Analytics of Surfactants in the Environment: Problems and Challenges

ARTICLE *in* CHEMICAL REVIEWS · JULY 2011

Impact Factor: 46.57 · DOI: 10.1021/cr100107g · Source: PubMed

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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

Received: April 7, 2010
Published: July 11, 2011

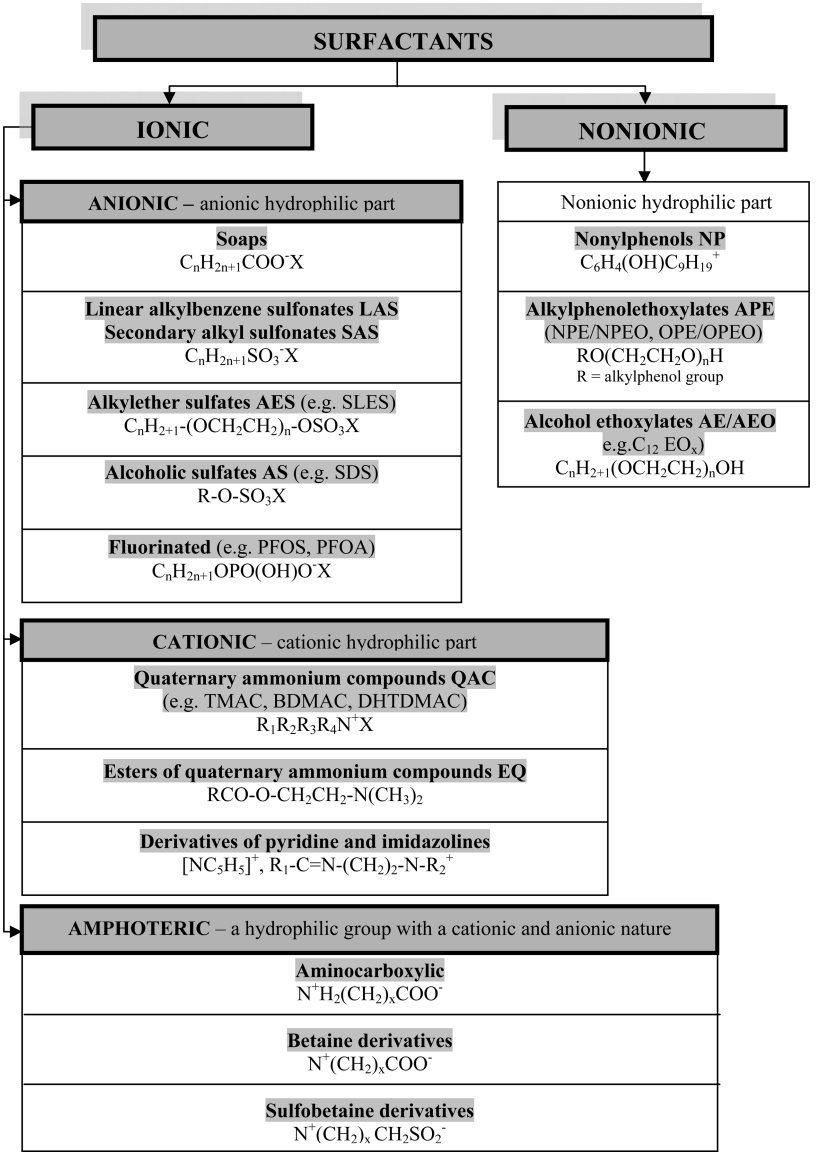

Figure 1. Classification of surface active compounds according to their chemical structure.

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

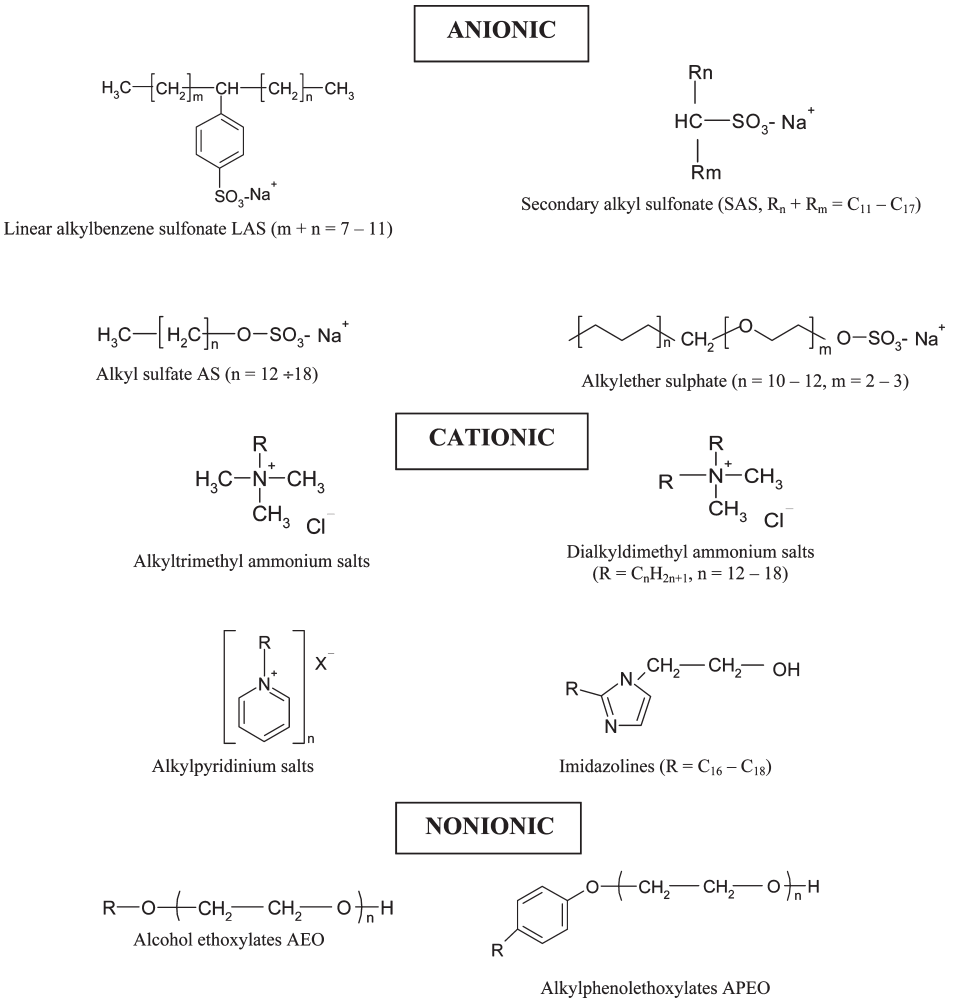

Figure 2. Structural formulas of selected surfactants.

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

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 μg/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 μg/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 2. color reaction with BTDAB 3. mixing 4. determination after 10 min	96−103	• good determination of SAAs in wastewater • 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 2. addition of sample 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^- 2. filtration through PTFE membrane filter 3. washing of filter (EB and acetate buffer) 4. elution of analytes	92	• method for the determination of trace ionic and NS using spectrophotometric techniques • isolation of analytes without toxic organic solvents • simple techniques	• only for the determination of total SAAs	43
anionic				1. addition to sample $CTMA^+$ 2. filtration through PTFE membrane filter 3. washing of filter (EB and acetate buffer) 4. elution of analytes	94−98			
nonionic			90 mL	1. dissolving KCl in sample 2. filtration through MCE membrane filter 3. washing of filter (EB and acetate buffer) 4. elution of analytes				
solvent sublation → liquid sample								
anionic	total	river water	1000 mL	1. solvent, ethyl acetate 2. time, 20 min (**3**)		• procedures for the determination of higher concentrations SAAs (for sewage or sewage treatment plant liquors and effluents) (**3**) higher recovery obtained with the addition of NaCl and $NaHCO_3$	• large volumes of solvent • process separates only dissolved SAAs • removal of surfactant from the solid particles takes a very long time • interferents also separated	44
nonionic		wastewater	5000 mL	1 solvent: ethyl acetate 2 time: n.g. 3 cleanup (reaction with modified Dragendorff reagent): glacial acetic acid	-			45

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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

dx.doi.org/10.1021/cr100107g |Chem. Rev. 2011, 111, 5667–5700

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 II − NPE_{1-2}	river water lake water	500−1000 mL	1. solvent, I fraction = hexane, II fraction = dichloromethane 2. time, 18 h	80			55
				microporous membrane liquid−liquid extraction (MMLLE) → liquid sample				
cationic	QAC	river water waste water	80 mL	1. solvent, 1-chlorobutane 2. ion reagent, heptanoic acid 3. flow rate, 8 mL/min 4. time, 25 min one analysis		• easy online connection to NP-LC (easy to automate) • no premixing in system, minimizes the risk of foam and emulsion formation	• chloroform leakage to aqueous phase • 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 mineral water well water	5 mL	1. solvent, chloroform (extraction solvent), ethanol (dispersant solvent) 2. time, 3 min 3. centrifuging, 5500 rpm	93−96	• very small amounts of microextraction solvent (<200 μL) required	• difficult to automate • the need to use a disperser solvent lowers the partition coefficient of analytes into the extractant solvent • solvent drop is vulnerable to physical forces • analytes are subsequently desorbed into methanol and then analyzed by HPLC	20
nonionic	NPEO OPEO NP OP	tap water river water		1. solvent, trichloroethylene (extraction solvent), acetone (dispersant solvent) 2. time, 10 min 3. centrifuging, 5000 rpm	71−75	• technique cheap, straightforward and quick • high level of preconcentration		57
	NP OP	river water		1. solvent, chloroform (extraction solvent), methanol/pyridine (dispersant solvent and catalyst), MCF (derivatization) (**7**) 2. time, 5 + 5 min (sonication + centrifuging) 3. centrifuging, 5000 rpm	88−106	(**7**) in situ derivatization		58
		tap water river water wastewater	20 mL	1. solvent, octanol 2. time, 2 + 2 min (sonication + centrifuging) 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**) 2. time, 24 h (with stirring)				60
				solid−liquid extraction (SLE) → solid sample				
cationic	DTDMAC	sewage sludge marine sediments	0.5 g 5 g	1. solvent, methanolic HCl 2. ion-pair reagent, LAS 3. cleanup, LLE (chloroform), SAEC (methanol)	91	• extraction is fast, simple and cost-effective • 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 • 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 2. ion-pair reagent, MB 3. time of extraction, 1.5 min				61
	LAS	sewage sludge	0.2 g	1. solvent, methanol 2. cleanup, with or without SPE (**9**)	44−96 33−70			62
		floor dust	1 g	1. solvent, ethanol 2. time, 4 h 3. temperature, 60 °C 4. cleanup, SPE (SAX, C18)	20−95			63
	PFOA PFOS	river sediment	5 g	1. solvent, water, MTBE 2. ion-pair reagent, TBAHS 3. time, 20 + 30 min (shaking + centrifuging)	81−108			33
		sludge	0.5 g	1. solvent, acetonitrile/methanol 2. time, 1 h 3. cleanup, SPE (HLB) (**10**)	91−99 82−99			64
nonionic	NP OP	river/lake sediment	10 g	1. solvent, dichloromethane 2. time, 20 min 3. cleanup, LLE (dichloromethane), removing sulfur (copper powder), silylation (Florisil)	91−97 87−100			27
				Soxhlet extraction → solid sample				
cationic	DDAC BAC ATAC	sludge [33] / river sediment	1 g 5 g	1. solvent, methanol 2. time, 18 h 3. cleanup, LLE (chloroform, water)	67−95	• technique for extracting nonvolatile and semivolatile compounds from solid samples (soils, sludge, and sediment) • equipment uncomplicated and inexpensive • one batch of solvent is recycled during extraction	• long extraction time • uses large volumes of organic solvents (toxic, expensive, and inflammable) • recoveries generally low • 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 SPC	soil	5 g	1. solvent, methanol 2. time, 16 h 3. cleanup, SPE (C18)	77−93 13−74 (**11**)			34
	LAS TPS	lake sediment	5−20 g	1. solvent, methanol 2. time, 15 h 3. cleanup, SPE (SAX) 4. derivatization and cleanup (1.5 g alumina)	79−113			67
	LAS AES AS	sediment	5 g	1. solvent, methanol 2. time, 5 h 3. cleanup, SPE	94−112 61−109			68
	PFOA PFOS	sewage sludge	2 g	1. solvent, methanol/water (99:1, v/v) 2. time, 6 h	48			69
nonionic	NPE NP, OP	river/lake sediment	5 g	1. solvent, dichloromethane 2. time, 6 h	80			55
	NP OP		10 g	1. solvent, dichloromethane 2. time, 18 h	<80			27

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

Table 2. Continued

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

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

Table 2. Continued

type of surfactant	analytes	type of sample	volume/weight of sample	conditions of isolation/ preconcentration	recovery (%)	advantages	disadvantages	refs
		sludge sediment	1 g 5 g	1. solvent, methanol 2. time, 30 min 3. cleanup, SPE (Envi-Carb)	82−83			86
nonionic	NPEO, PEG, NP, OP	sewage sludge	2 g	1. solvent, methanol/dichloromethane 2. cleanup, SPE (C18)	67−101			82
	NP OP	river sediment	5 g	1. solvent, methanol 2. time, 15 min 3. cleanup (silica gel, sodium sulfate)	90 123			87
	NPEO AEO	sludge	10 g	1. solvent, dichloromethane 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 2. pressure, 40.53 MPa; temperature, 85 °C 3. time, 45 min 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 marine sediments	0.5 g 5 g	1. medium, CO_2 modified with methanol 2. pressure, 38.50 MPa; temperature, 100 °C 3. time, 17 min 4. cleanup (SPE)	96			32
anionic	LAS AS SAS AES	sewage sludge	15 mg	1. medium, subcritical water (**20**) 2. pressure, 10 MPa; temperature, 200 °C 3. time, 15 min 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 SAS		100 mg	1. pressure, 40.53 MPa; temperature, 80 °C 2. time, 15 min	86−91 89−94			91
nonionic	NPE NP OP	sediment	0.25−1 g	1. medium, CO_2 2. pressure, 35.14 MPa; temperature, 80 °C 3. time, 25 min 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 NPEO	sewage sludge	0.1−1 g	as above	86−105			92
	AE NPE NPEC NP		15 g	1. medium, subcritical water (**20**, **21**) 2. pressure, 10 MPa; temperature, 200 °C 3. time, 15 min 4. cleanup (Carbograph)	>86	(**20**) water under subcritical conditions efficiently extracts polar and nonpolar compounds from solid matrices (**21**) fractionation of nonacidic and weakly acidic compounds	(**22**) the recovery of NP_3EC or NP_4EC by this method was not evaluated	90

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 2. pressure, 15 MPa; temperature, 75 °C 3. time, 20 min 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 2. time, 7 min 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 (**23**) no purification of the samples is required for the final determination (HPLC) (**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 (**24**) low recoveries for NP	83, 94
nonionic	NP, OP	river sediment	5 g	1. solvent, hexane/ethyl acetate 2. time, 15 min 3. pressure, 1.4 MPa; temperature, 130 °C 4. cleanup (silica gel)	96−103			87
				1. solvent, methanol 2. time, 15 min 3. pressure, 1.4 MPa; temperature, 100 °C 4. cleanup, SPE (HBL)	94−102			65
		marine sediment	1 g	1. solvent, dichloromethane/methanol 2. time, 25 min 3. pressure, 1.4 MPa; temperature, 130 °C 4. cleanup, SPE (Envi-Chrom P)	60 (**24**) 86			96
	NP NP_1EC NP_2EC	sediment (Atlantic Ocean)	1 g	1. solvent, acetone (**25**) 2. time, 15 min 3. pressure, 0.145 MPa 4. cleanup, SPE (Florisil)				21
		sediment		1. solvent, methanol 2. time, 15 min 3. pressure, 0.159 MPa 4. cleanup, SPE (Lichrolut)				28

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 • high recoveries of ionic and anionic analytes • low consumption of organic solvents • elimination of highly toxic solvent (chloroform) from sample preparation step • smaller amount of sample needed • automation of isolation step is possible (**26**) online SPE (**27**) SDS hemimicelle-based SPE (**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) (**29**) determination of the concentration, both total surfactant and individual homologue (LAS) or oligomer (APEO), possible (**30**) isolation LAS + APE (**31**) separation from sample different homologues of analytes (LAS, BS, NPS)	• samples may not contain large amounts of particulate matter • sorbent size must be adapted to the contents of analytes in the sample • relatively high price of cartridges • 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) • 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 1. conditioning, acetonitrile, water 2. washing, water/acetic acid 3. elution, acetonitrile/acetic acid/water	80−105			97
	BAC	tap water wastewater	50 mL	type of cartridge, Hysphere or PLRP-s (**26**) 1. conditioning, acetonitrile, water 2. elution, acetonitrile/ammonium buffer	71−90			98
		river water wastewater	250−1000 mL	type of cartridge: Alumina (**27**) 1. passing sample solution with SDS 2. elution, methanol	95−106			99, 100
anionic	LAS	sewage	10−100 mL	type of cartridge, GCB (**28**) 1. conditioning (TMAOH/dichloromethane/ methanol/water) 2. washing (water/methanol) 3. elution, fraction = TMAOH/dichloromethane	91−100			22
	LAS, DATS	sewage river water groundwater	10−1000 mL	type of cartridge, GCB 1. conditioning, water 2. washing, water, methanol, dichloromethane/ methanol/formic acid 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 2. washing, water/methanol 3. elution, methanol	96−120			103
				type of cartridge, C18 (**30**)				104
		surface water		1. conditioning, methanol, water 2. elution, methanol	>90			105
		wastewater	10−250 mL	type of cartridge, C18 1. conditioning, methanol, water 2. washing, methanol/water 3. elution, methanol	98−101			106
	LAS, ASE, AS	sea water	100 mL	type of cartridge, C18 1. conditioning, methanol, water 2. washing, water 3. elution, methanol				68

dx.doi.org/10.1021/cr100107g |Chem. Rev. 2011, 111, 5667–5700

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 1. conditioning, methanol, water 2. washing, water, water/methanol 3. elution, methanol	99−101			107
	LAS (**31**)	wastewater	200 mL	type of cartridge, Isolute ENV+ 1. conditioning, methanol, water 2. washing, water/methanol 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+ 1. conditioning, methanol, water 2. elution, methanol	77−93			109
	sulfated and sulfonated surfactants	seawater	10 mL	type of cartridges, SDB (**33**) 1. conditioning, methanol, water 2. washing, water 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**) 1. addition of SDS and filtration (PTFE filter) 2. washing filter, water, methanol 3. passing methanolic solution through SCX 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 2. washing, methanol/water 3. elution, methanol 1. conditioning, methanol 2. washing, methanol/acetic acid 3. elution, methanol/HCl	92−107			62
		coastal marine water	250 mL	type of cartridges, Isolute ENV+ SAX (**35**) 1. first elution, methanol 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 1. conditioning, methanol, water 2 washing: methanol/water 3 elution: methanol				112

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 1. conditioning, methanol, water 2. washing, water 3. elution, methanol	80−109 49−130			113
		sea water	100 mL	type of cartridge, Oasis WAX 1. conditioning, ammonium hydroxide/methanol, methanol, water 2. washing, ammonium acetate buffer 3. fractionation, methanol or ammonium hydroxide/methanol	99−103			114
		rain water		type of cartridge, Oasis WAX 1. conditioning, methanol, water 2. washing, water/ammonium hydroxide 3. fractionation, acetonitrile or methanol/ ammonium hydroxide	55−137			115
		river water	500 mL	type of cartridges, Oasis WAX 1. conditioning, methanol, water 2. washing, sodium acetate buffer, methanol 3. elution, ammonium hydroxide/water/ methanol/MTBE				116
		surface river water	5000 mL	type of cartridge, Strata XAW 1. conditioning, methanol, water 2. washing, formic acid 3. elution, ammonium hydroxide/methanol				117
		river water wastewater	250 mL	type of cartridge, Oasis HLB 1. conditioning, methanol, water 2. washing, methanol/water 3. elution, methanol	>50−105			118, 119 86
		rain snow	2000 mL 2 kg	type of cartridges, Oasis HLB+Presep-C Agri 1. conditioning, methanol, water 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**) 1. conditioning, methanol, water 2. washing, water 3. elution, acetic acid, ammonium acetate/ methanol	90−106	(**36**) semiautomated system		121

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 1. washing, acetonitrile/water 2. elution, dichloromethane/methanol				122
	NPEO, NP	sewage	10−100 mL	type of cartridge, GCB (**29**) 1. conditioning, TMAOH/dichloromethane/ methanol/water 2. washing, water 3. elution, dichloromethane/methanol and formic acid/dichloromethane/methanol	89−99			22
	NPE, AE	wastewater	500 mL	type of cartridge, GCB 1. conditioning, TMAOH/dichloromethane/ methanol/water 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 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 2. elution, methanol	72−98			124, 125
	NPEO, OPEO, NP, OP	wastewater	250 mL	type of cartridge, C18 (**37**) 1. conditioning, methanol, water 2. washing, water 3. elution, methanol	60−108	(**37**) reduction of volume of solvent for elution analytes (2 mL)		70
				type of cartridges, C18 1. conditioning, methanol, water 2. washing, elution, hexane/dichloromethane	75−102			126
		river water	4000 mL	type of cartridges, Isolute ENV+ or C18 (**38**) 1 conditioning, dichloromethane, acetone, water 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 1. conditioning, ethyl acetate, methanol 2. washing, water 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 1. conditioning, methanol, methanol/acetonitrile, methanol, water 2. elution, methanol/acetonitrile				123, 127

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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**) 1. conditioning, methanol, water 2. elution, methanol 1. conditioning, chloroform/methanol, hexane 2. washing, hexane 3. elution, chloroform/methanol		(**43**) the second extraction procedure was a SSPE for the preconcentration of nonionic polar surfactants present in highly contaminated matrices (**44**) procedure is good for analyte fractionation (**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) (**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**) 1. conditioning, methanol 2. washing, water/methanol 3. elution, methanol				102
	A, AEO_n $n > 15$ B, AEO C, NPEO D, PEG	wastewater (**43**)	200 mL	type of cartridges, LiChrolut RP-18 + EN 1. conditioning, water/methanol 2. acidification residual water and loading on second cartridge 3. elution, RP-18 A, hexane; B, dichloromethane/ hexane; C, methanol/dichloromethane; EN D, methanol (**44**)	74−82 92−94 72−73			107
	$C_{12}EO_7$ $C_{12}EO_5$	river water	500 mL	type of cartridges, C18 +S CX + SAX (**45**) 1. conditioning, SCX, SAX-methanol, methanol/ HCl/water; C18, acetone, methanol, water 2. isolation, methanol/water 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**) 1. conditioning, water, acetonitrile, methanol/ ethyl acetate/water, methanol, acetone/ dichloromethane, acetonitrile; C2−water 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 1. conditioning, water 2. passing solution containing SDS 3. elution, methanol	95−106	SDS hemimicelle-based SPE		131

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 2. temperature, room 3. time, 60 min 4. stirring 500 rpm (**47**)		• small sample volume • simplicity of extraction • solvent-free isolation (**48**) in situ acylation may be useful for hydrophilic analytes (**50**) in-tube silylation may be useful for hydrophobic analytes	(**47**) SBSE without derivatization, lowest extraction efficiency (**49**) SBSE with in situ derivatization, extraction less effective than in tube	132
				1. addition of derivatization reagent to sample 2. 1−4 as above (**48**, **49**)	93 96 94 95			
				1. coating of stir bar, polydimethylsiloxane 2. temperature, room 3. time, 60 min 4. stirring 500 rpm 5. derivatization in-tube (**50**)				
				solid-phase microextraction (SPME) → liquid/solid sample				
anionic	LAS	sea water		1. nondepletive SPME 2. type of fiber, PA (**51**)		•. reduction and simplification of sample preparation •. use of organic solvents unnecessary •. small sample volume •. high sensitivity of isolation •. automation possible hydrophobic analytes sampled onto the fiber can be directly desorbed in the GC injection port (**53**) compounds containing polar groups in their structures should be derivatized before analysis with GC to improve the quality and sensitivity of separation (**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 (**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) (**52**) background adsorption and matrix effects problematic (reduction during headspace extraction) (**55**) silyl derivatives with limited stability to hydrolysis; moisture content may affect derivatization (**56**) extractionequilibria of most analytes achieved after 80 min SPME	133
			5−7 mL	1. direct immersion with in-port derivatization 2. type of fiber, PDMS 3. time, 30 min 4. temperature, 25 °C				111
	PFOA, PFOS	river water/ wastewater	1 mL	online in-tube SPME	81−83 82−85			134

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 2. type of fiber, CWAX/TRCF 3. time: 60 min 4. temperature, 25 °C				135
	BPA, NP	wastewater	9.5 mL	1. direct immersion without derivatization (**52**) 2. type of fiber, PDMS/DVB 3. time, 60 min 4. temperature, 30 °C				136
	NP, $NPEO_n$	tap water river water	40 mL	1. direct immersion without derivatization (**52**) 2. type of fiber, DVB/CAR/PDMS 3. time, 60 min 4. temperature, 50 °C 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**) 2. type of fiber, PDMS, PDMS-DVB, PA 3. time, 90 min				138, 139
	NP, OP	river water	100 mL	1. direct immersion with derivatization on-fiber (silylation, BSTFA) (**52**, **54**, **55**) 2. types of fiber, PA 3. time, 60 min 4. temperature, 25 °C				140
		tap/lake water	2 mL	1. direct immersion with derivatization on-fiber (MTBSTFA/TBDMCS) (**52**) 2. types of fiber, PA, PDMS-DVB 3. time, 30 min 4. temperature, 65 °C				141

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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) • extraction into organic solvent • measurement of organic phase absorbance	linearity = 0.05 − 50 mg/L LOD = >0.22 mg/L RSD =4.9%	• analysis quick and simple • for determining total contents of a particular group of SAAs • uncomplicated apparatus • 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) • susceptible to interferents in the sample • no possibility of determining individual homologues or isomers • production of very toxic wastes **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-) • extraction into organic solvent • measurement of the organic phase absorbance	linearity = 0.05−2 mg/L LOD = 1.7 μg/L RSD = 0.64−5.9%			
nonionic	• formation of a ion-pairs with suitable reagent (modified Dragendorff reagent - BiAS, Pb(II)−T(DBHP)P) • determination of Bi (or Pb) ion content	linearity = 0.2−200 mg/L precision = 1.8−3.0% LOD = 20 μg/L RSD = 0.8−10%			
			flow injection analysis (FIA)		
cationic anionic	• based on ion-pair formation between analytes and reagent (MB, Fe(III)-SCN-, Bi(III)-I • online measurement of organic phase absorbance	LOD = 110−140 μg/L RSD = 0.7−2.4%	• technique simple and rapid • minimal consumption of organic solvents	• total analyte content determined	151−153
			potentiometric titration		
cationic anionic	• measurement of the change in EMF of the measurement cell caused by the addition of the titrant • 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 LOD = 4.0×10^{-6} mol/L RSD = 1.13%	• fast analysis • for determining total contents of a particular group of SAAs • uncomplicated apparatus	• no possibility of determining individual homologues or isomers • nonionic SAAs cannot be determined	154, 155

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

Table 3. Continued

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

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

Table 3. Continued

analytes	measurement principle	metrological parameters	advantages	disadvantages	refs
		high performance liquid chromatography (HPLC)			
cationic anionic nonionic	• technique for separating ionic and nonionic SAAs, quantitative and qualitative determination • mobile phase, liquid • ionization, atmospheric pressure chemical ionization, electrospray ionization • detector: UV* FLD** CD (for ionic SAAs) MS*** MS-MS****	LOD [μg/kg or μg/L] = * 0.03 or 0.0067 ** 3.7 or 0.03 *** 0.026 or 0.00021 **** 0.000033 μg/L RSD = 6−15%	• all groups of SAAs can be determined • single analytes can be analyzed and at lower concentrations • low-volatility analytes with large molar masses can be determined • addition of a standard enables e stimation of analyte recovery from environmental samples • 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 • complicated and expensive apparatus • analysis is costly (use of high-purity eluents, creation of a vacuum) • 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

dx.doi.org/10.1021/cr100107g |Chem. Rev. 2011, 111, 5667–5700

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

type of analyte	analytes	type/source of sample	concentration	refs
		soils [μg/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 μM/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 [μg/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 μg/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	

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 [μg/l]		
cationic	total	atmospheric water	1.0−11.7 pmol/m^3	163
		aerosols	26.1−129.6 pmol/m^3	39

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 μg/L	36
	PFOA	rain	0.0001−0.0033 μg/L	115
	PFOS		0.0004−0.0093 μg/L	
			0.0329−0.0408 μg/L	120
			0.00992−0.113 μg/L	
		snow	0.00774−0.0567 μg/L	
			0.0375−0.182 μg/L	
		street runoff	0.09 μg/L	112
			0.05 μg/L	
nonionic	NP	rain	0.3−0.95 μg/L	164
		snow	n.d.−0.802 μg/L	
		ground/well/mineral water [μg/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 [μg/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

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 [μg/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 μg/L	168
			0.014−3.5 μg/L	
			n.d.−1.1 μg/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	

dx.doi.org/10.1021/cr100107g |*Chem. Rev.* 2011, 111, 5667–5700

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 [μg/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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Prof. Jacek Namieśnik, Ph.D., D.Sc. Gdańsk, Poland Studies in chemistry at the Gdańsk University of Technology. PhD in 1978, professor for Analytical Chemistry since 1996. From 1996 to 2002 and from 2005, Dean of Chemical Faculty, Gdańsk University of Technology. Additionally, he served as Head of Analytical Chemistry Department since 1995. Major research interests included elaboration of new analytical procedures for determination of trace and ultratrace constituents in samples characterized by complex composition of the matrix, design and testing of specific (fit for purpose) analytical units and measuring devices, production of new types of matrix-free reference materials. He is the author and editor of 8 books, author and coauthor of over 300 papers and over 400 lectures and communications published in conference proceedings, and 10 patents. For many years, he was a member of the several Editorial Boards, for example, *Journal of Chromatography A*, *Critical Reviews in*

Analytical Chemistry, The Open Analytical Chemistry Journal, Regional Environmental Change, and *Toxicological and Environmental Chemistry*. Prof. Namieśnik has been the recipient of several awards, including the Award of Prime Minister of Poland in 2008, the Kemula Medal for achievements in the field of analytical chemistry in 2007 and Town Gdańsk Jan Hevelius Scientific Award in 2002. Professor honoris causa, University of Bucharest (Romania) since 2000.

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

REFERENCES

(1) Myers, D. *Surfactant Science and Technology*; John Wiley & Sons: Hoboken, NJ, 2005.
(2) Ying, G. G. *Environ. Int.* **2006**, *32*, 417.
(3) Rosen, M. J.; Dahanayake, M. *Industrial Utilization of Surfactants: Principles and Practice*; AOCS: Champaign, IL, 2000.
(4) Merretting-Bruns, U.; Jelen, E. *Materials* **2009**, *2*, 181.
(5) Nollet, L. M. L. *Chromatographic Analysis of the Environment*; CRC Press/Taylor & Francis Group: Boca Raton, FL, 2005.
(6) Ostroumov, S. A. *Biological Effects of Surfactants*; CRC Press/Taylor & Francis Group: Boca Raton, FL, 2005.
(7) Utsunomiya, A.; Watanuki, T.; Matsushita, K.; Nishina, M.; Tomita, I. *Chemosphere* **1997**, *35*, 2479.
(8) Garcia, M. T.; Ribosa, I.; Guindulain, T.; Sanchez-Leal, J.; Vives-Rego, J. *Environ. Pollut.* **2001**, *111*, 169.
(9) Lewis, M.; Wee, V. *Environ. Toxicol. Chem.* **1983**, *2*, 105.
(10) Singh, R. P.; Gupta, N.; Singh, S.; Singh, A.; Suman, R.; Annie, K. *Bull. Environ. Contam. Toxicol.* **2002**, *69*, 265.
(11) Verge, C.; Moreno, A.; Bravo, J.; Berna, J. L. *Chemosphere* **2000**, *44*, 1749.
(12) Liwarska-Bizukojc, E.; Miksch, K.; Malachowska-Jutsz, A.; Kalka, J. *Chemosphere* **2005**, *58*, 1249.
(13) Van Ewijk, P. H.; Hoekstra, J. A. *Ecotoxicol. Environ. Saf.* **1993**, *25*, 25.
(14) Figge, K.; Schöberl, P. *Tenside, Surfactants, Deterg.* **1989**, *26*, 122.
(15) Sandbacka, M.; Christianson, I.; Isomaa, B. *Toxicol. in Vitro* **2000**, *14*, 61.
(16) Pavlic, Z.; Vidakovic-Cifrek, Z.; Puntaric, D. *Chemosphere* **2005**, *61*, 1061.

(17) Naylor, C. G. *Text. Chem. Color.* **1995**, *27*, 29.
(18) Hall, W. S.; Potoczka, J. B.; Mirenda, R. J.; Porter, B. A.; Miller, E. *Arch. Environ. Contam. Toxicol.* **1988**, *18*, 765.
(19) Petrovic, M.; Lacorte, S.; Viana, P.; Barcelo, D. *J. Chromatogr. A* **2002**, *959*, 15.
(20) Bidari, A.; Ganjali, M. R.; Norouzi, P. *Cent. Eur. J. Chem.* **2010**, *8*, 702.
(21) Bartolomé, L.; Cortazar, E.; Raposo, J. C.; Usobiaga, A.; Zuloaga, O.; Etxebarria, N.; Ferńandez, L. A. *J. Chromatogr. A* **2005**, *1068*, 229.
(22) Di Corcla, A.; Samperi, R.; Marcomini, A. *Environ. Sci. Technol.* **1994**, *28*, 850.
(23) Łukaszewski, Z.; Szymański, A. *Mikrochim. Acta* **1996**, *123*, 185.
(24) Barceló, D. *TrAC, Trends Anal. Chem.* **2004**, *23*, 677.
(25) Chen, Y.; Guo, Z.; Wang, X.; Qiu, Ch. *J. Chromatogr. A* **2008**, *1184*, 191.
(26) Vogt, C.; Heinig, K. *Fresenius' J. Anal. Chem.* **1999**, *363*, 612.
(27) Li, D.; Oh, J. R.; Park, J. *J. Chromatogr. A* **2003**, *1012*, 207.
(28) Cortazar, E.; Bartolomé, L.; Delgado, A.; Etxebarria, N.; Ferńandez, L. A.; Usobiaga, A.; Zuloaga, O. *Anal. Chim. Acta* **2005**, *534*, 247.
(29) Shao, B.; Hu, J.; Yang, M.; An, W.; Tao, S. *Arch. Environ. Contam. Toxicol.* **2005**, *48*, 467.
(30) Wurl, O.; Miller, L.; Röttgers, R.; Vagle, S. *Mar. Chem.* **2009**, *115*, 1.
(31) Krogh, K. A.; Bugel Mogensen, B.; Halling-Sorensen, B.; Cortes, A.; Vejrup, K. V.; Barcelo, D. *Anal. Bioanal. Chem.* **2003**, *376*, 1089.
(32) Fernandez, P.; Alder, A. C.; Suter, M. J.-F.; Giger, W. *Anal. Chem.* **1996**, *68*, 921.
(33) Bao, J.; Jin, Y.; Liu, W.; Ran, X.; Zhang, Z. *Chemosphere* **2009**, *77*, 652.
(34) Andreu, V.; Picó, Y. *Anal. Chem.* **2004**, *76*, 2878.
(35) Sablayrolles, C.; Montréjaud-Vignoles, M.; Silvestre, J.; Treilhou, M. *Int. J. Anal. Chem.* **2009**, *2009*, 6.
(36) Cini, R.; Prodi., F.; Santachiara, G.; Porcu, F.; Bellandi, S.; Stortini, A. M.; Oppo, C.; Udisti, R.; Pantani, F. *Atmos. Res.* **2002**, *61*, 311.
(37) Ghose, N. C.; Saha, D.; Gupta, A. J. *Water Res. Protect.* **2009**, *4*, 290.
(38) Idouhar, M.; Tazerouti, A. *J. Surfactants Deterg.* **2008**, *11*, 263.
(39) Roslan, R. N.; Hanif, N. M.; Otoman, M. R.; Azmi, W. N. F. W.; Yan, X. X.; Ali, M. M.; Mohamed, C. A. R.; Latif, M. T. *Mar. Pollut. Bull.* **2010**, *60*, 1584.
(40) *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; American Public Health Association: Washington, DC., 1989; p 5540D.
(41) Li, S.; Zhao, S. *Anal. Chim. Acta* **2004**, *501*, 99.
(42) Zhu, Z.; Li, Z.; Hao, Z.; Chen, J. *Water Res.* **2003**, *37*, 4506.
(43) Yamamoto, K.; Oka, M.; Murakami, H. *Anal. Chim. Acta* **2002**, *455*, 83.
(44) Pastewski, S.; Mędrzycka, K. *Pol. J. Environ. Stud* **2003**, *12*, 643.
(45) Wickbold, R. *Tenside Deterg.* **1972**, *9*, 173.
(46) Radke, M.; Behrends, T.; Forster, J.; Herrmann, R. *Anal. Chem.* **1999**, *71*, 5362.
(47) Martınez-Carballo, E.; Gonzaez-Barreiro, C.; Sitka, A.; Kreuzinger, N.; Scharf, S.; Gans, O. *Environ. Pollut.* **2007**, *145*, 489.
(48) Jurado, E.; Fernandez-Serrano, M.; Nunez-Olea, J.; Luzon, G.; Lechuga, M. *Chemosphere* **2006**, *65*, 278.
(49) Mohd Hanif, N.; Talib Latif, M.; Mohd Ali, M.; Rozali Otoman, M. *Europ. J. Sci. Res.* **2009**, *32*, 268.
(50) Koga, M.; Yamamichi, Y.; Nomoto, Y.; Irie, M.; Tanimura, T.; Yoshinaga, T. *Anal. Sci.* **1999**, *15*, 563.
(51) Akyüz, M. *Talanta* **2007**, *71*, 471.
(52) Wyrwas, B.; Szymański, A.; Łukaszewski, Z. *Talanta* **1998**, *47*, 325.
(53) Nagarnaik, P. M.; Mills, M. A.; Boulanger, B. *Chemosphere* **2010**, *78*, 1056.
(54) Szymański, A.; Wyrwas, B.; Łukaszewski, Z. *Anal. Chim. Acta* **1995**, *305*, 256.
(55) Bennie, D. T.; Sullivan, C. A.; Lee, H.-B.; Peart, T. E.; Maguire, R. J. *Sci. Total Environ.* **1997**, *193*, 263.
(56) Norberg, J.; Thordarson, E.; Mathiasson, L.; Jönsson, J. Å. *J. Chromatogr. A* **2000**, *869*, 523.
(57) Zgoła-Grześkowiak, A. *J. Chromatogr. A* **2010**, *1217*, 1761.
(58) Luo, S.; Fang, L.; Wang, X.; Liu, H.; Ouyang, G.; Lan, C.; Luan, T. *J. Chromatogr. A* **2010**, *1217*, 6762.
(59) Yiantzi, E.; Psillakis, E.; Tyrovola, K.; Kalogerakis, N. *Talanta* **2010**, *80*, 2057.
(60) Liu, J.; Hu, X.; Peng, J.; Jönsson, J.Å.; Mayer, P.; Jiang, G. *Anal. Chem.* **2006**, *78*, 8526.
(61) Selberga, A; Budashovaa, J.; Tennoa, T. *Proc. Est. Acad. Sci., Chem* **2007**, *56*, 87.
(62) Heinig, K.; Vogt, C.; Werner, G. *Analyst* **1998**, *123*, 349.
(63) Vejrup, K. V.; Wolkoff, P. *Sci. Total Environ.* **2002**, *300*, 51.
(64) Yoo, H; Washington, J. W.; Jenkins, T. M.; Libelo, E. L. *J. Chromatogr. A* **2009**, *1216*, 7831.
(65) Martınez-Carballo, E.; Gonzaez-Barreiro, C.; Sitka, A.; Kreuzinger, N.; Scharf, S.; Gans, O. *Environ. Pollut.* **2007**, *146*, 543.
(66) Kreuzinger, N.; Fuerhacker, M.; Scharf, S.; Uhl, M.; Gans, O.; Grillitsch, B. *Desalination* **2007**, *215*, 209.
(67) Reiser, R.; Toljander, H. O.; Giger, W. *Anal. Chem.* **1997**, *69*, 4923.
(68) Lara-Martin, P. A; Gomez-Parra, A.; Gonzalez-Mazo, E. *J. Chromatogr. A* **2006**, *1114*, 205.
(69) Schröder, H.Fr. *J. Chromatogr. A* **2003**, *1020*, 131.
(70) Chiron, S.; Sauvard, E.; Jeannot, R. *Analusis* **2000**, *28*, 535.
(71) Ferrer, I.; Furlong, E. T. *Anal. Chem.* **2002**, *74*, 1275.
(72) Lara-Martin, P. A.; Gomez-Parra, A.; Gonzalez-Mazo, E. *Environ. Pollut.* **2008**, *156*, 36.
(73) Murakami, M.; Takada, H. *Chemosphere* **2008**, *73*, 1172.
(74) Petrovic, M.; Barceló, D.; Diaz, A.; Ventura, F. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 516.
(75) Petrovic, M.; Tavazzib, S.; Barcelo, D. *J. Chromatogr. A* **2002**, *971*, 37.
(76) Loyo-Rosales, J. E.; Schmitz-Afonso, I.; Rice, C. P.; Torrents, A. *Anal. Chem.* **2003**, *75*, 4811.
(77) Loyo-Rosales, J. E.; Rice, C. P.; Torrents, A. *Environ. Sci. Technol.* **2007**, *41*, 6815.
(78) Andreu, V.; Ferrer, E.; Rubio, J. L.; Font, G.; Picó, Y. *Sci. Total Environ.* **2007**, *378*, 124.
(79) Jiménez-Díaz, I.; Ballesteros, O.; Zafra-Gómez, A.; Crovetto, G.; Vílchez, J. L.; Navalón, A.; Verge, C.; de Ferrer, J. A. *Chemosphere* **2010**, *80*, 248.
(80) Sun, H. F.; Takata, A.; Hata, N.; Kasahara, I.; Taguchi, S. *J. Environ. Monit.* **2003**, *5*, 891.
(81) Sanderson, H.; Price, B. B.; Dyer, S. D.; DeCarvalho, A. J.; Robaugh, D.; Waite, S. W. *Sci. Total Environ.* **2005**, *367*, 312.
(82) Petrovic, M.; Barcelò, D. *Anal. Chem.* **2000**, *72*, 4560.
(83) Villar, M.; Fernández-Torres, R.; Callejón, M.; Villar, P.; Jiménez, J. C. *Microchem. J.* **2008**, *90*, 164.
(84) D'Hollander, W.; Roosens, L.; Covaci, A.; Cornelis., C.; Reynders, H.; Van Campenhout, K.; de Voogt, P.; Bervoets, L. *Chemosphere* **2010**, *81*, 478.
(85) Li, F.; Zhang, C.; Qu, Y.; Chen, J.; Chen, L.; Liu, Y.; Zhou, Q. *Sci. Total Environ.* **2010**, *408*, 617.
(86) Ma, R.; Shih, K. *Environ. Pollut.* **2010**, *158*, 1354.
(87) Liu, R; Zhou, J. L.; Wilding, A. *J. Chromatogr. A* **2004**, *1038*, 19.
(88) Cohen, A.; K. Klint, K.; Bøwadt, S.; Persson, P.; Jönsson, J.Å. *J. Chromatogr. A* **2001**, *927*, 103.
(89) Breen, D.G.P A.; Horner, J. M.; Bartle, K. D.; Clifford, A. A.; Waters, J.; Lawrecne, J. G. *Wat. Res.* **1996**, *30*, 476.
(90) Bruno, F.; Curie, R.; Di Corcia, A.; Fochi, I.; Nazzari, M.; Samperi, R. *Environ. Sci. Technol.* **2002**, *36*, 4156.

(91) Field, J. A.; Miller, D. J.; Field, T. M.; Hawthorne, S. B.; Gigert, W. *Anal. Chem.* **1992**, *64*, 3161.
(92) Lee, H. B.; Peart, T. E.; Bennie, D. T.; Maguire, R. J. *J. Chromatogr. A* **1997**, *785*, 385.
(93) Field, J. A.; Reed, R. L. *Environ. Sci. Technol.* **1999**, *33*, 2782.
(94) Villar, M.; Callejón, M.; Jiménez, J. C.; Alonso, E.; Guiráum, A. *Anal. Chim. Acta* **2007**, *599*, 92.
(95) Hibberd, A.; Maskaoui, K.; Zhang, Z.; Zhou, J. L. *Talanta* **2009**, *77*, 1315.
(96) Stuart, J. D.; Capulong, C. P.; Launer, K. D.; Pan, X. *J. Chromatogr. A* **2005**, *1079*, 136.
(97) Bassarab, P. *J. Chromatogr. A* **2011**, *1218*, 673.
(98) Ferrer, I.; Furlong, E. T. *Environ. Sci. Technol.* **2001**, *35*, 2583.
(99) Merino, F.; Rubio, S.; Pérez-Bendito, D. *Anal. Chem.* **2003**, *75*, 6799.
(100) Luque, N.; Merino, F.; Rubio, S.; Pérez-Bendito, D. *J. Chromatogr. A* **2005**, 1094.
(101) Crescenzi, C.; Di Corcia, A.; Marchiori, E.; Samperi, R.; Marcomini, A. *War. Res.* **1996**, *30*, 722.
(102) Scullion, S. D.; Clench, M. R.; Cooke, M.; Ashcroft, A. E. *J. Chromatogr. A* **1996**, *733*, 207.
(103) Bradley, C.; Bérubé, P. R. *J. Environ. Eng. Sci.* **2008**, *7*, 63.
(104) Tubau, I.; Vázquez-Suńé, E.; Carrera, J.; González, S.; Petrovic, M.; de Alda, M. J. L.; Barceló, D. *J Hydrology* **2010**, DOI: 10.1016/j.jhydrol.2009.11.030.
(105) Sander, S.; Henze, G. *Electroanalysis* **1997**, *9*, 619.
(106) Fabios, R.; Sicilia, M. D.; Rubio, S.; Pérez-Bendito, D. *Anal. Chem.* **2003**, *75*, 601.
(107) Castillo, M.; Alonso, C.; Priu, J.; Barceló, D. *Environ. Sci. Technol.* **1999**, *33*, 1300–1306.
(108) Riu, J.; Eichhorn, P.; Guerrero, J. A.; Knepper, Th.P.; Barceló, D. *J. Chromatogr. A* **2000**, *889*, 221.
(109) Pedraza, A.; Sicilia, M. D.; Rubio, S.; Pérez-Bendito, D. *Anal. Chim. Acta* **2007**, *588*, 252.
(110) Bruzzoniti, M. C.; De Carlo, M. R.; Sarzanini, C. *Talanta* **2008**, *75*, 734.
(111) Alzaga, R.; Peña, A.; Ortiz, L.; Bayona, J. M. *J. Chromatogr. A* **2003**, *999*, 51.
(112) Murakami, M.; Kuroda, K.; Sato, N.; Fukushi, T.; Takizawa, S.; Takada, H. *Environ. Sci. Technol.* **2009**, *43*, 3480.
(113) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Anal. Chem.* **2001**, *73*, 2200.
(114) Ahrens, L.; Taniyasu, S.; Yeung, L. W. Y.; Yamashita, N.; Lam, P. K. S.; Ebinghau, R. *Chemosphere* **2010**, *79*, 266.
(115) Dreyer, A.; Matthias, V.; Weinberg, I.; Ebinghaus, R. *Environ. Pollut.* **2010**, *158*, 1221.
(116) Nakayama, S .F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B. *Environ. Sci. Technol.* **2010**, *44*, 4103.
(117) Ahrens, L.; Felizeter, S.; Ebinghaus, R. *Chemosphere* **2009**, *76*, 179.
(118) Weremiuk, A. M.; Gerstmann, S.; Frank, H. *J. Sep. Sci* **2006**, *29*, 2251.
(119) Becker, A. M.; Gerstmann, S.; Frank, H. *Chemosphere* **2008**, *72*, 115.
(120) Liu, W.; Jin, Y. H.; Quan, X.; Sasaki, K.; Saito, N.; Nakayama, S. F.; Sato, I.; Tsuda, S. *Environ. Int.* **2009**, *35*, 737.
(121) Ahrens, L.; Gerwinski, W.; Theobald, N.; Ebinghaus, R. *Mar. Pollut. Bull.* **2010**, *60*, 255.
(122) Komori, K.; Okayasu, Y.; Yasojima, M.; Suzuki,Y; Tanaka, H. PROGRAM and ABSTRACTS of IWA International Conference Sustainable Development of Chemical Industries with the Environment, Waste and Wastewater Management, International Water Association 2005.
(123) Marcomini, A.; Pojana, G.; Patrolecco, L.; Capri, S. *Analusis* **1998**, *26*, 64.
(124) Martianóv, A. A. *Talanta* **2005**, *65*, 367.
(125) Petrovic, M.; Diaz, A.; Ventura, F.; Barcelo, D. *Anal. Chem.* **2001**, *73*, 5886.
(126) Vega-Morales, T. T.; Sosa-Ferrera, Z.; Santana-Rodríguez, J. J. *J. Hazard. Mat.* **2010**, *183*, 701.
(127) Fries, E.; Püttmann, W. J. *Environ. Monit.* **2003**, *5*, 598.
(128) Quednow, K.; Püttmann, W. *Environ. Pollut.* **2008**, *152*, 476.
(129) Yokoyama, Y.; Okabe, T.; Kubo, H.; Sato, H. *Microchim. Acta* **2005**, *149*, 287.
(130) Eadsforth, C. V.; Sherren, A. J.; Selby, M. A.; Toy, R.; Eckhoff, W. S.; McAvoy, D. C.; Matthijs, E. *Ecotoxicol. Environ. Saf* **2006**, *64*, 14.
(131) Cantero, M.; Rubio, S.; Pérez-Bendito, D. *J. Chromatogr. A* **2005**, *1067*, 161.
(132) Kawaguchi, M.; Sakui, N.; Okanouchi, N.; Ito, R.; Saito, K.; Nakazawa, H. *J. Chromatogr. A* **2005**, *1062*, 23.
(133) Rico-Rico, A.; Droge, S. T. J.; Widmer, D.; Hermes, J. L. M. *J. Chromatogr. A* **2009**, *1216*, 2996.
(134) Saito, K.; Uemura, E.; Ishizaki, A.; Kataoka, H. *Anal. Chim. Acta* **2010**, *658*, 141.
(135) Boyd-Boland, A. A.; Pawliszyn, J. B. *Anal. Chem.* **1996**, *68*, 1521.
(136) Braun, P.; Moeder, M.; Schrader, St.; Popp, P.; Kuschk, P.; Engewald, W. *J. Chromatogr. A* **2003**, *988*, 41.
(137) Diaz, A.; Ventura, F.; Galceranb, M. T. *J. Chromatogr. A* **2002**, *963*, 159.
(138) Basheer, C.; Parthiban, A.; Jayaraman, A.; Lee, H. K.; Valiyaveettil, S. *J. Chromatogr. A* **2005**, *1087*, 274.
(139) Li, D.; Park, J.; Oh, J. R. *Anal. Chem.* **2001**, *73*, 3089.
(140) Yang, L.; Luan, T.; Lan, C. *J. Chromatogr. A* **2006**, *1104*, 23.
(141) Pan, Y.-P.; Tsai, S.-W. *Anal. Chim. Acta* **2008**, *624*, 247.
(142) Tobiszewski, M.; Mechlińska, A.; Zygmunt, B.; Namieśnik, J. *TrAC, Trends Anal. Chem.* **2009**, *28*, 943.
(143) Tobiszewski, M.; Mechlińska, A.; Namieśnik, J. *Chem. Soc. Rev.* **2010**, *39*, 2869.
(144) Hultgren, S.; Larsson, N.; Nilsson, B. F.; Jönsson, J. Å. *Anal. Bioanal. Chem.* **2009**, *393*, 929.
(145) Larsson, N.; Mizera, P.; Villar, M.; Petersson, E.; Jönsson, J.Å. In press
(146) Shrivas, K.; Wu, H. F. *Anal. Chim. Acta* **2008**, 198.
(147) Feng, S.; Chen, X.; Fan, J.; Hu, Z.; Internat., J. *Environ. Anal. Chem.* **2005**, *85*, 63.
(148) Tersutaro, Y.; Yasuyuki, S.; Masarki, K.; Toshifumi, T. *Anal. Sci.* **1999**, *15*, 563.
(149) Ródenas-Torralba, E.; Reis, B. F.; Morales-Rubio, Á.; de la Gwardia, M. *Talanta* **2005**, *66*, 591.
(150) Li, S.; Zhao, S. *Anal. Chim. Acta* **2004**, *501*, 99.
(151) Patel, R.; Singh Patel, K. *Talanta* **1999**, *48*, 923.
(152) Agrawal, K.; Agnihotri, G.; Shrivas, K.; Mundhare, G. L.; Patel, S. K.; Hoffmann, P. *Microchem, Acta* **2004**, *147*, 273.
(153) Aydan, T.; Takeuchi, M.; Tanaka, H. *J. Flow Injection Anal.* **2009**, *26*, 133.
(154) Khaled, E.; Mohamed, G. G.; Awad, T. *Sens. Actuators, B* **2008**, *135*, 74.
(155) Lizondo-Sabater, J.; Martínez-Máñez, R.; Sancenón, F.; Seguí, M. J.; Soto, J. *Talanta* **2008**, *75*, 317.
(156) Szymański, A.; Wyrwas, B.; Jesiołowska, A.; Kaźmierczak, S.; Przybysz, T.; Grodecka, J.; Łukaszewski, Z. *Pol. J. Environ. Stud.* **2001**, *10*, 371.
(157) Martianova, A. A.; Dzantieva, B. B.; Zherdeva, A. V.; Ereminb, S. A.; Cespedesc, R.; Petrovic, M.; Barcelo, D. *Talanta* **2005**, *65*, 367.
(158) Kot, A.; Namieśnik, J. *TrAC, Trends Anal. Chem.* **2000**, *19*, 69.
(159) Wasik, A.; Namieśnik, J. *Pol. J. Environ. Stud.* **2001**, *10*, 405.
(160) Namieśnik, J.; Szefer, P. *Ecol. Chem. Eng. S* **2008**, *15*, 167.
(161) Nitschke, L.; Muller, R.; Metzner, G.; Huber, L. *Fresenius' J. Anal. Chem.* **1992**, *342*, 711.
(162) Cantarero, S.; Zafra-Gómez, A.; Ballesteros, O.; Navalón, A.; Vílchez, J. L.; Verge, C.; De Ferrer, J. A. *Environ. Toxicol. Chem.* **2011**, DOI: 10.1002/etc.447.
(163) Latif, M. T.; Brimblecombe, P. *Environ. Sci. Technol.* **2004**, *38*, 6501.
(164) Fries, E.; Puttmann, W. *Atmos. Environ.* **2004**, *38*, 2013.

(165) Patel, R.; Singh Patel, K. *Talanta* **1999**, *48*, 923.
(166) Takagi, S.; Adachi, F.; Miyano, K.; Koizumi, Y.; Tanaka, H.; Mimura, M.; Watanabe, I.; Tanabe, S.; Kannan, K. *Chemosphere* **2008**, *72*, 1409.
(167) Becker, A. M.; Suchan, M.; Gerstmann, S.; Frank, H. *Environ . Sci. Pollut. Res.* **2010**, *17*, 1502.
(168) Clara, M.; Scharf, S.; Scheffknecht, C.; Gans, O. *Water Res.* **2007**, *41*, 4339.