	5 µg/L	Mackay et al. (1997)

to 16)

sludge	NPnEO (n=1 to 17)	SFE (CO ₂ modified with water)	LC/FL, Hypersil APS	0.2 to 2 µg/g	Lee et al. (1997)
spiked sediment	NPnEO (n=13) Triton X-100	SFE (CO ₂ modified with MeOH)	LC/FL, RP-18	10 ng	Kreisselmeier and Dürbeck (1997)

Table 3. Methodologies for the determination of AP in water/wastewater and sediment/sludge samples.

Matrix	Parameter	Extraction	Analysis	Detection limit	Reference
wastewater sediment	NP, OP	DCM, water Soxhlet (isopropanol), sediment	GC/FID, 3% SP-2100, SE-52		Jungclaus et al. (1978)
sewage	NP	steam distillation	GC/EI/MS, OV-1		Giger et al. (1981)
sewage	NP	continuous liquid-liquid extraction (DCM)	GC/FID, OV-73 GC/EI/MS	10 µg/L	Stephanou and Giger (1982)
sludge	NP	steam distillation (cyclohexane)	GC/FID, OV-73 LC/UV, Lichrosorb NH2	<80 µg/g	Giger et al. (1984)
wastewater sludge	NP	steam distillation (cyclohexane)	LC/UV, Lichrosorb NH2	0.5 µg/L, water low µg/g, sludge	Ahel and Giger (1985a)
sewage wastewater	NP	SPE (ODS)	LC/FL, Lichrosorb RP-8		Marcomini et al. (1987) Brunner et al. (1988)
sediment sludge	NP	Soxhlet (MeOH), sediment steam distillation, sludge	LC/UV, Lichrosorb RP-8 LC/FL, Hypersil APS	65 ng	Marcomini et al. (1987) Brunner et al. (1988)
sewage	OP and BrOP	diethyl ether, methylation	GC/EI/MS, DB-5	0.005 µM	Ball et al. (1989)
wastewater sludge	NP	DCM, water acetone/water/ether, sludge	GC/ECD and GC/EI/NCI/MS of PFB and HFB derivatives		Wahlberg et al. (1990)
sludge	NP	Soxhlet (hexane)	LC/FL, Hypersil APS		Marcomini et al. (1991)
river water river sediment	NP	steam distillation	LC/FL, Microsorb CN	0.107 µg/L, water 2.93 µg/g, sediment	Naylor et al. (1992)
sludge	NP	steam distillation	LC/UV, Hypersil APS		Sweetman (1994)

sewage, river water	NP	steam distillation	LC/UV, Hypersil APS	10 g/L	Ahel et al. (1994a and b, 1996)
sewage	NP	SPE (graphitized carbon black)	LC/FL, C8		Di Corcia et al. (1994)
sludge river sediment	NP	Soxhlet (DCM/MeOH, 2:1), pentafluorobenzyl ether derivatives	GC/ECD, DB-5 GC/EI/MS, DB-5MS GC/NCI/MS, DB-5MS	2.9 pg/g, ECD 1.4 pg/g, EI/MS 0.3 pg/g, NCI/MS	Chaloux et al. (1994)
sludge	NP, OP	pet ether or SFE (CO ₂) with in situ acetylation	GC/EI/MS of acetyl derivatives, HP-5MS	0.1 µg/L or µg/g (NP) 0.01 µg/L or µg/g (OP)	Lee and Peart (1995)
river water	NP, OP	SPE (ODS)	GC/EI/MS, DB-5	30-200 ng/L (NP) 50-250 ng/L (OP)	Blackburn and Waldock (1995)
wastewater	NP, OP	SPE (ODS)	GC/EI/MS	0.5 µg/L	Paxéus (1996)
spiked sediment	NP	SFE (CO ₂ modified by MeOH)	LC/FL, RP-18	10 ng	Kreisselmeier and Dürbeck (1997)

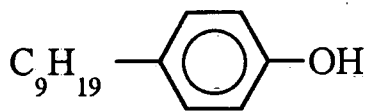
Table 4. Methodologies for the determination of APEC in water/wastewater and sediment/sludge samples.

Matrix	Parameter	Extraction	Analysis	Detection limit	Reference
wastewater	brominated APEC	SPE (XAD-8), methylation	GC/EI/MS, SE-52		Reinhard et al. (19812)
sewage	NP1EC, NP2EC	CHCl ₃ or gaseous stripping, methylation	GC/EI/MS, SE-54 LC/UV, Lichrosorb NH ₂	1 µg/L	Ahel et al. (1987)
raw and tap water	NPnEC (n=1 to 4) and halogenated derivatives	granular activated carbon then Soxhlet (DCM)	GC/EI/MS, BP-5 FAB/MS	qualitative	Ventura et al. (1988)
sewage	OPnEC (n=1 to 6) and Br derivatives	diethyl ether, methylation	GC/EI/MS, DB-5	0.005 µM	Ball et al. (1989)
raw and drinking water	NPnEC	SPE (XAD-2) or granular activated carbon	FAB/MS and FAB/MS/MS	qualitative	Ventura et al. (1991, 1992)
sewage	NP1EC, NP2EC	SPE (ODS)	LC/FL, Lichrosorb RP-18		Marcomini et al. (1993)
sewage	NPnEC (n=1 to 10)	SPE (graphitized carbon black)	LC/FL, C8		Di Corcia et al. (1994)
sewage, river water	NP1EC, NP2EC	CHCl ₃	LC/UV, Lichrosorb NH ₂	1 µg/L (1994) 100 ng/L (1996)	Ahel et al. (1994a and b, 1996)
sewage, paper mill effluent	NPnEC (n=1 to 4)	SPE (SAX), methylation	GC/PCI/MS, SE-54	0.2-2 µg/L	Field and Reed (1996)
sludge	NP1EC, NP2EC	SFE (CO ₂ modified by water), methylation	GC/EI/MS, HP-5MS	0.5 µg/g	Lee et al. (1997)
ground water	brominated OP1EC	DCM, methylation	GC/EI/MS, DB-5		Fujita and Reinhard (1997)
sewage	NP1EC, OP1EC	SPE (ODS), methylation	GC/EI/MS, HP-5MS	0.5 µg/L (NP1EC) 0.05 µg/L (OP1EC)	Lee et al. (1998)

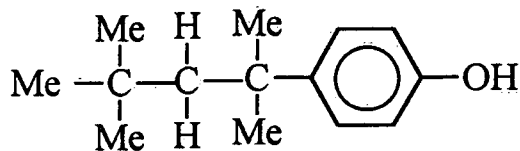
LIST OF FIGURES

- Figure 1. Chemical structures for NP, OP, APEO, AP1EC, and AP1EC.
- Figure 2. Liquid chromatogram of a NP_nEO (n=1 to 17) standard obtained by a 100 x 2.1 mm I.D. Hypersil APS column and a fluorescence detector (230 nm excitation, 300 nm emission). Gradient elution with mixtures of n-hexane/2-propanol (98:2, v/v) and isopropanol/water (9:1, v/v) was used. See Lee et al. (1997) for further details.
- Figure 3. LC/fluorescence chromatogram of an extract indicating the occurrence of NP_nEO in a pulp and paper mill sludge (Lee et al., unpublished results). See Figure 2 for experimental conditions.
- Figure 4. TIC (EI/GC/MS) of a NP/OP standard in the acetylated form using a 30 m x 0.25 mm I.D. HP-5MS column. The oven temperature was programmed from 70 to 160 and then to 240°C at 30 and 5°C/min, respectively. See Lee and Peart (1995) for further detail. The peak at 8.74 min and those from 9.8 to 10.9 min are derived from OP and NP, respectively.
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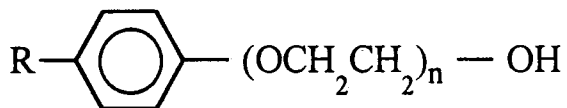
Figure 1



4-nonylphenol (NP)

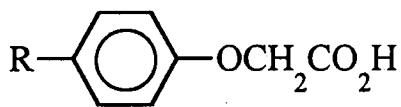


4-tert-octylphenol (OP)



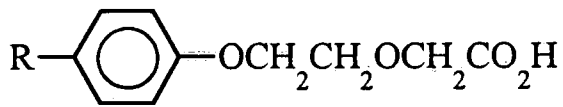
R=C₉H₁₉, nonylphenol ethoxylates (NPEO)

R=C₈H₁₇, octylphenol ethoxylates (OPEO)



R=C₉H₁₉, nonylphenoxyacetic acid (NP1EC)

R=C₈H₁₇, octylphenoxyacetic acid (OP1EC)



R=C₉H₁₉, nonylphenoxyethoxyacetic acid (NP2EC)

R=C₈H₁₇, octylphenoxyethoxyacetic acid (OP2EC)

Figure 2

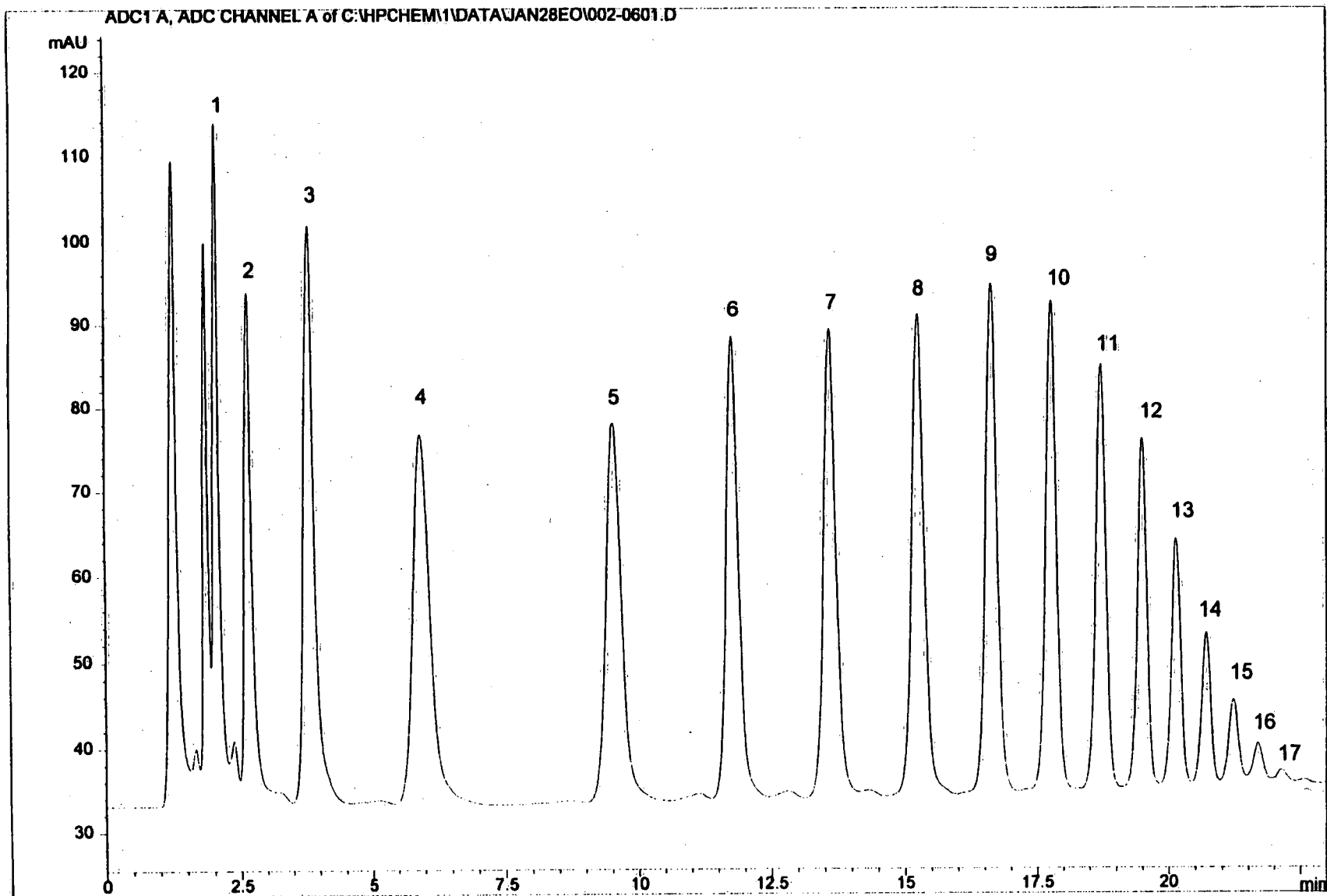


Figure 3

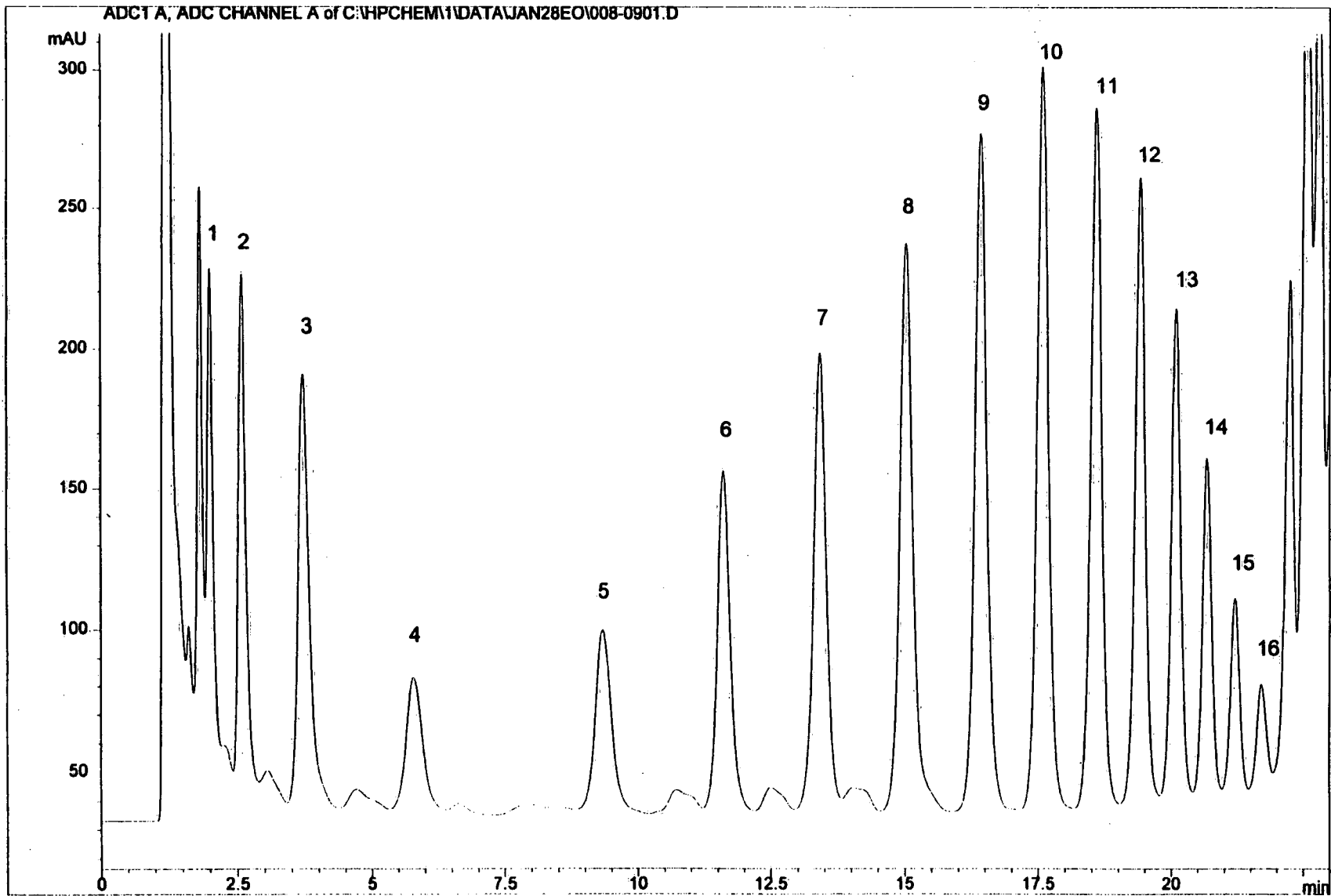


Figure 4

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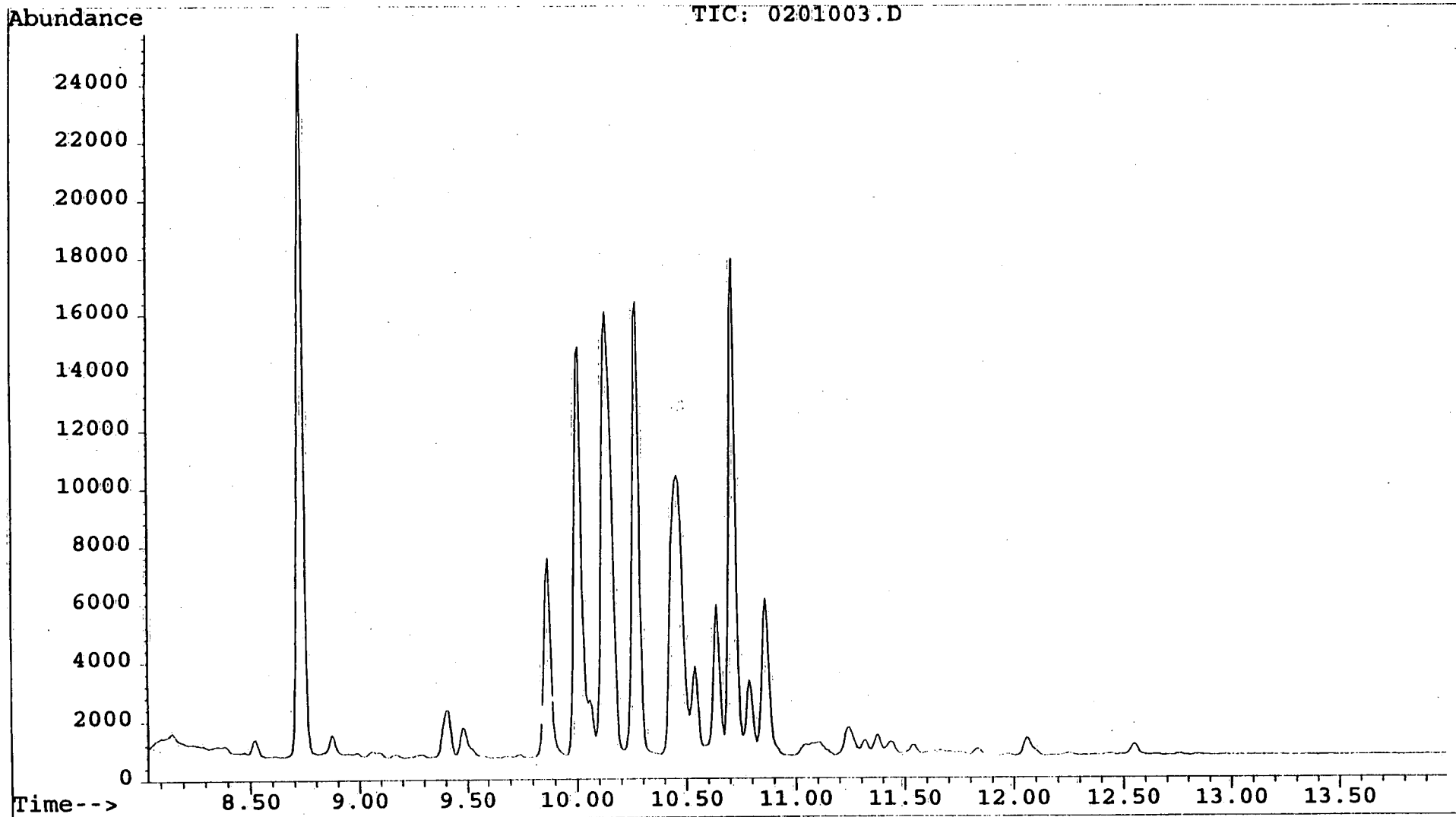


Figure 5

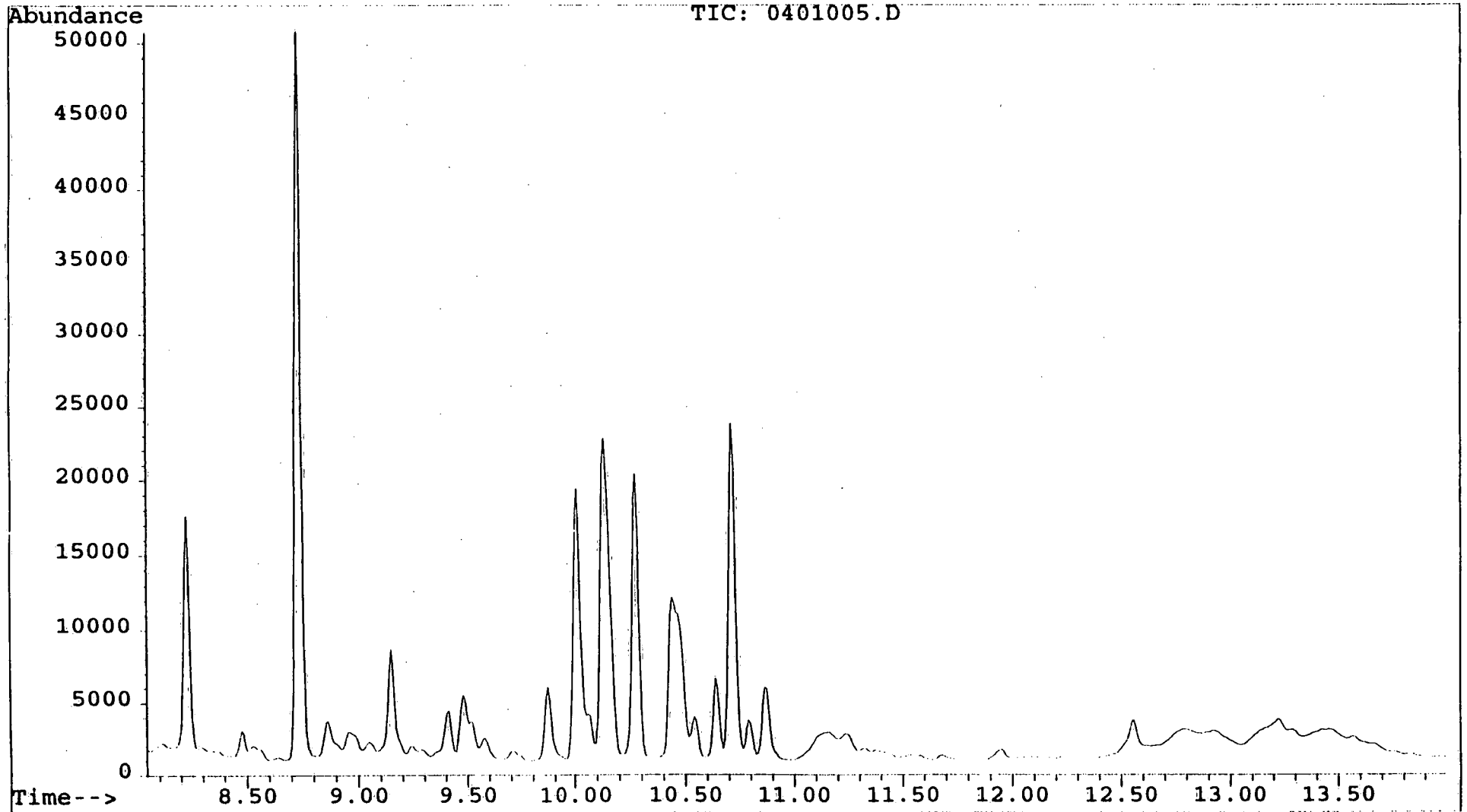


Figure 6

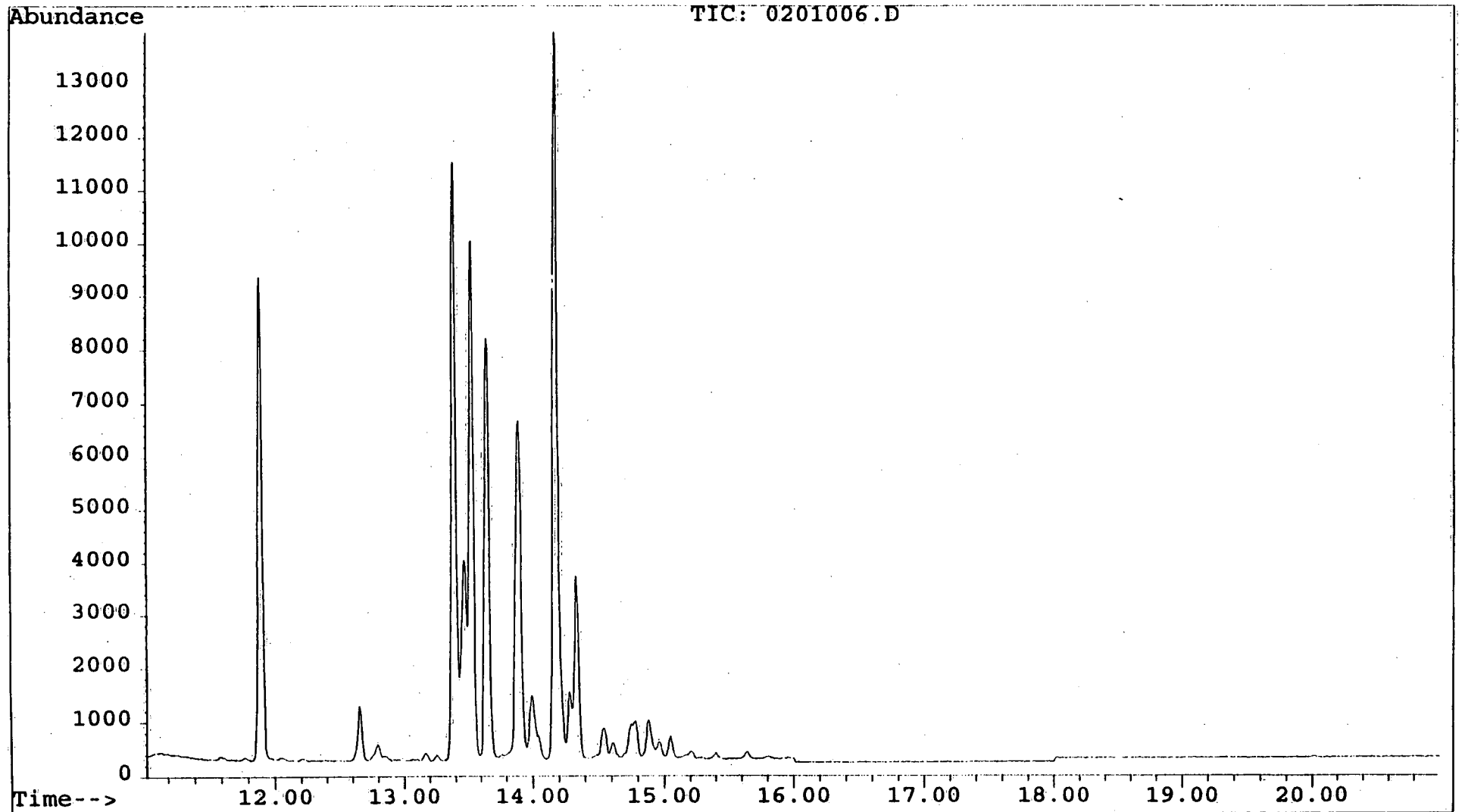
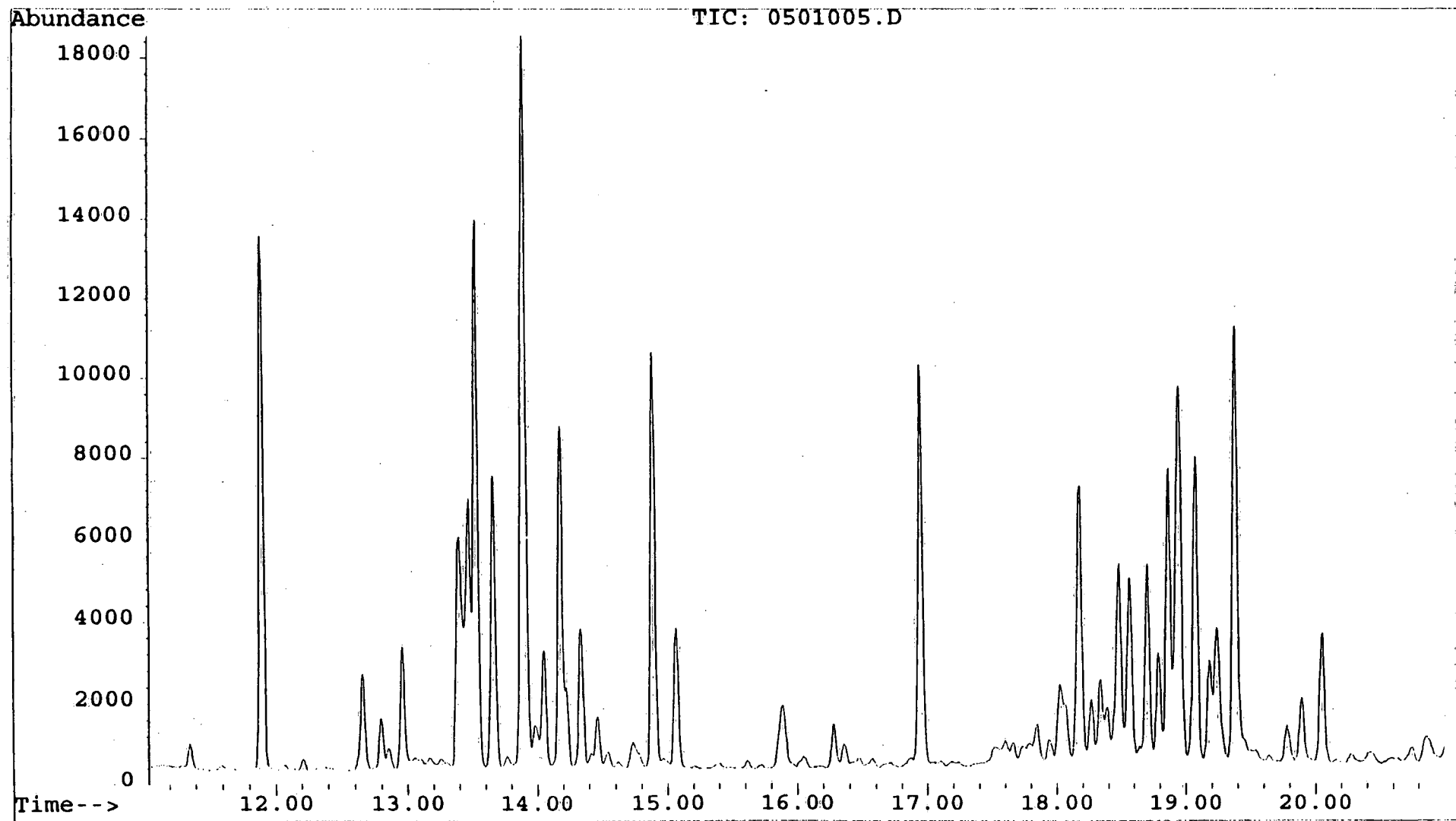
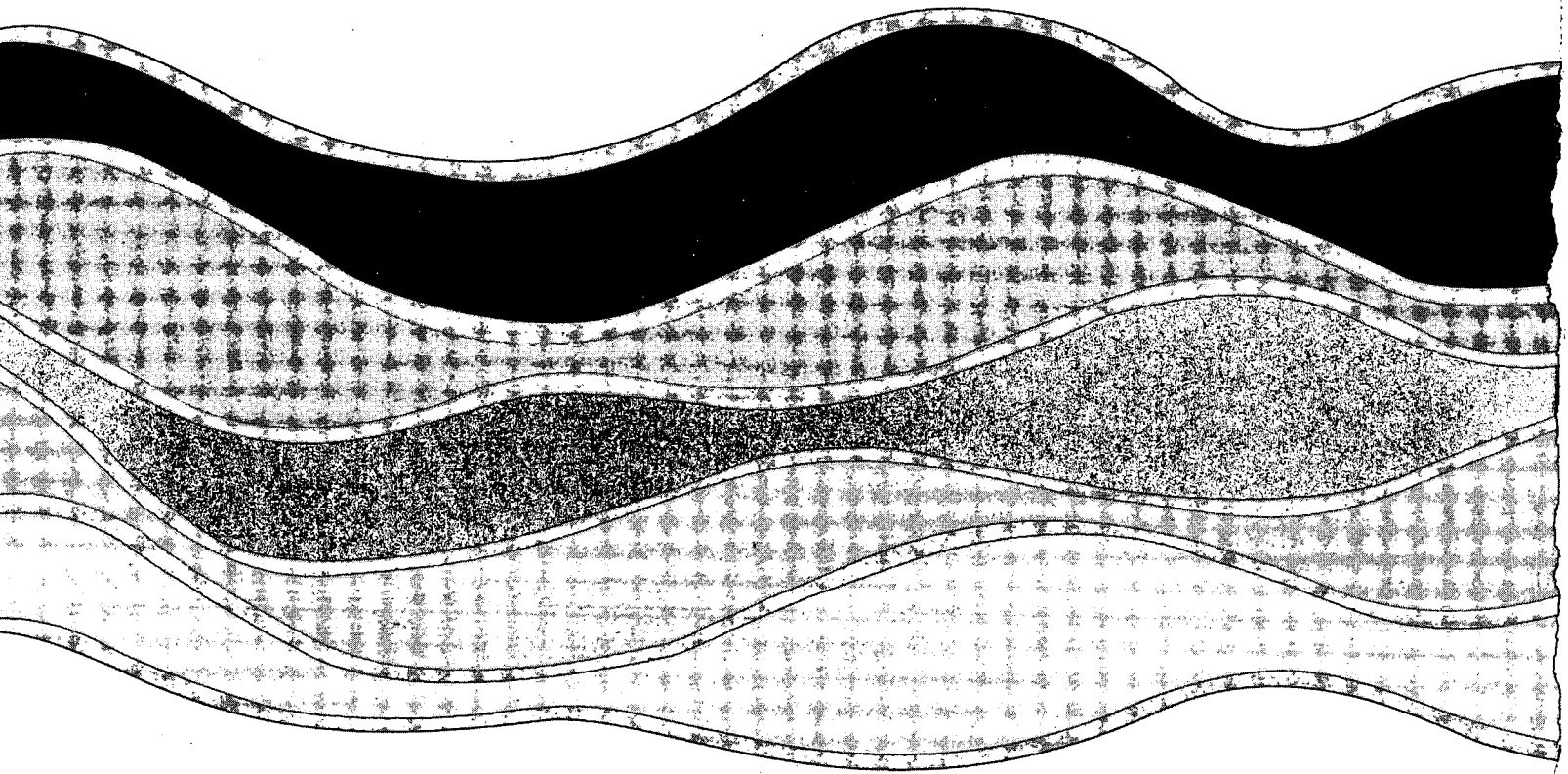


Figure 7





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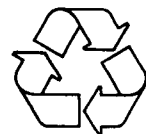


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