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DETERMINATION OF SURFACTANTS IN ENVIRONMENTAL SAMPLES. PART II. ANIONIC COMPOUNDS

OZNACZANIE POZIOMÓW ZAWARTOŚCI SURFAKTANTÓW W PRÓBKACH ŚRODOWISKOWYCH. CZĘŚĆ II. ZWIĄZKI ANIONOWE

Abstract: *Surface active agents* (SAA) with negative charge of polar group are named as anionic compounds. They are the main constituent of most products containing synthetic surfactants. The *linear alkylbenzene sulfonates* (LAS), *alkyl ethoxysulfates* (AES) and *alkyl sulfates* (AS) are typically applied from this class of compounds. Those surfactants are ingredients of household detergents and cleaners, laundry detergents, cosmetic etc. Moreover they can be applied in the paper, textile and tanning industry as optical brighteners, dispersant, wetting and suspending agents. They can be substrates in the formulation of different products like dyes, pigments, pesticides, exchange resins, plasticizers and pharmaceuticals. Anionic surfactants after use are passed into sewage-treatment plants, where they are partially degraded and adsorbed to sewage sludge (applied in agriculture fields). Finally, the anionic SAA or their degradation products are discharged into surface waters and onto bottom sediments, soils or living organisms. Therefore, it is important (widely application, bioaccumulation, toxicity for living organisms) to investigate the environmental fate of those class of compounds in more details. This research involves determination the concentration of anionic surfactants with use appropriated analytical techniques in environmental samples. The official methodology for determination of anionic SAA in liquid samples is based on the ion-pair reaction of these analytes compounds with *methylene blue* (MB) and an extraction with toxic solvent chloroform. During isolation step of anionic compounds from solid samples are employed Soxhlet and ultrasonic-assisted extraction techniques with use of methanol or mixture of other organic solvents as extraction medium. To overcome disadvantages of those traditional techniques were applied following techniques at sample preparation step from liquid and solid matrices: *solid-phase extraction* (SPE) and *solid-phases microextraction* (SPME); *accelerated solvent extraction* (ASE), *microwave-assisted extraction* (MAE), *supercritical fluid extraction* (SFE), respectively. For estimate total concentration of anionic analytes in extracts the spectrophotometric technique is used (as official regulation). For determination concentration of individual analytes were applied gas (derivatization step requires) and liquid chromatography mainly with mass spectrometry technique. The presence of anionic surface active agents was confirmed in various ecosystems (liquid and solid environmental samples).

Keywords: anionic surfactants, isolation and/or enrichment, final determination stage, environmental samples

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Introduction

Surfactant is an abbreviation from surface active agent. All compounds from this group have specific chemical composition of their molecules. They consist two parts: one is soluble in water (hydrophilic, lipophobic) and second soluble in non-polar medium (hydrophobic, lipophilic). Generally, those parts are referred as the head and as the tail, respectively. The amphiphilicity term describes the fact that surfactants contain two different chemical groups (polar and non-polar) [1].

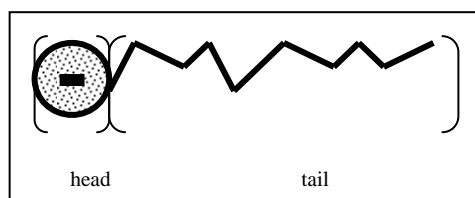


Fig. 1. Schematic structure of anionic surfactants molecule

This group of compounds is named due to their tendency to adsorb at different types surfaces and interfaces. Another important property of surfactants is that those compounds in solution have tendencies to form micelles. The term micelle formation (micellization) means that surface active agents are adsorbed at the interfaces for removing hydrophobic tails from water to reduce the free energy of the system. This property allows for applied surfactants as wetting or foaming agent. Due to those specific properties surfactants are applied in different areas of human activity [2-4].

The main classification of surface active agents is based on the basis of the charge of heads: cationic, anionic, non-ionic and zwitterionic compounds. Approximately 65% (6.5 million Mg per year) of total world production corresponds to the compounds classified as anionic surfactants [5]. For the ionic SAA the choice of ion type plays a role in their properties. Anionic compounds have such ion like sodium, potassium, lithium, calcium, protonated amines as counterions and carboxylate, sulfate, sulfonate and phosphate as polar group. The Figure 2 shows main compounds from the group of anionic surfactants [3].

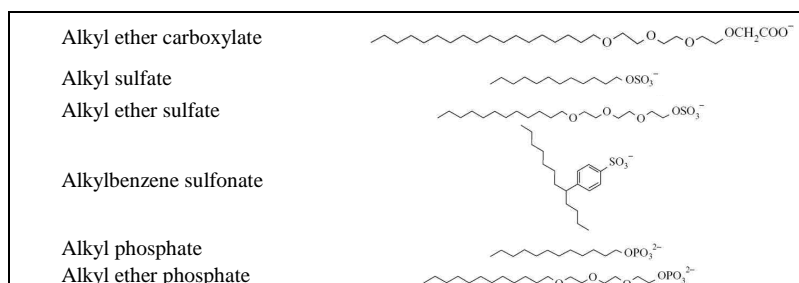


Fig. 2. The structure of some anionic surface active agents [3]


The linear alkylbenzene sulfonates (LAS) typically have 10 to 14 carbon units and their homologues consist of a varying number of positional isomers in the alkyl chain. The alkyl

ethoxysulfates (AES) and alkyl sulfates (AS) are placed second in the production volume ranking after LAS. These chemicals are formed by sulphation from alcohol ethoxylates (AEs) which are composed of a long-chain fatty alcohol with an ether linkage to a chain of ethoxylated units. Typically, in the alkyl ethoxysulfates, the alkyl chain length is from 12 to 18 carbon and the ethylene oxide group has an average number of 1-5 units [5, 6].

Compounds from group of anionic surfactants are generally used in household detergents and surface cleaners, shampoos, hand dishwashing liquids, laundry detergents and cosmetic care products [5]. Anionic surfactants are used as starting materials in the production of dyes, pigments, catalysts, pesticides, water-soluble and ion exchange resins, plasticizers, pharmaceuticals. Moreover, they can be applied in the paper, textile and tanning industry as optical brighteners, dyes, dispersant, wetting and suspending agents [7].

Table 1

The toxicity of several anionic surfactants

Analyt	Structure of surfactant molecule	Test organism	Toxicity factor	Concentration [mg/dm ³]	Literature		
Sum of LAS C ₁₀ LAS C ₁₂ LAS C ₁₄ LAS	$\text{H}_3\text{C}-[\text{CH}_2]_m-\text{CH}-[\text{CH}_2]_n-\text{CH}_3$ 	<i>Raphidocelis subcapitata</i>	*IC ₅₀ (72 h)	112	[8]		
		<i>Physella acuta</i>	*LC ₅₀ (24 h)	9.2-26			
		<i>Artemia salina</i>		39-48			
				<i>Helianthus annuus</i>	*EC ₅₀ (21 days)	120-307 mg/kg	[9]
				<i>Daphnia magna</i>	LC ₅₀ (48 h)	12-17	[10]
				<i>Dunaliella salina</i>	EC ₅₀ (24 h)	3.5	[11]
				<i>Daphnia magna</i>	LC ₅₀ (48 h)	8.1	[10]
			1.2				
SDS	$\begin{array}{c} \text{Rn} \\ \\ \text{H}-\text{C}-\text{SO}_3^- \\ \\ \text{Rm} \end{array}$	<i>Raphidocelis subcapitata</i>	*IC ₅₀ (72 h)	36	[8]		
		<i>Physella acuta</i>	*LC ₅₀ (24 h)	17-38			
		<i>Artemia salina</i>		36-49			
				<i>Daphnia magna</i>	*EC ₅₀ (24 h)	29	[12]
				<i>Salmo gairdneri</i>	EC ₅₀ (48 h)	34	[13]
					LC ₅₀ (24 h)	42	[12]
		<i>Carassius auratus</i>	EC ₅₀ (48 h)	38	[13]		
AES	$\text{H}_3\text{C}-[\text{CH}_2]_m-[\text{OCH}_2\text{CH}_2]_n-\text{OSO}_3^-$	<i>Raphidocelis subcapitata</i>	IC ₅₀ (72 h)	36	[8]		
		<i>Physella acuta</i>	LC ₅₀ (24 h)	17-38			
		<i>Artemia salina</i>		36-49			
			<i>Skeletonema costatum</i>	EC ₅₀ (72 h)	0.37	[14]	
			<i>Pseudokirchneriella subcapitata</i>		3.5		

*IC₅₀ - **inhibitory concentration** - causes weakness in a specific process of 50% of its maximum value after 24, 48 or 72 hours

*LC₅₀ - **lethal dose** - concentration of substance, which kills 50% of the population after 24, 48 or 72 hours

*EC₅₀ - **effective concentration** - concentration of substance that causes specific biological effect of 50% of its maximum value after 24, 48 or 72 hours



After use surfactants are discharged into domestic or industrial wastewater. Next, they are discharged via wastewater treatment plants (WWTPs) into surface waters. Due to specific properties, anionic compounds (like LAS) can be accumulated in aquatic organisms and interact with their cell membranes, proteins and enzymes. It causes the disturbances of their biological functions, cell lysis or even death (see toxic parameters of some anionic compounds in Table 1). Moreover, the decrease in surface tension properties makes easier the migration of other toxic pollutants into living organisms [15-17].

During biological degradation of linear alkylbenzene sulfonates are formed short-chain *sulfophenylcarboxylates* (SPC). Determination of those biotransformation products occurred in liquid or solid environmental samples is important because it may indicate ongoing biodegradation of compounds from the group of LAS [18-21].

Consequently, the environmental fate of anionic SAA and their effects (behavior during wastewater treatment, distribution pathways) and concentration in different type of waters, soils and sediments were thoroughly investigated. Therefore, monitoring anionic surface active agents levels in environmental samples is important for the protection of human health and the different ecosystems [22].

Sample preparation step

Liquid samples

The liquid-liquid extraction with addition of *methylene blue active substances* (MBAS, cationic ion-pair reagent) is the most frequently used sample preparation technique during the determination of anionic surfactants (*eg* LAS) in aqueous samples such as wastewaters and surface waters [23, 24]. Mainly, analytes are isolated from environmental matrices with use of toxic chloroform. During LLE for elimination of emulsion's formulation is applied also other ion-pair reagent: *methylene green* (MG) [22] or *crystal violet* (CV) [25].

The isolation of anionic surfactants from liquid environmental samples is usually carried out by means of solid phase extraction (SPE). The linear alkylbenzene sulfonates (LAS), sometimes products of their degradation (long-chain *sulfophenyl carboxylate compounds* - SPC, *dialkyltetralinsulfonates* - DATS) were isolated from untreated and treated sewage, river water, sea water and groundwater with use of sorbent different types of sorbents like *graphitized black carbon* (GBC) [26, 27], *strong anion exchange resins* (SAX) [28, 29], octyl silica (C₈) [30], hydroxylated polystyrene divinylbenzene co-polymer (Isolute ENV+) [31]. But the octadecyl silica sorbent has been the most widely employed for extraction of LAS from liquid samples with high recoveries (from 90 to 120%) [27-36].

The *sequential solid-phase extraction* (SSPE) gives higher recoveries of analytes from the group of linear alkylbenzene sulfonates than single SPE. In this modification of SPE technique were applied combinations of following types of sorbents: C18 coupled with SAX [37] and Isolute ENV+ coupled with SAX [31]. For simultaneous isolation of different compounds from the group of anionic surfactants (LAS, AES, AS) were applied two sorbents: octadecyl silica [5] and hydroxylated polystyrene divinylbenzene co-polymer [36]. Moreover, the application of graphitized black carbon or octadecyl silica sorbents allows for simultaneous isolation from environmental samples of anionic (LAS, AES) and non-ionic (APEO, NP) surfactants or their degradation products (SPC, APEC) during one extraction [26, 39, 40].



The *solid-phases microextraction* (SPME) is modification of SPE technique, which allows for elimination of organic solvent from sample preparation step. In this analytical technique analytes were adsorbed directly on the surface of special fiber. During application of SPME technique for isolation of anionic surfactants (individual LAS homologues from seawater and urban wastewater samples) from liquid samples has been tested two different materials of fibers: *polyacrylate* (PA) [41] and *polydimethylsiloxane* (PDMS) [37]. Then analytes adsorbed on SPME device were analyzed on a LC-MS/MS system without derivatization [41] or as ion-pairs of LAS with tetrabutylammonium hydrogensulfate on GC-MS system with derivatization in-port [37].

Other organic solvent-free colorimetric technique allows for screening determination of anionic surface active agents in aqueous samples without use of complicated laboratory apparatuses (for in situ analysis). In this technique is applied chromo- and fluorogenic reaction (discoloration) on sorption element name as S1 with cationic dye (methylene blue) [42, 43]. The modifications of presented procedure for determination of anionic compounds involve application of different type of solid material (*eg* silica nanoparticles) or type of dye [44, 45].

Solid samples

During recent decades different analytical techniques have been used to isolate anionic surfactants from solid environmental samples (bottom sediments, sewage sludges and soils). Traditional techniques solid-liquid extraction [46], extraction in Soxhlet apparatus [5, 28, 47] and ultrasonic extractions [48-50] are required the use of high amount of organic solvent. The analytes were extracted with use of pure methanol or as mixture with other solvents (acetone, dichloromethane) [5].

The less time- and solvent-consuming new techniques have emerged during the last years and these have been also employed to extract different compounds from the group of anionic compounds from solid environmental samples due to requirements of green analytical chemistry [51]. To group of environmental friendly techniques are included: *accelerated solvent extraction* (ASE) [52-54], *microwave-assisted extraction* (MAE) [55, 56] and *supercritical fluid extraction* (SFE) [54, 57]. The two first techniques with use of solvents (methanol) are assisting by elevated temperature and pressure or microwave radiation. Third one use properties of fluids at supercritical condition and for isolation of anionic analytes was applied water.

Final determination step

At final determination step different techniques were used for determination of total amount of anionic surfactants or individual compounds. The total content of anionic surface active compounds in environmental samples was determined with three techniques: *spectrophotometry* [22-25], *potentiometric titrametration* (PT) [58] and *tensammetry* [59].

The spectrophotometric determinations of anionic surfactants are relied on measuring of absorbance of ion-pairs with analytes occurred in appropriated solvent extracts. This technique allows for quick and simple determination of SAAs concentration with use of uncomplicated apparatuses, so it is applied in routine environmental analysis. On the other hand, the spectrophotometric technique causes production of very toxic wastes (contain



chloroform - extracts contain of cationic analytes) and is not selective only for compounds from the group of anionic surfactants [51, 60].

Second technique used for determination of total concentration of anionic surface active agent is named as the potentiometric titrametration. First researches in this field were beginning about 40 years ago [61-65]. Several types of sensitive potentiometric electrodes were investigated during measuring total content of anionic surfactants in wastewater [64, 66-68].

The last technique allows for determination of anionic compounds in liquid environmental samples is tensammetry. During analysis the changes of the double layer differential capacity are measured. Those changes are caused by the adsorption of surface active agents on the electrode's surface. So far, the tensammetry was applied during determination of anionic analytes in river water samples [59].

The information about total concentration of SAA in different environmental samples gives only basic information about pollution of the various ecosystems. Next, it should be determined concentration of individual compounds from mixtures with following steps: separation, qualitatively and quantitatively determination [60].

These problems are solved during analysis of solvent extracts with use chromatographic (gas and liquid chromatography) or related (capillary electrophoresis) techniques. The gas chromatography is limited to volatile analytes and because of it anionic surfactants have to be derivatized with specific agents (additional stage during preparation of samples). This technique coupled with mass spectrometry allows for separation of homologues and isomers of anionic compounds (*eg* linear alkylbenzene sulfonates). But GC technique was applied only several times for analysis of individual anionic analytes in environmental samples [28, 52].

The most universal technique used during analysis in extracts from environmental samples for determination of concentration of single surfactants from all classes is *liquid chromatography* (LC). The liquid chromatographer coupled with fluorescence detector (HPLC-UV) offers an easier way to separation, detection and quantification of linear alkylbenzene sulfonates [55, 56, 69]. The lack of a chromophore group of analytes (*eg* AES) makes it impossible to determine them by means of HPLC-UV technique. This problem was resolved as a result of the development of the different types of ionization interfaces (*electrospray* - ESI, *atmospheric pressure chemical ionization* - APCI) in liquid chromatography - mass spectrometry. The *negative ionization* (NI) mode is employed for detection for all anionic SAAs. Nowadays, the LC-MS has become the powerful tool for surfactant analysis in environmental samples due to its possibility of identification homologues and ethoxymers and of the simultaneous determining surfactants from different classes (anionic and non-ionic compounds) without influence of the interferences on results [5, 70].

The concentration of anionic surfactants in environmental samples

Anionic compounds are one of the most important surfactants, which are used in different areas of human activity (cosmetics, detergent, laundry agents etc.). Analysis of different types of environmental samples confirmed occurrence of compounds from the group of anionic surface active agents in different ecosystems. Mainly, in liquid and solid samples, were determined total concentrations of anionic analytes [49, 50, 71] or individual



linear alkylbenzene sulfonates [28, 55, 72]. There are few papers about determination also (beyond LAS) individual AES and AS in solid matrices [5, 48, 57, 73].

Table 2
The analytical procedures used during determination of anionic surfactants and their levels in liquid environmental samples

Analytes	Type of sample	Isolation technique	Final determination technique	Concentration of analytes	Literature
Sum of anionic	Wastewater	SPE	LC-MS-MS	307-1920 $\mu\text{g}/\text{dm}^3$	[34]
	Tap water			1 $\mu\text{g}/\text{dm}^3$	
	Lake water	LLE	Spectrophotometry	0.01 $\mu\text{mol}/\text{dm}^3$	[50]
	River water			13-50 $\mu\text{g}/\text{dm}^3$	[74]
	Sea water			0.11-0.21 $\mu\text{mol}/\text{dm}^3$	[49]
Sum of LAS	Wastewater - influent	SPE	LC-FL	2.4-6.8 mg/dm^3	[75]
	Wastewater - effluent			4.2-40 $\mu\text{g}/\text{dm}^3$	
	Sea water		LC-MS	10.7-17.4 mg/dm^3	[39]
	River water			0.24-3955 $\mu\text{g}/\text{dm}^3$	[48]
	Wastewater - influent			2.4-4.0 mg/dm^3	
	Wastewater - effluent			0.25-34 $\mu\text{g}/\text{dm}^3$	
C ₁₀ LAS	River water		9.3-19.9 $\mu\text{g}/\text{dm}^3$	[5]	
C ₁₁ LAS			8.9-26.6 $\mu\text{g}/\text{dm}^3$		
C ₁₂ LAS			4.5-12 $\mu\text{g}/\text{dm}^3$		
C ₁₃ LAS			2.4-5.9 $\mu\text{g}/\text{dm}^3$		
Sum of AES	Sea water	SPE	LC-MS	n.d.-0.1 $\mu\text{g}/\text{dm}^3$	[39]
Sum of AS/AES	River water			0.01-200 $\mu\text{g}/\text{dm}^3$	[48]
	Wastewater - influent			0.77-5.32 mg/dm^3	
	Wastewater - effluent			10.8-67 $\mu\text{g}/\text{dm}^3$	
C ₁₂ AES	River water			2.7-7.4 ng/dm^3	[5]
C ₁₃ AES				n.q.	
C ₁₄ AES				1.8-4.4 ng/dm^3	
C ₁₅ AES				n.d.	
C ₁₆ AES				n.d.-n.q.	

The analytical procedures allowed for determination of concentration of anionic surface agents in solid and liquid environmental samples are showed in Tables 2 and 3.

Table 3
The analytical procedures used during determination of anionic surfactants and their levels in solid environmental samples

Analytes	Type of sample	Isolation technique	Final determination technique	Concentration of analytes	Literature
Sum of anionic	Soil	SLE	Spectrophotometry	0.33 $\mu\text{mol}/\text{dm}^3$	[50]
Sum of LAS	Sea sediment	ASE	LC-MS	0.29-1.9 mg/kg	[39]
	Lake sediment	Soxhlet extraction	GC-MS	0.19-2.4 mg/kg	[28]
	River sediment	Soxhlet extraction		0.23-0.72 mg/kg	



Analytes	Type of sample	Isolation technique	Final determination technique	Concentration of analytes	Literature
C ₁₀ LAS	River sediment	ASE	LC-MS	0.026-0.068 mg/kg	[5]
	Sewage sludge (digested)	UAE	LC-FL	907 mg/kg	[55]
	Sewage sludge (compost)	UAE		89 mg/kg	
	Sludge	UAE	LC-MS	78-210 mg/kg	[40]
	Soil	Soxhlet extraction		0.05-18 mg/kg	[47]
C ₁₁ LAS	River sediment	ASE		0.13-0.23 mg/kg	[5]
	Sewage sludge (digested)	UAE	LC-FL	3147 mg/kg	[55]
	Sewage sludge (compost)			527 mg/kg	
	Sewage sludge		LC-MS	763-2850 mg/kg	[40]
Soil	Soxhlet extraction		0.95-15 mg/kg	[47]	
C ₁₂ LAS	River sediment	ASE	LC-MS	0.17-0.36 mg/kg	[5]
	Sewage sludge (digested)	UAE	LC-FL	4207 mg/kg	[55]
	Sewage sludge (compost)			887 mg/kg	
	Sewage sludge		LC-MS	671-4130 mg/kg	[40]
Soil	Soxhlet extraction		0.71-14 mg/kg	[47]	
C ₁₃ LAS	River sediment	ASE	LC-MS	0.216-0.339 mg/kg	[5]
	Sewage sludge (digested)	UAE	LC-FL	3602 mg/kg	[55]
	Sewage sludge (compost)			876 mg/kg	
	Sewage sludge			547-4240 mg/kg	[40]
Soil	Soxhlet extraction		0.7-10 mg/kg	[47]	
C ₁₄ LAS	Sewage sludge	UAE		n.d.-182 mg/kg	[40]
Sum of AES	Sediment	ASE	LC-MS	0.043-0.164 mg/kg	[39]
C ₁₂ AES	River sediment			0.030-0.196 mg/kg	[5]
C ₁₃ AES				0.052-0.105 mg/kg	
C ₁₄ AES				0.085-0.225 mg/kg	
C ₁₅ AES				n.d.-n.q. mg/kg	
C ₁₆ AES				n.q.-0.01 mg/kg	

Summary

Anionic surface active agents are a class of compounds which find the largest application in different fields of human activity. The environmental fate of anionic SAA and concentration in surface waters, soils or bottom sediments is investigated in details. Therefore, monitoring the occurrence of anionic surfactants in different types of samples is important for the protection of quality of environment and living organisms. At sample preparation step and final determination step were applied different analytical techniques (eg LLE, SPE, ASE, MAE, spectrophotometry, GC-MS, LC-MS). Those tools allow for increase of degree of knowledge about pollution various ecosystems. Generally, in



environmental samples was determined total concentration of anionic analytes or individual compounds from the group of linear alkylbenzene sulfonates.

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References

- [1] Rosen MJ, Dahanayake M. *Industrial Utilization of Surfactants: Principles and Practice*, Champaign: AOCS; 2000.
- [2] Thiele B. *Surfactants*. In: Nolle LML, editor. *Chromatographic Analysis of the Environment*. Boca Raton: CRC Press; 2005.
- [3] Holmberg K, Jönsson B, Kronberg B, Lindman B. *Surfactants and Polymers in Aqueous Solution*. The Atrium: John Wiley & Sons; 2003.
- [4] Toedt J, Koza D, Van Cleef-Toedt K. *Chemical Composition of Everyday Products*. Westport: Greenwood Publishing Group; 2005.
- [5] Lara-Martin P, Gomez-Parra A, Gonzalez-Mazo E. *J Chromatogr A*. 2006;1114:205-210. DOI: 10.1016/j.chroma.2006.03.014.
- [6] Fendinger NJ, Versteeg DJ, Weeg E, Dyer S, Rapaport RA. *Environmental behavior and fate of anionic surfactants*. In: Baker LA, editor. *Environmental chemistry of lakes and reservoirs*. ACS Advances in Chemistry Series No. 237. Washington DC: American Chemical Society; 1994.
- [7] Sütterlin H, Alexy R, Coker A, Kümmerer K. *Chemosphere*. 2008;72:479-484 DOI: 10.1016/j.chemosphere.2008.03.008.
- [8] Liwarska-Bizukojc E, Miksch K, Malachowska-Jutz A, Kalka J. *Chemosphere*. 2005;58:1249-1253. DOI: 10.1016/j.chemosphere.2004.10.031.
- [9] Van Ewijk PH, Hoekstra JA. *Ecotoxicol Environ Saf*. 1993;25:25-32.
- [10] Verge C, Moreno A, Bravo J, Berna JL. *Chemosphere*. 2001;44:1749-1757. DOI: 10.1016/S0045-6535(00)00574-9.
- [11] Utsunomiya A, Watanuki T, Matsushita K, Nishina M, Tomita I. *Chemosphere*. 1997;35:2479-2490. DOI: 10.1016/S0045-6535(97)00316-0.
- [12] Sandbacka M, Christianson I, Isomaa B. *Toxicol Vit*. 2000;14:61-68. DOI: 10.1016/S0887-2333(99)00083-1.
- [13] Singh RP, Gupta N, Singh S, Singh A, Suman R, Annie K. *Bull Environ Contam Toxicol*. 2002;69:265-270. DOI: 10.1007/s00128-002-0056-z.
- [14] Pavlic Z, Vidakovic-Cifrek Z, Puntaric D. *Chemosphere*. 2005;61:1061-1068. DOI: 10.1016/j.chemosphere.2005.03.051.
- [15] Nomura Y., Ikebukuro K., Yokoyama K., Takeuchi T., Arikawa Y., Ohno S. et al. *Biosens Bioelectron*. 1998;13:1047-1053. DOI: 10.1016/S0956-5663(97)00077-8.
- [16] Jensen J. *Sci Total Environ*. 1999;226:93-111. DOI: 10.1016/S0048-9697(98)00395-7.
- [17] Bliefert C. *Umweltchemie*. Weinheim: VCH; 1994.
- [18] Swisher RD. *Surfactant Biodegradation*, second ed., *Surfactant Science Series*, v. 18. New York: Marcel Dekker; 1987.
- [19] Schöberl P. *Tenside Surfact Det*. 1989;26:86-94.
- [20] Zhang C, Valsaraj KT, Constant WD, Roy D. *Water Res*. 1999;33(1):115-124. DOI: 10.1016/S0043-1354(98)00170-5.
- [21] Cavalli L, Gellera A, Landone A. *Environ Toxicol Chem*. 1993;12:1777-1788.
- [22] Akyüz M. *Talanta*. 2007;71:471-478. DOI: 10.1016/j.talanta.2006.06.014.
- [23] Sanemasa I., Oota E, Aoi K, Zheng J-Z. *Anal Sci*. 2002;18:347-350. DOI: 10.2116/analsci.18.347.
- [24] Koga M, Yamamichi Y, Nomoto Y, Irie M, Tanimura T, Yoshinaga T. *Anal Sci*. 1999;5:63-68. DOI: 10.2116/analsci.15.563.



- [25] Sar SK, Verma C, Pandey PK, Bhui A. *J Chin Chem Soc.* 2009;56:1250-125.
- [26] Di Corcia A, Samperi R, Marcomini A. *Environ Sci Technol.* 1994;28:850-858.
- [27] Crescenzi C, Di Corcia A, Marchiori E, Samperi R, Marcomini A. *Water Res.* 1996;30:722-730. DOI: 10.1016/0043-1354(95)00209-X.
- [28] Reiser R, Toljander HO, Giger W. *Anal Chem.* 1997;69:4923-4930.
- [29] Leon VM, Gonzalez Mazo E, Gomez Parra A. *J. Chromatogr A.* 2000;889:211-219. DOI: 10.1016/S0021-9673(00)00569-0.
- [30] Trehy ML, Gledhill WE, Orth RG. *Anal Chem.* 1990;62:2581-2586.
- [31] Riu J, Eichhorn P, Guerrero JA, Knepper ThP, Barceló D. *J Chromatogr A.* 2000;889:221-229. DOI: 10.1016/S0021-9673(00)00400-3.
- [32] Scullion SD, Clench MR, Cooke M, Ashcroft AE. *J Chromatogr A.* 1996;733:207-216. DOI: 10.1016/0021-9673(95)01188-9.
- [33] Bradley C, Bérubé PR. *J Environ Eng Sci.* 2008;7:63-70. DOI: 10.1139/S07-036.
- [34] Tubau I, Vázquez-Suñé E, Carrera J, González S, Petrovic M, de Alda MJL, Barceló D. *J Hydrology.* 2010;383:83-92. DOI: 10.1016/j.jhydrol.2009.11.030.
- [35] Sander S, Henze G. *Electroanal.* 1997;9:619-624.
- [36] Fabios R, Sicilia M.D, Rubio S, Pérez-Bendito D. *Anal Chem.* 2003;75:6011-6016. DOI: 10.1021/ac030105v.
- [37] Alzaga R, Peña A, Ortiz L, Bayona JM. *J Chromatogr A.* 2003;999:51-60. DOI: 10.1016/S0021-9673(03)00493-X.
- [38] Pedraza A, Sicilia MD, Rubio S, Pérez-Bendito D. *Anal Chim Acta.* 2007;588:252-260. DOI: 10.1016/j.aca.2007.02.011.
- [39] Lara-Martin PA, Gomez-Parra A, Gonzalez-Mazo E. *Environ Poll.* 2008;156:36-45. DOI: 10.1016/j.envpol.2008.01.005.
- [40] Petrovic M, Barceló D. *Anal Chem.* 2000;72:4560-4567. DOI: 10.1021/ac000306o.
- [41] Rico-Rico A, Droge STJ, Widmer D, Hermes JLM. *J Chromatogr A.* 2009;1216:2996-3002. DOI: 10.1016/j.chroma.2009.01.090.
- [42] Coll C, Marínez-Máñez R, Marcos MD, Sancenón F, Soto J. *Angew Chem Int Ed.* 2007;46:1675-1678. DOI: 10.1002/anie.200603800.
- [43] Coll C, Ros-Lis JV, Marínez-Máñez R, Marcos MD, Sancenón F, Soto J. *J Mater. Chem.* 2010;20:1442-1451.
- [44] Coll C, Aznar E, Marínez-Máñez R, Marcos MD, Sancenón F, Soto J, Amorós P, Cano J, Ruiz E. *Chem Eur J.* 2010;16:10048-10061. DOI: 10.1002/chem.200903125.
- [45] Climent E, Giménez C, Marcos MD, Marínez-Máñez R, Secenón F, Soto J. *Chem Commun.* 2011;47:6873-6875. DOI: 10.1039/C1CC11393C.
- [46] Heinig K, Vogt C, Werner G. *Analyst.* 1998;123:349-353. DOI: 10.1039/A705929I.
- [47] Andreu V, Picó Y. *Anal Chem.* 2004;76:2878-2885. DOI: 10.1021/ac035483e.
- [48] Sanderson H, Price BB, Dyer SD, DeCarvalho AJ, Robaugh D, Waite SW. *Sci Total Environ.* 2006;367:312-323. DOI: 10.1016/j.scitotenv.2005.11.021.
- [49] Roslan RN, Hanif NM, Otoman MR, Azmi WNF, Yan XX, Ali MM, Mohamed CAR, Latif MT. *Mar Poll Bull.* 2010;60:1584-1590. DOI: 10.1016/j.marpolbul.2010.04.004.
- [50] Mohd Hanif N, Talib Latif M, Mohd Ali M, Rozali Otoman M. *Europ J Sci Res.* 2009;32:268-276.
- [51] Olkowska E, Polkowska Ż, Namieśnik J. *Chem Rev.* 2011;111:5667-5700. DOI: 10.1021/cr100107g.
- [52] Gonzalez S, Petrovic M, Barcelo D. *J Chromatogr A.* 2004;1052:111-120. DOI: 10.1016/j.chroma.2004.08.047.
- [53] Eichhorn P, Lopez O, Barcelo D. *J Chromatogr A.* 2005;1067:171-179. DOI: 10.1016/j.chroma.2005.01.014.
- [54] Lara Martin PA, Gomez Parra A, Gonzalez Mazo E. *Int J Environ Anal Chem.* 2005;85:293-303. DOI: 10.1080/03067310412331330785.
- [55] Villar M, Fernández-Torres R, Callejón M, Villar P, Jiménez JC. *Microchem J.* 2008;90:164-170. DOI: 10.1016/j.microc.2008.05.005.
- [56] Villar M, Callejón M, Jiménez JC, Alonso E, Guiráum A. *Anal Chim Acta* 2007;599:92-97. DOI: 10.1016/j.aca.2007.07.065.
- [57] Bruno F, Curini R, di Corcia A, Fochi I, Nazzari M, Samperi R. *Environ Sci Technol.* 2002;36:4156-4761. DOI: 10.1021/es020002e.
- [58] Madunic-Cacic D, Sak-Bosnar M, Matešic-Puac R. *Int J Electrochem Sci.* 2011;6:240-253. DOI: 10.1166/sl.2008.040.



- [59] Szymański A, Wyrwas B, Jesiołowska A, Kazmierczak S, Przybysz T, Grodecka J, Łukaszewski Z, Pol. J Environ Stud. 2001;10:371-376.
- [60] Olkowska E, Polkowska Ż, Namieśnik J. Talanta. 2012;85:1-13. DOI: 10.1016/j.talanta.2011.10.034.
- [61] ISO 16265:2009. Water quality - Determination of the methylene blue active substances (MBAS) index - Method using continuous flow analysis (CFA). International Organization for Standardization, Geneva, Switzerland.
- [62] Gavach TC, Bertrand C. Anal Chim Acta. 1971;55:385-393.
- [63] James H, Carmack G, Freiser H. Anal Chem. 1972;44:856-875.
- [64] Birch BJ, Clarke DE. Anal Chim Acta. 1973;67:387-393.
- [65] Fujinaga T, Okazaki S, Freiser H. Anal Chem. 1974;46:1842-1844.
- [66] Sanchez J, del Valle M. Crit Rev Anal Chem. 2005;35:15-29. DOI: 10.1080/10408340590947899.
- [67] Zelenka Lj, Sak-Bosnar M, Marek N, Kovacs B. Anal Lett. 1989;22:2791-2802. DOI: 10.1080/00032718908052395.
- [68] Sak-Bosnar M, Matesic-Puac R, Madunic-Cacic D, Grabaric Z. Tenside Surf Det. 2006;43:82-87.
- [69] Vejrup KV, Wolkoff P. Sci Total Environ. 2002;300:51-58. DOI: [http://dx.doi.org/10.1016/S0048-9697\(02\)00280-2](http://dx.doi.org/10.1016/S0048-9697(02)00280-2).
- [70] Stuart JD, Capulong CP, Launer KD, Pan X. J Chromatogr A. 2005;11079:136-145. DOI: 10.1016/j.chroma.2005.03.075.
- [71] Selberga A, Budashovaa J, Tennoa T. Proc Estonian Acad Sci Chem. 2007;56:87-97.
- [72] D'Hollander W, Roosens L, Covaci A, Cornelis C, Reynnders H, Van Campenhout K et al. Chemosphere. 2010;81:478-487. DOI: 10.1016/j.chemosphere.2010.07.043.
- [73] Field JA, Miller DJ, Field TM, Hawthorne SB, Gigert W. Anal Chem. 1992;64:3161-3167.
- [74] Pastewski S, Mędrzycka K. Pol J Environ Stud. 2003;12:643-646.
- [75] Clara M, Scharf S, Scheffknecht C, Gans O. Water Res. 2007;41:4339-4348. DOI: 10.1016/j.watres.2007.06.027.

OZNACZANIE POZIOMÓW ZAWARTOŚCI SURFAKTANTÓW W PRÓBKACH ŚRODOWISKOWYCH - CZĘŚĆ II. ANIONOWE ZWIĄZKI

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Abstrakt: Związki powierzchniowo czynne (SAA) o ujemnym ładunku polarnej części cząsteczek określane są jako anionowe surfaktanty. Ich wielkość produkcji jest najwyższa wśród syntetycznych związków. Z tej grupy analitów są zazwyczaj stosowane liniowe alkilobenzen sulfoniany (LAS), alkilo etoksyciarczany (AES) oraz alkilo siarczany (AS). Tego typu surfaktanty są składnikami detergentów i produktów czyszczących używanych w gospodarstwach domowych, środkach piorących, kosmetykach. Są one wykorzystywane w przemyśle papierniczym, tekstylnym i garbarskim jako optyczne wybielacze, środki rozpraszające, zwilżające i rozpraszające. Co więcej, są one używane przy wytwarzaniu barwników, pestycydów, żywic jonowymiennych, plastyfikatorów oraz farmaceutyków. Anionowe surfaktanty wraz ze ściekami trafiają do oczyszczalni ścieków, gdzie są poddawane degradacji oraz dochodzi do zjawiska adsorpcji w osadzie czynnym (wykorzystywanym w rolnictwie). Ostatecznie, związki z grupy anionowych SAA lub produkty ich degradacji są emitowane do wód powierzchniowych, a następnie do osadów dennych, gleby i są akumulowane przez organizmy żywe. Stąd istotne staje się poznanie w sposób bardziej szczegółowy losu środowiskowego tej klasy związków (ze względu na ich szerokie wykorzystywanie, podatność na zjawisko bioakumulacji oraz toksyczności względem organizmów żywych). Tego rodzaju badania obejmują określanie poziomów zawartości surfaktantów w różnego typu próbkach z użyciem odpowiednich narzędzi analitycznych. Oficjalne metodyki analityczne dotyczące określania zawartości anionowych związków w ciekłych próbkach środowiskowych są oparte na reakcji tworzenia par jonowych z błękitem metylenowym (MB), a następnie ekstrakcji do toksycznego rozpuszczalnika chloroformu. Na etapie izolacji anionowych analitów ze stałych próbek stosowane są techniki ekstrakcji za pomocą rozpuszczalnika w aparacie Soxhleta lub ekstrakcji wspomagananej falami ultradźwiękowymi (z użyciem jako medium ekstrakcyjnego metanolu lub mieszaniny z innymi rozpuszczalnikami). By wyeliminować wady tego typu tradycyjnych technik, na etapie przygotowania próbek do analizy stosowane są odpowiednio: ekstrakcja do fazy stałej (SPE) oraz mikroekstrakcja do fazy stałej (SPME) - próbki ciekłe; przyspieszona ekstrakcja za pomocą



rozpuszczalnika (ASE), ekstrakcja za pomocą rozpuszczalnika wspomaganą promieniowaniem mikrofalowym (MAE) lub ekstrakcja za pomocą płynu w stanie nadkrytycznym (SFE). W celu określenia sumarycznej zawartości anionowych analitów w ekstraktach stosowana jest technika spektrofotometrii (według obowiązujących regulacji prawnych). Określenie poziomów stężeń indywidualnych analitów odbywa się z reguły z użyciem chromatografii gazowej (konieczny etap derywatyzacji analitów) bądź cieczonej w połączeniu ze spektrometrią mas. Obecność anionowych związków powierzchniowo czynnych została potwierdzona w różnorodnych ekosystemach (ciekłych i stałych próbkach środowiskowych).

Słowa kluczowe: anionowe surfaktanty, izolacja i/lub wzbogacanie, etap oznaczania końcowego, próbki środowiskowe