30 Surfactants

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I. INTRODUCTION

Surfactants have amphiphilic structures consisting of a hydrophilic and a hydrophobic part. These special structures cause their surface-active properties like concentration at surfaces, reduction of the surface tension, and formation of micelles in bulk solution. Therefore, they are widely used in formulations for washing, wetting, emulsifying, and dispersing. Laundry detergents, cleaning agents, and personal care products are by far the largest class of surfactant containing products for domestic use. After use, they are mainly discharged into municipal wastewaters which enter sewage treatment plants. The different ingredients of a detergent formulation are eliminated there by biodegradation or adsorption. In the case of insufficient biological degradability, however, they are potential sources of environmental pollution. Tetrapropylenebenzene sulfonate (TPS) is a typical example of a persistent anionic surfactant which was used in detergents between 1946 and 1965. As a consequence of rising TPS concentrations in German rivers during dry years of 1959/1960, visible foam formed on the water surface.

As a reaction, strict standards were applied to surfactants with regard to their biodegradability. In a directive of the European Community (73/404/EEC),[1] an average biodegradation rate of at least 90% for all surfactants (referring to a certain residence time in a municipal sewage treatment plant) is required. Consequently, TPS was replaced by readily biodegradable linear alkylbenzenesulfonates (LAS) in the 1960s. The dramatic increase in the production of detergents during the second part of the last century still has an enormous impact on the environment. In order to evaluate the ecological risks of the different components of detergent formulations their levels in the different environmental compartments have to be determined. The analytical methods for the determination of surfactants as the main risk factors in environmental matrices have been continuously improved with regard to reproducibility, selectivity, and sensitivity over last few years. This chapter describes the broad spectrum of different analytical methods for these analytes beginning with correct sampling, followed by matrix-specific enrichment procedures, and finally the determination by colorimetric, spectroscopic, electrochemical, or chromatographic methods.

A. General Remarks

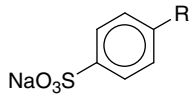
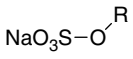
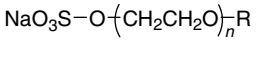
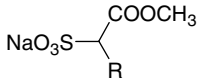
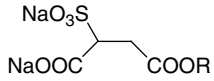
Depending on the nature of the hydrophilic groups of surfactants, they can be divided into anionic, nonionic, cationic, and amphoteric surfactants. The last-mentioned class only plays a minor role with respect to domestic and industrial applications and practically no methods for the environmental analysis of amphoteric surfactants have been published so far.

1. Anionic Surfactants

The hydrophilic groups of anionic surfactants consist in most cases of sulfonate, sulfate, or carboxyl groups (Table 30.1). Amongst them, LAS are produced in the largest quantities worldwide. These are mainly used in powdery and liquid laundry detergents and household cleaners.

Abbreviations: AEO, alcohol ethoxylates; AES, alcohol ethoxy sulfates; AP, alkylphenols; APCI, atmospheric pressure chemical ionization; APEC, alkylphenoxy carboxylates; APEO, alkylphenol ethoxylates; APG, alkyl polyglucosides; AS, alcohol sulfates; BGE, background electrolyte; BiAS, bismuth active substance; CAD, collisionally activated decomposition; CI, chemical ionization; DBAS, disulphine blue active substances; DEEDMAC, diethylester dimethylammonium chloride; DEQ, diesterquaternary; DSDMAC, distearyldimethylammonium chloride; DTDMAC, ditallowdimethylammonium chloride; ECD, electron capture detector; EI, electron impact ionization; ESI, electrospray ionization; FAB, fast atom bombardment; FD, field desorption; FID, flame ionization detector; GC, gas chromatography; GCB, graphitized carbon black; HPLC, high performance liquid chromatography; IR, infrared; LAB, linear alkylbenzenes; LAS, linear alkylbenzene sulfonates; LC, liquid chromatography; MBAS, methylene blue active substances; MS, mass spectrometry; NCI, negative chemical ionization; NMR, nuclear magnetic resonance spectroscopy; NP, nonylphenols; NPEC, nonylphenoxy carboxylates; NPEO, nonylphenol ethoxylates; SAS, secondary alkane sulfonate; SFC, supercritical fluid chromatography; SFE, supercritical fluid extraction; SIM, selected ion monitoring; SPC, sulphophenyl carboxylates; SPE, solid-phase extraction; SPME, solid-phase micro-extraction; TPS, tetrapropylenebenzene sulfonate; UV, ultraviolet.

TABLE 30.1
Classification of Anionic Surfactants

Type	Formula	
Linear alkylbenzene sulfonates (LAS)		$R = C_{10}-C_{13}$
Alkylsulfonates	NaO_3S-R	$R = C_{11}-C_{17}$
α-Olefine sulfonates	$NaO_3S-(CH_2)_mHC{=}CH(CH_2)_nCH_3$	$m + n = 9-15$
Alkylsulfates		$R = C_{11}-C_{17}$
Fatty alcohol ether sulfates		$R = C_{12}-C_{14}$; $n = 1-4$
α-Sulfo fatty acid methyl esters		$R = C_{14}-C_{16}$
Sulfo succinate esters		$R = C_{12}$
Soaps	$NaOOC-R$	$R = C_{10}-C_{16}$

2. Nonionic Surfactants

The hydrophilic behavior of nonionic surfactants is caused by polymerized glycol ether or glucose units (Table 30.2). They are almost exclusively synthesized by addition of ethylene oxide or propylene oxide to alkylphenols (AP), fatty alcohols, fatty acids, or fatty acid amides. Nonionic surfactants found major applications as detergents, emulsifiers, wetting agents, and dispersing agents. They are used in many sectors, including household, industrial and institutional cleaning products, textile processing, pulp and paper processing, emulsion polymerization, paints, coatings, and agrochemicals.

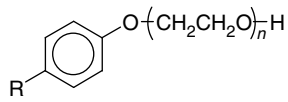
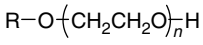
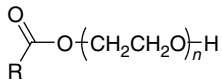
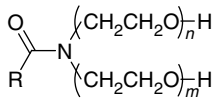
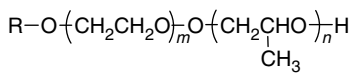
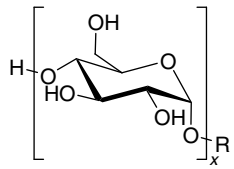
3. Cationic Surfactants

Cationic surfactants contain quaternary ammonium ions as their hydrophilic parts (Table 30.3). This class of surfactants has gained importance because of its bacteriostatic properties. Therefore, cationic surfactants are applied as disinfectants and antiseptic components in personal care products and medicine. Because of their high adsorptivity to a wide variety of surfaces, they are used as antistatic agents, textile softeners, corrosion inhibitors, and flotation agents.

II. SAMPLING

Correct sampling and storage of environmental samples are indispensable in environmental analysis. On the one hand, the samples must be representative of the environmental compartment from which they were taken and, on the other hand, it must be guaranteed that the chemical composition of the samples does not change during storage. The main problem in the analysis of surfactants is that they tend to concentrate at all interfaces due to their amphiphilic nature. Consequently, losses from aqueous solutions occur because of adsorption of the surfactants to

TABLE 30.2
Classification of Nonionic Surfactants

Type	Formula	
Alkylphenolethoxylates (APEO)		R = C_8–C_{12}; n = 3–40
Alcoholethoxylates (AEO)		R = C_9–C_{18}; n = 1–40
Fatty acid ethoxylates		R = C_{12}–C_{18}; n = 4
Fatty acid alkanolamide ethoxylates		R = C_{11}–C_{17}; m = 0, 1; n = 1, 2
Fatty alcohol polyglycol ethers		R = C_8–C_{18}; m = 3–6; n = 3–6
Alkylpolyglucosides (APG)		R = C_8–C_{16}; x = 1–4

laboratory apparatus or suspended particles. Especially for matrices like sewage sludges, sediments, and biological samples, the quantitative recovery of the analytes becomes a major problem. For this reason, internal standards are added to the samples in order to correct for nonquantitative recovery. This approach, however, is restricted to chromatographic determination methods because less selective methods such as the determination of summary parameters cannot discriminate surfactant initially present from added internal standards. Table 30.4 contains a selection of internal standards used in surfactant analysis.

Irrespective of the surfactants to be determined, water samples are immediately preserved upon collection by the addition of formaldehyde up to a concentration of 1% and stored at 4°C in the dark.[2–4] In order to prevent adsorption of LAS to laboratory apparatus, sodium dodecylsulphate is added to water samples.[5]

Sewage sludges are either preserved like water samples by the addition of formaldehyde up to 1% and storage at 4°C in the dark[6] or immediately filtrated and air-dried.[3]

Fertilization of agricultural land with sewage sludge has resulted in the need to monitor surfactant concentrations in sludge-amended soils. Soil samples are collected from the upper 5 cm with a stainless steel corer, dried at 60°C, pulverized, and stored at 4°C in the dark.[7]

III. ISOLATION AND ENRICHMENT

The concentrations of surfactants in environmental samples are usually below the limit of the analytical method. Therefore, preconcentration is necessary before analysis. Interfering substances

TABLE 30.3
Classification of Cationic Surfactants

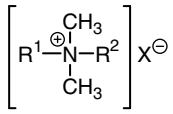
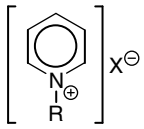
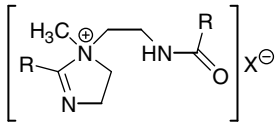
Type	Formula	
Tetraalkylammonium salts		$R^1, R^2 = C_1, C_{16}-C_{18}$ $R^1, R^2 = C_{16}-C_{18}$ $R^1 = C_8-C_{18}, R^2 = CH_2C_6H_5$
Alkylpyridinium salts		$R = C_16-C_{18}$
Imidazoliumquaternary-ammonium salts		$R = C_{16}-C_{18}$

TABLE 30.4
Selected Internal Standards Used in Determination Procedures for Surfactants in Different Environmental Matrices

Surfactant	Matrix	Determination Method	Internal Standard	Reference
LAS	Water	HPLC	C_9-, C_{15}-LAS or 1-C_8-LAS, 3-C_{15}-LAS	6,57
LAS	Water	GC–MS	CF_3CH_2-LAS	78
AEO	Sewage sludge, water	GC	1-Octanol and 1-eicosanol	67
AEO, APEO	Water	LC–MS	Hexylphenol5EO and ethylphenol5EO	33
APEO, AP	Sewage sludge, water	GC	*n*-Nonylbenzene or tribromophenol	31,43
APEO, AP	Water	HPLC	2,4,6-Trimethylphenol	2
NPEO, NP	Water, sediments	LC–MS	4-*n*-NP3EO, 4-*n*-NP	32

from the matrix have to be removed in an additional prepurification step prior to quantitative determination of the surfactants.

A. Solid-Phase Extraction

Solid-phase extraction (SPE) has gained importance for the extraction and isolation of surfactants from aqueous samples over the last few years. It has advantages of very low solvent consumption, little time consumption, easy handling, and a broad spectrum of different exchange resins with regard to polarities and functionalities. SPE works on the principle that organic substances adsorb from aqueous solutions to exchange resin. The adsorbed substances are then eluted with small amounts of organic solvents.

1. Anionic Surfactants

Anionic surfactants are efficiently concentrated at reversed-phase (RP) materials consisting of silica gel modified with alkyl groups of different chain lengths or graphitized carbon black (GCB). LAS have been extracted by C2-,[8] C8-,[3,9] or C18-silica gels,[10–13] as well as by GCB stationary phases.[14]

The RP cartridges are usually rinsed with methanol/water before the adsorbed LAS is eluted with methanol. For further purification, these extracts are passed through an anionic exchange resin.[12,15] After passing water samples through GCB cartridges coextracted matrix substances are washed out by a formic acid-acidified solvent mixture. LAS are then eluted by CH_2Cl_2:methanol (9:1) containing 10 m*M* tetramethylammoniumhydroxide.[16] C_2 resins have been applied for the enrichment of alcohol ethoxy sulfates (AES) and alcohol sulfates (AS) from water. Afterwards the analytes have been eluted with methanol/2-propanol (8:2).[17] Marcomini et al. have developed a method for the simultaneous determination of LAS and nonylphenol ethoxylates (NPEO) as well as their metabolites sulphophenyl carboxylates (SPC) and nonylphenoxy carboxylates (NPEC), respectively. Wastewater or river water samples are adjusted to pH 2 with HCl and passed through C18 cartridges. The adsorbed analytes are eluted with methanol.[18] Solid-phase micro-extraction (SPME) has been proved an alternative technique for extraction of LAS. Desorption of the extracted LAS from a Carbowax/Templated Resin-coated fiber in a specially designed SPME–LC interface enable the analysis with HPLC and ESI–MS.[19]

2. Nonionic Surfactants

Nonionic surfactants like alkylphenol ethoxylates (APEO) and their biodegradation products alkylphenol diethoxylate (AP2EO), alkylphenol monoethoxylate (AP1EO), and AP are isolated from aqueous solutions with a number of different stationary phases. Kubeck et al.[20] used C18 cartridges to adsorb NPEO, but first the water samples were passed through a mixed-bed ion exchange resin to remove all ionic species. For SPE of alcohol ethoxylates (AEO) C8 cartridges have been successfully applied from which the surfactants were eluted with methanol followed by 2-propanol.[21] Alkyl polyglucosides (APG) are becoming more and more interesting because of their production from renewable raw materials (fatty alcohol and glucose or starch) and their good toxicological, dermatological, and ecological properties. Of the few analytical methods presently available for APG, C18 cartridges are employed to enrich APG from water. Desorption from the cartridges is carried out with methanol.[22] Amberlite XAD-2 and XAD-4 have been proved to extract APEO and AP from water samples with high selectivity. These resins are based upon a styrene structure cross-linked with divinylbenzene. Water samples saturated with NaCl are passed through a XAD-2 column, and the analytes are eluted with acetone/water (9:1) with a recovery of 91 to 94%.[23] Isolute ENV is a hyper-cross-linked hydroxylated poly(styrene–divinylbenzene) copolymer, which allows the extraction of APEO/AP from large sample volumes with similar recoveries compared to C18 cartridges.[24] GCB is a nonporous material with positively charged active centers on the surface. Therefore, it is employed for separation of NPEO/nonylphenol (NP) from acidic NPEC as well as LAS and SPC. The procedure involves the stepwise desorption of the adsorbed analytes from the GCB cartridges with different solvent systems.[25,26] SPME coupled to GC–MS was developed for analysis of NP in water. Optimal conditions were found with an 85 μm polyacrylate fiber, 1 g NaCl per 9.5 ml water sample, pH 2 and an extraction time of 1 h at 30°C.[27]

B. Liquid–Liquid Extraction

The attempt to extract surfactants directly from aqueous solutions into organic solvents without auxiliary measures is usually futile. The tendency of surfactants to concentrate at phase boundaries leads to the formation of emulsions and phase separation becomes very difficult.

Formation of lipophilic ion pairs between ionic surfactants and suitable counterions, however, avoids these problems. Hon-Nami et al.[28] developed a method of extracting LAS as these ion pairs with methylene blue using chloroform from river water. This method is also often applied to purify LAS extracts. Afterwards the ion pair is cleaved on a cationic exchange resin.[29]

Analogously to anionic surfactants, cationic surfactants are also extracted, e.g., into methylene chloride by the formation of ion pairs with LAS.[4,30]

Because of the formation of emulsions, the liquid–liquid extraction (LLE) of nonionic surfactants, e.g., APEO, is restricted to these less surface-active metabolites, i.e., APEO with one to three ethoxy units, APEC, and AP. Noncontinuous LLE of water samples with methylene chloride using a separatory funnel has been applied for NP and NPEO (one to three ethoxy units).[31,32] In addition, an ultrasonic bath has been shown to be suitable for the LLE of APEOs and AEOs form water samples.[33] Continuous LLE (percolation) has been successfully used for concentration of short-chained APEO and AP too.[31] Steam distillation/solvent extraction using an apparatus designed by Veith and Kiwus[34] is a sophisticated method of concentrating steam-distillable AP and APEO (one to three ethoxy units) from water samples.[2,35] AEOs have been efficiently extracted by combination of reflux hydrolysis with sulfuric acid and steam distillation with a "Karlsruhe Apparatus."[36]

C. Solvent Sublation

Solvent sublation is a technique capable of selectively concentrating surfactants free from nonsurface-active materials. In the original procedure by Wickbold,[37] the water sample is placed into a sublation apparatus and overlaid by ethyl acetate. Then ethyl acetate-saturated nitrogen is purged through the liquids whereupon surfactants are enriched at the gas–liquid phase boundary and carried by gas stream into the organic layer. This method has often been applied for the enrichment of nonionic surfactants and has now been standardized.[38] Waters et al.[39] optimized the Wickbold procedure and additionally purified the sublation extracts by passing them through a cation/anion exchanger.

Kupfer[40] applied the same sublation procedure for isolation of cationic surfactants. For separation of anionic and nonionic surfactants, the sublation extract is passed through a cation exchanger. Afterwards, the adsorbed cationic surfactants are eluted with methanolic HCl.

D. Solid–Liquid Extraction

The method of choice for the extraction of surfactants from sewage sludges or sediments is solid–liquid extraction (SLE). In most cases, however, further purification of the extracts is necessary prior to quantitative determination. LAS are desorbed from sewage sludge either in a noncontinuous procedure by extraction into chloroform as ion pairs with methylene blue[41] or in a continuous procedure by the application of a Soxhlet apparatus and addition of solid NaOH to the dried sludge in order to increase extraction efficiency.[6] Heating of sludge or sediment samples in methanol under reflux for 2 h is also sufficient to extract LAS with recoveries of 85%.[3]

Extraction of APEO from solid matrices is performed in the same way as for LAS, i.e., Soxhlet extraction with methanol in combination with NaOH.[6] In addition to methanol, methanol:ethylene chloride (1:2)[23] and hexane[42] are used as extraction solvents. Steam distillation–solvent extraction is especially suitable for extraction of the APEO metabolites AP and APEO (one to three ethoxy units) from solid matrices.[2,43]

Quite drastic conditions are required to desorb cationic surfactants from solids. Extraction with methanolic HCl resulted in optimum recovery.[44,45] However, the extract has to be purified by extraction into chloroform in the presence of disulphine blue[44] or LAS.[45] Finally, cleavage of the ion pairs is done on ion exchangers. Hellmann[46] used an Al_2O_3 column to purify sewage sludge extracts. In this way, he was not only able to separate impurities but also to elute cationic and anionic surfactants stepwise with different solvent systems.

Supercritical fluid extraction (SFE) turns out to be very effective in the isolation of all three surfactant classes from solid matrices. While supercritical CO_2 alone did not affect significant recovery of surfactants, the addition either of modifiers or of reactants resulted in nearly quantitative recoveries. Thus, LAS and secondary alkane sulphonates (SAS) are extracted from sewage sludges in the form of tetrabutylammonium ion pairs.[47] Lee et al. extracted NP from sewage

sludge spiked with acetic anhydride and a base with supercritical CO_2. In this way NP is, *in situ*, converted into its acetyl derivative.[48] Ditallowdimethylammonium chloride (DTDMAC) is quantitatively extracted from digested sludges and marine sediments using supercritical CO_2 modified with 30% methanol.[49]

IV. DETERMINATION PROCEDURES

A. Colorimetry/Titrimetry

Nonspecific analytical methods, such as colorimetry and titrimetry, for determination of summary parameters were the earliest attempts to analyze surfactants in the environment. The main disadvantage of these methods is that, apart from surfactants, other interfering organic compounds from the environmental matrices are recorded too, resulting in systematic errors. Nevertheless, colorimetric and titrimetric methods are still widely used for determination of anionic, nonionic, and cationic surfactants because of their easy handling and the need for relatively simple apparatus.

1. Anionic Surfactants

Anionic surfactants are determined with methylene blue. The procedure is based on the formation of ion pairs between the cationic dye methylene blue and anionic surfactants, which are extractable into chloroform. The concentrations of anionic surfactants are determined colorimetrically at 650 nm after separation of the organic phase.[38] Other anionic organic compounds also form extractable complexes with methylene blue resulting in high values for methylene blue active substances (MBAS). On the other hand, cationic substances lead to low values because of formation of ion pairs with anionic surfactants. Osburn, therefore, eliminated interfering compounds by several clean-up steps. Concentration of all organic compounds on an XAD-2 resin eliminates inorganic salts; the following anion exchange step separates all interfering cationic surfactants.[50]

2. Nonionic Surfactants

The bismuth active substances (BiAS) method for the determination of nonionic surfactants with barium tetraiodobismuthate ($BaBiI_4$, modified Dragendorff reagent) is used in the standardized (DIN-Norm) procedure in Germany,[38] as well as in other countries. Ba^{2+} as a hard Lewis acid forms cationic coordination complexes with the polyethoxylate chain of the nonionic surfactants, which are precipitated by $[BiI_4]^{2-}$ in the presence of acetic acid. The orange precipitate is then dissolved with ammonium tartrate solution, and the released bismuth ions are determined by potentiometric titration with pyrrolidinedithiocarbamate solution.[38,51] Waters et al.[39] optimized the BiAS procedure by introduction of a cation/anion exchange clean-up of the sublation extracts. The BiAS procedure fails to determine ethoxylates with less than five ethoxy units because these compounds are not precipitated by barium tetraiodobismuthate. Thus, this procedure is not suitable for determination of APEO metabolites, i.e., the shorter APEO and AP.[31]

3. Cationic Surfactants

Cationic surfactants form ion pairs with suitable anionic dyes that are extractable into organic solvents. The anionic dye most widely used is disulphine blue. After extraction of the ion pair into chloroform the extinction is determined at 628 nm. The presence of anionic surfactants results in serious interferences, and therefore they have to be separated by anion exchange before the addition of disulphine blue.[52,53] The determination of cationic surfactants is hampered by some problems not encountered with MBAS. In particular, cationic surfactants are strongly adsorbed to almost any surface, so that all apparatus has to be specially pretreated.

B. High-Performance Liquid Chromatography (HPLC)

The ultimate goal in environmental analysis is the quantification of individual compounds separated from all their isomers and/or homologues. Chromatographic methods like HPLC, GC, or SFC are amongst the most powerful analytical instruments with regard to separation efficiency and sensitivity. Because of the low volatility of surfactants, HPLC is used far more often than GC. Since the launch of atmospheric pressure ionization (API) interfaces, LC–MS coupling is increasingly used for determination of surfactants (Table 30.5).

1. Anionic Surfactants

The majority of HPLC applications in determination of anionic surfactants are only concerned with the analysis of LAS, which are surfactants in the largest quantities in present detergent formulations. Individual homologues of LAS are typically separated on reversed-phase columns with a $NaClO_4$-modified mobile phase using UV or fluorescence detection. Application of C18 columns with gradient elution results in the separation not only of the LAS homologues but also of their isomers (Figure 30.1).[3,6,54,55] While information on individual isomers could be valuable for studies on the biological degradation of LAS this is a hindrance in routine trace analysis because of the high number of peaks resulting in higher detection limits. By the use of short-chain alkyl bonded reversed phases like C8[6,11,56] and C1 columns[57] or long-chain C18 phases with isocratic elution,[58,59] however, the isomers of every single LAS homologue are eluted as one peak. Thus, the interpretation of the chromatograms becomes easier because of a greatly reduced number of peaks. Fluorescence detection is more selective and more sensitive than UV detection resulting in lower detection limits. Detection limits of 2 μg/l for water using fluorescence detection[57] compared to 10 μg/l for water using UV detection[3] have been reported for determination of LAS by HPLC.

For the analysis of aliphatic anionic surfactants by HPLC other detection systems than UV or fluorescence detection have to be used because of the lack of chromophoric groups. Refractive index detection and conductivity detection provide a solution for this type of anionic surfactants but their detection limits are rather high and gradient elution is not usually possible. Another possibility is the application of indirect photometric detection which is based on the formation of ion pairs between UV-active cationic compounds, such as *N*-methylpyridinium chloride, used as mobile-phase additives and the anionic surfactants followed by UV detection.[60] Gradient elution with indirect photometric detection is possible in principle but the detection limits increase considerably.[61] A selective and sensitive method for the determination of aliphatic anionic surfactants is reversed-phase HPLC combined with postcolumn derivatization and fluorescence detection.[62] After HPLC separation of the surfactants on a C1 column an UV-active cationic dye is added to the eluate in order to form fluorescent ion pairs. Then $CHCl_3$ is added to the eluent stream as the extraction solvent for the ion pairs. The two phases are conducted through a sandwich-type phase separator where the major part of the organic phase is separated. Finally, the amount of ion pairs extracted into $CHCl_3$ is determined by a fluorescence detector.

Simultaneous determination of LAS and their main metabolites SPC was enabled by LC–MS with an electrospray ionization (ESI) interface. Problems with high salt loads of the mobile phase due to the ion pair reagent have been overcome by incorporation of a suppressor between the LC column and the mass spectrometer.[63] A LC–MS method for the determination of AES and AS was introduced by Popenoe et al.[17] After separation on a C8 column the analytes are determined by ion spray LC–MS. The mass chromatograms obtained give information about both the distribution of the alkyl homologues and distribution of the oligomeric ethoxylates as well.

2. Nonionic Surfactants

The main nonionic surfactants are AEO, APEO, and recently APG. The hydrophobic part of AEO consists of *n*-alkanols with chain lengths between 8 and 20, typical AP are branched-chain octyl- or

TABLE 30.5
HPLC Methods for the Analysis of Surfactants

Compound	Matrix	Column	Mobile Phase	*Derivatization* Detector	LOD [μg/l]	Ref.
			Anionic Surfactants			
LAS	Sewage sludge	C-18 (Spherisorb S3 ODS II, 3 μm), 250 × 4 mm C-8 (LiChrosorb RP8, 10 μm), 100 × 4 mm	A: iPrOH B: H_2O C: CH_3CN:H_2O (45:55) + 0.02 *M* $NaClO_4$	UV (225 nm) or Fluorescence (230/295 nm)[a]	80 ng	6
LAS	River water	C-18 (μ-Bondapak, 10 μm), 300 × 3.9 mm	A: H_2O + 0.15 *M* $NaClO_4$ B: CH_3CN:H_2O (70:30) + 0.15 *M* $NaClO_4$	UV (230 nm)	10	3
LAS	Sea water	C-18 (Spherisorb S3 ODS II, 3 μm), 250 × 4 mm	A: CH_3CN B: CH_3CN:H_2O (25:75) + 10 g/l $NaClO_4$	Fluorescence (225/295 nm)[a]	-	54
LAS	River water	C-18 (Chromasil), 250 × 3.1 mm	A: CH_3CN:H_2O (50:50) B: CH_3CN:H_2O (70:30) Both containing 0.1 *M* $NaClO_4$	UV (225 nm)	100 (C-11 LAS)	55
LAS, SPC	Sea water	C-8 (LiChrosorb RP-8, 10 μm), 250 × 4.6 mm, gradient elution	A: MeOH:H_2O (80:20) + 1.25 m*M* TEAHS[b] B: H_2O	Fluorescence (225/295 nm)[a]	0.2	11
LAS	River water, waste water	C-8 (C_8-DB, 5 μm), 250 × 4.6 mm	H_2O:MeOH (20:80) + 0.1 *M* $NaClO_4$ Isocratic elution	Fluorescence (225/290 nm)[a]	0.8	56
LAS	River water, waste water	C-1 (Spherisorb, 5 μm), 250 × 4 mm	THF:H_2O (45:55) + 0.1 *M* $NaClO_4$ Isocratic elution	Fluorescence (225/290 nm)[a]	2.0	57
LAS, SPC	Waste water	C-8 (Eclipse XDB, 3.5 μm), 150 × 3 mm	MeOH:0.01 *M* CH_3COONH_4 (75:25) Isocratic elution	Fluorescence (220/290 nm)[a]	5.0	19

LAS, SPC	River water	C-18 (LiChrospher 100 RP-18, 5 μm), 250 × 4 mm	A: CH_3CN B: 0.008 *M* KH_2PO_4 + H_3PO_4 (pH 2.2)	UV (215 nm)	20 (SPC)	13
LAS, SPC	River water	C-18 (Hypersil ODS, 5 μm), 250 × 2.1 mm	A: H_2O + 5 m*M* TEAAc B:CH_3CN:H_2O (80:20) + 5 m*M* TEAAc	ESI-MS (suppressor before MS), full-scan *m/z* 170–400		63
SAS, AS	Water	C-1 (Spherisorb S5-C1), 40 × 4 mm	A: 0.01 *M* trisodium citrate + 5 μ*M* HCl B: CH_3CN:H_2O (50:50) + 0.01 *M* trisodium citrate + 5 μ*M* HCl	*Post-column derivatization with CTBI*[c] Fluorescence (285/485 nm)[a]	3–30 ng	62
AS, AES	Waste water	C-8 (Baker, 5 μm), 250 × 4.6 mm	A: CH_3CN:H_2O (20:80) + 0.3 m*M* CH_3COONH_4 B: CH_3CN:H_2O (80:20) + 0.3 m*M* CH_3COONH_4	Ion spray-MS	-	17
			Nonionic Surfactants			
AP, APEO	Waste water	C-8 (LiChrosorb RP8, 10 μm), 250 × 3 mm	MeOH:H_2O (8:2) Isocratic elution	UV (277 nm)	0.5	43, 2
AP, APEO	Waste water	NH_2 (LiChrosorb- NH_2, 10 μm), 250 × 4.6 mm	A: hexane B: hexane:iPrOH (1:1)	UV (277 nm)	0.5	2
APEO	Waste water	NH_2 (Hypersil APS, 3 μm), 100 × 4 mm	A: hexane:iPrOH (98:2) B: iPrOH:H_2O (98:2)	UV (277 nm)	1.0	64
APEO	Waste water	NH_2 (Zorbax NH_2), 250 × 4.6 mm	A: MTBE[d] + 0.1% acetic acid B: CH_3CN:MeOH (95:5) + 0.1% acetic acid	Fluorescence (230/302 nm)[a]	0.2 ng	65

Continued

TABLE 30.5
Continued

Compound	Matrix	Column	Mobile Phase	*Derivatization* Detector	LOD [μg/l]	Ref.
APEO, LAS	Waste water	C-18 (LiChrosopher RP-18, 5 μm), 250 × 4 mm	A: MeOH B: H_2O + 0.14 g/l trifluoroacetic acid C: H_2O + 14 g/l $NaClO_4$ D: H_2O	Fluorescence-detection[a]	-	18, 66
NPEO, AEO	Waste water	C-18 (Phenomex Luna, 5 μm), 250 × 2 mm	A: H_2O B: MeOH Both containing 5 m*M* CH_3COONH_4 and 0.5 m*M* trichloroacetic acid	ESI-MS: *m/z* 300–1400	1–10	33
NPEO, NP	Waste water	Poly(vinylalcohol) (Shodex MSpak GF-310 4D), 150 × 4.6 mm	A: H_2O B: MeOH Both containing 5 μ*M* CH_3COONH_4	$[^{13}C_6]$NP and $[^{13}C_6]$NPEO as surrogate standards ESI-MS	1–55 pg	32
OPEO, NPEO, OP, NP	River water	Poly(vinylalcohol) (Shodex MSpak GF-310 4D), 150 × 4.6 mm	A: H_2O:MeOH (50:50) + 10 m*M* CH_3COONH_4 B: MeOH	ESI-MS/MS: e.g. *m/z* 219 → 133 (NP), *m/z* 205 → 133 (OP) in the electrospray negative mode	0.1–9 pg	24
NPEO, AEO, LAS	Waste water	C-18 (Nucleosil C_{18}, 5 μm), 250 × 4.6 mm	A: H_2O:CH_3CN (20:80) + 0.5 m*M* CH_3COONH_4 B: H_2O:CH_3CN (80:20) + 0.5 m*M* CH_3COONH_4	APCI-MS and -MS/MS	-	71, 72
AEO	Waste water	C-18 (μBondapak C_{18}), 300 × 3.9 mm	A: H_2O B: MeOH	*Derivatization with phenylisocyanate* UV (235 nm)	100	67, 68, 69
APG	Technical APGs	C-18 (LiChrospher RP-18)	MeOH:H_2O (80:20) Isocratic elution	Refractive index	-	70

Cationic Surfactants						
DTDMAC, DSDMAC	River water	NH_2/CN (Partisil PAC, 5 or 10 μm), 250 mm	$CHCl_3$:MeOH (80:20)	Conductivity	3–16	4, 73, 74
			Isocratic elution			
DTDMAC, DSDMAC	River water	NH_2/CN (Partisil PAC, 10 μm), 250 × 4.6 mm	A: $CHCl_3$	*Post-column ion pair formation with methyl orange or DAS*[e]	0.01 by use of DAS[e]	45, 49, 75
			B: MeOH	Fluorescence (383/452 nm)		
			C: CH_3CN			
DTDMAC, DEEDMAC, DEQ	River water	NH_2/CN (Partisil PAC, 5 μm), 150 × 1 mm	A: $CHCl_3$ + 4% CH_3CN	ESI-MS	-	30
	Waste water		B: MeOH + 2% CH_3CN			

[a] Fluorescence ($\lambda_{ex}/\lambda_{em}$).

[b] TEAHS: Tetraethylammonium hydrogensulfate.

[c] CTBI: 1-Cyano-[2-(2-trimethylammonio)ethyl]benz(f)isoindole.

[d] MTBE: Methyl *tert*-butyl ether.

[e] DAS: 9,10-Dimethoxyanthracene-2-sulfonate.

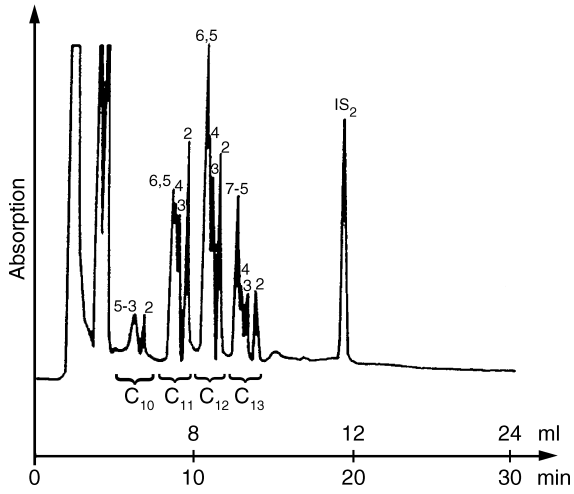


FIGURE 30.1 Reversed-phase high performance liquid chromatogram of LAS from digested sludge. C_{10}, C_{11}, C_{12}, and C_{13}: LAS homologues; the numbers above the LAS peaks indicate the position of the phenyl group on the alkyl chain; IS_2: 3-pentadecylbenzenesulphonate (3-C_{15}-LAS). (From Marcomini, A. and Giger, W., *Anal. Chem.*, 59, 1709–1715, 1987.)

nonylphenol, and APG typically have alkyl groups with chain lengths in the range of 8 to 18. The degrees of polymerization of the polyethoxylate chains of AEO and APEO vary from 3 to 40 ethoxy units, while the average polymerization degree of APG is in the range of 1.3 to 1.7 moles glucose per mole of fatty alcohol. Consequently, HPLC separation of these surfactants into individual compounds is a two-dimensional problem best solved by the use of different HPLC stationary phases. Reversed-phase columns separate these compounds by their interaction with the hydrophobic alkyl chains, only eluting the hydrophilic oligomers as a single peak, while normal phase columns separate them by interaction with the hydrophilic polyethoxylate and polyglucoside chains without resolving the hydrophobes. Giger et al.[2,43] described a reversed-phase HPLC method for the determination of APEO on a C8 column with isocratic water/methanol elution and UV detection at 277 nm. Under these conditions, the homologous compounds octylphenol ethoxylates (OPEO) and NPEO are separated into two peaks. Normal phase HPLC is mostly applied to obtain information about the ethoxylate chain distribution of APEO. Aminosilica columns with gradient elution and UV detection are well suited to determine the individual oligomers of APEO.[2,6,64] An increase in sensitivity and selectivity for APEO is attained using a fluorescence detector. Thus, each single oligomer of APEO is determined by normal phase HPLC and fluorescence detection with a minimum detection of 0.2 ng.[65] Fluorescence detection is also used for the simultaneous determination of LAS and APEO as well as these corresponding metabolites SPC and NPEC, respectively, by reversed-phase HPLC and gradient elution.[18,66]

AEO can be sensitively determined in the form of these corresponding UV-active phenylisocyanate derivatives by UV detection. In this case, the residue of the extraction of a water sample or a solid matrix is dissolved in dichloromethane or dichloroethane. This solution is mixed with phenylisocyanate as well as 1-octanol and/or 1-eicosanol as internal standards and heated to 55 to 60°C for 45 to 120 min. Then the AEO derivatives are separated either by reversed-phase HPLC with regard to different alkyl chain lengths[67–69] or by normal phase HPLC with regard to different ethoxylate oligomers.[67,69] The addition of the internal standard is imperative for quantitative determination because derivatization is not completed even after 2 h.[69]

HPLC analysis of APG is carried out with C8[22] or C18 columns[70] by use of a refractive index detector[70] or a conductivity detector after the addition of 0.3 mol/l NaOH to the eluate in a postcolumn reactor.[22]

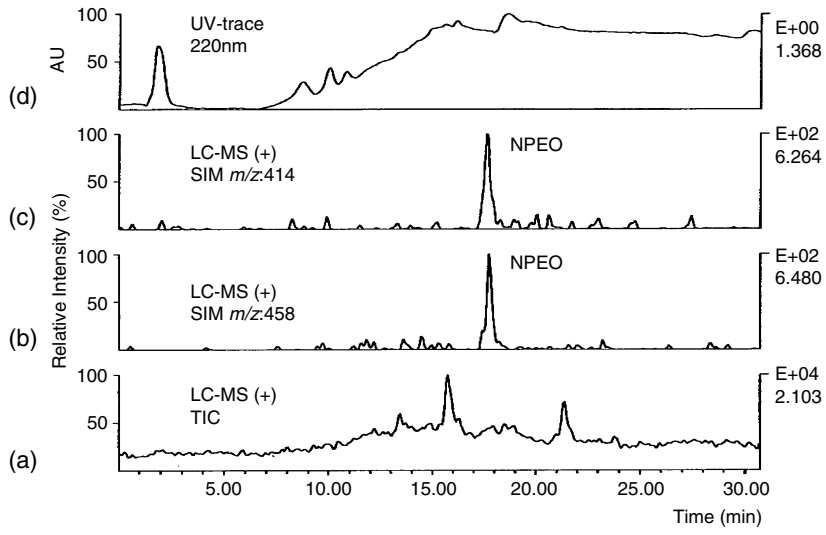


FIGURE 30.2 LC–APCI–MS total ion current chromatogram of wastewater (a); LC–MS mass trace *m/z* 458 (b); LC–MS mass trace *m/z* 414 (c); UV trace (220 nm) (d). (From Li, H. Q., Jiku, F., and Schröder, H. F., *J. Chromatogr. A*, 889, 155–176, 2000.)

Several LC–MS methods using an ESI interface have been published for the analysis of APEO and AEO. The formation of crown ether-type complexes between the ethoxylate chain and cations like NH_4^+ or Na^+ leads to efficient ion formation of the APEO and AEO surfactants during the electrospray process.[24,32,33] By use of a C-18 HPLC column NPEO and AEO are separated according to these aliphatic chain lengths. In the subsequent MS analysis, coeluting ethoxylate homologues are individually detected because of their mass differences of 44 mass units (CH_2CH_2O, *m/z* 44).[33] The comprehensive analysis of APEO and AP by LC–ESI–MS is enabled in a single chromatographic run by mixed-mode HPLC, using a Shodex MSpak GF-310 4D gel filtration column. This column operates with size-exclusion and reversed-phase mechanisms.[24,32] Complex water samples have been analyzed by LC–APCI–MS–MS in order to characterize the different surfactant classes (APEO, AEO, LAS) with the help of parent-ion and neutral-loss scans (Figure 30.2).[71,72]

3. Cationic Surfactants

DTDMAC and distearyldimethylammonium chloride (DSDMAC), which have long been amongst the most important cationic surfactants, are traditionally analyzed by normal phase HPLC with conductivity detection.[4,73,74] However, with conductivity detection an isocratic elution mode is mandatory, resulting in a steady broadening of the peaks with increasing retention time thus leading to higher detection limits. An alternative method for the quantitative analysis of cationic surfactants is the combination of HPLC separation with postcolumn ion pair formation and fluorescence detection.[45,49,75] Analogous to the method described for anionic surfactants (see above), an UV-active anionic dye is added to the HPLC eluate. The ion pairs formed are extracted online into a nonpolar organic phase in a phase separator and detected by a fluorescence detector. The application of LC–ESI–MS has enabled the homologue-specific analysis of esterquats and DTDMAC in environmental samples.[30]

C. Gas Chromatography (GC)

As a separation technique GC is inherently more powerful than HPLC; however, it is limited by the volatility of the compounds to be analyzed. For this reason, only nonionic surfactants with

low degrees of ethoxylation are amenable to direct determination using GC. High-molecular nonionic surfactants as well as ionic surfactants must be derivatized prior to GC analysis in order to transform them into more volatile compounds. Apart from the flame ionization detector (FID), MS is increasingly becoming the dominant determination method for surfactants in environmental matrices. MS is not only a very sensitive and selective detection method but also provides valuable information on the molecular weight and structure of separated compounds (Table 30.6).

1. Anionic Surfactants

GC analysis of LAS is only possible after derivatization into volatile derivatives. Desulfonation of LAS in the presence of strong acids like phosphoric acid leads to linear alkylbenzenes (LAB). The identification of every single LAB isomer by GC–FID is achieved with detection limits lower than 1 μg/l.[76] In an alternative derivatization method, LAS are converted into their alkylbenzene sulfonyl chlorides by PCl_5, which can be directly analyzed by GC–FID.[41] Derivatization reactions for aliphatic anionic surfactants have mainly been described for product analysis. Among the very few methods for environmental analysis, the derivatization of alkyl sulfates to their corresponding trimethylsilylesters followed by determination with GC–FID is mentioned here.[77]

Several GC–MS methods are described for LAS in the literature. McEvoy et al. accomplished GC analysis by formation of the corresponding sulfonyl chlorides and subsequent mass spectrometric detection employing electron impact ionization (EI) and chemical ionization (CI) modes. The mass chromatograms obtained are complementary with regard to their qualitative and quantitative information. In the EI modus the mass spectra are characterized by fragment ions, which allow conclusions to be drawn on the distribution of LAS isomers, whereas CI-induced mass spectra give very reliable information on homologous distributions due to the presence of protonated molecular ions $(M + 1)^+$.[41] In other GC–MS methods LAS are converted in a two-step derivatization procedure to the corresponding trifluoroethyl sulfonate derivatives which are analyzed by GC–MS with EI and low-pressure CI modes[78,79] or with negative chemical ionization (NCI) mode in order to enhance sensitivity and selectivity due to the high electron affinity of the CF_3 group.[9] Direct derivatization in the hot injection port is carried out with LAS–tetraalkylammonium ion pairs to form the corresponding alkyl esters, which are subsequently determined by GC–MS.[14,47] Suter et al. developed a GC–MS–MS method to differentiate LAS and branched alkylbenzenesulfonates (ABS). Despite partial overlapping of LAS and ABS homologues, tandem mass spectrometric detection enabled the homologue-specific determination of these compounds due to their different fragmentation behaviors (Figure 30.3).[79]

2. Nonionic Surfactants

APEO analysis by GC without derivatization has been mainly used on the more volatile biodegradation products like NPEO (one to four ethoxy units) and NP. Using capillary columns a complex pattern is obvious for every ethoxylate oligomer, indicating that each single alkyl chain isomer is separated.[31,80] Quantification is performed by the addition of internal standards with a detection limit of 10 μg/l.[31] Derivatization of APEO not only increases their volatility but also, by an intelligent choice of derivatization reagent, more specific or sensitive detectors can be used. Thus, using perfluoroacid chlorides to derivatize NPEO the resulting perfluoroesters can be detected with the very sensitive electron capture detector (ECD) achieving detection limits lower than 1 μg/l.[81]

Because of the low volatility of APG, high-temperature GC with temperature programs up to 400°C in combination with silylation prior to GC analysis is required for these determination. The GC system allows detection of the separated oligomeric glucosides up to five units. While monoglucosides are well separated into these individual isomers, glucosides with higher degrees of polymerization are not resolved.[22]

TABLE 30.6
GC Methods for the Analysis of Surfactants

Analyte	Matrix	Injector	Column	Oven Program	*Derivatization* Detector	LOD [μg/L]	Ref.
			Anionic Surfactants				
LAS	River water	Splitless (1 μl), 275°C	OV-101 (30 m × 0.5 mm)	140°C, 3°C/′–240°C (4′)	*Desulfonation with phosphoric acid* FID	1.0	76
LAS	Sewage sludge	Splitless (0.5–1 μl), 275°C	Fused silica coated with PS 255 (19 m × 0.31 mm)	50°C, 4°C/′–300°C	*Formation of sulfonyl chlorides with PCl_5* FID	-	41
LAS	River water, waste water	230°C	DB-5 (15 m × 0.25 mm, 0.25 μm film)	125°C (1′), 5°C/′–230°C (5′)	*Two-step PCl_5 - trifluoroethanol derivatization* MS (NCI): SIM *m/z* 380, 394, 408, 422, 436	1.0	9
LAS, SAS	Sewage sludge	Split (1:7)	HP-5 (20 m × 0.2 mm, 0.33 μm film)	110°C, 10°C/′–220°C, 6°C/′–300°C	*Injection port derivatization with tetraalkylammonium salts* MS (EI): Full scan *m/z* 50– 400	-	47
LAS	River water	Large-volume (10–20 μl) direct sample introduction	DB-5MS (30 m × 0.25 mm, 0.25 μm film)	100°C (3′), 7°C/′–300°C (7′)	*Injection port derivatization with tetraalkylammonium salts* MS (EI): Full scan *m/z* 50–550	0.1	14
LAS, SPC	River water	Splitless (1 μl) 250°C	DB-5MS (30 m × 0.25 mm, 0.25 μm film)	60°C (2′), 8°C/′–180°C, 3°C/′–230°C, 10°C/′–250°C (10′)	*Two-step thionyl chloride - trifluoroethanol derivatization* MS (EI): Full scan *m/z* 50–500 MS (CI): Methane as reagent gas	0.01	78
LAS, ABS	LAS and ABS standards	On-column (1 μl)	Fused silica coated with PS089 (15 m × 0.25 mm)	60°C, 8°C/′–180°C, 3°C/′–230°C	*Two-step thionyl chloride - trifluoroethanol derivatization* MS (CI): Isobutane as reagent gas, full scan *m/z* 80–500 MS/MS (CI): Argon as collision gas, *m/z* 295 → 167 (LAS), *m/z* 295 → 181 (ABS)	-	79
AS	Waste water	Splitless (1 μl) 200°C	Rt_x − 1 (60 m × 0.25 mm, 0.25 μm film)	50°C (1′), 10°C/′–215°C (20′)	*Silylation with BSTFA*[a] + 1% *TMCS*[b] FID	1 ng	77

Continued

TABLE 30.6
Continued

Analyte	Matrix	Injector	Column	Oven Program	*Derivatization* Detector	LOD [μg/L]	Ref.
			Nonionic Surfactants				
NPEO, NP	Waste water	Splitless (1–2 μl), 250°C	Glass capillary coated with OV-73 (15 m × 0.3 mm)	50°C, 2°C/′–280°C	FID	10	31,80
NPEO, NP	Waste water	Splitless (1–2 μl) 280°C	Glass capillary coated with OV-1 (20 m × 0.3 mm)	50°C, 3°C/′–270°C	MS (EI): Full scan *m/z* 45–480	-	35, 2
NPEO, NP	Waste water	Splitless (2 μl) 250°C	SGE BP-1 (25 m × 0.22 mm, 0.25 μm film)	80°C (1′), 30°C/′– 210°C, 10°C/′–300°C (15′)	*Derivatization with pentafluorobenzoyl chloride* MS (EI) MS (CI): methane as reagent gas	0.1 (NP) 0.2–1 (NPEO)	81
OPEO, OP, AEO	Waste water	-	DB-5 (30 m × 0.25 mm, 0.25 μm film)	70°C (1′), 3°C/′–300°C (10′)	MS (EI): Full scan *m/z* 45–500 MS (CI): methane as reagent gas	-	82, 83
NP	Effluent water	Splitless 250°C	HP-5-MS (30 m × 0.25 mm, 0.25 μm film)	70°C (1′), 30°C/′–160°C, 5°C/′–240°C	*In situ derivatization with acetic anhydride during extraction* MS (EI): SIM *m/z* 107, 121, 135, 1613, 191, 262	0.1	48
NP	Biological samples	Splitless (2 μl), PTV[c]: 50°C (0.6′), 12°C/s–285°C	DB-5-MS (60 m × 0.25 mm, 0.25 μm film)	50°C (0.8′), 20°C/′–110°C (1′), 4°C/′–230°C, 20°C/′–285°C (20′)	MS (EI): SIM *m/z* 121, 135, 149, 163, 177, 191 (NP); *m/z* 107, 220 (4-n-NP)	15 ng (NP)	84
NPEO, NP, NPEC	River water, sewage effluent	Large-volume (10 μl) direct sample introduction	DB-5MS (30 m × 0.25 mm, 0.25 μm film)	100°C (5′), 8.5°C/′–280°C (15′)	*Derivatization of NPEC to the propyl esters* MS (EI): Full scan *m/z* 50–500 MS (CI): Methane or acetone as reagent gases	0.01	85
NP	Waste water	SPME, desorption at 280°C for 3 min	HP-5 MS (30 m × 0.25 mm, 0.25 μm film)	50°C (4′), 20°C/′–140°C (1′), 10°C/′–280°C (8′)	MS (EI): SIM *m/z* 107, 135 (NP), *m/z* 107, 220 (4-n-NP)	0.2–0.8	27

[a] BSTFA: Bis(trimethylsilyl)trifluoroacetamide.
[b] TMCS: Trichloromethylsilane.
[c] PTV: programmed temperature vaporization.

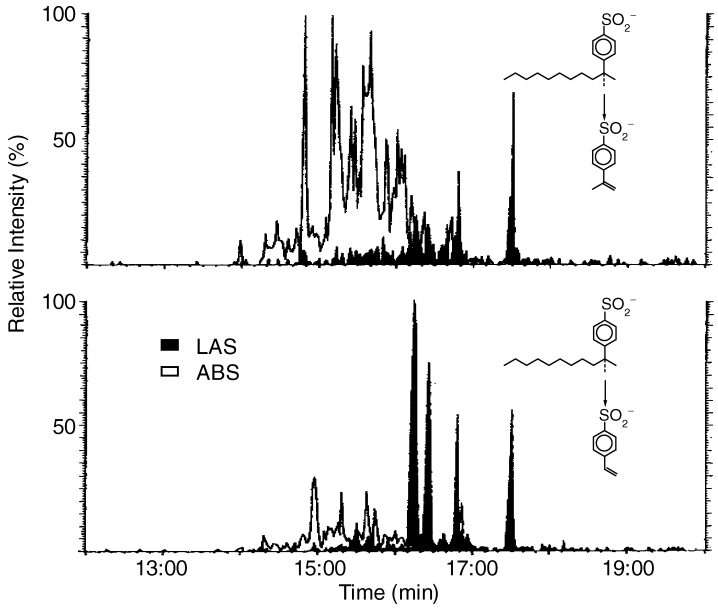


FIGURE 30.3 Superimposed reconstructed GC–MS–MS chromatograms of LAS obtained in the negative CI mode (parent ion *m/z* 295). The top trace corresponds to *m/z* 295 → 181 and the bottom trace to *m/z* 295 → 167, both recorded for C_{11}-LAS (solid peaks) and C_{11}-ABS (open peaks). (From Suter, M. J. F., Reiser, R., and Giger, W., *J. Mass Spectrom.*, 31, 357–362, 1996.)

GC–MS in the EI mode is well established for the identification and sensitive quantification of APEO and AP in environmental matrices.[31,35] Moreover, the fragmentation patterns in the mass spectra allow the structural characterization of the nonyl side-chain isomers; however, valuable information on the distribution of the oligomeric ethoxylates is lost due to very weak intensities of the molecular ions. The distribution of the ethoxylates is determined by CI–MS as a complementary method to EI–MS because of the presence of intensive adduct ions like, e.g., $(MH)^+$.[82,83] Lee et al. developed an *in situ* derivatization procedure in which NP is simultaneously extracted and converted into the corresponding acetyl derivatives. Quantification of NP from effluent water and sewage sludge is carried out by GC–EI–MS in the selected ion monitoring (SIM) mode with detection limits of 0.1 μg/l and 0.1 μg/g.[48] Günther et al. used an off-line coupling of normal phase HPLC and GC–EI–MS in the SIM mode to determine the individual isomers of NP in biological matrices. The HPLC step serves as clean-up of the extracts by collection of the NP containing eluate after passing the HPLC column.[84] Simultaneous determination of NPEO and their degradation products, NP and NPEC, is accomplished by GC–MS with EI, CI, and CI–MS–MS modes. Prior to the GC analysis NPEC is derivatized with propanol/acetyl chloride. Sensitivity has been increased by use of a large-volume direct sample introduction device.[85]

3. Cationic Surfactants

GC analysis is not of practical relevance for the determination of cationic surfactants in environmental matrices.

D. Supercritical Fluid Chromatography (SFC)

SFC combines the advantages of HPLC and GC into one method. Gases above their critical temperatures and conditions are used as mobile phases in order to separate analytes with a

TABLE 30.7
CE Methods for the Analysis of Surfactants

Analyte	Matrix	Injection	Column	BGE	Detection	LOD (μg/L)	Reference
			Anionic Surfactants				
LAS	Detergents	Large volume sample stacking: Sample injection (4 psi/90 sec) followed by injection of a buffer plug, stacking voltage of 15 kV at reversed polarity, voltage of 20 kV at normal mode	Fused silica (60 cm × 50 μm i.d., 50 cm eff.)	20 m*M* sodium tetraborate + 30% acetonitrile, pH 9.0	UV (200 nm)	2 to 10	90
LAS, SPC	Wastewater	Pressure (0.5 psi/20 sec)	Fused silica (80 to 100 cm × 75 μm i.d.)	10 m*M* ammonium acetate +16% CH_3CN, pH 9.8	ESI–MS: *i*PrOH:H_2O (80:20) + 0.1% ammonia as makeup solvent	4 to 23	91
LAS	Wastewater	Pressure (5 sec)	Fused silica (57 cm × 75 μm i.d., 50 cm eff.)	250 m*M* borate + 30% CH_3CN, pH 8.0	UV (200 nm)	1000	12
LAS, aliphatic anionic surfactants	Detergents	Pressure (50 mbar/4 sec)	Fused silica (48.5 cm × 75 μm i.d., 40 cm eff.)	NACE[a]: 15 m*M* naphthalene sulfonic acid, 15 mM triethyl-amine in CH_3CN: MeOH (75:25)	Indirect UV (280 nm)	—	94
LAS	Detergents, river water	Pressure (5 sec)	Fused silica (57 cm × 25, 50 or 75 μm i.d., 50 cm eff.)	A: 50 m*M* borate, pH 8.2 B: 100 m*M* phosphate + 30% CH_3CN, pH 6.8 C: 100 m*M* phosphate + 30% CH_3CN 20 m*M* α-CD[b], pH 6.8	UV (200 nm)	5900 (C11-LAS)	55,88
AS	Detergents	Pressure (5 or 10 sec)	Fused silica (57 cm × 75 μm i.d., 50 cm eff.)	20 m*M* salicylate + 30% CH_3CN, pH 6	Indirect UV (214 nm)		88

SAS, tetraalkylammonium halides	Surfactants	Pressure (25 mbar/12 sec)	Fused silica (60 cm × 50 μm i.d., 60 cm eff.)	20 m*M* NaF, 1 mM triethanolamine + 10% CH_3CN	Indirect conductivity	6000	89
			Nonionic Surfactants				
NPEO	Surfactants	Pressure (5 to 10 sec)	Fused silica (57 cm × 75 μm i.d., 50 cm eff.)	10 m*M* phosphate, 70 m*M* SDS[c] +35% CH_3CN, pH 6.8	UV (200 nm)	—	88
			Cationic Surfactants				
Alkylbenzylammonium salts, alkyl pyridinium salts	Detergents	Pressure (5 to 10 sec)	Fused silica (57 cm × 75 μm i.d., 50 cm eff.)	50 m*M* phosphate + 58% THF, pH 6.8	UV (200 nm)	—	92
Alkyltrimethylammonium salts	Detergents	Pressure (5 sec)	Fused silica (57 cm × 75 μm i.d., 50 cm eff.)	20 m*M* phosphate, 5 mM C_{12}-benzyl-DMA[d] +50% THF, pH 4.4	UV (214 nm)	—	93

[a] NACE: Nonaqueous CE.
[b] α-CD: α-Cyclodextrin.
[c] SDS: Sodium dodecyl sulfate.
[d] C_{12}-benzyl-DMA: Dodecylbenzyldimethylammonium salt.

conventional HPLC column. Under these conditions the supercritical fluids have densities of liquids while retaining the diffusion coefficients of typical gases. The universal and sensitive FID detector can be applied to SFC. Consequently, no derivatization of analytes is required, either to increase volatility or to increase detectability.

Until now applications of SFC have been limited to product analysis of, e.g., nonionic surfactants but here with great success.[86,87] No reports on the determination of surfactants in environmental matrices using SFC is known to the authors.

E. Capillary Electrophoresis (CE)

CE is a separation technique which uses empty capillaries to effect separation by the electrophoretic movement of charged compounds. Therefore, CE is not a chromatographic method in the strict sense. Recently CE has been applied for the separation and determination of all three surfactant classes (Table 30.7).

1. Anionic Surfactants

LAS are analyzed in river water by CE using UV detection. The efficiency of separating LAS homologues and isomers significantly depends on the addition of organic modifiers to the buffers. In phosphate and borate buffers without an organic modifier only one peak is obtained in the electropherogram for all LAS isomers and homologues.[55,88] The addition of 20 to 30% acetonitrile to the buffer leads to a separation of homologues and with buffers containing α-cyclodextrin (α-CD) even a complete separation of isomers is possible (Figure 30.4).[55,88] Aliphatic anionic surfactants can be determined by CE with indirect UV detection using salicylate as chromophore in the buffer[88] or indirect conductivity detection.[89] CE of LAS with large-volume sample stacking technique has been shown to improve the peak shapes, the efficiency, and the sensitivity.[90] CE–ESI–MS has been used for the simultaneous determination of LAS and their metabolites, SPC. Limits of detection of 4.4 to 23 μg/l could be reached for the quantification of LAS homologues.[91]

2. Nonionic Surfactants

Nonionic surfactants of the ethoxylate type are not so efficiently separated compared to ionic surfactants.[88] The complexity of the surfactant mixtures and the lack of charge leads to insufficient peak resolution and high detection limits.

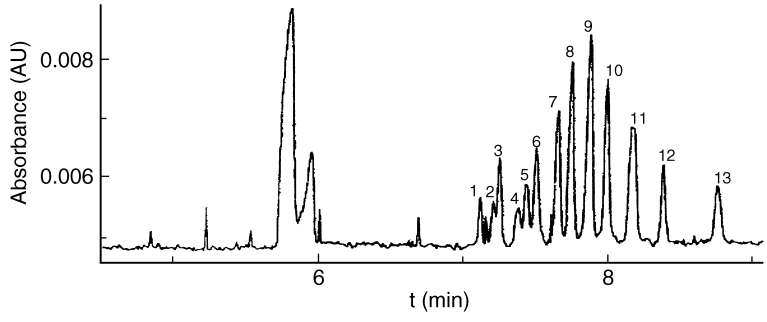


FIGURE 30.4 CE electropherogram of a LAS detergent (Marlon A-390), buffer: 100 m*M* phosphate, pH 6.8, 15 m*M* α-CD, 20% (v/v) acetonitrile. Numbered peaks correspond to LAS isomers (From Heinig, K., Vogt, C., and Werner, G., *J. Chromatogr. A*, 745, 281–292, 1996): (1) 2-C_{13}, (2) 3-C_{13}, (3) 2-C_{12}, (4) 4-C_{13}, (5) 3-C_{12}, 5-C^*_{13}, (6) 2-C_{11}, 5-C^*_{13}, 4-C^*_{12}, (7) 5-C^*_{13}, 4-C^*_{12}, (8) 3-C_{11}, 6-C_{13}, 4-C^*_{12}, (9) 4-C_{11}, 2-C_{10}, 5-C_{12}, 7-C^*_{13}, (10) 3-C_{10}, 6-C^*_{12}, 7-C^*_{13}, (11) 5-C_{11}, 4-C_{10}, 6-C^*_{12}, 7-C^*_{13}, (12) 6-C_{11}, (13) 5-C_{10} (∗denotes supposed).

3. Cationic Surfactants

Cationic surfactants are separated using direct UV detection[92] or indirect UV detection with a chromophore as electrolyte additive.[93] The addition of organic solvents as modifiers to the electrolytes is essential to obtain efficient separations because of the ability of cationic surfactants to adsorb onto the capillary surface.

F. Mass Spectrometry (MS)

MS is a reliable method for the determination of molecular weight distributions of homologous and/or oligomeric surfactants as well as for the determination of molecular structures, e.g., the position of side chains or the degree of branching. Soft ionization methods like fast atom bombardment (FAB) or field desorption (FD) are well suited for the formation of molecular ions of high molecular surfactants. For this reason, they are not only used in product analysis for the determination of molecular weight distributions but also in biodegradation studies of surfactants.

1. Anionic Surfactants

FAB–MS was successfully employed for the identification of LAS in groundwater. The mass spectra obtained from the samples, which were slurred in glycerol as matrix show molecular ions $(M)^+$ separated by 14 mass units corresponding to the different LAS homologues.[8] Triethanolamine or thioglycerol in combination with NaCl is alternatively used as matrix but then quasimolecular ions $(M + H)^+$ and $(M + Na)^+$, respectively, are formed.[95] Moreover, FAB spectra exhibit fragment ions, which are in part structure specific.[96] FD-MS spectra obtained in the positive or negative mode only contain quasimolecular ions while fragment ions are missing.[96] Therefore, FD spectra are well suited for determining the molecular weight distribution of surfactants but less suited for structure elucidation.

2. Nonionic Surfactants

FAB–MS spectra of APEO and AEO are preferentially obtained by thioglycerol saturated with NaCl as matrix due to the formation of strong $(M + Na)^+$ ions.[95,97,98] The characteristic appearance of these spectra is a series of $(M + Na)^+$ ions separated by 44 units corresponding to different degrees of ethoxylation. Cleavage of the alkyl constituents and the ethoxylate chains lead to fragmentation patterns in the lower mass range, which make it possible to elucidate the structures of nonionic surfactants. The clarity of FD–MS spectra due to the dominance of quasimolecular ions $(M + H)^+$ and missing fragment ions caused Levsen et al.[99] to monitor the biodegradation of NPEO in surface water. FD–MS is also used for the identification of APEO in water samples after separation by reversed-phase HPLC and collection of the APEO-containing eluate.[100,101]

3. Cationic Surfactants

Conventional ionization techniques like EI or CI are less well suited for the characterization of quaternary amines, which are the most common cationic surfactants. Because of their thermal instability and low volatility their corresponding mass spectra only show decomposition products and fragment ions which make it impossible to analyze environmental samples of unknown composition. By the use of FAB–MS and FD–MS, however, ionization of quaternary amines can be achieved without decomposition. FAB spectra are characterized by strong quasimolecular ions as well as structure specific ions.[95,102] FAB in combination with collisionally activated decomposition (CAD) in a tandem mass spectrometer enables a clear differentiation between quasimolecular and fragment ions, which is often difficult using FAB alone.[102] FD spectra of quaternary amines are dominated by quasimolecular ions as already described for other surfactant

types.[102] By combining FD and CAD in a tandem MS it is even possible to obtain fragment ions for the structure elucidation of individual cationic surfactants in environmental samples.[103]

Quantitative determinations of surfactants by FAB or FD–MS are rather difficult because of the need for isotopically labeled internal standards.

G. Infrared Spectroscopy (IR)

IR spectroscopy is used for the qualitative identification of surfactants and for differentiating between them and nonsurfactant compounds. Prior to IR spectroscopy, however, separation of the organic compound complex into different fractions, performed by, e.g., the use of thin-layer chromatography, is required to obtain meaningful spectra.[104,105] By comparing the IR spectra of the isolated fractions with IR spectra of standard compounds with regard to characteristic bands, the qualitative determination of surfactants in environmental samples is possible. The method is equally applicable to anionic,[105] nonionic,[104] and cationic surfactants.[106] The prerequisite for a clear identification of surfactants, however, is the availability of suitable standards. Moreover, considerable experience and knowledge are needed to interpret IR spectra of environmental samples.

H. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra regularly contain far more information on the molecular structure of the particular compound investigated than IR spectra. However, the complex compound mixture in environmental samples has to be thoroughly separated in order to obtain meaningful NMR spectra. Furthermore, the amount of analyte needed for NMR is relatively high; therefore, NMR spectroscopy is exclusively used in product analysis for the characterization of pure compounds and is of no importance in environmental analysis.

REFERENCES

1. EEC (European Economic Community) (73/404/EEC), Off. J.E.C. No. L 347/51, 1973.
2. Ahel, M. and Giger, W., *Anal. Chem.*, 57, 1577–1583, 1985.
3. Matthijs, E. and De Henau, H., *Tenside Surf. Det.*, 24, 193–199, 1987.
4. Wee, V. T. and Kennedy, J. M., *Anal. Chem.*, 54, 1631–1633, 1982.
5. Marcomini, A., Capri, S., and Giger, W., *J. Chromatogr.*, 403, 243–252, 1987.
6. Marcomini, A. and Giger, W., *Anal. Chem.*, 59, 1709–1715, 1987.
7. Marcomini, A., Capel, P. D., Liechtensteiger, T., Brunner, P. H., and Giger, W., *J. Environ. Qual.*, 18, 523–528, 1989.
8. Field, J. A., Barber, L. B. II, Thurman, E. M., Moore, B. L., Lawrence, D. L., and Peake, D. A., *Environ. Sci. Technol.*, 26, 1140–1148, 1992.
9. Trehy, M. L., Gledhill, W. E., and Orth, R. G., *Anal. Chem.*, 62, 2581–2586, 1990.
10. Kikuchi, M., Tokai, A., and Yoshida, T., *Water Res.*, 20, 643–650, 1986.
11. Leon, V. M., Gonzalez-Mazo, E., and Gomez-Parra, A., *J. Chromatogr. A*, 889, 211–219, 2000.
12. Heinig, K., Vogt, C., and Werner, G., *Analyst*, 123, 349–353, 1998.
13. Sarrazin, L., Arnoux, A., and Rebouillon, P., *J. Chromatogr. A*, 760, 285–291, 1997.
14. Ding, W. H. and Chen, C. T., *J. Chromatogr. A*, 857, 359–364, 1999.
15. Schöberl, P., Klotz, H., Spilker, R., and Nitschke, L., *Tenside Surf. Det.*, 31, 243–252, 1994.
16. Crescenzi, C., DiCorcia, A., Marchiori, E., Samperi, R., and Marcomini, A., *Water Res.*, 30, 722–730, 1996.
17. Popenoe, D. D., Morris, S. J. III, Horn, P. S., and Norwood, K. T., *Anal. Chem.*, 66, 1620–1629, 1994.
18. Marcomini, A., Di Corcia, A., Samperi, R., and Capri, S., *J. Chromatogr.*, 644, 59–71, 1993.
19. Ceglarek, U., Efer, J., Schreiber, A., Zwanziger, E., and Engewald, W., *Fresenius J. Anal. Chem.*, 365, 674–681, 1999.
20. Kubeck, E. and Naylor, C. G., *J. Am. Oil Chem. Soc.*, 67, 400–405, 1990.

21. Evans, K. A., Dubey, S. T., Kravetz, L., Dzidic, I., Gumulka, J., Mueller, R., and Stork, J. R., *Anal. Chem.*, 66, 699–705, 1994.
22. Steber, J., Guhl, W., Stelter, N., and Schröder, F. R., *Tenside Surf. Det.*, 32, 515–521, 1995.
23. Valls, M., Bayona, J. M., and Albaiges, J., *J. Environ. Anal. Chem.*, 39, 329–348, 1990.
24. Loyo-Rosales, J. E., Schmitz-Afonso, I., Rice, C. P., and Torrents, A., *Anal. Chem.*, 75, 4811–4817, 2003.
25. Di Corcia, A., Samperi, R., and Marcomini, A., *Environ. Sci. Technol.*, 28, 850–858, 1994.
26. Crescenzi, C., Di Corcia, A., Samperi, R., and Marcomini, A., *Anal. Chem.*, 67, 1797–1804, 1995.
27. Braun, P., Moeder, M., Schrader, S., Popp, P., Kuschk, R., and Engewald, W., *J. Chromatogr. A*, 988, 41–51, 2003.
28. Hon-Nami, H. and Hanya, T., *J. Chromatogr.*, 161, 205–212, 1978.
29. Takada, H. and Ishiwatari, R., *Environ. Sci. Technol.*, 24, 86–91, 1990.
30. Radke, M., Behrends, T., Förster, J., and Herrmann, R., *Anal. Chem.*, 71, 5362–5366, 1999.
31. Stephanou, E. and Giger, W., *Environ. Sci. Technol.*, 16, 800–805, 1982.
32. Ferguson, P. L., Iden, C. R., and Brownawell, B. J., *J. Chromatogr. A*, 938, 79–91, 2001.
33. Cohen, A., Klint, K., Bowadt, S., Persson, P., and Jönsson, J. A., *J. Chromatogr. A*, 927, 103–110, 2001.
34. Veith, G. D. and Kiwus, L. M., *Bull. Environ. Contam. Toxicol.*, 17, 631–636, 1977.
35. Giger, W., Stephanou, E., and Schaffner, C., *Chemosphere*, 10, 1253–1263, 1981.
36. Meissner, C. and Engelhardt, H., *Chromatographia*, 49, 12–16, 1999.
37. Wickbold, R., *Tenside Surf. Det.*, 8, 61–63, 1971.
38. DIN 38409, Teil 23, 1980.
39. Waters, J., Garrigan, J. T., and Paulson, A. M., *Water Res.*, 20, 247–253, 1986.
40. Kupfer, W., *Tenside Surf. Det.*, 19, 158–161, 1982.
41. McEvoy, J. and Giger, W., *Environ. Sci. Technol.*, 20, 376–383, 1986.
42. Marcomini, A., Pavoni, B., Sfriso, A., and Orio, A. A., *Mar. Chem.*, 29, 307–323, 1990.
43. Giger, W., Brunner, P. H., and Schaffner, C., *Science*, 225, 623–625, 1984.
44. Osburn, Q. W., *J. Am. Oil Chem. Soc.*, 59, 453–457, 1982.
45. De Ruiter, C., Hefkens, J. C. H. F., Brinkman, U. A. Th., Frei, R. W., Evers, M., Matthijs, E., and Meijer, J. A., *Int. J. Environ. Anal. Chem.*, 31, 325–339, 1987.
46. Hellmann, H., *Z. Wasser Abwasser Forsch.*, 22, 4–12, 1989.
47. Field, J. A., Miller, D. J., Field, T. M., Hawthorne, S. B., and Giger, W., *Anal. Chem.*, 64, 3161–3167, 1992.
48. Lee, H. B. and Peart, T. E., *Anal. Chem.*, 67, 1976–1980, 1995.
49. Fernandez, P., Alder, A. C., Suter, M. J. F., and Giger, W., *Anal. Chem.*, 68, 921–929, 1996.
50. Osburn, Q. W., *J. Am. Oil Chem. Soc.*, 63, 257–263, 1986.
51. Wickbold, R., *Tenside Surf. Det.*, 9, 173–177, 1972.
52. Waters, J. and Kupfer, W., *Anal. Chim. Acta*, 85, 241–251, 1976.
53. DIN 38409, Teil 20, 1989.
54. Marcomini, A., Stelluto, S., and Pavoni, B., *Int. J. Environ. Anal. Chem.*, 35, 207–218, 1989.
55. Vogt, C., Heinig, K., Langer, B., Mattusch, J., and Werner, G., *Fresenius J. Anal. Chem.*, 352, 508–514, 1995.
56. Di Corcia, A., Marchetti, M., Samperi, R., and Marcomini, A., *Anal. Chem.*, 63, 1179–1182, 1991.
57. Castles, M. A., Moore, B. L., and Ward, S. R., *Anal. Chem.*, 61, 2534–2540, 1989.
58. Nakae, A., Tsuji, K., and Yamanaka, M., *Anal. Chem.*, 52, 2275–2277, 1980.
59. Holt, M. S., Matthijs, E., and Waters, J., *Water Res.*, 23, 749–759, 1989.
60. Liebscher, G., Eppert, G., Oberender, H., Berthold, H., and Hauthal, H. G., *Tenside Surf. Det.*, 26, 195–197, 1989.
61. Pietrzyk, D. J., Rigas, P. G., and Yuan, D., *J. Chromatogr. Sci.*, 27, 485–490, 1989.
62. Schoester, M. and Kloster, G., *Fresenius J. Anal. Chem.*, 345, 767–772, 1993.
63. Knepper, T. P. and Kruse, M., *Tenside Surf. Det.*, 37, 41–47, 2000.
64. Ahel, M. and Giger, W., *Anal. Chem.*, 57, 2584–2590, 1985.
65. Holt, M. S., McKerrel, E. H., Perry, J., and Watkinson, R. J., *J. Chromatogr.*, 362, 419–424, 1986.
66. Marcomini, A., Tortato, C., Capri, S., and Liberatori, A., *Ann. Chim.*, 83, 461–484, 1993.

67. Schmitt, T. M., Allen, M. C., Brain, D. K., Guin, K. F., Lemmel, D. E., and Osburn, Q. W., *J. Am. Oil Chem. Soc.*, 67, 103–109, 1990.
68. Kiewiet, A. T., van der Steen, J. M. D., and Parsons, J. R., *Anal. Chem.*, 67, 4409–4415, 1995.
69. Nitschke, L. and Huber, L., *Fresenius J. Anal. Chem.*, 345, 585–588, 1993.
70. Spilker, R., Menzebach, B., Schneider, U., and Venn, I., *Tenside Surf Det.*, 33, 21–25, 1996.
71. Schröder, H. F., *J. Chromatogr. A*, 777, 127–139, 1997.
72. Li, H. Q., Jiku, F., and Schröder, H. F., *J. Chromatogr. A*, 889, 155–176, 2000.
73. Wee, W. T., *Water Res.*, 18, 223–225, 1984.
74. Nitschke, L., Müller, R., Metzner, G., and Huber, L., *Fresenius J. Anal. Chem.*, 342, 711–713, 1992.
75. Schoester, M. and Kloster, G., *Vom Wasser*, 77, 13–20, 1991.
76. Waters, J. and Garrigan, J. T., *Water Res.*, 17, 1549–1562, 1983.
77. Fendinger, N. J., Begley, W. M., McAvoy, D. C., and Eckhoff, W. S., *Environ. Sci. Technol.*, 26, 2493–2498, 1992.
78. Ding, W. H., Lo, J. H., and Tzing, S. H., *J. Chromatogr. A*, 818, 270–279, 1998.
79. Suter, M. J. F., Reiser, R., and Giger, W., *J. Mass Spectrom.*, 31, 357–362, 1996.
80. Ahel, M., Conrad, T., and Giger, W., *Environ. Sci. Technol.*, 21, 697–703, 1987.
81. Wahlberg, C., Renberg, L., and Wideqvist, U., *Chemosphere*, 20, 179–195, 1990.
82. Stephanou, E., *Chemosphere*, 13, 43–51, 1984.
83. Stephanou, E., *Org. Mass Spectrom.*, 19, 510–513, 1984.
84. Günther, K., Dürbeck, H. W., Kleist, E., Thiele, B., Prast, H., and Schwuger, M. J., *Fresenius J. Anal. Chem.*, 371, 782–786, 2001.
85. Ding, W. H. and Tzing, S. H., *J. Chromatogr. A*, 824, 79–90, 1998.
86. Brossard, S., Lafosse, M., and Dreux, M., *J. Chromatogr.*, 591, 149–157, 1992.
87. Silver, A. H. and Kalinoski, H. T., *J. Am. Oil Chem. Soc.*, 69, 599–608, 1992.
88. Heinig, K., Vogt, C., and Werner, G., *J. Chromatogr. A*, 745, 281–292, 1996.
89. Gallagher, P. A. and Danielson, N. D., *J. Chromatogr. A*, 781, 5331997.
90. Ding, W. H. and Liu, C. H., *J. Chromatogr. A*, 929, 143–150, 2001.
91. Riu, J. and Barcelo, D., *Analyst*, 126, 825–828, 2001.
92. Heinig, K., Vogt, C., and Werner, G., *Fresenius J. Anal. Chem.*, 358, 500–505, 1997.
93. Heinig, K., Vogt, C., and Werner, G., *J. Chromatogr. A*, 781, 17–22, 1997.
94. Grob, M. and Steiner, F., *Electrophoresis*, 23, 1921–1927, 2002.
95. Ventura, F., Caixach, J., Figueras, A., Espalder, I., Fraisse, D., and Rivera, J., *Water Res.*, 23, 1191–1203, 1989.
96. Schneider, E., Levsen, K., Dähling, P., and Röllgen, F. W., *Fresenius J. Anal. Chem.*, 316, 488–492, 1983.
97. Ventura, F., Figueras, A., Caixach, J., Espadaler, I., Romero, J., Guardiola, J., and Rivera, J., *Water Res.*, 22, 1211–1217, 1988.
98. Ventura, F., Fraisse, D., Caixach, J., and Rivera, J., *Anal. Chem.*, 63, 2095–2099, 1991.
99. Schneider, E. and Levsen, K., In *Identification of Surfactants and Study of These Degradation in Surface Water By MS*, Bjoerseth, A. and Angeletti, G., Eds., D. Reidel Publ., Dordrecht, p. 14, 1986.
100. Otsuki, A. and Shiraishi, H., *Anal. Chem.*, 51, 2329–2332, 1979.
101. Shiraishi, H., Otsuki, A., and Fuwa, K., *Bull. Chem. Soc. Jpn.*, 55, 1410–1415, 1982.
102. Schneider, E., Levsen, K., Dähling, P., and Röllgen, F. W., *Fresenius J. Anal. Chem.*, 316, 277–285, 1983.
103. Weber, R., Levsen, K., Louter, G. J., Henk Boerboom, A. J., and Haverkamp, J., *Anal. Chem.*, 54, 1458–1466, 1982.
104. Hellmann, H., *Fresenius Z. Anal. Chem.*, 321, 159–162, 1985.
105. Hellmann, H., *Tenside Surf. Det.*, 28, 111–117, 1991.
106. Hellmann, H., *Z. Wasser Abwasser Forsch.*, 16, 174–179, 1983.