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Review

Analytical procedures for the determination of surfactants in environmental samples

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ABSTRACT

Because of their specific physical and chemical properties (amphiphilicity, solubility in polar and nonpolar liquids, ability to form micelles, adsorption at phase boundaries, low toxicity) surfactants (surface-active compounds) are widely applied in industry and in the household. As their applications are on a very large scale, it has become necessary to acquire a more detailed understanding of their environmental fate.

In the methodologies for analysing environmental samples, the isolation and/or preconcentration of analytes constitutes an important step. The usual techniques are liquid–liquid extraction (LLE), solid-phase extraction (SPE – also used for extract clean-up contains following analytes isolated by another technique) or accelerated solvent extraction (ASE).

For the analysis of samples/extracts, depending on whether information is required – the total concentration or the levels of particular surface-active compounds in environmental samples – spectrophotometry, tensammetry or electrophoresis, and chromatography may be used. Nowadays, high-performance liquid chromatography (HPLC) is usually coupled with a universal mass spectrometry detector (MS) (or tandem mass spectrometry detector MS–MS), what allows for detection, identification and quantification the various compounds in a particular group of surfactants in suitably prepared solvent extracts.

Contents

Abbreviations: AA, Acetic acid; ACN, Acetonitrile; AE/AEO, Alcohol ethoxylates; AES, Alkylethoxysulfates; AMAC, Ammonium acetete; AMF, Ammonium formate; APEO, Alkylphenol ethoxylates; APCI, Atmospheric pressure chemical ionization; AS, Alkylsulfates; ASo, Alkyl sulfonates; ASE, Accelerated solvent extraction; ATAC, Alkyl trimethyl ammonium chloride; BAC, Benzyl ammonium chloride; BDMAC, Alkyl benzyl dimethyl ammonium chloride; BSTFA, Bis(trimethylsilyl)trifluoroacetamide; CD, Conductometric detector; CDEA, Coconut diethanol amides; CTAB, Cetyltrimethylammonium bromide; CWAX/TR, Carbowax/template resin-coated fiber; DCM, Dichloromethane; DDAC, Dialkyl dimethyl ammonium chloride; DHTDMAC, Dihydrogenated tallow dimethylammonium chloride; DiSB, Disulfine blue dyes; DDLME, Dispersive liquid–liquid microextraction; DEEDMAC, Diethylester dimethylammonium chloride; DEQ, Diesterquaternary; DTDMAC, Ditallowdimethylammonium chloride; DVB, Divinylobenzene; EA, Etyhyl acetate; EI, Electron impact ionization; FA, Formic acid; FLD, Fluorescence detector; ESI, Electrospray ionization; GAA, Glacial acetic acid; GC, Gas chromatography; GCB, Graphitized carbon black; HF-LPME, Hollow-fiber liquid phase microextraction; HPLC, High-performance liquid chromatography; LAS, Linear alkylbenzenesulfonates; LLE, Liquid–liquid extraction; LOD, Limit of detection; MAE, Microwaves-assisted extraction; MB, Methylene blue dyes; MBSTFA, *N-tert*-butyl-dimethylsilyl *N*-methyltrifluoroacetamide; MG, Methylene green dyes; MH-AB, Mixed hemimicelle/admicelle-based; MLD, Method limit detection; MMLLE, Microporous membrane liquid–liquid extraction; MS, Mass spectrometry; MS–MS, Tandem mass spectrometry; NI, Negative ionization; NP, Nonylphenol; NPEC, Nonylphenol ethoxy carboxylates; NPEO, Nonyl phenol ethoxylates; OP, Octylphenol; OPEC, Octylphenol ethoxy carboxylates; OPEO, Octylphenol ethoxylate; PA, Polyacrylate; PDMS, Polydimethoxysilane; PEG, Poly(ethylene glycols); PFC, Perfluorinated compounds; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctane sulfonate; PI, Positive ionization; PT, Potentiometry titrametration; SAS, Secondary alkyl sulfate; SAX, Strong anion exchange; SBSE, Stir bar sorptive extraction; SCX, Strong cation exchange; SDS, Sodium dodecyl sulfate; SEC, Size exclusion; SFE, Supercritical fluid extraction; SLE, Solid–liquid extraction; SPC, Sulfophenylcarboxylates; SPE, Solid-sample extraction; SPME, Solid-phase microextraction; TBA, Tribytuloamine; TEA, Triethyleamine; TMAC, Dodecyl trimethyl ammonium; TPS, Tetrapropylenebenzenesulfonate; TQ, Triple quadrupole; Q, Single quadrupole; QAC, Quaternary ammonia compounds; QIT, Quadrupole-ion-trap; Q-TOF, Quadrupole time-of-flight; QIT-TOF, Quadrupole ion-trap time-of-flight.

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1. Introduction

Surface Active Agents (SAAs) constitute a group of compounds which contain in molecules hydrophobic and hydrophilic parts. This phenomenon is defined as amphiphilicity and it causes their specific physical and chemical properties like solubility in polar and nonpolar liquids, ability to form micelles, adsorption at phase boundaries and reduction of the surface tension. These compounds are categorised on the basis of different parameters, but usually surfactants are classified according to their chemical character of the hydrophobic groups (the acronyms of main compounds belonging to a particular group are given in parentheses):

- ionic:
  - cationic (e.g. BAC, BDMAC, TMAC, DDAC, DHTDMAC);
  - anionic (e.g. LAS, SAS, SDS, PFOA, PFOS);
- non-ionic: (e.g. NP, OP, NPEO, OPEO).

Nowadays, surface-active compounds are widely applied in formulation of agents used in the industry and household which possessing specific properties (washing, wetting, emulsifying, dispersing). As a consequence, different types of surfactants are added to laundry and cleaning detergents, personal-care products, food, paints, pesticides and petroleum products [1–3].

As the everyday increase in the production of SAAs and their possible usage, it has become necessary to monitor their levels and impact on different parts of the environment. Released into different ecosystems the surfactants are subject to a variety of physical and chemical changes. The structures of SAAs are such that they can be adsorbed on the surface of solid particles or be absorbed in droplets of water vapour, as a result of which they can occur in the atmosphere in aerosol form. Moreover, the amphiphilic properties of surfactants and wet deposition facilitate the presence of these compounds in wet and dry atmospheric precipitation, as well as the transport of contaminants to surface and runoff waters (and then to ground waters) [4]. In addition, the volatility of some surfactants enables them to evaporate into the atmospheric air. SAAs are then transported with the air and eventually deposited (often a long distance from the point of emission), after which they find their way into living organisms (in which they bioaccumulate) [5]. Consequently, there is a need to develop appropriate analytical procedures enabling the determination of a wide range of surface active agents in different types of environmental sample.

In this paper we present main problems posed by analysis of SAAs in environmental sample. We also review the analytical techniques used to:

- isolation and/or preconcentration surfactants from different types of samples;
- identification and quantification analytes in properly prepared extracts.

It should be noted that the review is devoted to compounds named as traditional surfactants (produced from raw materials from non-renewable sources). However, the discussion about analysis of PFOA and PFOS in different environmental samples is associated with presentation of procedures the determination of the whole group of PFCs compounds, not only surface active agents depend to them, so hence this problem will be omitted in the review (to ensure its readability).

Presently, the scientists work on formulation more "greener" compounds than traditional SAA – biosurfactants produced from renewable resources. Currently, that group of compounds is very promising because of their possibility of application in different areas of human activity, their high degree of biodegradation and lower toxicity than traditional SAA [6–8]. The more frequent application of biosurfactants, as we mentioned before, makes it necessary to develop analytical methodologies allow for the determination such compounds in different ecosystems. The existing researches only focus on the analytical characterization of products synthesized by various types of microorganisms [9–11]. However, no information is available about determination of biosurfactants in environmental samples and this issue will not be discussed in this work.

2. Determination of surfactants in different types of samples

Surface-active compounds (due to their specific physical and chemical properties) are widely applied in industry, in household and elsewhere. Therefore, surfactants (or their metabolites) will inevitably get into different compartments of ecosystems. The determination of SAAs levels in different environmental samples becomes a crucial analytical problem which could be resolve by the development of new analytical methodologies. However, the analysis of surface active compounds in these samples is difficult becouse of [12]:

- the complex matrix composition;
- the low concentrations of individual analytes;
- the various chemical structures of SAAs;
- the amphiphilicity of surfactants molecules.

The complex matrix composition of environmental samples and the low concentration of SAAs mean that suitable extraction techniques have to be applied at the sample preparation stage for isolation and/or enrichment of analytes. On the preparation stage errors may be committed which will affect on the final result of the analysis, so it is important to select such conditions for analytes preconcentration that will ensure appropriate sensitivity and reproducibility [13].

The various molecular structures of surfactants and their properties cause that required the separation during sample preparation (application to the analysis extraction techniques). For example surfactants like QAC can underestimate the levels of anionic SAAs [14]. On the other hand, it is sometimes advantageous to simultaneously isolate anionic and non-ionic surfactants and next to fractionation using appropriate solvents before their quantitative determination [15,16].

The amphiphilicity of SAAs cause that these compounds may be adsorbed on the different surfaces (e.g. on solid particles contained in the environmental samples, on the laboratory glassware

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and apparatus used during the analytical procedures). As a consequence of amphiphilic nature of surfactants molecules during isolation and preconcentration stage an internal standard has to be added to the sample before the solvent extraction (for estimation the losses of targets analytes). This approach is taken with respect to chromatographic techniques during the identification and quantities determination of the contents of compounds in the various groups of surfactants [17,18].

However, addition the internal standard and plotting appropriate calibration curves are problematic. The three main reasons of which are [12]:

- the limited availability of commercial standard solutions of surfactants (e.g. only available are standards of anionic SAA: LAS or non-ionic SAA: NP, NPEO);
- the application of standard solutions prepared from technically pure products (instead of commercial standard solutions);
- the need to synthesize specific compounds or purification commercial products containing selected surfactants.

In Table 1 information on compounds and/or mixtures used in previous research of occurrance of the surface active agents in environmental samples are collected.

2.1. Sample pre-treatment

The collection and storage of environmental samples, both solid and liquid, should provide a representative sample and the compounds should not be allowed to decompose [1].

Solid samples like soils, sediments and sewage sludges after sampling are drying (e.g. in an oven [21], at room temperature [41]) or subjected to freeze-drying (after frozen at −20 °C) [42]. After drying samples are grinding, sieving and then stored at a low temperature (at 4 to −20 °C) before analysis.

In the aquatic environment many organic pollutants undergo biodegradation, especially when liquid samples are rich in microorganisms such as sewage as well as surface water [43]. A biocide is therefore added to aqueous media immediately after sampling in order to minimize the biodegradation of surfactants – the usual one is a solution of formaldehyde, mineral acids (to pH ∼2) [21,44,45] or sodium azide [43]. Then samples are stored at a low temperature (at 4 °C).

2.2. Sample preparation

In environmental samples the surface active agents are usually at trace levels bellow the limit of detection of most analytical techniques used for identification and quantities determination. Because of this limitation necessary is involve techniques for isolation or/and preconcentration on the sample preparation stage. During last years, on the isolation stage of surfactants from liquid environmental samples, were used following techniques:

- liquid–liquid extraction (LLE) [19,20,44,46–49];
- solid-phase extraction (SPE) [33,34,40,50–64]

and solid samples:

- solid–liquid extraction (SLE) [24,55,56].

Below will be presented the operations and processes used at this stage of the analytical procedure (with division due to the solid and liquid samples).

2.3. Liquid samples

2.3.1. Liquid–liquid extraction (LLE)

The liquid–liquid extraction has been widely used for the determination of ionic and non-ionic SAAs. Separation of analytes in LLE is based on distribution of compounds between two immiscible or partially miscible liquid phases. Due to those rudiments to aqueous samples are added appropriate organic solvents – chloroform to extraction of anionic and cationic SAAs [19,20,47,48], dichloromethane (DCM) and ethyl acetate to isolation non-ionic SAAs [44,49]. Table 2 shows details of the conditions for carrying out isolation step with this extraction technique.

The main advantages of LLE technique is ability to use during determination total concentration of cationic, anionic or non-ionic surfactants in environmental samples, which often contain a lot of solid particles matter. This isolation technique is used in routine analysis of occurrence surface active agents in different ecosystems. Moreover, LLE is considered to be the most effective technique for extraction of cationic surfactants from liquid samples [43].

On the other hand, LLE is time-consuming (clean-up step is involve), consumption of organic solvent and production of toxic wastes in this technique is very high. The isolation of analytes requires large volumes of samples (usually 100–500 mL). Furthermore, the tendency of SAAs to the formation of emulsion causes difficulties during the phase separation. This disadvantage can be avoided by formation of hydrophobic ion-pairs between surfactant and specific ion-pair reagent [1] (e.g. disulfine blue dyes (DiSB) or LAS for cationic SAAs [20,43,46], methylene blue (MB) [20,47] or methylene green (MG) for anionic SAAs [28], modified Dragendorff reagent for non-ionic [49]).

2.3.2. Solid-phase extraction (SPE)

Solid-phase extraction (SPE) at present is the most popular sample preparation technique for determination of surfactants in liquid samples. This technique applies to a wide range of compound classes and has undergone considerable development in the last years, with many improvements like automation or introduction of new sorbents or medium for elution of analytes. Table 2 contains general information of isolation procedures with use of solid-phase extraction technique.

This analytical technique allows for reduction volume of organic solvents in comparison with LLE and give possibility to eliminate of chloroform from sample preparation stage. During use of SPE the analytes from liquid samples are adsorb to appropriate sorbents like: GCB, C18, SDVB, SAX, SCX with different recovery. After washing exchange resins (to remove water, salts or other contaminations) the adsorbed surfactants are eluted with use of appropriate organic solvents like: ACN, MeOH, water, different types of buffers [45,50–65]. Table 3 gives overview about conditions of isolation cationic, anionic and non-ionic analytes from liquid samples with use of SPE technique.

Cartridges contain octadecylsilica phase are universal sorbent for extraction surface active agents from environmental samples. However, isolation of cationic analytes associated with strong interaction with silanol groups of sorbent and it results in very broad elution bands [57]. During comparison of application two different sorbents (polymeric and octadecylsilica) for extraction of non-ionic SAA from aqueous sample found that both phases give similar recovery of analyzed compounds, but polymeric sorbent allows for faster isolation and use larger volume of sample (it is important when analytes in samples are at trace levels) [66,67]. Moreover, application of SPE sorbent like GCB or C18 allows for simultaneous separation of anionic (LAS, SPC, AES) and non-ionic (APEO, APEC, NP) surfactants during one extraction [16,35,42]. Cassani et al. [68] describe determination of AE in sludge samples with use of SPE techniques for isolation (application of Resprep disk)

Table 1
Compounds or mixtures used as standards in analysis of SAAs in environmental samples.

Analytes	Sample	Compounds and mixtures used as standard	References
Total of cationic SAAs	River water	Cetyltrimethylammonium bromide (CTAB)	[19]
	Sea-surface water	Benzyldimethyltetradecylammonium chloride (Zephiramine), benzyldimethyltetradecylammonium chloride dihydrate	[20,21]
Total of anionic SAAs		Sodium dodecyl sulfate	[20]
Total of non-ionic SAAs	River water	Triton X-100	[22]
DDAC, BAC, ATAC	–	C_{10-18}DDAC, C_{10-14}BAC, C_{12-18}ATAC	[23]
DTDMAC	Sewage sludge	DTDMAC (97%), didecyldimethylammonium chloride (DDDMAC, surrogate standard)	[24]
BAC	River sediment	Technical mixture of BAC, atrazine (surrogate standard)	[25]
LAS		C_{n-m}-LAS (n – length of the alkyl chain and m – position of the phenyl group in the alkyl chain, purity > 97%)	[26]
		Marlon A (commerial mixture of C_{10}–C_{14} LAS)	[27]
	River and sea water	Arylan SE (commercial mixture contains 14 homologues and isomers of C_{10}–C_{12}LAS)	[28]
	Sewage sludge	Commercial LAS mixture: C_{10} (13.5%), C_{11} (33.1%), C_{12} (29.3%), C_{13} (23.1%), others 1% 2-Octylbenzenesulfonic acid sodium salt (81%), 2-hexadecylbenzenesulfonic acid sodium salt (95%, internal standards)	[29]
LAS, AES	River water Sediment	Commercial LAS mixture: C_{10} (10.9%), C_{11} (35.3%), C_{12} (30.4%), C_{13} (21.2%), C_{14} (1.1%) and AES mixture: C_{12} (68.5%), C_{14} (29.8%), C_{16} (1.7%) or C_{12} (17.5%), C_{13} (28.2%), C_{14} (32.1%) C_{15} (22.2%), 2ΦC$_{16}$ LAS (internal standard)	[30]
LAS, AES	River sediment	Deuterated d_4-C_{12} LAS, deuterated sodium d_{25} dodecyl sulfate (SDS)	[31]
SAS	Sewage sludge	Hostapur 60 (commercial mixture), C_{12}, C_{18}SAS (surrogate standard)	[32]
LAS		Dobane 113 (commercial mixture), C8-LAS (surrogate standard)	
	Wastewater	LAS-M (LAS concentration 20%), Petrelab P-550 (9.6% C_{10}, 38.1% C_{11}, 31.3%, C_{12}, 19.1% C_{13}, 1% C_{14})	[33]
	River water		
AES		EMAL 270E (3% C_{12}, 27% C_{14} with EO_2)	
AS, ASo		SDeS, SDS, STS, SHS, SOS, SdeSo, SDSo, STSo, SHSo (pure)	
LAS	Sludge	Commercial LAS mixture: C_{10} (3.9%), C_{11} (37.4%), C_{12} (35.4%), C_{13} (23.1%)	[34]
OP, NP	Wastewater	4-*tert*-OP, 4-NP, 4-n-NP-d8 (internal standard)	
OPEC, NPEC		OP_1EC, OP_2EC (laboratory-synthesized), NP_1EC, NP_2EC (laboratory-synthesized)	
LAS, AES, NPEO, AEO	Sediment	C_{16} LAS	[35]
AES	Sewage sludge	Commercial mixture of C_{12} to C_{15} AES	[36]
NPEO		Marlophen 810 (mixture of NPE)	
AE		Lialet 125 (mixture of AE), $A_{10}E_6$–$A_{18}E_6$ and $A_{12}E$ with 2, 3, 4, 6, 8 EO units	
NP, OP		Branched NP, 4-*tert*-OP	
NPE_1C		Calibrated solution of NPE_1C	
NP, OP	Sludge	4-NP, 4-OP	[37]
AEO	Wastewater	$C1_6EO_6$ and $C_{18}EO_6$ (pure), NEODOL 25-9 contains: C_{12}-EO_x (21%), $C_{13}EO_x$ (20%), $C_{14}EO_x$ (28%), $C_{15}EO_x$ (31%)	
OPEO, NPEO		Triton X-100 (contains 4-*tert*-$OPEO_9$), Nonidet P40 (contains $NPEO_9$)	
OPEO, NPEO, C_xEO	Sludge, wastewater	Hexylphenol pentaethylene glycol, ethylphenol pentaethylene glycol	[38]
APEO	River sediment	NP_1EO, NP_2EO, OP_1EO, OP_2EO (laboratory-synthesized)	[39]
NPEC, OPEC		Findet 9Q/22 (mixture contain $NP_{10}EO$), NP_1EC, NP_2EC, Findet S8Q/21 (mixture contains OP_9EO), OP_1EC, OP_2EC	
OP, NP		4-*tert*-octylphenol (98%), 4-nonylphenol (technical mixture)	
AP_nEOs ($n \leq 2$)	Wastewater	AP_nEO (pure)	[40]
AP_nEOs ($n \geq 3$)		Igepal CO-210, CO-520 and CO-720 (contained NP_nEO_{3-12})	
		Igepal CA-210, CA-520 and CA-720 (contained OP_nEO_{3-12})	

and clean-up of extracts. The novel procedure involves application at clean-up stage two times LC–Alumina sorbent (before and after derivatization). The derivatization process modifies the polarity of non-ionic compounds like AE what allows to improve samples clean-up (during elution under mild condition the elimination of desorption polar compounds) and transform them to compounds more volatile ions during chromatographic analysis. Moreover, the sorption SPE cartridges contain Florisil were involve to isolate low mole ethoxymers (C_nEO_{0-3}).

Summarized, SPE is simple and rapid isolation technique for analysis with high recovery of analytes (about 90% in the most cases). Generally, this technique allows for using significantly lower sample volume consumption (7–100 mL) against to LLE. However, samples can not contain large amount of solid particles and exchange sorbent size must be appropriated suitable to the concentration of analytes in different environmental samples [33,34,40,45,50–65,69].

2.3.3. *"Green" isolation techniques*

Over the last years, in many researching centers chemists working on a new extraction technique which give possibility to reduce or eliminate use of solvent during samples preparation stage. Examples of these isolation techniques:

- dispersive liquid–liquid microextraction (DLLME) [14,70];
- hollow-fiber liquid phase microextraction (HF-LPME) [71];
- solid-phase microextraction (SPME) [26,72,73];
- stir bar sorptive extraction (SBSE) [74];
- two-step colorimetric technique (chromo-fluorogenic sensing protocole) [75–78].

The mentioned technique give a possibility to simple, low cost and rapid sample preparation with use very small amount of solvents (usually <200 μL) [79].

DLLME is based on migration analytes to appropriate solvent. In this technique is employing a mixture of two solvents: dispersing (soluble in water, e.g. acetone) and extracting (low soluble in water, e.g. trichloroethylene). The addition of organic solvents to water samples cause formation of stable dispersed phase in which are extracted analytes. The dispersed phase is separated by centrifugation and surfactants (OPEO, OP, NP) are dissolved in the extracting solvent (on the bottom of tube) [70]. However, the main drawbacks associated with DLLME are the difficulties to automation and vulnerability of solvent drop to physic forces. The solution of these problems could be application the hollow-fiber supported liquid membranes during isolation analytes like cationic alkyldimethylbenzylammonium chloride or non-ionic NP and OP (techniques

Table 2
General information about preparation of environmental samples prior to their analysis for the presence of SAAs with used LLE and SPE techniques.

Analytes	Volume of sample	Extraction technique	Condition of isolation	Clean-up	References
Total cationic SAAs	100 mL	LLE	Solvent: chloroform (15 mL) Ion-pair reagent: patent blue V	LLE (water)	[19]
	20 mL		Solvent: chloroform (3 × 50 mL) Ion-pair reagent: DiSB	–	[20]
DTDMAC DEEDMAC DEQ	100–500 mL		Solvent: chloroform (3 × 50 mL) Ion-pair reagent: LAS	LLE (8 mL $CHCl_3$, 4 mL water)	[46]
Total anionic SAAs	5–50 mL		Solvent: chloroform Ion-pair reagent: MB	LLE (water)	[20,47,48]
Total non-ionic SAAs	200 mL		Solvent: EA Ion-pair reagent: modified Dragnedorff reagent	LLE (isooctane)	[49]
APE	300 mL		Solvent: DCM Ion-pair reagent: –	–	[44]
QAC	10 mL	SPE	Type of cartridge: Strata-X 1. Conditioning: ACN, water 2. Washing: water/AA 3. Elution: ACN/AA/water	–	[50]
BAC	250–1000 mL		Type of cartridge: alumina 1. Passing solution with SDS 2. Elution: methanol	–	[45]
LAS	7–250 mL		Type of cartridge: C18 1. Conditioning: MeOH/water 2. Washing: water/MeOH 3. Elution: MeOH	–	[33,34,51,52]
NPEO, OPEO NP, OP NPEC, OPEC	100–250 mL		Type of cartridge: C18 1. Conditioning: MeOH, water 2. Washing: water/MeOH 3. Elution: MeOH	–	[34,40,53]
C_xEO_{0-18}	4000 mL		Type of cartridge: C2 + SCX + SAX 1. Conditioning: MeOH, water, ACN, DCM 2. Fractionation: ACN 3. Fractionation: MeOH/EA/water	–	[54]

name as hollow-fiber membrane-assisted liquid-phase microextraction) [71,80,81].

The solid-phases microextraction and the stir bar sorptive extraction are modification of SPE technique. SPME give possibility to eliminate organic solvent from isolation step, because SAAs analytes are diffuse directly into the fiber made of specific materials. Then SPME device is transfer to injection port of the GC or HPLC, where compounds are desorbed into stream of mobile phase [72,82]. The analytes contain polar groups in their molecules should be derivatized (to methyl, acetyl and silyl derivatives) before analysis with gas chromatography. Those procedures improve GC parameters like sensitivity, accuracy, reproducibility and resolution [68,83,84]. During application of solid-phases microextraction have been tested different types of fibers for isolation anionic (PA [26], PDMS [82]) and non-ionic (CWAX/TR [72], PA, PDMS, PDMS/DVB [83,85]) SAAs.

SPME and SBSE are very similar techniques, but they are differ the amount of polymers in adsorb device. The fibers contain about 0.5 μL of polymers while stir bars usually 300 μL (it improve sensitivity of extraction analytes) [86]. The stir bar sorptive extraction has been used only for separation non-ionic surfactants (NP, OP) from liquid sample with thermally desorption for direct analysis by GC. The recoveries of analytes from river water sample after used this isolation techniques (with in-tube derivatization) were high (93–96%) [74].

The other group of techniques consistent with the principles of green analytical chemistry includes selective and sensitive chromo-and fluorogenic processes. The novel organic solvent-free colorimetric method allows for screening determination of ionic surfactants in liquid environmental samples without use of complicated laboratory apparatuses (allows for in situ measurement). The two step protocol involves using silica functionalized with suitable binding groups (sorption element name as S1 for anionic SAA and S2 for cationic SAA). The first step involves interaction with appropriated surface with molecules of surfactants. The second step involves addition of suitable dyes – cationic (MB) to anionic SAA and anionic (Patent Blue V) to cationic SAA. After two steps was observed discoloration or coloration S1 and S2 solids related to concentration of ionic SAA in aqueous solutions [75,76]. Also are carried out the modifications of this procedure of determination anionic SAA which go in the direction application new solid material (e.g. silica nanoparticles) or type of dye [77,78].

2.4. Solid samples

The preparation step of solid samples is based on extraction and next often clean-up of solvent extracts. For a long time, the traditional isolation techniques like solid–liquid extraction (SLE) or solvent extraction in a Soxhlet apparatus have been using in the preparation stage of solid environmental samples (soils, sediment, sludge) for analysis. These technique have similar advantages (fast, simple, does not require expensive apparatuses) and disadvantages (required large amounts of solvents – e.g. from 250 to 500 mL of methanolic HCl [24], MeOH [55], DCM [56]; production highly toxic wastes) to liquid–liquid extraction. Furthermore, Soxhlet extraction takes long time (usually 5–18 h [27,43,87]) so it was improved to deduce the solvent consumption to 100 mL and the process time to 45 min in Soxtec extraction (semiautomatic techniques) [37,88].

In the past decades different parameters (high temperature and pressure, application of ultrasounds) have been investigated to accelerate sample preparation stage with reduction use of organic solvent. These factors influencing the improvement of solubility of solid samples, the diffusion rates and mass transfer stability of liquid phase [89]. Table 4 contains general information about techniques used for preparation solid environmental samples prior to their analysis for the presence of SAAs.

The accelerated solvent extraction (ASE) give ability to faster isolation of wide range of surfactant from solid samples with

Table 3
Conditions of isolation cationic, anionic and non-ionic analytes from liquid samples with use of SPE technique.

Analytes	Sorbents	Solvent	Details of isolation	References
Cationic SAAs	C18 Alumina SCX Strata X	Conditioning: ACN, water Elution: ACN, AA, water, MeOH, ammonium buffer	Analytes associated with the strong interaction of the silanol groups (RF sorbents) which results in very broad elution bands Neutral sorbents could solve this problems, but recovery of analytes are about 75% Adsorption analytes on SDS-γ alumina admicelles with good recovery (95–106%) Use of cation-exchange cartridge with good recovery (95–97%) Polymeric SPE cartridges (Strata-X) – recovery of analytes from 80% to 105%	[45,57,58]
Anionic SAAs	GCB SDB-1 C18 Isolute ENV+	Conditioning: MeOH or MeOH/water Elution: MeOH	Analytes contain anionic hydrophobic groups (e.g. LAS, AES, AS) are ability to adsorb at various sorbents Two last exchange sorbents are mostly used during samples preparation stage Recovery of analytes from 91% to 133%	[16,30,33,34,52,59–62]
Non-ionic SAAs	GCB C18 Alumina [SDS hemimicelle-based SPE] Oasis HLB SDVB C18 + SAX C18 + SCX + SAX	Conditioning: TMAOH/DCM/MeOH/water, MeOH/water, ethyl acetate/MeOH, MeOH Elution: MeOH, acetone, ACN, MeOH/DCM	NPEO, NP, NPEC adsorb on GCB (conditioning with mixture of TMAOH/DCM/MeOH/water, elution with DCM/MeOH, recovery 89–99%) NPEO, OPEO, NP, OP, NPEC, OPEC adsorb on C18 silica sorbent (conditioning with MeOH/water, elution MeOH, recovery 89–108%) Sorbents Isolute ENV+ and C18 – similar recovery of the analytes but first SPE sorbent better for extraction larger volumes samples GCB and C18 phases for simultaneous separation of APEO, APEC, NP, LAS, SPC	[16,34,37,40,53,63–65]

decreased amount of organic solvent (due to SLE) [39]. The optimalization of ASE parameter is associated only with the choice of extracting solvent, temperature and time of isolation SAAs compounds and gives possibility to automatic. Ionic and non-ionic analytes were extracted with acetonitrile, water, methanol, acetone, dichloromethane or mixture of them [25,27,30,66]. Petrovic et al. [13,39] had investigated that alkylphenol ethoxylates (APEO) and their metabolites at temperature above 60 °C could be depredated so they prepare analytical methodologies at lower temperature. Isolation of analytes with ASE could be performed automatically but the main problem of use ASE technique is the high apparatus cost.

Supercritical fluid extraction (SFE) has been applicable only several times to isolation compounds from all groups of surfactants: cationic [93], anionic [32] and non-ionic [87,36]. The lower interest in mentioned techniques is because of acceptation ASE as recommended extraction for isolation SAA. The extractants (water [94] or CO_2 [95]) used in SFE are non-toxic and could be easily remove from samples. The modification of extracting medium (CO_2) with low molecular weight alcohol (e.g. MeOH) resolves problems with isolation polar or ionic compounds [24,93].

The application of ultrasound during isolation of analytes increases efficiency of SAAs extraction in shorter time [92]. Ultrasound assisted-extraction (UAE) does not require costly equipment so it is eliminating the financial barrier (opposite to ASE, MAE or SFE). On the other side, large volumes of organic solvents and production of toxic wastes are similar to SLE and Soxhlet extraction. Sonication often can produce emulsions which are difficulties to separate and it is result in long phase separation time [89].

In the past years, microwave-assisted extraction (MAE) has become a technique which is widely applied to isolate analytes from solid samples. MAE alternatively has such improvement as simultaneous isolation different anionic [88,89] and non-ionic compounds from many samples [15], small volume of solvent (mainly MeOH [88], DCM/MeOH [94], small amount of samples and short time of isolation. The high initial cost of MAE equipment is pay-back because of solvent amount saving and short time of extraction.

2.5. Identification and quantities determination of different types of SAAs

During the last years, different techniques have been used for determination of sum amount of surfactants or individual compounds. The techniques applied to measure total content of surface active compounds in environmental samples belong to different group are usually:

- spectrophotometry [95–101];
- potentiometric titrametration (PT) [102–104];
- tensammetry [22,49,106].

In general, the spectrophotometric techniques are based on the formation of ion associates of analytes with ions-pair reagent and their extraction into appropriated organic solvents. After phase

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Table 4
General information about preparation of solid environmental samples prior to their analysis for the presence of SAAs.

Analytes	Weight of sample	Extraction technique	Condition of isolation	Clean-up	References
DTDMAC	0.5 g	SLE	Solvent: methanolic HCl Ion-pair reagent: LAS	LLE ($CHCl_3$) SAEC (MeOH)	[24]
LAS	1 g		Solvent: water/MeOH Ion-pair reagent: MB Time of extraction: 1.5 min	–	[55]
NP OP	10 g		Solvent: DCM Time of extraction: 20 min	LLE (DCM)	[56]
DDAC BAC ATAC	1 g	Soxhlet extraction	Solvent: MeOH Time of extraction: 18 h	LLE ($CHCl_3$, water)	[43]
LAS AES AS	5 g		Solvent: MeOH Time of extraction: 5 h	SPE	[27]
NPE NP OP	5 g		Solvent: DCM Time of extraction: 6 h	–	[87]
BAC	10 g	ASE	Solvent: ACN/water Pressure: 10.34 MPa Temperature: 120 °C Time: 30 min	SPE	[25]
LAS AES AS	5 g		Solvent: MeOH Pressure: 10.34 MPa Temperature: 125 °C Time: 15 min	SPE (C18)	[27]
NPEO OPEO NP OP	5 g		Solvent: acetone/MeOH Pressure: 10.34 MPa Temperature: 50 °C Time: 15 min	SPE (OSP-2A)	[39]
BAC	10 g	UAE	Solvent: MeOH/HCl Time of extraction: 30 min	SPE (SCX)	[21]
AS AES	30–40 g		Solvent: MeOH Time of extraction: 20 + 10 min	–	[90]
NPEO OPEO NP, OP PEG	2 g		Solvent: MeOH/DCM Time of extraction: 20 + 10 min	SPE (C18)	[42]
LAS	0.5 g	MAE	Solvent: MeOH Time of extraction: 7 min	–	[91,92]
NP NPEC	1 g		Solvent: acetone Time of extraction: 15 min Pressure: 0.145 MPa	SPE (Florisil)	[15]

separation the absorbance of organic phase is measured. This technique has several advantages like quick and simple determination SAAs with use of uncomplicated equipment. Due to this characteristic it was the purpose of routine environmental analysis. Main drawbacks of this technique are: impossibility of determination individual compounds and production of very toxic wastes (contain chloroform). Moreover, prepared samples contain other than surfactants organic compounds what is resulting in errors during analysis [95–101].

A PT technique is based on the changes in electromotive force (EMF) of the measurement cell after the addition of the titrant. The end point of titration is defined with ion-selective detector. Potentiometric titration is limited only to determination sum of ionic compounds. Main drawbacks of this technique are problems related basically to reproducibility and signal stability [102–104].

In tensammetric technique, the changes of the double layer differential capacity are measured caused by the adsorption of surfactants on the electrode surface [105]. Tensammetry is limited to the determination only of anionic and non-ionic SAAs [22,49,106].

Nowadays, the determination of the total concentration of surfactants in environmental samples could be only the first step in evaluation of pollution of the various ecosystems. Next steps are following: separation, detection and quantitatively determination individual SAAs compounds from mixtures. Chromatographic techniques (gas chromatography, high-performance liquid chromatography, or related-capillary electrophoresis) coupled with different types of detections are suitable to resolve these analytical problems. The applications of these techniques always require isolation and preconcentration of analytes with use of appropriated extraction techniques.

Gas chromatography is limited to volatile analytes and this requirement meet only low molecular mass non-ionic (contain low number of ethoxylated groups) [86]. Technique is suitable to determination of contents of other non-ionic and anionic those have been derivatizated with specific agents. Often gas chromatography coupled with mass spectrometry is use for complete separation of homologues and isomers of compounds like linear alkylbenzene sulfonates (LAS) after derivatization. The employment of GC–MS in such analysis resolves important problem because susceptibility for biodegradation and toxicity of LAS depend on length of alkyl chain and position of the phenyl ring [107]. In the literature data not mentioned about application of GC to separation cationic SAAs [1].

Generally, analytes were separated using nonpolar capillary columns contain 5%-phenyl–95%-methylpolysiloxane (e.g. HP-5 [108–110], ZB-5 [111], DB-5 [28,73]). The carrier gas was high purity helium with flow rate from 0.58 to 3.4 mL/min. Gas chromatography is mainly coupled with single or tandem mass spectrometry (LOD about of the sub ng/L [74]). Analytes from the group of surfactants can be detected by chemical ionization, but more often mass spectrometer works in the electron impact ionization (EI). Table 5 summarizes the information on the analytical

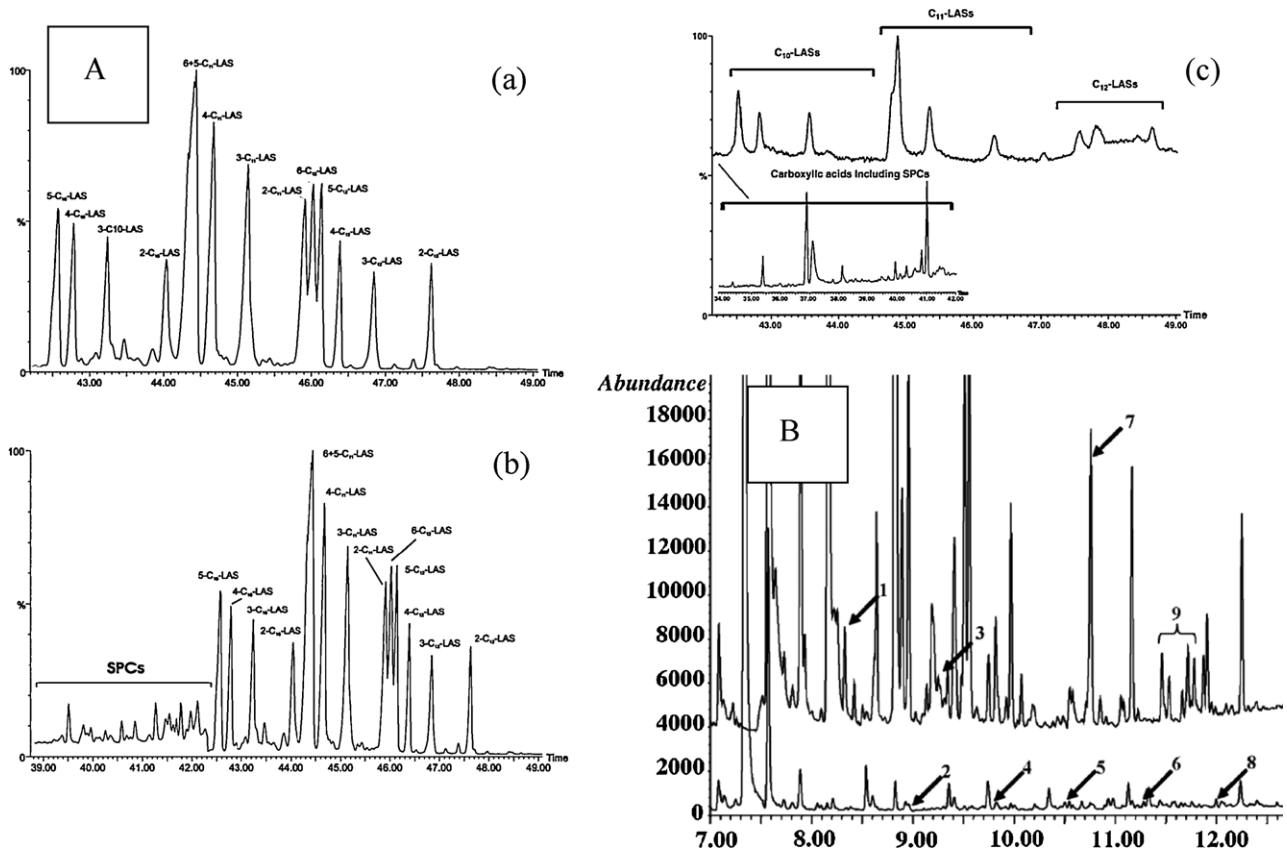

Fig. 1. Reconstructed ion chromatograms obtained by GC–MS for A – (a) standard solution sample methyl derivatives of LAS, (b) derivatives of LAS in spiked water sample, (c) derivatives of LAS in seawater sample [28]; B – derivatives of OP and NP in river water sample where (7) tOP, (8) nOP, (9) NP, (10) nNP [74].

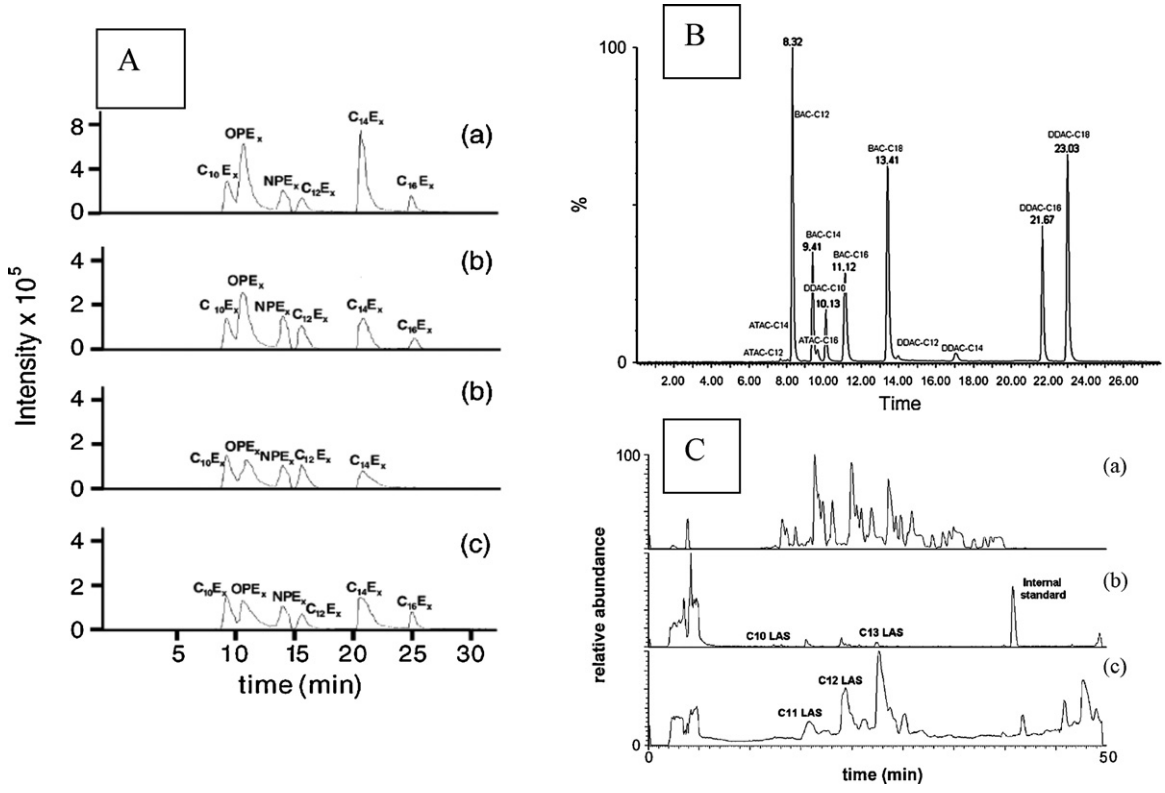

Fig. 2. Reconstructed ion chromatograms obtained by LC–MS for A – (a) standard solution sample contain NPEO, OPEO and C_{12-16} AE, (b) wastewater sample, (c) river water sample [65]; B – sediment sample [23]. C – (a) standard solution sample contain LAS and AES, (b) water sample after SPE, (c) sediment sample after ASE + SPE – the use of the LC/MS technique allows us to distinguish analytes because of their specific fragment ions, *m*/*z* 183 for LAS and *m*/*z* 97 for AES and quasimolecular ions $[M-H]^-$ [30].

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Table 5
The analytical procedures (involve gas chromatography) for the determination of surfactants in environmental samples.

Analytes	Sample type	Sample preparation	Recovery [%]	Mobile phase	Type of column	Detection	MLD/LOD	References
LAS/TPS	Lake sediment	Soxhlet extraction SPE Derivatization ($SOCl_2$)	79–113	–	HP-5 (capillary column, 20 m, 0.25 mm ID, 0.25 μm)	CI(+)-MS	60–210 μg/L	[108]
LAS/SPC	River and sea water	Ion-pair LLE Hydrolysis Derivatization (CH_2N_2)	98	– (0.7 mL/min)	DB-5 (fused silica capillary column, 50 m, 0.25 mm ID, 0.25 μm)	MS	<4 μg/L	[28]
NPEO NP	River water	SPME (without derivatization)	–	Helium	DB-5 (fused silica capillary column, 30 m, 0.25 mm ID, 0.25 μm)	EI(+)-MS	0.09–0.45 μg/L	[73]
OPEO NP OP	Soil	ASE SPE Derivatization (BSTFA)	96–104	Helium (1 mL/min)	ZB-5 (capillary column, 30 m, 0.25 mm ID, 0.25 μm)	EI-MS	3–126 μg/kg 9 μg/kg 9–10 μg/kg	[111]
NP NPEC	Sediment	MAE SPE	–	Helium (3.4 mL/min)	HP-5 (capillary column, 30 m, 0.25 mm ID, 0.25 μm)		300 ng	[109]
NP OP	Marine sediment	MAE SPE Derivatization (PTA-OH)	60–86	Helium (0.58 mL/min)	HP-1 (capillary column, 12 m, 0.20 mm ID, 0.33 μm)		0.01 ng	[96]
	River water	SPME Derivatization on-fiber (BSTFA)	–	Helium (1 mL/min)	HP-5 (capillary column, 30 m, 0.25 mm ID, 0.25 μm)	EI(+)-MS	3 ng/L 72 ng/L	[110]
		SBSE Derivatization in-tube (MBSTFA)	93–96	Helium (1.2 mL/min)	DB-5 (fused silica capillary column, 30 m, 0.25 mm ID, 0.5 μm)	EI-MS	0.001–0.05 ng/L	[74]
		SPE Derivatization (BSTFA and pyridine)	94–102	Helium (1 mL/min)	HP-5 (capillary column, 30 m, 0.25 mm ID, 0.25 μm)	EI(+)-MS–MS	0.01 ng/L 0.1 ng/L	[112]

procedures which involve application of GC techniques for final determination of anionic and non-ionic SAAs contained in environmental samples (along with information about recoveries of analytes during preparation stage, parameters of separations and detection). Inclusion of chromatograms obtained by GC technique gives good overview of results for analysis of environmental sample (Fig. 1).

Presently, liquid chromatography (LC) is the most used analytical technique during analysis of surface active agents from all classes in environmental samples. In the most cases derivatization of analytes is not necessary, because LC is suitable to determination low-volatility analytes with large-molecules. It gives possibility to exclusion this operation from analytical procedures due to the green analytical chemistry concept.

Mostly, the chromatographic separations of compounds from different groups of surfactants were done using a reverse-phase analytical columns like RP-C18 [26,29,96] or RP-C8 [80,91,92] and methanol, acetonitrile, deionized water (their mixtures with ammonium acetate (AMAC), formic acetate (FA), acetic acid (AA)) as mobile phase. Addition of formic or acetic acid to mobile phases improves separation of analytes and peak shape) [29]. Ferguson et al. [113] tested an application of mixed-mode HPLC–ESI-MS for analysis of non-ionic SAAs (NP, NPEO). Farther modifications of this technique give possibility to quantify (beyond NP, and NPEO) also OP, and OPEO in different types of environmental samples (e.g. water, sediment) [66,114]. Other scientists applied a polar-embedded stationary phase for the simultaneous separation of cationic, anionic and non-ionic surfactants. The packing material contains hydrophobic (alkyl chains, tertiary amino) and hydrophilic (amide) functional groups, what is resulting in a multi-mode separation mechanism (reversed-phase, anion-exchange, and dipole–dipole interactions). New stationary phase offers good selectivity for different types of surface active agents (better peak shapes and resolution for oligomers in ethoxylated SAAs) and is compatibility with highly aqueous mobile phases [80].

High-performance liquid chromatography can be coupled with following types of detectors to determination singles analytes from group of SAAs in suitable solvent extracts: fluorescence (FLD) [51,88], ultra-violet (UV) [115], conductometric (CD, ionic surfactants) [93], mass spectrometry (MS) [46,73], tandem mass spectrometry (MS–MS) [34,43] or UV–FLD [91] and UV–MS [42].

Nowadays, other detectors are replaced by mass spectrometers work in the electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) interface [89]. The positive ionization (PI or "+") mode is employed for detection for all cationic SAAs [43,45], NPEO, AEO, CDEA, PEG and the negative ionization (NI or "–") for anionic SAAs [94], APEO and NPEC [42].

During application of high-performance liquid chromatography coupled with mass spectrometry (or MS–MS) techniques compounds are transform to appropriate ions and the data on the fragmentation process of specific analytes from a group of surfactants can be found in the relevant original publications (cationic SAA [23,45,50], anionic SAA [26,30,31], non-ionic SAA [111,117] or in either review materials [67,70,89]). For the recognition and identification appropriate fragmentation ion of surfactants are used various types of analyzers such as: single (Q) or triple quadrupole (TQ), quadrupole-ion-trap (QIT), time of flight (TOF), or hybrids like quadrupole time-of-flight (Q-TOF), quadrupole ion-trap time-of-flight (QIT-TOF) [25,26,44,45,86,116–118]. Generally, QIT analyzer

Table 6
The analytical procedures (involve high performance liquid chromatography) for the determination of surfactants in environmental samples.

Analytes	Sample type	Sample preparation	Recovery [%]	Mobile phase	Column	Detection	MLD/LOD	References
QAC	River water Waste water	MMLLE	–	$CHCl_3$:EtOH:NH_3:heptanoic acid (70:28:1:1, v/v/v/v)	NP cyanopropyl column (250 mm, 2.1 mm)	UV	0.7–5 μg/L	[81]
	Sea water	SPE	80–105	ACN (+AC) with 50 mM AMAC buffer (pH = 3.6)	C18 XTerra (50 mm, 4.6 mm, 2.5 μm)	ESI(+)-MS	0.03–0.06 μg/L	[50]
BAC	River water	SPE (MH/AB)	95–106	MeOH with 50 mM AMF buffer (pH = 3.5)	Nova-Pack C8 (150 mm, 3.8 mm, 5 μm)	ESI(+)-MS	0.004 μg/L	[45]
	Waste water	SPE	71–90	A: ACN B: 10 mM AMF	RP-C18 (250 mm, 3 mm, 5 μm)	ESI(+)-MS–MS	0.009–0.025 μg/L	[57]
ATAC BAC DDAC	River sediment Sludge	Soxhlet extraction LLE	67–95	A: ACN:water (1:4, v/v) + 1% AA B: ACN:water (95:5, v/v) + 10 mM AMAC C: isopropanol + 0.1% FA	Luna C18 (150 mm, 2 mm, 5 μm)	ESI(+)-MS–MS	0.0004–0.002 μg/L	[43]
LAS	Indoor dust	SLE SPE	20–95	A: ACN:water (1:4, v/v) B: ACN:water (75:25, v/v)	Nucleosil 100–5 C18 (125 mm, 4.6 mm)	FLD	3 mg/kg	[115]
	Sewage sludge	MAE	–	A: water:ACN (95:5) + 5 mM TEA + 5 mM AA B: ACN	LiChrospher 100 RP-18 (250 mm, 4 mm, 5 μm)	FLD	0.0033–0.0054 mg/kg	[29]
AES, AS LAS, SAS		SFE SPE	>86	A: MeOH contains 0.2 mM AMAC B: water contains 0.2 mM AMAC	Alltima (250 mm, 4.6 mm, 5 μm)	ESI(−)-MS	–	[36]
LAS SPC	Soil	Soxhlet extraction SPE	77–93 13–74	A: MeOH–water B: MeOH Both contain 10 mM TBA, 10 mM AMAC, 10 mM AA	Zorbax SB-Aq – C18 (150 mm, 4.6 mm, 5 μm)	ESI(−)-MS	0.1–15 mg/kg	[116]
LAS	Sea water	SPME	–	10 mM AMAC with MeOH–water (4:1, v/v)	RP-C18 (50 mm, 3 mm, 3 μm)	ESI(−)-MS–MS	0.1 μg/L	[26]
	Sewage sludge	MAE Filtration	94–102	ACN–water with 0.1 M $NaClO_4$ (65:35, v/v)	XDB-C8 (150 mm, 4.6 mm, 5 μm)	UV–FLD	1.1–6.09 mg/kg	[91,92]
LAS CDEA	Sewage sludge	UAE SPE	67–101	A: ACN–MeOH (+0.5% AA) B: water (+0.5% AA)	LiChrospher 100 RP-18 (250 mm, 4 mm, 5 μm)	UV–APCI(+)-MS	0.012–0.036 mg/kg	[42]
NP OP	Waste water River water	HFLME	–	ACN with phosphate buffer (75:25, v/v, buffer – pH 7)	Zorbax XDB-C8 (150 mm, 4.6 mm, 5 μm)	FLD	60–100 μg/L	[80]
APEO NP, OP	Tap water	DLLME	71–75	MeOH:ACN:water (50:15:35, v/v/v)	Inertsil ODS3 (150 mm, 4.6 mm, 4 μm)	FLD	0.1–0.3 μg/L 0.1–0.3 μg/L	[70]

Table 6 (*Continued*)

Analytes	Sample type	Sample preparation	Recovery [%]	Mobile phase	Column	Detection	MLD/LOD	References
NP OP	Marine sediment	MAE SPE Derivatization	60–86	UV – A: ACN–water (+0.1% FA), B: ACN MS – ACN–water or MeOH	Aquasil C-18 (100 mm, 2.0 mm (MS) or 4.6 mm (UV), 5 μm)	UV or ESI-MS	3.4–4.7 ng or 1.3–2.2 ng	[94]
APEO NP, OP	Soil	ASE SPE		A: MeOH (+5 mM AMAC) B: water (+5 mM AMAC)	Luna C18 (150 mm, 4.6 mm, 5 μm)	APCI-MS	0.001–0.1 μg/kg	[41]
AE NPEO NPEC NP, OP	Sewage sludge	SFE SPE	>86	A: MeOH contains 0.2 mM AMAC B: water contains 0.2 mM AMAC	Alltima (250 mm, 4.6 mm, 5 μm)	ESI-MS AE, NPEO (ESI+) NPEC, AP (ESI−)	–	[36]
$NP_{1-14}EO$ $OP_{1-14}EO$ NP, OP	Wastewater	SPE	60–108	A: water B: MeOH (+0.1% GAA, 15 mM AMAC)	Pursuit XRs Ultra–C18 (50 mm, 2 mm, 2.8 μm)	ESI-MS–MS APEO (ESI+) AP (ESI−)	0.0005–0.006 μg/L	[40]
$NP_{1-2}EO$ NP	Marine sediment	MAE SPE	–	A: water B: MeOH	Hydro-RP 80 A C18 (150 mm, 4.6 mm, 4 μm)	UV–FL	–	[109]
NPEO PEG NP*, OP* NPEC*	Sewage sludge	UAE SPE	67–101	A: ACN:MeOH (+0.5% AA) B: water (+0.5% AA) A*: ACN:water (5 mM TEA + AA) B*: water (+5 mM TEA + AA)	LiChrospher 100 RP-18 (250 mm, 4 mm, 5 μm)	UV–APCI(+)-MS UV–ESI(−)-MS*	0.19 mg/kg 1.68 mg/kg 0.45; 0.42 mg/kg 0.22 mg/kg	[42]
NPEO OPEO NP, OP	River sediment River water	ASE + SPE SPE	38–110	A: MeOH:water (1:1, v/v) + 10 mM AA B: methanol	MSpak GF-310 4B Mixed-mode column (150 mm, 4.6 mm, 4 μm)	ESI-MS–MS APEO (ESI+) AP, APEC (ESI−)	0.009–0.04 mg/kg 0.001–0.014 μg/L	[66,114]
$NP_{3-18}EO$ $OP_{2-12}EO$ NP, OP	Wastewater	Filtration	–	A: ACN B: water C: 0.1 mM AA	Atlantic TM MS C18 (150 mm, 2.1 mm, 3 μm)	ESI(+)-MS–MS	–	[44]

can be used for control of different ionic and non-ionic surfactants in environmental samples because its selectivity, very low levels of analytes can be detected and its capability to analyzed samples contain high amount of interferences like sludges or soil [67]. On the other hand, time-of-flight LC–MS systems become useful analytical tools for determination of polar compounds in all kinds of matrices because of the full scan spectral sensitivity in a wide mass range, high resolving power and accurate mass measurement. Moreover, TOF analyzer can be use for identification and quantification of large number of target and non-target surfactants and their metabolites [118].

Because of giving possibility of simultaneous identification of analytes retention time, they molecular weight and mass spectra, HPLC–MS technique is widely applied in environmental analysis [86]. Moreover, different surfactants (e.g. LAS, CDEA, PEG, APEO, NPEC) can be analyzed during in one analysis [42]. In addition, application of MS–MS detector improves the selectivity of analytes from group of SAAs separation and leads to lower value LOD parameter (especially during analysis of solvent extracts which contain compounds with the same molecular ions as analytes) [57].

Examples of chromatograms obtained during analysis of environmental sample with use HPLC technique are shown in Fig. 2. Table 6 lists information of condition during determination of different surfactants using high-performance liquid chromatography.

3. Conclusion

The assessment of the degree of environmental contamination by SAAs is a crucial matter, because 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 qualitative and quantitative determination of different types of surfactant in environmental samples.

The different techniques have been used for the isolation and/or preconcetration, detection, identification and quantitative determination of surface active agents in environmental samples. Nowadays, mostly in sample preparation stages are used following techniques: SPE and SPME – liquid samples; UAE, ASE, MAE – solid samples. In recent years those techniques had been modified to eliminate use of organic solvents and production of toxic wastes with high recoveries of analytes due to the principles of green analitical chemistry.

For routine determination of total concentration of ionic and non-ionic surfactants in various types environmental samples still used spectrophotometric and titrametric techniques (simple and rapid measurement, no required complicated apparatuses).

High-performance liquid chromatography coupled with mass spectrometer MS (or tandem MS) became most universal technique used during detection, identification and quantitative determination of individual SAAs in different environmental samples.

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