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# Analytics of Surfactants in the Environment: Problems and Challenges

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## 1. INTRODUCTION

Surfactants (surface active agents = SAAs) are a group of compounds with specific physicochemical properties (amphiphilicity, solubility in polar and nonpolar liquids, ability to form micelles, adsorption at phase boundaries).[1,2] Because of their properties, surface-active compounds are widely applied in industry and the household (e.g., in detergents, personal-care products, paints, pesticides, petroleum products). As their applications are on a very large scale, it has become imperative to monitor SAAs levels in environmental samples with regard to the protection of human health and various aspects of the ecosystems. Consequently, there is a need to develop appropriate analytical methodologies enabling the determination of a wide range of SAAs in different types of environmental sample. The measurement data obtained thereby should be reliable and comply with quality assurance and control systems (QA/QC).

We give a general classification of SAAs (with examples of the structural formulas of selected compounds) and of their toxicity to living organisms. Next, we review the problems posed by the analysis of surfactants in environmental samples and the analytical techniques used to isolate and/or preconcentrate, identify and quantify a broad spectrum of analytes (i.e., ionic and nonionic compounds and their metabolites). Finally, we provide information on surfactants levels determined in environmental samples.

### 1.1. Classification of Surfactants

A number of criteria can be applied to classify surfactants. These compounds are usually categorized on the basis of

- the raw material used for their production (from renewable and nonrenewable sources)
- their effect on the environment (chemodegradable, biodegradable, hardly degradable and nondegradable)
- their possible applications (as wetting, dispersing and foaming agents, detergents, emulsifiers and antiemulsifiers solubilizers)
- their chemical structure (Figure 1).

To a large extent the chemical structure of surfactants determines their influence on different compartments of the biotic and abiotic environment and also the applicability of different analytical procedures for determining them in environmental samples.[1,3,4] In the context of this criterion, it is useful to present the structural formulas of a number of SAAs (Figure 2), which may give some idea of their specific physicochemical properties.[5]

### 1.2. Toxicity of Surfactants

Because of their specific physical and chemical properties surface-active compounds are widely applied in industry, in the household and elsewhere. This means that they will inevitably get into the different compartments of the environment. It is therefore essential to ascertain whether these compounds adversely affect fauna and flora (especially aquatic organisms). Analysis of the literature data indicates that surfactants affect living organisms to different extents. Cationic SAAs, in particular, possess biostatic and biocidal properties. These properties are made use of in antibacterial and fungicidal preparations to retard the growth of or kill microorganisms like bacteria, yeasts and fungi.[6]

The toxicity of surfactants (Table 1) is a significant parameter, which determines the extent of their applicability. A variety of indices are used to assess the toxic properties of these chemicals: in the case of ionic and nonionic SAAs two parameters, $EC_{50}$ and $LC_{50}$, are measured after a fixed period of exposure. Such tests are usually carried out with the aid of indicator organisms, mostly daphnia (*Daphnia magna*) and algae, but sometimes fish as well. It has been reported that algae are highly variable in their sensitivity to surfactants, with short response times. This means that algae can be used as organisms warning of the contamination of ecosystems by SAAs.[16] For some compounds, concentrations have been established at which a given effect occurs or which lead to the death of half the population of higher organisms (rats or rabbits). In humans, contact with SAAs may cause irritation or burning sensations of the skin or eyes, and also irritation of the respiratory system. Manufacturers include warnings of such effects on their product labels.

## 2. PROBLEMS AND CHALLENGES POSED BY THE ANALYSIS OF SURFACTANTS IN ENVIRONMENTAL SAMPLES

The very extensive application of products containing surfactants (often with a broad diversity of structure and toxicity to

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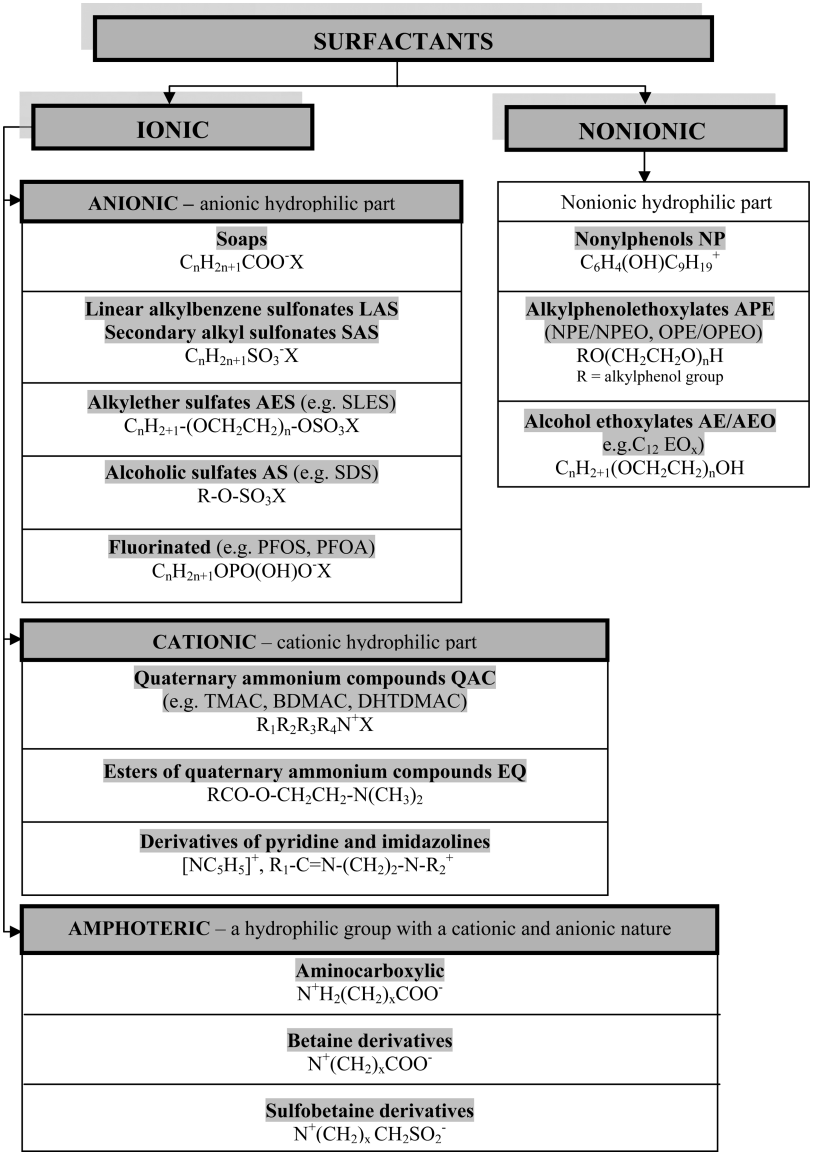


**Figure 1.** Classification of surface active compounds according to their chemical structure.

different organisms) both in everyday life and in industry requires an assessment of the extent to which these substances (or their degradation products) get into different compartments of the environment; this is a crucial analytical problem. It is imperative to have the appropriate analytical tools to hand in order to monitor their presence in the various compartments of the environment. These tools include

- appropriate analytical procedures ensuring the preparation of suitable representative extracts, in which target analytes are present at levels sufficiently high for their quantitative determination
- appropriate analytical techniques for detection, identification, and quantitative determination
- reference materials for the validation of analytical procedures, the calibration of the several stages or the whole of the analytical process, and the calibration of the measurement instrumentation used.

As a consequence, new analytical methodologies need to be developed for SAAs that will enable very low concentrations of these compounds to be determined in different types of environmental sample (soil, bottom sediments, dusts, atmospheric air, surface waters, sewage) in a short time.

A particular challenge faced by chemical analysts is the development of analytical methodologies ensuring the detection, identification and quantitative determination of a broad spectrum of surfactants in the various compartments of the environment. The determination of SAAs in different types of environmental samples causes a lot of problems, mainly because of

- the complex composition of such samples
- the low concentrations of individual surfactants in such samples
- the diverse chemical structures of surfactants
- the amphiphilic nature of surfactants (a consequence of their chemical structure).

The complex and frequently variable matrix composition of environmental samples and the low levels of target SAAs mean that suitable isolation or preconcentration techniques have to be

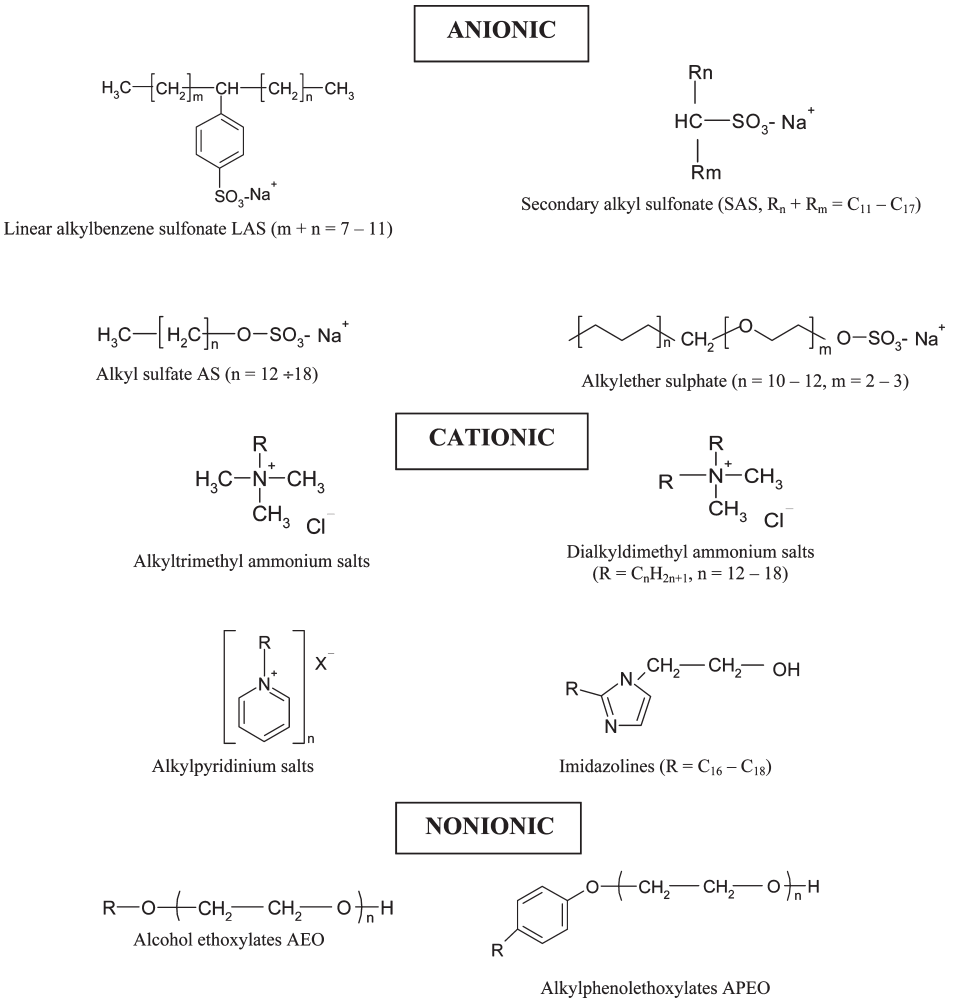


**Figure 2.** Structural formulas of selected surfactants.

applied at during sample preparation. The operations to be carried out during this stage involve

- the removal (masking) of interferents
- the isolation or preconcentration of target analytes.

During these operations, however, errors may be committed that will affect the final result of the analysis; hence it is crucial to select such conditions for analyte preconcentration that will ensure maximum sensitivity and reproducibility.[19] Interferents can usually be divided into those that overestimate SAAs levels (e.g., nonorganic and organic ions, chlorides, nitrates, cyanates, thiocyanates, sulfonates, carboxylates, phosphates, phenols) those that underestimate them (e.g., amines like QAC).[20] The various groups of techniques for preparing samples for analysis of their SAAs content will be discussed in the next section.

In view of the characteristic molecular structures of surfactants and their properties, they have to be separated into subgroups during sample preparation; it is this that will determine the techniques applicable to the analysis of the solvent extracts.

Nevertheless, it is sometimes advantageous to isolate anionic and nonionic surfactants simultaneously (e.g., by SPE) and only then to separate them prior to their quantitative determination (fractionation using appropriate solvents). With this approach it becomes possible to determine a whole range of SAAs in a single analytical run without jeopardizing the reliability of the results.[21,22]

The amphiphilic properties of surfactants mean that these compounds may be adsorbed on the surface of solid particles contained in the environmental samples and on the surfaces of the laboratory glassware used at the sample preparation stage. Moreover, during the filtration of liquid samples, analytes may be lost through absorption on the membrane filter surface (the filter material and pore size are thus significant).[23] In the next step any surfactants retained on the filter surface have to be removed, after which this extract is combined with the solvent extract obtained during the isolation of analytes from the filtrate. During the preparation of solid samples (soil, bottom sediments, sewage sludge) for analysis, it is exceedingly difficult to obtain quantitative recoveries of analytes because SAAs are adsorbed on the solid particle surfaces as a result of strong hydrophobic or electrostatic interactions.[24] As a consequence of the amphiphilic properties of SAAs, an internal standard (the relevant SAAs analyte or a compound with similar properties) has to be added to the sample before solvent extraction so that the loss of target analytes during isolation and preconcentration can be estimated. This approach is taken with respect to chromatographic techniques during the final determination of the contents of compounds in various SAAs.[25,26]

At this point it is relevant to draw attention to the fact that preparing suitable solutions of standard surfactants, adding an


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Table 1. **Toxicity of Surfactants**

| type of surfactant | surfactant (acronym) | organism | parameter/exposure time | concentration range [mg/L] | references |
|---|---|---|---|---|---|
| cationic | TMAC | green algae (*Dunaliella salina*) | $EC_{50}$/24 h | 0.79 | 7 |
| | | daphnia (*Daphnia magna*) | $IC_{50}$/24 h | 0.13−0.38 | 8 |
| | BDMAC | green algae (*Dunaliella salina*) | $EC_{50}$/24 h | 1.3 | 7 |
| | | daphnia (*Daphnia magna*) | $IC_{50}$/24 h | 0.13 − 0.22 | 8 |
| | DTDMAC | daphnia (*Daphnia magna*) | $LC_{50}$/48 h | 0.49 | 9 |
| | | goldfish (*Carassius auratus*) | *$EC_{50}$/48 h | 2.37 | 10 |
| | | rainbow trout (*Salmo gairdneri*) | | 0.74 | |
| anionic | Na($C_{10}$ LAS) | daphnia (*Daphnia magna*) | $LC_{50}$/48 h | 13.9 (11.7−17.2) | 11 |
| | Na($C_{12}$ LAS) | green algae (*Dunaliella salina*) | $EC_{50}$/24 h | 3.5 | 7 |
| | | daphnia (*Daphnia magna*) | $LC_{50}$/48 h | 8.1 | 11 |
| | Na($C_{14}$ LAS) | daphnia (*Daphnia magna*) | | 1.22 | |
| | LAS | algae (*Raphidocelis subcapitata*) | $IC_{50}$/72 h | 112.4 | 12 |
| | | acute bladder snail (*Physella acuta*) | $LC_{50}$/24 h | 16.65 (9.2−26) | |
| | | *Artemia salina* | | 40.4 (38.7−48.5) | |
| | | sunflower (*Helianthuus annuus*) | increase in $EC_{50}$/21 days | 260 (120−307) mg/kg | 13 |
| | | potatoes (*Solanum tuberosum*) | efficiency and increase in NOEC/106 days | 16 mg/kg | 14 |
| | SDS | algae (*Raphidocelis subcapitata*) | $IC_{50}$/72 h | 36.58 | 12 |
| | | acute bladder snail (*Physella acuta*) | $LC_{50}$/24 h | 27.2 (17.6−37.9) | |
| | | *Artemia salina* | | 41.04 (35.9−49.6) | |
| | | daphnia (*Daphnia magna*) | $EC_{50}$/24 h | 28.77 | 15 |
| | | rainbow trout (*Salmo gairdneri*) | *$EC_{50}$/48 h | 33.61 | 10 |
| | | | $LC_{50}$/24 h | 42.04 | 15 |
| | | goldfish (*Carassius auratus*) | *$EC_{50}$/48 h | 38.04 | 11 |
| | AES | algae (*Raphidocelis subcapitata*) | $IC_{50}$/72 h | 36.58 | 12 |
| | | acute bladder snail (*Physella acuta*) | $LC_{50}$/24 h | 27.2 (17.6−37.9) | |
| | | *Artemia salina* | | 41.04 (35.9−49.6) | |
| | | algae (*Skeletonema costatum*) | $EC_{50}$/72 h | 0.37 ± 0.08 | 16 |
| | | *Pseudokirchneriella subcapitata* | | 3.5 ± 0.66 | |
| nonionic | NP | daphnia (*Daphnia magna*) | $LC_{50}$/48 h | 0.19 | 17 |
| | NPE | daphnia (*Daphnia magna*) | | 14 | |
| | | *Mysidopsis bahia* | | 1.23−1.89 | 18 |
| | AE | algae (*Raphidocelis subcapitata*) | $IC_{50}$/72 h | 6.87 | 12 |
| | | acute bladder snail (*Physella acuta*) | $LC_{50}$/24 h | 5.33 (4.0−7.4) | |
| | | *Artemia salina* | | 0.62 (0.58−0.67) | |
| | | goldfish (*Carassius auratus*) | *$EC_{50}$/48 h | 29.26 | 10 |
| | | rainbow trout (*Salmo gairdneri*) | | 22.38 | |

internal standard, and plotting appropriate calibration curves are problematic for several reasons, the most important of which are

- the limited availability of commercial standard solutions of surfactants (standards of only certain analytes are available, LAS, ABS, PFOA, PFOS, OPEO, NPEO, OP, NP)
- the application of standard solutions prepared from technically pure products that are mixtures of isomers, homologues or oligomers of compounds from the relevant group of SAAs (instead of commercial standard solutions)
- the occurrence of foaming or the formation of highly viscous solutions during the preparation of aqueous solutions of surfactant standards.

The analytical methodologies enabling the determination of a wide assortment of SAAs present at different levels in environmental samples with various matrix compositions should be validated against certified reference materials. At present only liquid reference materials are available on the market; they can be used to validate methodologies for determining total contents of ionic (cationic or anionic) and nonionic surfactants. On the other hand, there are no reference materials suitable for validating entire analytical procedures. All we can do in these circumstances is to add a standard solution to a certified reference material,[27] and then re-extract the same samples under optimal conditions to check that extraction of analytes is complete,[21] or else to compare two different analytical methodologies.[28]

### 2.1. Analytical Procedures for Determining Surfactants in Environmental Samples

Analysis of the subject literature indicates that the determination of surfactants in environmental samples requires different methodological approaches depending on whether the information required concerns the total SAAs content or the levels of individual SAAs in the sample.

During the collection and storage of environmental samples, no matter whether they are liquid or solid, the target compounds should not be allowed to decompose. A biocide is therefore added to aqueous media immediately after sampling in order to minimize the biodegradation of SAAs: the usual one is a solution of formaldehyde. Samples are then stored at a low temperature and in the dark until they need to be prepared for final determination.[4,25,29,30] Solid samples (bottom sediments, sewage sludges, soils) are first desiccated, then stored at a low temperature.[31−35]

Apparatus and glassware likely to come into contact with the samples are first flushed with a mixture of acids and then rinsed with deionized water. During this procedure detergents (themselves containing SAAs) must not be used, as they could contaminate the environmental samples. The samples are stored in amber glass or polypropylene bottles.

The analytical procedures for determining surfactants in environmental samples can be divided into two types:

- determination of the total content of surfactants of a given group (cationic, anionic, nonionic)
- determination of analytes belonging to different classes of chemical compounds.

In the first case, the preparation of samples for analysis is relatively straightforward, as only a few operations like extraction (LLE or SLE) with ion-pair formation and photometric analyte determination need to be carried out.[36−40] In the second, analytes have first to be isolated and/or preconcentrated before the final determination (using the appropriate extraction techniques). Table 2 lists information on the extraction techniques commonly used in the preparation of environmental samples whose SAAs content is to be determined. The table also lists the operating parameters for analyte isolation, as well as the advantages and disadvantages of each technique. Perusal of the subject literature shows that the usual techniques for isolating and/or preconcentrating SAAs analytes from solid or liquid environmental samples are

- liquid−liquid extraction (LLE[38−55] or solid−liquid extraction (SLE)[27,32,33,61−64]
- solvent extraction in a Soxhlet apparatus[27,34,55,65−69]
- solid phase extraction (SPE).[22,62,65,68,70,74,76,77,81,86,97−131]

For a long time, the traditional extraction techniques (solvent sublation,[44,45] LLE, SLE, Soxhlet extraction) used in the preparation of various types of environmental samples for analysis required large amounts of organic solvents for isolating the analytes, which itself produced highly toxic effluents.

These techniques do not ensure desirable analyte recoveries (they are often <50%); they are also time-consuming and labor-intensive. But the search is now on for new analytical techniques, and existing ones are being modified, so that samples can be prepared in accordance with the principles of "green analytical chemistry"; analyses can then be carried out with minimal adverse effects on the environment.[142,143] The use of techniques assisting extraction, such as elevated temperature and pressure, microwave radiation, and ultrasound improve the efficacy of analyte isolation. In comparison with traditional solvent extraction, accelerated solvent extraction (ASE),[19,27,68,69,71−79] microwave-assisted extraction (MAE),[21,28,93,87,94−96] supercritical fluid extraction (SFE),[32,55,89−93] or ultrasound-assisted liquid extraction (USE)[39,49,80−88] shorten the sample preparation time and reduce the quantities of solvents required in the analytical procedure; these procedures also lend themselves to automation. On the one hand, ultrasound-assisted solvent extraction requires the use of considerable amounts of organic solvents, but the cost of the apparatus is far less than in the case of ASE, MAE or SFE. Nowadays, SPE is the usual technique for isolating analytes from liquid samples. This technique is also used for cleaning up solvent extracts containing analytes obtained during the extraction of solid samples. With SPE the use of highly toxic chloroform can be wholly eliminated (at the sample preparation stage). It is also possible to isolate anionic and nonionic SAAs simultaneously (they are fractionated during analyte elution from SPE columns) and to automate sample preparation.

Researchers in many centers are working on new methodological approaches to extraction that are compliant with the requirements of sustainable development (solventless sample preparation techniques). These techniques are a major element of green analytical chemistry (GAC). Here are some examples of such methods (the SAAs analytes to which they are relevant are given in parentheses):

- DLLME (anionic and nonionic SAAs)[20,57−60]
- membrane−MMLLE (cationic SAAs[56]); HF-LPME (cationic[144] and anionic[145] SAAs)
- SBSE (nonionic SAAs)[132]
- SPME (anionic and nonionic SAAs)[111,133−141]
- sorption of analytes from liquid samples on the surfaces of suitable materials (PTFE, compounds from all SAAs groups; MCE, nonionic SAAs; O-MWCNT, cationic SAAs[146])

The following techniques provide information on the total content of particular groups of SAAs (the groups of compounds to which they are applicable are given in parentheses):

- spectrophotometry (ionic and nonionic)
- flow injection analysis (ionic)
- potentiometric titration (ionic)
- tensammetry (anionic, nonionic)
- immunoanalysis (nonionic)

These techniques are quick, simple, and cheap, with limits of detection (LODs) between 110 and 1.7 $\mu$g/L. The apparatus for such determinations is fairly straightforward, so the financial outlay is not great. These techniques are applied in the routine monitoring of various kinds of environmental samples and can be used in small laboratories not equipped with specialist apparatus. Spectrophotometry is a universal technique, as it can be applied to both ionic and nonionic surfactants. But its application is limited by the high LODs values and the considerable influence of organic interferents on the results.

The determination of the total content of particular groups of SAAs should be treated as the first step in studies aiming to measure the degree of contamination of particular environmental compartments by these analytes. The next step involves individual chemical speciation.[158−160], during which individual surfactants are detected and quantitatively determined. This becomes possible with the use of suitable equipment (in combination with a sensitive detector) for separating complex mixtures of analytes (present, for example, in a solvent extract) into separate chemical species; in most cases these are chromatographic and related techniques (the types of SAAs analytes to which they are applicable are given in parentheses):

- capillary electrophoresis (CE) (anionic)
- gas chromatography (GC) (anionic and nonionic)
- liquid chromatography (LC) (ionic and nonionic)

Chromatographic techniques require environmental samples to be prepared appropriately to preconcentrate the analytes they contain and to remove interferents (using extraction techniques).

The use of CE (LOD = 1 $\mu$g/L) is limited to anionic surfactants, because cationic compounds can be adsorbed on

Table 2. **Techniques for the Preparation of Environmental Samples Prior to Their Analysis for the Presence of Surfactants**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| isolation of SAAS without extraction and membrane filters → liquid sample | | | | | | | | |
| cationic (**1**) | total | wastewater | 250 mL | 1. addition of EDTA and standard<br>2. color reaction with BTDAB<br>3. mixing<br>4. determination after 10 min | 96−103 | • good determination of SAAs in wastewater<br>• simple, reproducible, selective and sensitive techniques | • only for the determination of total SAAs | 41 |
| nonionic (**2**) | | | n.g. | 1. transferring Pb(II)−T(DBHP)P complex and Triton X-100 to flask<br>2. addition of sample<br>3. dilution to the mark with water | 98−104 | (**2**) ionic SAAs cannot interfere in this method | (**1**) anionic SAAs caused negative interference | 42 |
| isolation of SAAS with membrane filters (without extraction) → liquid sample | | | | | | | | |
| cationic | total | river water | n.g. | 1. addition to sample $LS^-$<br>2. filtration through PTFE membrane filter<br>3. washing of filter (EB and acetate buffer)<br>4. elution of analytes | 92 | • method for the determination of trace ionic and NS using spectrophotometric techniques<br>• isolation of analytes without toxic organic solvents<br>• simple techniques | • only for the determination of total SAAs | 43 |
| anionic | | | | 1. addition to sample $CTMA^+$<br>2. filtration through PTFE membrane filter<br>3. washing of filter (EB and acetate buffer)<br>4. elution of analytes | 94−98 | | | |
| nonionic | | | 90 mL | 1. dissolving KCl in sample<br>2. filtration through MCE membrane filter<br>3. washing of filter (EB and acetate buffer)<br>4. elution of analytes | | | | |
| solvent sublation → liquid sample | | | | | | | | |
| anionic | total | river water | 1000 mL | 1. solvent, ethyl acetate<br>2. time, 20 min (**3**) | | • procedures for the determination of higher concentrations SAAs (for sewage or sewage treatment plant liquors and effluents)<br>(**3**) higher recovery obtained with the addition of NaCl and $NaHCO_3$ | • large volumes of solvent<br>• process separates only dissolved SAAs<br>• removal of surfactant from the solid particles takes a very long time<br>• interferents also separated | 44 |
| nonionic | | wastewater | 5000 mL | 1 solvent: ethyl acetate<br>2 time: n.g.<br>3 cleanup (reaction with modified Dragendorff reagent): glacial acetic acid | - | | | 45 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | | | | liquid−liquid extraction → liquid sample | | | | |
| cationic | total | wastewater | 100 mL | 1 solvent, chloroform<br>2. ion-pair reagent, Patent Blue V<br>3. time, 15 min<br>4. cleanup, water | | • widely used for the determination of surfactants in different types of samples<br>• samples with even a high content of particulate matter can be extracted (unlike SPE)<br>• overall concentration of SAAs determined in aqueous and particulate phases<br>• requires no sophisticated equipment or well-trained staff<br>(4) hydrolysis at lower temperature of LAS-MG than LAS-MB<br>(6) reduction of sample volume from 5000 to 100 mL | • the procedures are very complicated and time-consuming but modifications can simplify them<br>• the consumption of organic solvents used in the liquid extraction is about 550 mL<br>• production of toxic wastes (5) because of the formation of emulsions with long-chain nonionics only short-chain nonionics and their degradation products can be efficiently recovered | 38 |
| | | sea-surface water | 20 mL | 1. solvent, chloroform<br>2. ion-pair reagent, disulfine blue<br>3. time, 1 min | 80 | | | 39 |
| | DTDMAC<br>DEEDMAC<br>DEQ | sewage<br>river water | 100−200 mL<br>500 mL | 1. solvent, chloroform<br>2. ion-pair reagent, LAS<br>3. cleanup, chloroform, water | 95−97 | | | 46 |
| | DDAC<br>BAC<br>ATAC | wastewater<br>surface water | 500 mL | 1. solvent, chloroform<br>2. ion-pair reagent, LAS<br>3. cleanup, chloroform, water | 80−99 | | | 47 |
| anionic | total | wastewater | 5 mL | 1. solvent, chloroform<br>2. ion-pair reagent, MB<br>3. time, 0.5 min | | | | 48 |
| | | sea-surface water | 20 mL | 1. solvent, chloroform<br>2. ion-pair reagent, MB<br>3. time, 4 min<br>4. cleanup, water (shaking 2 min) | 90 | | | 39, 49 |
| | | tap water | 50 mL | 1. solvent, 5 mL chloroform<br>2. ion-pair reagent, MB<br>3. time, 1 min | | | | 50 |
| | LAS<br>SPC | river water<br>sea water | 250 mL<br>500 mL | 1. solvent, chloroform<br>2. ion-pair reagent, MG (methylene green) (4)<br>3. time, 1 min | 98 | | | 57 |
| nonionic (5) | total | water<br>wastewater | | 1. solvent, dichloromethane<br>2. ion-pair reagent, cobalt thiocyanate<br>3. time, 1 min | 87−97 | | | 40 |
| | | river water | 200 mL | 1. solvent, ethyl acetate<br>2. ion-pair reagent, modified Dragendorff reagent<br>3. cleanup, isooctane | 83−100 | | | 52 |
| | APE, AP | wastewater | 300 mL | 1. solvent, dichloromethane<br>2. time, 18 h | 60−140 | | | 23 |
| | total | river water | 100 mL | 1. solvent, ethyl acetate (6)<br>2. cleanup, water | 54−110 | | | 54 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | I − NP, OP<br>II − $NPE_{1-2}$ | river water<br>lake water | 500−1000 mL | 1. solvent, I fraction = hexane, II fraction = dichloromethane<br>2. time, 18 h | 80 | | | 55 |
| | | | | microporous membrane liquid−liquid extraction (MMLLE) → liquid sample | | | | |
| cationic | QAC | river water<br>waste water | 80 mL | 1. solvent, 1-chlorobutane<br>2. ion reagent, heptanoic acid<br>3. flow rate, 8 mL/min<br>4. time, 25 min one analysis | | • easy online connection to NP-LC (easy to automate)<br>• no premixing in system, minimizes the risk of foam and emulsion formation | • chloroform leakage to aqueous phase<br>• low solubility of ion-pair reagents in organic solvent | 56 |
| | | | | dispersive liquid−liquid microextraction (DLLME)/thin liquid film extraction (TLFE) → liquid sample | | | | |
| anionic | total | tap water<br>mineral water<br>well water | 5 mL | 1. solvent, chloroform (extraction solvent), ethanol (dispersant solvent)<br>2. time, 3 min<br>3. centrifuging, 5500 rpm | 93−96 | • very small amounts of microextraction solvent (<200 $\mu$L) required | • difficult to automate<br>• the need to use a disperser solvent lowers the partition coefficient of analytes into the extractant solvent<br>• solvent drop is vulnerable to physical forces<br>• analytes are subsequently desorbed into methanol and then analyzed by HPLC | 20 |
| nonionic | NPEO<br>OPEO<br>NP<br>OP | tap water<br>river water | | 1. solvent, trichloroethylene (extraction solvent), acetone (dispersant solvent)<br>2. time, 10 min<br>3. centrifuging, 5000 rpm | 71−75 | • technique cheap, straightforward and quick<br>• high level of preconcentration | | 57 |
| | NP<br>OP | river water | | 1. solvent, chloroform (extraction solvent), methanol/pyridine (dispersant solvent and catalyst), MCF (derivatization) (**7**)<br>2. time, 5 + 5 min (sonication + centrifuging)<br>3. centrifuging, 5000 rpm | 88−106 | (**7**) in situ derivatization | | 58 |
| | | tap water<br>river water<br>wastewater | 20 mL | 1. solvent, octanol<br>2. time, 2 + 2 min (sonication + centrifuging)<br>3. centrifuging, 3500 rpm | 63−111 | (**8**) vortex mixing (a mild emulsification procedure) prevents the problems associated with the use of ultrasound | | 59 |
| | | | 100 mL | 1. solvent, octanol (**8**)<br>2. time, 24 h (with stirring) | | | | 60 |
| | | | | solid−liquid extraction (SLE) → solid sample | | | | |
| cationic | DTDMAC | sewage sludge<br>marine sediments | 0.5 g<br>5 g | 1. solvent, methanolic HCl<br>2. ion-pair reagent, LAS<br>3. cleanup, LLE (chloroform), SAEC (methanol) | 91 | • extraction is fast, simple and cost-effective<br>• does not require expensive equipment (**10**) PFC: comparison of (WAX) with (HLB) cartridges − HLB gives higher recoveries and better-resolved peaks than WAX | • requires the use of large amounts of organic solvents which are toxic and inflammable<br>• production of toxic wastes (**9**) the low recoveries of all homologues caused by overloading and displacement of the LAS by matrix | 32 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| anionic | total | soil | 1 g | 1. solvent, water and chloroform<br>2. ion-pair reagent, MB<br>3. time of extraction, 1.5 min | | | | 61 |
| | LAS | sewage sludge | 0.2 g | 1. solvent, methanol<br>2. cleanup, with or without SPE (**9**) | 44−96 33−70 | | | 62 |
| | | floor dust | 1 g | 1. solvent, ethanol<br>2. time, 4 h<br>3. temperature, 60 °C<br>4. cleanup, SPE (SAX, C18) | 20−95 | | | 63 |
| | PFOA<br>PFOS | river sediment | 5 g | 1. solvent, water, MTBE<br>2. ion-pair reagent, TBAHS<br>3. time, 20 + 30 min (shaking + centrifuging) | 81−108 | | | 33 |
| | | sludge | 0.5 g | 1. solvent, acetonitrile/methanol<br>2. time, 1 h<br>3. cleanup, SPE (HLB) (**10**) | 91−99 82−99 | | | 64 |
| nonionic | NP<br>OP | river/lake sediment | 10 g | 1. solvent, dichloromethane<br>2. time, 20 min<br>3. cleanup, LLE (dichloromethane), removing sulfur (copper powder), silylation (Florisil) | 91−97 87−100 | | | 27 |
| | | | | Soxhlet extraction → solid sample | | | | |
| cationic | DDAC<br>BAC<br>ATAC | sludge [33] / river sediment | 1 g<br>5 g | 1. solvent, methanol<br>2. time, 18 h<br>3. cleanup, LLE (chloroform, water) | 67−95 | • technique for extracting nonvolatile and semivolatile compounds from solid samples (soils, sludge, and sediment)<br>• equipment uncomplicated and inexpensive<br>• one batch of solvent is recycled during extraction | • long extraction time<br>• uses large volumes of organic solvents (toxic, expensive, and inflammable)<br>• recoveries generally low<br>• techniques costly (**11**) lower recoveries obtained for the most polar SPCs (C2−C4 SPCs) - difficult to retain in the solid phase | 65, 66 |
| anionic | LAS<br>SPC | soil | 5 g | 1. solvent, methanol<br>2. time, 16 h<br>3. cleanup, SPE (C18) | 77−93<br>13−74 (**11**) | | | 34 |
| | LAS<br>TPS | lake sediment | 5−20 g | 1. solvent, methanol<br>2. time, 15 h<br>3. cleanup, SPE (SAX)<br>4. derivatization and cleanup (1.5 g alumina) | 79−113 | | | 67 |
| | LAS<br>AES<br>AS | sediment | 5 g | 1. solvent, methanol<br>2. time, 5 h<br>3. cleanup, SPE | 94−112<br>61−109 | | | 68 |
| | PFOA<br>PFOS | sewage sludge | 2 g | 1. solvent, methanol/water (99:1, v/v)<br>2. time, 6 h | 48 | | | 69 |
| nonionic | NPE<br>NP, OP | river/lake sediment | 5 g | 1. solvent, dichloromethane<br>2. time, 6 h | 80 | | | 55 |
| | NP<br>OP | | 10 g | 1. solvent, dichloromethane<br>2. time, 18 h | <80 | | | 27 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | | | | Soxtec extraction → solid sample | | | | |
| anionic | LAS | soil | 2 g | 1. solvent, 100 mL methanol<br>2. time, 45 min<br>3. temperature, 30 °C | 91 | • semiautomated apparatus<br>• quicker<br>• lower cost (better solvent recovery)<br>• safe (dissociation of extraction and heating units) | • equipment costly<br>• applicable only to anionic and nonionic SAAs | 35 |
| nonionic | APEO<br>AE | sludge | 10 g | 1. solvent, 50 mL methanol<br>2. time, 45 min<br>3. cleanup, SPE (C18) | 71−92 | | | 70 |
| | | | | accelerated solvent extraction (ASE) → solid sample | | | | |
| cationic | BAC | sediment | 10 g | 1. solvent, acetonitrile/water<br>2. pressure 10.34 MPa, temperature 120 °C<br>3. time, 30 min<br>4. cleanup, online SPE (PLRP) | 95−103 | • ionic and nonionic analytes can be isolated from solid samples<br>• faster sample preparation (this is important when analytes are volatile)<br>• lower volume of organic solvents<br>• high level of automation<br>• extraction pressure has no influence when samples are dry<br>(**12**) extraction efficiency better than Soxhlet<br>(**14**) small sample mass<br>(**15**) one extraction for nonionic and anionic analytes<br>(**16**) all steps performed automatically<br>(**17**) modification of cleanup increases the recovery of wide range of isolated nonionic SAAs<br>(**18**) milder extraction conditions with good recoveries of analytes | • high initial cost of ASE equipment<br>• ASE extractors can be automated but samples are always run one at a time<br>• extract purification required<br>• isolation of cationic SAAs requires a large amount of sample<br>• problems with degradation at temperatures above 60 °C for APEOs and their degradation products<br>(**13**) purification only by SPE not sufficient | 71 |
| anionic | LAS<br>AES<br>AS | | 5 g | 1. solvent, methanol<br>2. pressure, 10.34 MPa; temperature, 125 °C<br>3. time, 15 min<br>4. cleanup, SPE (C18) | 81−125<br>55−99 | | | 68 |
| | LAS<br>AES | | 4 g | 1. solvent, methanol<br>2. pressure, 10.34 MPa; temperature, 120 °C<br>3. time, 15 min<br>4. cleanup, SPE (C18) | 70−107 | | | 72 |
| | PFOA<br>PFOS | sewage sludge | 2 g | 1. solvents, EtOAc−DMF−MeOH−$H_3PO_4$<br>2. pressure, 14.28 MPa; temperature, 150 °C | 119 (**12**) | | | 69 |
| | | street dust | 1 g (**14**) | 1. solvents, methanol<br>2. pressure, 10.5 MPa; temperature, 100 °C<br>3. cleanup, SPE (C18), OT-GC (**13**) | 91−96 | | | 73 |
| nonionic | NPEC<br>NP | sludge | 1 g (**14, 15**) | 1. solvent, acetone/methanol<br>2. pressure, 10.34 MPa; temperature, 75 °C<br>3. time, 10 min<br>4. cleanup, SPE (C18) | 60−81 | | | 74 |
| | AEO<br>NPEO | sediment | 4 g | 1. solvent, methanol<br>2. pressure, 10.34 MPa; temperature, 120 °C<br>3. time, 15 min<br>4. cleanup, SPE (C18) | 70−107 | | | 72 |
| | NP<br>OP | river/lake sediment | 3 g | 1. solvent, dichloromethane<br>2. pressure, 13.17 MPa; temperature, 100 °C<br>3. time, 10 min | | | | 27 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | NPEO<br>OPEO<br>NP<br>OP | river sediment | 5 g | 1. solvent, acetone/methanol<br>2. pressure, 10.34 MPa; temperature, 50 °C<br>3. time, 2 × 5 min<br>4. cleanup, SPE (OSP-2A) (**16**) | 62−102 | | | 75 |
| | | | 5 g | 1−4 as above<br>5. cleanup, SPE (C18) (**17**) | 74−97 | | | 19 |
| | | | 1 g (**14**) | 1. solvent, acetone/hexane<br>2. pressure, 10.34 MPa; temperature, 100 °C<br>3. time, 45 min<br>4. cleanup ($NH_2$) | 67−110 | | | 76, 77 |
| | | soil | 5 g | 1. solvent, acetone/hexane<br>2. pressure, 3.79 MPa; temperature, 60 °C (**18**)<br>3. time, 16 min<br>4. cleanup, SPE (C18) | 89−91 | | | 78 |
| | OPEO<br>NP<br>OP | | 5 g | 1. solvent, methanol<br>2. pressure, 6.9 MPa; temperature, 70 °C<br>3. time, 12 min<br>4. cleanup, SPE (isolute ENV+) | 96−104 | | | 79 |
| | | | | ultrasound-assisted liquid extraction (USE) → solid and liquid sample | | | | |
| cationic | BAS | sediment river | 10 g | 1. solvent, methanol/hydrochloric acid<br>2. time, 30 min<br>3. cleanup, SPE (SCX) | >90 | • sonication systems do not face the financial barrier of the high initial outlay on SFE, PLE, or MAE equipment<br>• samples from a wide range of sources can be readily analyzed<br>• rapid extraction (5−45 min)<br>(**19**) extractions are not dependent on the length of the alkyl chain of LAS | • isolation of all SAAs classes requires a large amount of sample (10−40 g) large volumes of organic solvent used (toxic, expensive and inflammable)<br>• extraction often produces stable emulsions that result in long phase separation times<br>• low recoveries of some analytes (35−57%) | 80 |
| | total | aerosols | 20 mL (water solution) | 1. solvent, water<br>2. time, 45 min<br>3. cleanup, LLE (chloroform + DiSB) | 80 | | | 39 |
| anionic | | soil (only in [11]) aerosols | 50 mg | 1. solvent, water<br>2. time, 45 min<br>3. cleanup, LLE (chloroform, water, + MB) | 90 | | | 39, 49 |
| | AS, AES | river sediment | 30−40 g | 1. solvent, methanol<br>2. time, 20 + 10 min (shaking + sonication) | 35−106 | | | 81 |
| | LAS, CDEA | sewage sludge | 2 g | 1. solvent, methanol/dichloromethane<br>2. cleanup, SPE (C18) | 90 (CDEA) | | | 82 |
| | LAS | sewage sludge | 0.5 g | 1. solvent, methanol (**19**)<br>2. time, 7 min | 93−97 | | | 83 |
| | PFOA<br>PFOS | dust | 0.5 g | 1. solvent, acetonitrile<br>2. cleanup, SPE (Envi Carb) | | | | 84 |
| | | sludge<br>sediment<br>soil | 1 g<br>5 g | 1. solvent, methanolic acetic acid/acetic acid<br>2. time, 45 min<br>3. cleanup, SPE (WAX, EnviCarb) | 57−115 | | | 85 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | | sludge<br>sediment | 1 g<br>5 g | 1. solvent, methanol<br>2. time, 30 min<br>3. cleanup, SPE (Envi-Carb) | 82−83 | | | 86 |
| nonionic | NPEO, PEG, NP, OP | sewage sludge | 2 g | 1. solvent, methanol/dichloromethane<br>2. cleanup, SPE (C18) | 67−101 | | | 82 |
| | NP<br>OP | river sediment | 5 g | 1. solvent, methanol<br>2. time, 15 min<br>3. cleanup (silica gel, sodium sulfate) | 90<br>123 | | | 87 |
| | NPEO<br>AEO | sludge | 10 g | 1. solvent, dichloromethane<br>2. time, 5 min (+ 2 h shaking) | 30−61 | | | 88 |
| | | | | supercritical fluid extraction (SFE) → solid sample | | | | |
| cationic | DHTDMAC | sewage sludge | 0.5 g | 1. medium, $CO_2$ modified with methanol<br>2. pressure, 40.53 MPa; temperature, 85 °C<br>3. time, 45 min<br>4. cleanup (LLE, anion-exchange chromatography) | >70 | • a reduction in sample cleanup; more efficient and rapid extractions | • extraction of polar or ionic compounds with $CO_2$ problematic (because of poor solubility) | 89 |
| | DTDMAC | sewage sludge<br>marine sediments | 0.5 g<br>5 g | 1. medium, $CO_2$ modified with methanol<br>2. pressure, 38.50 MPa; temperature, 100 °C<br>3. time, 17 min<br>4. cleanup (SPE) | 96 | | | 32 |
| anionic | LAS<br>AS<br>SAS<br>AES | sewage sludge | 15 mg | 1. medium, subcritical water (**20**)<br>2. pressure, 10 MPa; temperature, 200 °C<br>3. time, 15 min<br>4. cleanup (Carbograph) | >86 | • extractant easy to remove, is nontoxic (water, $CO_2$) | • extractant has to be modified with a low molecular weight alcohol (methanol) | 90 |
| | LAS<br>SAS | | 100 mg | 1. pressure, 40.53 MPa; temperature, 80 °C<br>2. time, 15 min | 86−91<br>89−94 | | | 91 |
| nonionic | NPE<br>NP<br>OP | sediment | 0.25−1 g | 1. medium, $CO_2$<br>2. pressure, 35.14 MPa; temperature, 80 °C<br>3. time, 25 min<br>4. cleanup (silica gel) | 80 | • minimizes risk of laboratory contamination and considerably reduces the amounts of organic solvents used | • less interest partly because of the development of ASE, which has become a widely accepted extraction technique | 55 |
| | NPEC<br>NPEO | sewage sludge | 0.1−1 g | as above | 86−105 | | | 92 |
| | AE<br>NPE<br>NPEC<br>NP | | 15 g | 1. medium, subcritical water (**20**, **21**)<br>2. pressure, 10 MPa; temperature, 200 °C<br>3. time, 15 min<br>4. cleanup (Carbograph) | >86 | (**20**) water under subcritical conditions efficiently extracts polar and nonpolar compounds from solid matrices<br>(**21**) fractionation of nonacidic and weakly acidic compounds | (**22**) the recovery of $NP_3EC$ or $NP_4EC$ by this method was not evaluated | 90 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | NPEC (**22**) | | 0.25 g | 1. medium, water with ethanol<br>2. pressure, 15 MPa; temperature, 75 °C<br>3. time, 20 min<br>4. cleanup, SPE (SAX Empore disks) | 90−108 | | | 93 |
| | | | | microwave-assisted extraction (MAE) → solid sample | | | | |
| anionic | LAS | sewage sludge | 0.5 g | 1. solvent, methanol<br>2. time, 7 min<br>3. power of microwave irradiation, 250 W (**23**) | 94−102 | • MAE should be preferred to Soxhlet or sonication because it requires less time and solvent<br>(**23**) no purification of the samples is required for the final determination (HPLC)<br>(**25**) technique not only for a specific group of analytes (isolation of PAH, PE, NP, NPEO during one extraction) | • high initial cost of MAE equipment<br>(**24**) low recoveries for NP | 83, 94 |
| nonionic | NP, OP | river sediment | 5 g | 1. solvent, hexane/ethyl acetate<br>2. time, 15 min<br>3. pressure, 1.4 MPa; temperature, 130 °C<br>4. cleanup (silica gel) | 96−103 | | | 87 |
| | | | | 1. solvent, methanol<br>2. time, 15 min<br>3. pressure, 1.4 MPa; temperature, 100 °C<br>4. cleanup, SPE (HBL) | 94−102 | | | 65 |
| | | marine sediment | 1 g | 1. solvent, dichloromethane/methanol<br>2. time, 25 min<br>3. pressure, 1.4 MPa; temperature, 130 °C<br>4. cleanup, SPE (Envi-Chrom P) | 60 (**24**) 86 | | | 96 |
| | NP $NP_1EC$ $NP_2EC$ | sediment (Atlantic Ocean) | 1 g | 1. solvent, acetone (**25**)<br>2. time, 15 min<br>3. pressure, 0.145 MPa<br>4. cleanup, SPE (Florisil) | | | | 21 |
| | | sediment | | 1. solvent, methanol<br>2. time, 15 min<br>3. pressure, 0.159 MPa<br>4. cleanup, SPE (Lichrolut) | | | | 28 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | | | | solid-phase extraction (SPE) → liquid sample | | | | |
| cationic | DDAC, BAC, ATAC, | surface water wastewater | 500 mL | type of cartridge, C18 | 80−99 | • simple and rapid extraction<br>• high recoveries of ionic and anionic analytes<br>• low consumption of organic solvents<br>• elimination of highly toxic solvent (chloroform) from sample preparation step<br>• smaller amount of sample needed<br>• automation of isolation step is possible<br>(**26**) online SPE<br>(**27**) SDS hemimicelle-based SPE<br>(**28**) the extraction of complex mixtures from aqueous samples and their class fractionation by stepwise desorption can be rapidly and easily achieved by the use of a single GCB cartridge (LAS, SPC, NP, NPEO, NPEC)<br>(**29**) determination of the concentration, both total surfactant and individual homologue (LAS) or oligomer (APEO), possible<br>(**30**) isolation LAS + APE<br>(**31**) separation from sample different homologues of analytes (LAS, BS, NPS) | • samples may not contain large amounts of particulate matter<br>• sorbent size must be adapted to the contents of analytes in the sample<br>• relatively high price of cartridges<br>• the use of large volumes of organic solvents to elute analytes generally implies an evaporation step (the final extract has to be compatible with the mobile phase and analytical instrument)<br>• evaporation step prolongs analysis and causes loss of volatile analytes, which affects the quality of the results | 65 |
| | QAC | seawater | 10 mL | type of cartridge, Strata-X<br>1. conditioning, acetonitrile, water<br>2. washing, water/acetic acid<br>3. elution, acetonitrile/acetic acid/water | 80−105 | | | 97 |
| | BAC | tap water wastewater | 50 mL | type of cartridge, Hysphere or PLRP-s (**26**)<br>1. conditioning, acetonitrile, water<br>2. elution, acetonitrile/ammonium buffer | 71−90 | | | 98 |
| | | river water wastewater | 250−1000 mL | type of cartridge: Alumina (**27**)<br>1. passing sample solution with SDS<br>2. elution, methanol | 95−106 | | | 99, 100 |
| anionic | LAS | sewage | 10−100 mL | type of cartridge, GCB (**28**)<br>1. conditioning (TMAOH/dichloromethane/ methanol/water)<br>2. washing (water/methanol)<br>3. elution, fraction = TMAOH/dichloromethane | 91−100 | | | 22 |
| | LAS, DATS | sewage river water groundwater | 10−1000 mL | type of cartridge, GCB<br>1. conditioning, water<br>2. washing, water, methanol, dichloromethane/ methanol/formic acid<br>3. elution, dichloromethane/methanol/TMAOH | 94−98 | | | 101 |
| | LAS | river water | 7 mL | type of cartridge, C18 (**29**) | | | | 102 |
| | | wastewater [76, 77] groundwater river water | 50 mL | 1. conditioning, methanol<br>2. washing, water/methanol<br>3. elution, methanol | 96−120 | | | 103 |
| | | | | type of cartridge, C18 (**30**) | | | | 104 |
| | | surface water | | 1. conditioning, methanol, water<br>2. elution, methanol | >90 | | | 105 |
| | | wastewater | 10−250 mL | type of cartridge, C18<br>1. conditioning, methanol, water<br>2. washing, methanol/water<br>3. elution, methanol | 98−101 | | | 106 |
| | LAS, ASE, AS | sea water | 100 mL | type of cartridge, C18<br>1. conditioning, methanol, water<br>2. washing, water<br>3. elution, methanol | | | | 68 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | LAS, (**31**), AES, AS, ASo | tap water river water sewage | 100−200 mL | type of cartridges, C18<br>1. conditioning, methanol, water<br>2. washing, water, water/methanol<br>3. elution, methanol | 99−101 | | | 107 |
| | LAS (**31**) | wastewater | 200 mL | type of cartridge, Isolute ENV+<br>1. conditioning, methanol, water<br>2. washing, water/methanol<br>3. elution, TEA/acetic acid/methanol | 57−93 (**32**) 93 85−103 | (**32**) low recoveries of LAS C13 (57%) | | 108 |
| | LAS | | | type of cartridge, Isolute ENV+<br>1. conditioning, methanol, water<br>2. elution, methanol | 77−93 | | | 109 |
| | sulfated and sulfonated surfactants | seawater | 10 mL | type of cartridges, SDB (**33**)<br>1. conditioning, methanol, water<br>2. washing, water<br>3. elution, methanol | 16−133 | (**33**) addition to sample of ion-pair reagent (TBAOH) before SPE improves the extraction recovery; TBA+ has electrostatic interactions with hydrophobic anions such as surfactants and can ion-pair in the SDB substrate | | 110 |
| | AES, AS, LAS | river water | 100 mL | type of cartridges, PTFE and SCX (**34**)<br>1. addition of SDS and filtration (PTFE filter)<br>2. washing filter, water, methanol<br>3. passing methanolic solution through SCX<br>4. elution, NaCl/methanol | >90 | (**34**) ion-pair SPE | | 81 |
| | LAS | seawater | 25 mL | type of cartridges, C18, SAX (**35**) | 71−94 | | | 111 |
| | | wastewater | 100 mL | 1. conditioning, methanol, water<br>2. washing, methanol/water<br>3. elution, methanol<br>1. conditioning, methanol<br>2. washing, methanol/acetic acid<br>3. elution, methanol/HCl | 92−107 | | | 62 |
| | | coastal marine water | 250 mL | type of cartridges, Isolute ENV+ SAX (**35**)<br>1. first elution, methanol<br>2. second elution, HCl/methanol | 94−98 | (**35**) sequential solid-phase extraction (SSPE) = higher recoveries that single SPE | | 108 |
| | PFOA, PFOS | wastewater street runoff | 500−1000 mL | type of cartridge, C18<br>1. conditioning, methanol, water<br>2 washing: methanol/water<br>3 elution: methanol | | | | 112 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | | surface river water | 0.2−200 mL | type of cartridge, C18<br>1. conditioning, methanol, water<br>2. washing, water<br>3. elution, methanol | 80−109 49−130 | | | 113 |
| | | sea water | 100 mL | type of cartridge, Oasis WAX<br>1. conditioning, ammonium hydroxide/methanol, methanol, water<br>2. washing, ammonium acetate buffer<br>3. fractionation, methanol or ammonium hydroxide/methanol | 99−103 | | | 114 |
| | | rain water | | type of cartridge, Oasis WAX<br>1. conditioning, methanol, water<br>2. washing, water/ammonium hydroxide<br>3. fractionation, acetonitrile or methanol/ ammonium hydroxide | 55−137 | | | 115 |
| | | river water | 500 mL | type of cartridges, Oasis WAX<br>1. conditioning, methanol, water<br>2. washing, sodium acetate buffer, methanol<br>3. elution, ammonium hydroxide/water/ methanol/MTBE | | | | 116 |
| | | surface river water | 5000 mL | type of cartridge, Strata XAW<br>1. conditioning, methanol, water<br>2. washing, formic acid<br>3. elution, ammonium hydroxide/methanol | | | | 117 |
| | | river water<br>wastewater | 250 mL | type of cartridge, Oasis HLB<br>1. conditioning, methanol, water<br>2. washing, methanol/water<br>3. elution, methanol | >50−105 | | | 118, 119<br>86 |
| | | rain<br>snow | 2000 mL<br>2 kg | type of cartridges, Oasis HLB+Presep-C Agri<br>1. conditioning, methanol, water<br>2. elution, methanol | 97−104 96−103 (**35**, **36**) | | (**36**) changing the order in which the cartridges are connected leads to lower analyte recoveries | 120 |
| | | sea water | 10 L | type of cartridges, glass fiber cotton + Chromabond HR-P (**34**, **36**)<br>1. conditioning, methanol, water<br>2. washing, water<br>3. elution, acetic acid, ammonium acetate/ methanol | 90−106 | (**36**) semiautomated system | | 121 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| nonionic | NPEC | wastewater | 100 mL | type of cartridge, GL-Pak Carbograph<br>1. washing, acetonitrile/water<br>2. elution, dichloromethane/methanol | | | | 122 |
| | NPEO, NP | sewage | 10−100 mL | type of cartridge, GCB (**29**)<br>1. conditioning, TMAOH/dichloromethane/ methanol/water<br>2. washing, water<br>3. elution, dichloromethane/methanol and formic acid/dichloromethane/methanol | 89−99 | | | 22 |
| | NPE, AE | wastewater | 500 mL | type of cartridge, GCB<br>1. conditioning, TMAOH/dichloromethane/ methanol/water<br>2. elution, dichloromethane/methanol | 90−96 | | | 123 |
| | total NPEO | surface water | | type of cartridges, C18 | >80 | | | 105 |
| | NPEC, OPEC OP, NP | ground/river water | | 1. conditioning, methanol, water<br>2. elution, methanol | | | | 104 |
| | NPEC, NP | wastewater | 100−500 mL | type of cartridge, C18 | | | | 74 |
| | NPEC, NPEO, NP | tap/raw water wastewater | | 1. washing, water/methanol<br>2. elution, methanol | 72−98 | | | 124, 125 |
| | NPEO, OPEO, NP, OP | wastewater | 250 mL | type of cartridge, C18 (**37**)<br>1. conditioning, methanol, water<br>2. washing, water<br>3. elution, methanol | 60−108 | (**37**) reduction of volume of solvent for elution analytes (2 mL) | | 70 |
| | | | | type of cartridges, C18<br>1. conditioning, methanol, water<br>2. washing, elution, hexane/dichloromethane | 75−102 | | | 126 |
| | | river water | 4000 mL | type of cartridges, Isolute ENV+ or C18 (**38**)<br>1 conditioning, dichloromethane, acetone, water<br>2 elution, dichloromethane, methanol, acetone | 38−110 (**39**) | (**38**) ENV+, better for extracting large volumes of sample, faster isolationv | (**39**) low recoveries (38%) | 76, 77 (**40**) |
| | NP, OP | | 2500 mL | type of cartridges, Oasis HLB<br>1. conditioning, ethyl acetate, methanol<br>2. washing, water<br>3. elution, ethyl acetate | 94−102 | (**40**) modification allows a smaller amount of solvent to be used for extraction −10 mL for all steps | | 95 |
| | | | 2500−5000 mL | type of cartridge, SDVB<br>1. conditioning, methanol, methanol/acetonitrile, methanol, water<br>2. elution, methanol/acetonitrile | | | | 123, 127 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | NPEO, NP | wastewater | 1000 mL | type of cartridges, Sep-Pak PS-2+Sep-Pak Plus Silica (**35**, **41**)<br>1. conditioning, methanol, water<br>2. elution, methanol<br>1. conditioning, chloroform/methanol, hexane<br>2. washing, hexane<br>3. elution, chloroform/methanol | | (**43**) the second extraction procedure was a SSPE for the preconcentration of nonionic polar surfactants present in highly contaminated matrices<br>(**44**) procedure is good for analyte fractionation<br>(**45**) triple-stage SPE improved spectrophotometric determination of total polyoxyethylene nonionic surfactants (provides quantitative results with high sensitivity) and minimal release of chemical agents into the surroundings | (**41**) toxic solvent used for cleanup (chloroform)<br>(**42**) for samples containing a high level of sediment it is necessary to add a second cleanup stage (SPE) to remove all anionic components (LAS) | 122 |
| | NPEO, OPEO | river water | 7 mL | type of cartridges, C18 + SAX (**30**, **42**)<br>1. conditioning, methanol<br>2. washing, water/methanol<br>3. elution, methanol | | | | 102 |
| | A, $AEO_n$ $n > 15$<br>B, AEO<br>C, NPEO<br>D, PEG | wastewater (**43**) | 200 mL | type of cartridges, LiChrolut RP-18 + EN<br>1. conditioning, water/methanol<br>2. acidification residual water and loading on second cartridge<br>3. elution, RP-18 A, hexane; B, dichloromethane/ hexane; C, methanol/dichloromethane; EN D, methanol (**44**) | 74−82 92−94 72−73 | | | 107 |
| | $C_{12}EO_7$<br>$C_{12}EO_5$ | river water | 500 mL | type of cartridges, C18 +S CX + SAX (**45**)<br>1. conditioning, SCX, SAX-methanol, methanol/ HCl/water; C18, acetone, methanol, water<br>2. isolation, methanol/water<br>3. elution, acetone (C18) | | | (**46**) recovery values for C18 were the lowest, reflecting the higher hydrophobicity (cf. lower chain lengths $C_{12}$−$C_{16}$) and dependence on the quality (e.g., industrial composition) of the sample analyzed | 129 |
| | $C_{12-18}EO_{0-18}$ | wastewater | 4000 mL | type of cartridges, C2 + SCX + SAX (**46**)<br>1. conditioning, water, acetonitrile, methanol/ ethyl acetate/water, methanol, acetone/ dichloromethane, acetonitrile; C2−water<br>2. fractionation A, acetonitrile; B, methanol/ethyl acetate/water | 37−97 | | | 130 |
| | $C_{12-16}E$, $NPE_x$, $OPE_x$ | river water wastewater | 250−750 mL | type of cartridge, A Alumina<br>1. conditioning, water<br>2. passing solution containing SDS<br>3. elution, methanol | 95−106 | SDS hemimicelle-based SPE | | 131 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| | | | | stir bar sorptive extraction (SBSE) | | | | |
| nonionic | OP, NP | river water | 2 mL | 1. coating of stir bar, polydimethylsiloxane<br>2. temperature, room<br>3. time, 60 min<br>4. stirring 500 rpm (**47**) | | • small sample volume<br>• simplicity of extraction<br>• solvent-free isolation<br>(**48**) in situ acylation may be useful for hydrophilic analytes<br>(**50**) in-tube silylation may be useful for hydrophobic analytes | (**47**) SBSE without derivatization, lowest extraction efficiency<br>(**49**) SBSE with in situ derivatization, extraction less effective than in tube | 132 |
| | | | | 1. addition of derivatization reagent to sample<br>2. 1−4 as above (**48**, **49**) | 93 96 94 95 | | | |
| | | | | 1. coating of stir bar, polydimethylsiloxane<br>2. temperature, room<br>3. time, 60 min<br>4. stirring 500 rpm<br>5. derivatization in-tube (**50**) | | | | |
| | | | | solid-phase microextraction (SPME) → liquid/solid sample | | | | |
| anionic | LAS | sea water | | 1. nondepletive SPME<br>2. type of fiber, PA (**51**) | | •. reduction and simplification of sample preparation<br>•. use of organic solvents unnecessary<br>•. small sample volume<br>•. high sensitivity of isolation<br>•. automation possible hydrophobic analytes sampled onto the fiber can be directly desorbed in the GC injection port<br>(**53**) compounds containing polar groups in their structures should be derivatized before analysis with GC to improve the quality and sensitivity of separation<br>(**54**) the introduction of a silyl group to highly polar analytes improves various GC parameters (accuracy, reproducibility, sensitivity and resolution by suppressing tailing and enhancing thermal stability) | • predesorption with solvent is performed to combine this technique with HPLC<br>(**51**) the applicability of the current nondepletive SPME for environmental sampling is limited (small proportion of each LAS structure in commercial mixtures, relatively high background contamination from various sources)<br>(**52**) background adsorption and matrix effects problematic (reduction during headspace extraction)<br>(**55**) silyl derivatives with limited stability to hydrolysis; moisture content may affect derivatization<br>(**56**) extractionequilibria of most analytes achieved after 80 min SPME | 133 |
| | | | 5−7 mL | 1. direct immersion with in-port derivatization<br>2. type of fiber, PDMS<br>3. time, 30 min<br>4. temperature, 25 °C | | | | 111 |
| | PFOA, PFOS | river water/ wastewater | 1 mL | online in-tube SPME | 81−83 82−85 | | | 134 |



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**Table 2. Continued**

| type of surfactant | analytes | type of sample | volume/weight of sample | conditions of isolation/ preconcentration | recovery (%) | advantages | disadvantages | refs |
|---|---|---|---|---|---|---|---|---|
| nonionic | APE | sewage sludge | 4 mL | 1. direct immersion without derivatization<br>2. type of fiber, CWAX/TRCF<br>3. time: 60 min<br>4. temperature, 25 °C | | | | 135 |
| | BPA, NP | wastewater | 9.5 mL | 1. direct immersion without derivatization (**52**)<br>2. type of fiber, PDMS/DVB<br>3. time, 60 min<br>4. temperature, 30 °C | | | | 136 |
| | NP, $NPEO_n$ | tap water<br>river water | 40 mL | 1. direct immersion without derivatization (**52**)<br>2. type of fiber, DVB/CAR/PDMS<br>3. time, 60 min<br>4. temperature, 50 °C<br>5. addition organic modifier, methanol | | | | 137 |
| | BPA, NP, OP | seawater | 10 mL | 1. direct immersion with derivatization on-fiber (silylation, BSTFA) (**52**, **53**, **54**, **55**)<br>2. type of fiber, PDMS, PDMS-DVB, PA<br>3. time, 90 min | | | | 138, 139 |
| | NP, OP | river water | 100 mL | 1. direct immersion with derivatization on-fiber (silylation, BSTFA) (**52**, **54**, **55**)<br>2. types of fiber, PA<br>3. time, 60 min<br>4. temperature, 25 °C | | | | 140 |
| | | tap/lake water | 2 mL | 1. direct immersion with derivatization on-fiber (MTBSTFA/TBDMCS) (**52**)<br>2. types of fiber, PA, PDMS-DVB<br>3. time, 30 min<br>4. temperature, 65 °C | | | | 141 |



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Table 3. **Analytical Techniques for Determining SAAs Contents in Environmental Samples**

| analytes | measurement principle | metrological parameters | advantages | disadvantages | refs |
|---|---|---|---|---|---|
| | | | spectrophotometry | | |
| cationic | • formation of ion-pairs with suitable reagent (e.g., DBAS, Orange II, Patent Blue V, Bromophenol Blue, Fe(III)-SCN-, Bi(III)-I-, Cu(II)−TPPS)<br>• extraction into organic solvent<br>• measurement of organic phase absorbance | linearity = 0.05 − 50 mg/L<br>LOD = >0.22 mg/L<br>RSD =4.9% | • analysis quick and simple<br>• for determining total contents of a particular group of SAAs<br>• uncomplicated apparatus<br>• techniques can be modified (more effective techniques for isolating SAAs; determination of lower concentrations, reduction or elimination of solvents for extracting analytes) | • large-volume samples needed for preparation step (e.g., 5 L)<br>• susceptible to interferents in the sample<br>• no possibility of determining individual homologues or isomers<br>• production of very toxic wastes<br>**Only nonionic:** limited applicability (from 5 to 30 ethoxylated groups) | 38, 42, 43, 45, 129, 147−150 |
| anionic | • formation of ion-pairs with suitable reagent (e.g., MB, MG, EV, Azure A-)<br>• extraction into organic solvent<br>• measurement of the organic phase absorbance | linearity = 0.05−2 mg/L<br>LOD = 1.7 $\mu$g/L<br>RSD = 0.64−5.9% | | | |
| nonionic | • formation of a ion-pairs with suitable reagent (modified Dragendorff reagent - BiAS, Pb(II)−T(DBHP)P)<br>• determination of Bi (or Pb) ion content | linearity = 0.2−200 mg/L<br>precision = 1.8−3.0%<br>LOD = 20 $\mu$g/L<br>RSD = 0.8−10% | | | |
| | | | flow injection analysis (FIA) | | |
| cationic<br>anionic | • based on ion-pair formation between analytes and reagent (MB, Fe(III)-SCN-, Bi(III)-I<br>• online measurement of organic phase absorbance | LOD = 110−140 $\mu$g/L<br>RSD = 0.7−2.4% | • technique simple and rapid<br>• minimal consumption of organic solvents | • total analyte content determined | 151−153 |
| | | | potentiometric titration | | |
| cationic<br>anionic | • measurement of the change in EMF of the measurement cell caused by the addition of the titrant<br>• ion-selective electrode used to define the end point of the titration | linearity = $7.9 \times 10^{-6} - 2.0 \times 10^{-3}$ mol/L<br>LOD = $4.0 \times 10^{-6}$ mol/L<br>RSD = 1.13% | • fast analysis<br>• for determining total contents of a particular group of SAAs<br>• uncomplicated apparatus | • no possibility of determining individual homologues or isomers<br>• nonionic SAAs cannot be determined | 154, 155 |



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**Table 3. Continued**

| analytes | measurement principle | metrological parameters | advantages | disadvantages | refs |
|---|---|---|---|---|---|
| | | | tensammetry | | |
| anionic<br><br><br><br>nonionic | • measurement of the capacitive current due to the adsorption and desorption of surfactants at the electrode surface | linearity = 0.5−20 mg/L<br>precision = 0.42<br>LOD = 0.15 mg/L<br>RSD = 6−11% | • fast analysis<br>• for determining total contents of a particular group of SAAs**Only nonionic**:<br>• tolerance to the presence of anionic SAAs<br>• applicable to compounds containing 1−30 EO groups | • no possibility of determining individual homologues and isomers<br>• limited to the determination of anionic and nonionic SAAs | 52, 54, 156 |
| | | | immunoanalysis | | |
| nonionic | • based on the binding of antibodies to antigens (analytes) by means of selective bonds | LOD = 10 $\mu$g/L | • small sample volumes<br>• reduced demand for solvents<br>• for the determination of the total level of nonionic surfactants<br>• screening technique | • restricted to the analysis of nonionic SAAs<br>• the main problem preventing further development of surfactant immunoanalysis is the lack of antibodies with acceptable specificity spectra | 157 |
| | | | capillary electrophoresis (CE) | | |
| anionic | • based on the separation of analytes under the influence of an applied voltage<br>• detectors:<br>UV−vis<br>MS | linearity = 33−2057 $\mu$g/L<br>LOD = 1−23 $\mu$g/L<br>RSD = 6−24% | • reduced demand for organic solvents<br>• short analysis time, easy to carry out | • limited to the determination of anionic SAAs in environmental samples<br>• high limit of detection (analyte isolation necessary) | 62, 108, 161 |
| | | | gas chromatography (GC) | | |
| anionic<br><br><br>nonionic | • technique for separating analytes and determining their levels with a suitable detector<br>• mobile phase, gases<br>• various types of detectors:<br>NPD and FID*, limited applicability<br>MS** (MS-MS), universal detector | LOD [ng/L or ng/kg] =<br>* 300<br>** 0.0003 or 3<br>SD = 0.15%<br>RSD = 5−20% | • single analytes can be analyzed and at lower concentrations<br>• addition of a standard enables estimation of analyte recovery at the sample preparation stage<br>• tandem MS is a more selective analytical technique<br>• lower SAAs contents can be determined than with HPLC | • requires isolation and/or preconcentration of analytes<br>• limited to determination of anionic and nonionic SAAs<br>• limited applicability to compounds of low volatility<br>• derivatization essential (except for nonionic of low molecular mass)<br>• complicated and expensive apparatus | 21, 28, 49, 51, 55, 58, 65, 67, 87, 91, 93, 96, 111, 123, 127, 132, 137 |



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**Table 3. Continued**

| analytes | measurement principle | metrological parameters | advantages | disadvantages | refs |
|---|---|---|---|---|---|
| | | high performance liquid chromatography (HPLC) | | | |
| cationic<br><br><br><br><br><br><br><br><br><br>anionic<br><br><br><br><br><br>nonionic | • technique for separating ionic and nonionic SAAs, quantitative and qualitative determination<br>• mobile phase, liquid<br>• ionization, atmospheric pressure chemical ionization, electrospray ionization<br><br>• detector:<br>UV*<br>FLD**<br>CD (for ionic SAAs)<br>MS***<br>MS-MS**** | LOD [$\mu$g/kg or $\mu$g/L] =<br>* 0.03 or 0.0067<br>** 3.7 or 0.03<br>*** 0.026 or 0.00021<br>**** 0.000033 $\mu$g/L<br>RSD = 6−15% | • all groups of SAAs can be determined<br>• single analytes can be analyzed and at lower concentrations<br>• low-volatility analytes with large molar masses can be determined<br>• addition of a standard enables e stimation of analyte recovery from environmental samples<br>• the use of various types of detector makes HPLC the most universal technique for determining ionic and nonionic SAAs | • requires isolation and/or preconcentration of analytes<br>• complicated and expensive apparatus<br>• analysis is costly (use of high-purity eluents, creation of a vacuum)<br>• production of toxic wastes (organic solvents) | 19, 28, 30−32, 34, 35, 46, 47, 49, 55, 57, 63−66, 68−74, 76−78, 80−86, 88−90, 92, 94, 96−99, 101−104, 108, 112, 113, 115, 116, 118, 120, 121, 124, 125, 131, 134, 162, 164, 166, 168 |



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Table 4. **Literature Information on Surfactant Concentrations in Environmental Samples**

| type of analyte | analytes | type/source of sample | concentration | refs |
|---|---|---|---|---|
| | | soils [$\mu$g/kg] | | |
| anionic | LAS | | 50 000 | 35 |
| | LAS, SPC | forest area | 100−15 000 | 34 |
| | PFOA | | 3.28−47.5 | 85 |
| | PFOS | | 8.58−10.4 | |
| | total | soil surface | 330 ± 170 $\mu$M/kg | 49 |
| nonionic | AEO | urban area | 69−329 | 31 |
| | NPEO | forest area | 92−329 | 78 |
| | OPEO | | 87−369 | |
| | NP | | 142−500 | |
| | OP | | 125−238 | |
| | OPEO, NP, OP | agricultural area | 200−229 000 | 49 |
| | | dusts [$\mu$g/kg] | | |
| anionic | LAS | indoor dust | 34−1 500 000 (public buildings) | 63 |
| | PFOA | | 0.7−56.9 (house) | 84 |
| | PFOS | | 0.5−293 (office) | |
| | | street dust | 7.7 ± 0.9 | 73 |
| | | | 5.0 ± 0.9 | |
| | | sediments [mg/kg] | | |
| cationic | total | river sediment | 5−50 | 80 |
| | DDAC | | n.d.−2.1 | 66 |
| | BAC | | n.d.−3.6 | |
| | DDAC | | n.d.−2.1 | 65 |
| | BAC | | 0.002−3.6 | |
| | ATAC | | 0.01−0.12 | |
| | BAC | | 0.021−0.26 | 71 |
| | DTDMAC | marine sediment | 1140−42 300 | 32 |
| anionic | LAS, TPS | lake sediment | 0.19−3.4 | 67 |
| | LAS, AES, AS | river sediment | 0.225−2.065 $\mu$g/L (pore water) | 81 |
| | LAS | marine sediment | 0.54−1.01 | 68 |
| | AES | | 0.17−0.54 | |
| | LAS | | 0.29−1.94 | 72 |
| | AES | | 0.043−0.16 | |
| | PFOA | river sediment | 0.0052−0.203 | 85 |
| | PFOS | | 0.00157−0.00878 | |
| | | | <0.00008−0.00017 | 33 |
| | | | <0.00012−0.00037 | |
| | | wetland | n.d.−0.0029 | 86 |
| | | | 0.0026−0.0307 | |
| nonionic | NP | river sediment | <MDL−0.005 | 87 |
| | OP | | <MDL−0.008 | |
| | | | 0.0047−0.0313 | 95 |
| | | | <MLD−0.011 | |
| | NPE | river/lake sediment | n.d.−38 | 55 |
| | NP | | 0.17−72 | |
| | OP | | n.d.−1.8 | |
| | NPEO | river sediment | <MDL−395 | 19 |
| | OPEO | | <MDL−1170 | |
| | NP | | | |
| | OP | | 0.024−0.91 | |
| | | | | 76, 77 |
| | | | <MQL−0.41 | |
| | | | 0.41−6.7 | |


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**Table 4. Continued**

| type of analyte | analytes | type/source of sample | concentration | refs |
|---|---|---|---|---|
| | | <MQL−0.41 | | |
| | NP, OP | marine sediment | n.d.−0.023 | 96 |
| | AEO | | 0.11−2.7 | 72 |
| | NPEO | | 0.26−2.6 | |
| | NPEC | from Atlantic Ocean | <MDL−1.54 | |
| | | | | 21, 28 |
| | NP | | 0.14−0.41 | |
| | | sewage sludge [mg/kg] | | |
| cationic | DHTDMAC | Germany | 1600−3000 | 89 |
| | DTDMAC | Switzerland | 150−5870 | 32 |
| anionic | LAS | Germany | 110−1030 | 62 |
| | | Spain | 0.1−13.39 | 162 |
| | | | 89−4207 | |
| | | | | 83, 94 |
| | LAS + CDEA | | n.d.−4 340 | 82 |
| | LAS | Switzerland | 3830−7510 | 91 |
| | SAS | | 370−800 | |
| | AES | Germany | 1.0−22 | 90 |
| | AS | | 3.6−40 | |
| | LAS | | 66−1770 | |
| | SAS | | 6.4−23 | |
| | PFOA, PFOS | | 6−10 | 69 |
| nonionic | NPEC | U.S.A. | n.d−91.9 | 93 |
| | NPEC | Canada | n.d.−38 | 92 |
| | NPEO | | 4−304 | |
| | AE | Germany | 0.71−106 | 90 |
| | NPE | | 3.2−100 | |
| | NPEC | | 3.0−100 | |
| | NPEC | Spain | n.d.−14 | 82 |
| | NPEO | | 2.1−135 | |
| | $C_{10-18}$OE | | n.d.−98 | |
| | NP | | 25.5−601 | |
| | OP | | n.d. | |
| | PEG | | 1.7−31 | |
| | | sludge [mg/kg] | | |
| cationic | DDAC | Austria | n.d.−2.1 | 65 |
| | BAC | | n.d.−3.6 | |
| | ATAC | | n.d.−0.12 | |
| anionic | PFOA | China | 0.0052−0.2 | 85 |
| | PFOS | | 0.0016−0.0088 | |
| | | | n.d.−0.0157 | 86 |
| | | | 0.0031−7.3 | |
| | | U.S.A. | 0.0084−0.128 | 64 |
| | | | 0.032−0.417 | |
| nonionic | NPEO | France | 0.038 | 70 |
| | OPEO | | 0.15 | |
| | AE | | 0.032−1.5 | |
| | NPEC, NP | Spain | 0.105−0.15 | 74 |
| | NPEO | U.S.A. | n.d.−43.6 | 88 |
| | AEO | | 16.3−654 | |
| | | atmospheric water [pmol/$m^3$] or [$\mu$g/l] | | |
| cationic | total | atmospheric water | 1.0−11.7 pmol/$m^3$ | 163 |
| | | aerosols | 26.1−129.6 pmol/$m^3$ | 39 |


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**Table 4. Continued**

| type of analyte | analytes | type/source of sample | concentration | refs |
|---|---|---|---|---|
| anionic | | | 14.9−229.1 pmol/$m^3$ | |
| | | | 128 ± 62 pmol/$m^3$ | 49 |
| | | atmospheric water | 12.5−285 pmol/$m^3$ | 163 |
| | | | 39.4−932.2 pmol/$m^3$ | |
| | | cloud water | n.d.−960 $\mu$g/L | 36 |
| | PFOA | rain | 0.0001−0.0033 $\mu$g/L | 115 |
| | PFOS | | 0.0004−0.0093 $\mu$g/L | |
| | | | 0.0329−0.0408 $\mu$g/L | 120 |
| | | | 0.00992−0.113 $\mu$g/L | |
| | | snow | 0.00774−0.0567 $\mu$g/L | |
| | | | 0.0375−0.182 $\mu$g/L | |
| | | street runoff | 0.09 $\mu$g/L | 112 |
| | | | 0.05 $\mu$g/L | |
| nonionic | NP | rain | 0.3−0.95 $\mu$g/L | 164 |
| | | snow | n.d.−0.802 $\mu$g/L | |
| | | ground/well/mineral water [$\mu$g/l] (for pfoa and pfos [ng/l]) | | |
| cationic | total | ground water | 500−1300 | 165 |
| anionic | DATS | | n.d. | 101 |
| | total | tap water | 20−193 | 50 |
| | | tap water | 30−70 | 20 |
| | | mineral water | | |
| | | well water | | |
| | PFOA | ground water | 0.47−60 | 112 |
| | PFOS | | 0.28−133 | |
| | | raw water | n.d.−67 | 166 |
| | | | n.d.−22 | |
| | | tap water | n.d.−34 | |
| | | | n.d.−22 | |
| | | | <5−35.3 | 134 |
| | | | n.d. | |
| nonionic | NPE | ground water | <0.11−0.2 | 137 |
| | NP | | n.d.−0.32 | |
| | NPEO, OPEO, NP, OP | tap water | n.d. | 57 |
| | NPEO | raw water | 13 | 125 |
| | OPEO | | 1.2 | |
| | NPEC | | 2.2 −2.9 | |
| | OPEC | | n.d. | |
| | NP | | 0.45 | |
| | OP | | 0.12 | |
| | NPEC | ground/tap water | 0.1 | 104 |
| | OPEC | | <MDL | |
| | NP | | 0.1 | |
| | OP | | <MDL | |
| | NPEC | tap water | <0.001 | 124 |
| | NPEO | | <0.025−100 | |
| | NP | | <0.01 | |
| | | surface water [$\mu$g/L] (for PFOA and PFOS [ng/L]) | | |
| cationic | DDAC | surface water | <MDL−0.19 | 47 |
| | BAC | | 0.02−0.3 | |
| | ATAC | | 0.015−0.3 | |
| | DTDMAC, DEEDMAC, DEQ | river water | 0.11−75 | 46 |


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**Table 4. Continued**

| type of analyte | analytes | type/source of sample | concentration | refs |
|---|---|---|---|---|
| | BAC | | <MDL | 99 |
| | DTMABr | sea water | n.d. | 97 |
| | DDABr, DBDMAC | | 0.12−0.27 | |
| | | | n.d. | |
| | total | | 11−210 μmol/L | 39, 49 |
| anionic | | river water | 5−150 | 44 |
| | AES + AS | | 0.01−200 | 81 |
| | LAS | | 0.24−3955 | |
| | LAS | | 6−52 | 51 |
| | SPC | | total = 204 | |
| | LAS | | 5.6 | 102 |
| | | | 48 | 104 |
| | DATS | | 2.2−6.6 | 101 |
| | PFOA | | 24−287 | 116 |
| | PFOS | | 16.3−155 | |
| | | | 11−1130 | 113 |
| | | | n.d.−2 210 000 | |
| | | | 0.08−14 | 118 |
| | | | <0.06−15 | |
| | | | <0.06− 8 | 167 |
| | | | <0.12−32 | |
| | | | <5−14.6 | 134 |
| | | | n.d. | |
| | | lake water | 0.69−3.95 | 117 |
| | | | 2.67−7.83 | |
| | total | sea water | 5−360 pmol/L | |
| | | | | 39, 49 |
| | LAS | | n.d.−46 | 111 |
| | | | 739−911 | 108 |
| | LAS | | 4−24 | 57 |
| | SPC | | total = 83 | |
| | LAS | | 0.025−0.064 | 72 |
| | AES + AS | | 0.0045−0.017 | |
| | PFOA | | n.d.−0.00455 | 121 |
| | PFOS | | n.d.−0.00226 | |
| nonionic | total | river water | 27−222 | 54 |
| | NP | | <0.025−1.22 | 127 |
| | NPE | | 1.3−1.6 | 137 |
| | NP | | 1.4−2.2 | |
| | NP | | <0.01−0.77 | 123 |
| | OP | | <0.01−0.42 | |
| | | | 2.40 ± 0.16 | 58 |
| | | | 0.037 ± 0.001 | |
| | | | n.d.−0.018 | 132 |
| | | | n.d.−0.0597 | |
| | | | 4.67 | 140 |
| | | | 0.15 | |
| | | | 0.00001−0.0376 | 95 |
| | | | 0.0001−0.044 | |
| | NPE | | n.d.−0.15 | 55 |
| | NP | | n.d. | |
| | OP | | n.d.−0.013 | |
| | NPEO, OPEO | | 5.6 | 102 |
| | NPEO | | 0.3−0.5 | 57 |

**Table 4. Continued**

| type of analyte | analytes | type/source of sample | concentration | refs |
|---|---|---|---|---|
| | OPEO | | 0.1−0.3 | |
| | NP | | <MQL | |
| | OP | | 0.1 | |
| | | | 0.14−0.2 | 76 |
| | | | <MDL | |
| | | | <MDL−0.067 | |
| | | | <MDL | |
| | $C_{12-16}EO$ | | <MDL−8 | 131 |
| | NPE | | 4−12 | |
| | OPE | | <MDL−14 | |
| | NPEC | | 1.2−2.5 | 104 |
| | OPEC | | 0.1−0.3 | |
| | NP | | 0.6 | |
| | OP | | <MDL | |
| | NPE | lake water | n.d.−10 | 55 |
| | NP | | n.d.−0.92 | |
| | OP | | n.d.−0.47 | |
| | | wastewater [$\mu$g/L] | | |
| cationic | total | China | 374−2116 | 42 |
| | DDAC | Austria | n.d.−0.03 | 47 |
| | BAC | | n.d.−0.17 | |
| | ATAC | | n.d.−0.0066 | |
| | | | n.d.−0.83 $\mu$g/L | 168 |
| | | | 0.014−3.5 $\mu$g/L | |
| | | | n.d.−1.1 $\mu$g/L | |
| | CTAB | Algeria | >31 | 38 |
| | BAC | Spain | 0.1−49 | 99 |
| | BAC | U.S.A. | n.d.−36.6 | 98 |
| anionic | total | Canada | 120−9340 | 103 |
| | LAS | Germany | 126−1410 | 62 |
| | | Spain | 288−1630 | 108 |
| | | | 136−1309 | |
| | | | 1−16 | 107 |
| | | | 30.7−1635 | 104 |
| | | Austria | 4.2−40 | 168 |
| | PFOA | Germany | 0.0087−0.093 | 118 |
| | PFOS | | 0.012−0.014 | |
| | | | 0.020−3.9 | 167 |
| | | | 0.106−0.252 | |
| | | Japan | 0.01−0.07 | 112 |
| | | | 0.05−0.65 | |
| | | China | 0.019−0.0499 | 86 |
| | | | <3* 0.00286−4.1 | |
| nonionic | total | China | 374−2 116 | 42 |
| | NPEO | wastewater | n.d.−84 | 53 |
| | OPEO | U.S.A. | n.d.−6 | |
| | NP | | n.d. | |
| | OP | Spain | 0.0161−1.097 | 126 |
| | | | <MDL−0.2057 | |
| | | | 0.0097−0.0187 | |
| | | | 0.0061−0.0093 | |
| | NPEO | France | 38 | 70 |
| | OPEO | | 150 | |
| | AE | | 32−136 | |


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Table 4. Continued

| type of analyte | analytes | type/source of sample | concentration | refs |
|---|---|---|---|---|
| | NPEO | Austria | 0.042−0.83 | 168 |
| | NP | | 0.18−1.6 | |
| | OP | | 0.029−0.03 | |
| | AEO | Spain | 290−820 | 107 |
| | NPEO | | 49 | |
| | PEG | | n.d.−2340 | |
| | NPE | Italy | 5.9−284 | 123 |
| | AE | | <MDL−405 | |
| | $C_{12-16}EO$ | Spain | 0.6−30 | 131 |
| | NPE | | 25−222 | |
| | OPE | | <MDL−188 | |
| | AE | Canada/Europe | 0.95−22.71 | 130 |
| | NPEC | Spain/Russia | <0.01−0.82 | 124 |
| | NPEO | | <0.025−198 | |
| | NP | | <0.01−2.58 | |
| | | Japan | n.d. | 122 |
| | | | 1−58 | |
| | | | 0.5−66 | |
| | NPEC | Spain | n.d.−47.8 | 104 |
| | OPEC | | n.d | |
| | NP | | <MDL−18 | |
| | OP | | <MDL−14 | |
| | | sewage [$\mu$g/L] | | |
| cationic | DTDMAC | Germany | n.d.−140 | 46 |
| | DEEDMAC | | | |
| | DEQ | | | |
| anionic | LAS | | 3.6−290 | 101 |
| | DATS | | 0.52−106 | |
| | LAS | Italy | 7−2360 | 22 |
| nonionic | NPEO | | 3−208 | |
| | NP | | 0.3−13 | |

the inner surface of the fused silica capillary. A UV detector is usually used with this method.

Gas chromatography is a more universal means of analyzing surfactants, mainly in combination with single or tandem mass spectrometry. With GC−MS for the quantitative determination of SAAs in suitably prepared extracts, an LOD of the order of 0.02 ng/L is achievable. While GC-MS is suitable for determining highly volatile surfactants, with less volatile SAAs an additional derivatization step is needed. Indeed, this improves the selectivity of SAAs separation and leads to lower LODs and LOQs, which are the metrological parameters that determine the practicability of a methodology in routine monitoring. The derivatization step can be modified by the use of reagents that convert analytes to more stable derivatives (e.g., replacing BSTFA with MTBSTFA) or by using in-port,[91] on-fiber,[140] and in-tube[132] techniques. Like CE, GC cannot be used to determine the contents of cationic compounds in environmental samples.

High-performance liquid chromatography (HPLC) is suitable for determining levels of both ionic and nonionic surfactants; it also enables homologues, oligomers, and isomers of complex surfactant mixtures to be separated. For the quantitative determination of SAAs by HPLC the usual detectors are MS (MS−MS), UV, and FLD. The lowest LODs achieved using HPLC hyphenated with MS−MS was 0.03 ng/L. An undoubted advantages of HPLC is that SAAs levels can be measured in a short time. Sometimes, however, sample preparation can be time-consuming and laborious, and several extraction techniques may need to be applied. A disadvantage of chromatographic methods is the high cost of the apparatus and its operation.

Table 3 summarizes the information on the analytical techniques for determining SAAs contained in diverse types of environmental samples, along with their basic metrological parameters, advantages, and disadvantages.

## 3. LITERATURE DATA ON CONCENTRATIONS OF SURFACTANTS DETERMINED IN ENVIRONMENTAL SAMPLES

The literature provides a wealth of information concerning the presence and concentrations of a wide range of surfactants in environmental samples of different composition and origin. The research objects included soil, street and indoor dust, bottom sediments, sewage sludge, and liquid samples, including precipitation (rain, snow, and cloudwater), atmospheric deposits, aerosols, ground waters, surface waters (river, lake, and sea waters), and sewage.

SAAs concentrations in environmental samples can take values from the LOD of the analytical procedure to over a dozen milligrams per kilogram or milligrams per liter, depending on the type of sample in which the analytes have been determined. Table 4 lists information on SAAs contents determined in different environmental samples from all over the world (soil, dust, bottom sediments, sewage sludge, sewage, rain, snow, aerosols, cloudwater, road runoff, surface waters, sea waters, and ground waters).

## 4. SUMMARY

The diverse practical applications and specific properties of surfactants (including their toxicity toward living organisms) makes it essential to learn their environmental fate. These compounds can move freely within the atmosphere, waters and sediments of various types, soils and even living organisms.

To this end it is essential to develop analytical procedures enabling the simultaneous identification and quantitative determination of different types of surfactants in environmental samples. The biggest problems in selecting appropriate analytical procedures are the complex composition of the samples to be analyzed and the low levels of target analytes, their diverse chemical structures and amphiphilic nature (the tendency for analytes to adsorb on surfaces). Applying increasingly effective means of preparing environmental samples for analysis can solve these problems. An ever-widening spectrum of techniques is available for the detection, identification, and quantitative determination of surfactants in environmental samples with a complex matrix composition.

Analysis of papers reporting the presence of surfactants in different compartments of the environment indicates that our knowledge of the contents of surface active compounds, especially anionic and nonionic ones, in environmental samples is far from complete.

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## ABBREVIATIONS

| | |
|---|---|
| ABS | alkylbenzenesulfonates |
| AE | alcohol ethoxylates |
| AES | alkylethoxysulfates |
| AS | alkylsulfates |
| ATAC | alkyl trimethyl ammonium chloride |
| BAC | benzyl ammonium chloride |
| BDMAC | alkyl benzyl dimethyl ammonium chloride |
| BSTFA | bis(trimethylsilyl)trifluoroacetamide |
| BTDAB | benzothiaxolydiazoaminoazobenzene |
| CD | conductometric detector |
| CDEA | coconut diethanol amides |
| CTAB | cetyl trimethyl ammonium bromide |
| CTMA | cetyltrimethylammonium |
| CWAX-TR | carbowax/template resin-coated fiber |
| DATS | dialkyltetralinsulfonates |
| DBDMAC | dodecylbenzyldimethylammonium chloride |
| DEEDMAC | diethylester dimethylammonium chloride |
| DDAC | dialkyl dimethyl ammonium chloride |
| DDABr | didecyldimethylammonium bromide |
| DEQ_ | diesterquaternary |
| DiSB | disulfine blue |
| DMF | dimethylformamide |
| DTDMAC | ditallowdimethylammonium chloride |
| DTMABr | dodecyltrimethylammonium bromide |
| EB | erythrosine B |
| $EC_{50}$ | effective concentration |
| $^{*}EC_{50}$ | immobilization effective concentration |
| EDTA | ethylenediaminetetraacetic acid |
| $EO_x$ | polyethoxylate |
| FID | flame ionization detector |
| FLD | fluorescence detector |
| HLB | hydrophilic−lipophilic balanced |
| GCB | graphitized carbon black |
| GC-MS | gas chromatography−mass spectrometry |
| HF-LPME | hollow fiber liquid-phase microextraction |
| HPLC | high performance liquid chromatography |
| $IC_{50}$ | inhibitory concentration |
| LAS | linear alkylbenzenesulfonates |
| $LC_{50}$ | lethal concentration |
| LOD | limit of detection |
| LOQ_ | limit of quantification |
| LS | lauryl sulfate |
| MB | methylene blue |
| MCE | mixed cellulose ester |
| MCF | methyl chloroformate |
| MDL | method detection limit |
| MG | methylene green |
| MQL | method quantitation limit |
| MTBE | methyl *tert*-butyl ether |
| MTBSTFA | *N*-*tert*-butyl-dimethylsilyl *N*-methyltrifluoroacetamide |
| NOEC | no observed effect concentration |
| NP | nonylphenol |
| NPD | nitrogen phosphorus detector |
| NPE/NPEO | nonyl phenol ethoxylates |
| NPEC | nonylphenol ethoxy carboxylates |
| NP-LC | normal-phase liquid chromatography |
| NPS | naphthalene sulfonates |
| O-MWCNT | oxidized multiwalled carbon nanotubes |
| OP | octylphenol |
| OPE/OPEO | octylphenol ethoxylate |
| OT-GC | open-top gel chromatography |
| PA | polyacrylate |
| PDMS−DVB | polydimethoxysilane−divinylbenzene |
| PEG | poly(ethylene glycols) |
| PFOA | perfluorooctanoic acid |
| PFOS | perfluorooctane sulfonate |
| PLRP | polymer reversed phase |
| PTFE | polytetrafluoroethylene |
| RSD | relative standard deviations |
| SAEC | subsequent anion-exchange chromatography |
| SDS | sodium dodecyl sulfate |
| SAX or SCX | strong anion exchange or strong cation exchange |
| SLES | sodium lauryl ether sulfate |
| TBAHS | tetrabutylammonium hydrogen sulfate |
| TBAOH | tetrabutylammonium hydroxide |
| TBDMCS | *tert*-butyl-dimethylchlorosilane |
| T(DBHP)P | *meso*-tetra-(3,5-dibromo-4-hydroxyphenyl) porphyrin |
| TLFE | thin liquid film extraction |
| TMAOH | tetramethylammonium hydroxide |
| TPPS | tetrabromophenolphthalein ethyl ester |
| TPS | tetrapropylenebenzenesulfonate |
| UV−vis | ultra-violet detector |
| WAX | weak-anion exchange |

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