

Author's Accepted Manuscript

Paired-ion electrospray ionization - triple quadrupole tandem mass spectrometry for quantification of anionic surfactants in waters

Inês C. Santos, Hongyue Guo, Raquel B.R. Mesquita, António O.S.S. Rangel, Daniel W. Armstrong, Kevin A. Schug



PII: S0039-9140(15)00339-2
DOI: <http://dx.doi.org/10.1016/j.talanta.2015.04.081>
Reference: TAL15581

To appear in: *Talanta*

Received date: 28 February 2015
Revised date: 24 April 2015
Accepted date: 27 April 2015

Cite this article as: Inês C. Santos, Hongyue Guo, Raquel B.R. Mesquita, António O.S.S. Rangel, Daniel W. Armstrong and Kevin A. Schug, Paired-ion electrospray ionization - triple quadrupole tandem mass spectrometry for quantification of anionic surfactants in waters, *Talanta*, <http://dx.doi.org/10.1016/j.talanta.2015.04.081>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Paired-ion electrospray ionization - triple quadrupole tandem mass spectrometry for quantification of anionic surfactants in waters

Inês C. Santos^{a,b}, Hongyue Guo^b, Raquel B.R. Mesquita^a, António O.S.S. Rangel^a, Daniel W. Armstrong^b, Kevin A. Schug^{b,*}

^a CBQF – Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Universidade Católica Portuguesa/Porto, Rua Arquitecto Lobão Vital, Apartado 2511, 4202-401 Porto, Portugal

^b Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX, USA

* Corresponding author at: 700 Planetarium Pl.; Box 19065; Arlington, TX 76019-0065, USA.
Tel.: +1 817 272 3541; Fax: +1 817 272 3808; e-mail address: kschug@uta.edu.

Abstract

A new paired ion electrospray ionization tandem mass spectrometry method for determination of anionic surfactants in water samples was developed. In this method, dicationic ion-pairing reagents were complexed with monoanionic analytes to facilitate analyte detection in positive mode electrospray ionization – mass spectrometry. Single ion monitoring and selected reaction monitoring on a triple quadrupole instrument were performed and compared. Four dicationic reagents were tested for the determination of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), sodium dodecyl sulphate (SDS), dodecylbenzene sulfonic acid (DBS), and stearic acid (SA), among other common anions. The obtained limits of detection were compared with those from previous literature. Solid phase extraction using a C18 cartridge was performed in order to eliminate matrix interferences. A literature review was compiled for the methods published between 2010 and 2015 for determination of anionic surfactants. The optimized method was more sensitive than previously developed methods with LOD values of 2.35, 35.4, 37.0, 1.68, and 0.675 pg for SDS, SA, DBS, PFOS, and PFOA, respectively. The developed method was effectively applied for the determination of anionic surfactants in different water samples such as bottled drinking water, cooking water, tap water, and wastewater.

Keywords: anionic surfactants; water analysis; tandem mass spectrometry; solid phase extraction; perfluorinated compounds; ion pairing; PIESI

1. Introduction

The determination of anions, since they possess a negative charge, would be expected to be performed in the negative ionization mode of mass spectrometry. However, the use of electrospray ionization mass spectrometry (ESI-MS) in the negative ionization mode has been shown to have drawbacks [1,2]. The positive ion mode is usually preferred as it can provide lower detection limits and better baseline stability. The negative ionization mode requires application of high negative voltages to form the electrospray. Consequently, it is more susceptible to corona discharge than the positive ion mode, and it can result in higher background noise and poor spray stability. Water/methanol-based solvents are known to increase the likelihood of corona discharge. Also, anions of small mass that are below the mass cut-off of the mass spectrometer cannot be determined [3]. Association of these anions with a multiply-charged cationic reagent increases the mass-to-charge ratio of the “paired ion” species and this facilitates detection.

Martinelango et al. [4] initially reported paired ion electrospray ionization (PIESI) for perchlorate determination using the positive ionization mode in mass spectrometry. Later, PIESI was applied for the determination of different inorganic and organic anions [5]. Lower detection limits (LODs), in the picogram and subpicogram range, were obtained demonstrating the improvement in sensitivity when using the positive ion mode compared to the negative ion mode. Following these results, some studies were performed to understand why these ion-pairing reagents were improving the sensitivity for anions determination in mass spectrometry. According to Breitbach et al. [6], the binding between the anions and the ion-pairing reagents is enhanced during the electrospray desolvation process. They were able to observe that the complex was much more surface active than the analyte or reagent ions alone, and that this improved the ionization efficiency. Other dicationic and tricationic reagents were developed and applied for the determination of both mono and doubly charged anions [7,8]. The authors concluded that the structure of the reagent was an important factor in obtaining better sensitivity, as rigid structures did not perform as well [9]. Additional PIESI-MS applications have included the determination of metals [10,11] and acidic pesticides [12].

Surfactants are widely used in a variety of dispersants, detergents, personal care products, paints, and pharmaceuticals. Their ability to enhance solubilisation and act as cleaning, coating, and releasing agents makes them ubiquitous in modern society. Surfactant molecules possess hydrophilic and hydrophobic moieties, which give them amphiphilic properties and surface activity in aqueous solutions. These compounds can be divided into anionic, cationic, and non-ionic categories depending on the nature of their head group. Anionic surfactants are the most prevalent type and they have been released to the environment in appreciable quantities. They have been found in natural water systems and wastewaters [13]. There are several types of anionic surfactants, but among them, sodium dodecyl sulfate (SDS) and dodecylbenzenesulfonate (DBS) are the most widely used. Also, there is increasing concern about perfluorinated compounds, in particular perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) [14]. They are widely used in many industrial applications and they are more environmentally stable and persistent than most other surfactants. These compounds have been detected in human blood, water, soils, sediments, air, and biota. As a result, they have been added to the United States Environmental Protection Agency (US EPA) priority list for future regulation in drinking water [14,15]. Due to their high toxicity to humans [15,16], studies have been performed to understand the sources of these compounds, their fate, modes of human uptake and their potential health effects. Indeed, consumers are exposed to PFOA due to its usage in PFC-containing products [14,17]. PFOA is an essential polymerization aid for the production of fluoropolymers used in non-stick coating materials, such as those used in cooking pans (as a consequence, the use of Teflon® in cooking utensils is being phased out) [18].

In this work, a brief review of the literature on the determination of anionic surfactants (from 2010 to 2015) is presented, with an emphasis on the sensitivity of the methods, since the levels in environmental samples can be very low. Subsequently, a PIESI method is presented for the determination of anionic surfactants in water and compared to existing methods. Finally, the developed method was applied for the determination of SDS, DBS, PFOA, PFOS, and stearic acid (SA) in different water samples, including bottled drinking water, tap water and

wastewater. The possible release of PFOA from new and used anti-stick pans was also evaluated.

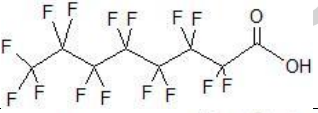
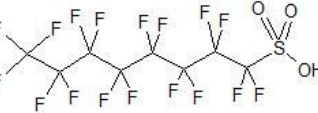
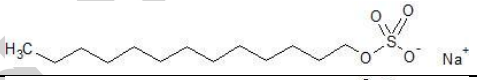
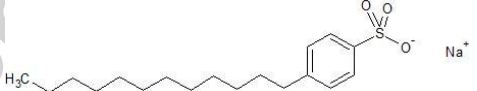
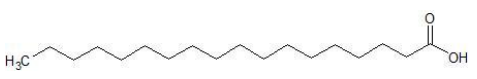
Accepted manuscript

2. Materials and Methods

2.1. Chemicals & Reagents

LC-MS grade analytical water and methanol were obtained from J.T. Baker (Phillipsburg NJ). Sodium bromide, potassium iodide, and sodium benzoate were purchased from Sigma-Aldrich (St. Louis MO, USA). The surfactants, perfluorooctanoic acid, perfluorooctanesulfonic acid, sodium dodecyl sulfate, sodium dodecylbenzenesulfonate, and stearic acid were also purchased from Sigma-Aldrich. The respective structures are presented in Table 1. Standard solutions in the range of 0.01 – 50 $\mu\text{g L}^{-1}$ were prepared.

Table 1. Structures of the surfactants studied in this work.

Group	Anionic surfactant	Structure	Molecular weight (g mol^{-1})
Perfluoroalkyl carboxylate	Perfluorooctanoic acid (PFOA)		414.07
Perfluoroalkyl sulfonate	Perfluorooctanesulfonic acid (PFOS)		500.13
Fatty alkyl sulfate	Sodium lauryl sulfate (SDS)		288.37
Linear alkylbenzene sulfonate	Sodium dodecylbenzenesulfonate (DBS)		348.48
Alkyl carboxylates (soap)	Stearic acid (SA)		284.48

Four types of dicationic ion-pairing reagents were used to carry out PIESI analysis. Their detailed information is given in Table 2. The reagents utilize charged moieties such as imidazolium (MeImC_9 and ButImC_{12}), pyrrolidinium ($\text{C}_5(\text{Bpyr})_2$), and phosphonium ($\text{C}_3(\text{tpr})_2$), and the alkyl linkage chain length differs from C_3 to C_{12} . These compounds were chosen as they present a more flexible structure which was previously indicated as ideal for anion determination; they gave more sensitive results when compared with dicationic ion-pairing reagents with more rigid structures [6].

Table 2. Structures of the dicationic ion-pairing reagents used in this work.

Name	Structure	Molecular weight (g mol ⁻¹)
1,3-Propanediyl-bis(tripropylphosphonium) difluoride [C ₃ (tpr) ₂]		400.55
1,5-Pentanediy-bis(1-butylpyrrolidinium) difluoride [C ₅ (Bpyr) ₂]		362.58
1,9-Nonanediy-bis(3-methylimidazolium) difluoride [MeImC ₉]		328.44
1,12-dodecanediyl-bis(butylimidazolium) difluoride [ButImC ₁₂]		470.65

The dication reagents were used in the fluoride form as it has been shown that this anion associates less strongly with the ion-pairing reagents. A concentration of 40 μ M for each was prepared in water and used.

2.2. Water Samples

For application of the PIESI method, different water samples, such as bottled drinking water, tap water, and wastewater, were analysed for the presence of anionic surfactants. The wastewater was obtained from an unconventional oil extraction site where hydraulic fracturing was utilized in West Texas. Water was also boiled in a new non-stick pan before and after being scratched to assess the possible release of PFOA. The same was done in a used non-stick pan and a plastic box indicated for microwave usage.

2.3. ESI-MS analysis

The mass spectrometer used in this study was an LCMS-8040 triple quadrupole (Shimadzu Corporation, Kyoto, Japan) equipped with an electrospray ionization (ESI) interface and LCMS LabSolutions software (version 5.53 SP2). The PIESI-MS was operated in the

positive ionization mode in either scan, single ion monitoring (SIM), or selected reaction monitoring (SRM) modes. The MS conditions were set as follows: Spray voltage, 4.5 kV; capillary temperature, 250°C; nebulizer gas, 2.0 L min⁻¹. The LC pumps were used to pump the mobile phase 75% MeOH/25% H₂O at a flow rate of 250 µL min⁻¹. An external syringe pump (KD scientific, Holliston, MA) with a 2.5 mL syringe (Hamilton, Reno, NV) was placed in-line to pump the 40 µM dicationic reagent at a flow rate of 75 µL min⁻¹. The dicationic reagent was introduced by using a T-shaped confluence, giving a final flow rate of 325 µL min⁻¹ and a dicationic reagent concentration of 9 µM. The injection volume was set at 40 µL.

The LODs were calculated according to Harris [68] by injecting a standard that was estimated to be 1-5 times the LOD seven times. After that, the standard deviation (s) of the signal was used as follows: LOD = 3s/m, where m is the slope of the calibration curve.

2.4. Solid Phase Extraction

Analytes were extracted using Supelclean LC-18 (500 mg/ 3 mL) cartridges from Supelco Analytical (Bellefonte PA, USA). Cartridges were preconditioned on a vacuum manifold with 3 mL of MeOH and equilibrated with 3 mL of LC-MS water. 3 mL of water samples were then passed through the cartridges at 1-2 drops per second. The matrix interferences were cleaned from the cartridge using 3 mL of a 40% MeOH solution. Afterwards, analytes were eluted using 3 mL of 90% MeOH into a test tube. The resulting solutions were transferred to 2 mL autosampler vials.

3. Results and Discussion

A review of the existing methods described in the literature between 2010 and 2015 for anionic surfactants determination was performed and is presented in Table 3. The most common methods used for surfactants determination are liquid chromatography coupled to mass spectrometry (LC-MS) or tandem mass spectrometry (LC-MS/MS). These are the more

sensitive methods for anionic surfactants determination. Liquid chromatography is more frequently used than gas chromatography. Fluorimetric, spectrophotometric, and potentiometric methods are also presented but clearly they are not as sensitive as the MS methods, in many cases due to lack of strong chromophores. This is a disadvantage for the determination of surfactants in environmental samples, as the levels of surfactants are expected to be in the ng L^{-1} range. Almost all the presented works require a sample pre-treatment before the determination step, and solid phase extraction is the most commonly used method. The lowest detection limit reported was 0.02 ng L^{-1} for PFOS and PFOA and the presented methods were mainly applied for the determination of anionic surfactants in water samples such as river, fresh, drinking, and tap water.

Table 3. Methods for anionic surfactants determination published from 2010-2015.

Analyte	Method/ Detector	Sample pre-treatment	LOD	RSD, %	Sample	References
SDS, DBS and PVS	Spectrophotometry	-	1 mg L ⁻¹	n.g.	Cleaning products	[20]
Alkylphenols, alkylphenols polyethoxylates, alkylphenoxy carboxylates	LC-MS/MS	SPE	0.52-7.5, 0.04-30, 0.22-0.24 µg L ⁻¹	n.g.	Wastewater and surface water	[21]
Fluorosurfactants	ESI-QToF	-	n.g.	n.g.	Municipal reverse osmosis concentrate	[22]
SDS and DBS	Potentiometry	-	60.6, 73.2 µg L ⁻¹	n.g.	Detergents	[23]
Anionic surfactants	Spectrophotometry	-	30 µg L ⁻¹	2.3-5.1	Water	[24]
Alkyl sulphates	IPC	-	10 mg L ⁻¹	0.62-4.24	River water and sewage	[25]
Perfluorinated compounds	LC-MS/MS	SPE	0.09-3 ng L ⁻¹ ; 0.15-1.5 ng g ⁻¹	<15	Wastewater and sewage sludge	[26]
SDBS	Spectrophotometry	LLE	16 µg L ⁻¹	1.3; 3.8	River water	[27]
Fatty alcohol ethoxylates, alkylether sulfates, LASs	LC	SPE	n.g.	n.g.	Industrial cleaners, laundry, shampoos, shower gel	[28]
LASs, alkyl sulfates, AESs, alcohol polyethoxylates	LC-MS/MS	Ultrasound-assisted extraction	0.02-7.0 µg Kg ⁻¹	2.0-8.2	Marine sediments	[29]
Alcohol sulfates and alcohol ethoxysulfates	LC-MS/MS	SPE	0.1, 0.2-0.5 µg L ⁻¹	<5	Wastewater	[30]
LASs	HPLC-FLD	µSPE	0.8-1.9 µg L ⁻¹	2.0-3.9	Tap and mineral water samples and seawater	[31]
SDBS, SDS	Spectrophotometry	-	0.059, 0.016 mg L ⁻¹	0.44-2.6	Domestic and industrial wastewaters	[32]

Analyte	Method/ Detector	Sample pre-treatment	LOD	RSD, %	Sample	References
SDS	Diffuse reflectance spectrophotometry	-	n.g.	n.g.	Natural and drinking water	[33]
Perfluorinated compounds	LC-MS/MS	SPE	0.040-0.125 $\mu\text{g L}^{-1}$	n.g.	Human milk	[34]
SDS	Potentiometry	-	1.44 mg L^{-1}	n.g.	Toothpastes	[35]
Secondary alkane sulfonates	LC-MS	LE/SPE	0.31-0.65/0.007-0.022 $\mu\text{g L}^{-1}$; 4-7/0.5-1.1 $\mu\text{g kg}^{-1}$	<20	Sediment, sludge, wastewater, surface water	[36]
LASs, nonylphenol, nonylphenol mono and diethoxylates, di-(2-ethylhexyl)phthalate	LC-MS	DLLME	0.009-0.224 $\mu\text{g L}^{-1}$	1.3-7.8	Tap water, wastewater	[37]
Alkyl polyglucoside, alpha olefin sulfonate	LC-evaporated light scattering detector	-	2.29; 16.55 mg L^{-1}	<1.0	Dishwashing detergents	[38]
SDS	Spectrophotometry	LLME	0.02 mg L^{-1}	1.5	Freshwaters	[39]
LASs	HPLC	SPE	0.013-0.021 $\mu\text{g L}^{-1}$	2.4-5.6	Environmental water	[40]
Alcohol sulfates	GC-MS	SPE	0.2-0.3 $\mu\text{g L}^{-1}$	<5	WWTP	[41]
PFOS and PFOA	LC-MS/MS	SPE	0.06, 0.10 ng L^{-1} ; 0.09, 0.10 ng g^{-1}	n.g.	Wastewater and sludge	[42]
Perfluorinated compounds	LC-MS/MS	SPE	0.11-0.35 ng L^{-1} ; 0.010-0.029 ng g^{-1}	n.g.	Water and sediment samples	[43]
Perfluorocarboxylic acids	GC-MS/MS	DLLME	0.037-0.051 $\mu\text{g L}^{-1}$	<13	River water	[44]

Analyte	Method/ Detector	Sample pre-treatment	LOD	RSD, %	Sample	References
Alkylphenol ethoxylates	LC-IM-MS	-	5-200/10-300 $\mu\text{g L}^{-1}$	12, 15	-	[45]
Perfluorinated alkylated substances	LC-MS/MS	SPE, LLE	2 pg g^{-1}	n.g.	Surface sediments and sediment core	[46]
Perfluorooctane sulfonates	LC-MS/MS	ASE/ SPE	0.4 $\mu\text{g m}^{-2}$	0.48-3.59	Nonstick pot, food packaging materials, waterborne coatings	[47]
Perfluorinated compounds	LC-MS/MS	Ultrasonic extraction, DSPE	<0.1 ng g^{-1}	0.6-11	Sludge amended soil	[48]
SLES	Potentiometry	-	n.g.	n.g.	Liquid detergents and personal care products	[49]
Perfluorinated compounds	LC-MS/MS	SPE	0.39-60.7 ng L^{-1} 0.09-112 ng g^{-1}	<20	Food and drinking water	[50]
Perfluorinated compounds	LC-MS/MS	MSPD	0.05-0.3 ng g^{-1}	<7.5	Mollusks	[51]
PFCAs	HPLC-fluorescence detection	-	5-10 $\mu\text{g L}^{-1}$	<1	River, lake and tap water	[52]
PFCAs	HPLC-fluorescence detection	SPE	43-75 ng L^{-1}	<1	Surface water	[53]
Perfluorinated compounds	LC-MS/MS	Extraction QA/QC	0.1-17 ng g^{-1}	n.g.	Plants	[54]
Anionic surfactants	Spectrophotometry	Ultrasonic-assisted extraction	0.010 mg L^{-1}	4.8	Water samples	[55]
Anionic surfactants	Spectrophotometry	-	n.g.	0.6-10	River, well, seawater	[56]
Perfluorooctane sulfonyl fluoride	LC-MS	LLE/SPE	0.5 $\mu\text{g L}^{-1}$	10.8	Water, soil	[57]

Analyte	Method/ Detector	Sample pre-treatment	LOD	RSD, %	Sample	References
SDS, DBS	Potentiometry	-	10 mg L ⁻¹	n.g.	-	[58]
LASs, AESs	LC-MS	SPE	0.04-2 µg L ⁻¹	<10	Seawater, river water, industrial and urban wastewater	[59]
LASs	LC-UV	IP-SPE	0.02-0.03 µg L ⁻¹	1.55-2.54	Tap and river water	[60]
LASs	LC-FLD	Microwave-assisted extraction	3.3-5.4 µg Kg ⁻¹	1.3-3.2	Sewage sludge samples	[61]
PFOS and PFOA	HPLC-MS/MS	SPE	0.1, 0.5 ng L ⁻¹	n.g.	Reservoirs, rivers/canals, coastal waters and treated effluents of WWTPs	[62]
Fluorochemicals	LC-MS/MS	SPE	0.5-5-4 ng L ⁻¹	<26	Landfill leachates	[63]
Perfluoroalkyl phosphonates, carboxylates, and sulfonates	ESI-QToF	SPE	0.095-0.17, 0.027-0.17, 0.014-0.052 ng L ⁻¹	3-83	Drinking water	[64]
LASs isomers	GC-MS	SPE	n.g.	n.g.	Water samples from WWTPs	[65]
Anionic surfactants	rFIA-spectrophotometry	-	2.4 µg L ⁻¹	0.38	Seawater	[66]
SDS	Fluorescence quenching	-	8.35x10 ⁻⁹ M	1.67	Natural and industrial water samples	[67]
PFOS and PFOA	LC-MS/MS	SPE/ silica clean-up	0.1, 0.5 µg L ⁻¹	n.g.	Reservoir water, river water, treated effluent and influent of WWTP	[68]
PFOS and PFOA	LC-MS/MS	SPE	0.02 ng L ⁻¹	≤15	River basin	[69]
LASs	HPLC	SPE	0.027 µg L ⁻¹	<10	Environmental water samples	[70]

Analyte	Method/ Detector	Sample pre-treatment	LOD	RSD, %	Sample	References
Anionic surfactants	Sorption-photometric	-	0.001-0.003 mg L ⁻¹	0.04-0.08	Water from the central water supply	[71]

* LC-MS/MS, Liquid chromatography-Tandem mass spectrometry; IPC, Ion-pair chromatography; ESI-QToF, electrospray ionization-time of flight; LC, Liquid chromatography; HPLC-FLD, high pressure liquid chromatography with fluorescence detection; HPLC, high pressure liquid chromatography; LC-MS, liquid chromatography-mass spectrometry; GC-MS, gas chromatography-mass spectrometry; LC-IM-MS, liquid chromatography-ion mobility-mass spectrometry; rFIA, reverse flow injection analysis; SPE, solid phase extraction; LLE, liquid liquid extraction; DLLME, dispersive liquid liquid microextraction; LLME, liquid liquid microextraction; ASE, Accelerated solvent extraction; DSPE, dispersive solid phase extraction; MSPD, matrix solid-phase dispersion; IP-SPE, ion pair-solid phase extraction; SDS, sodium lauryl sulfate; DBS/SDBS, sodium dodecylbenzenesulfonate; PVSK, potassium polyvinylsulfate; LASs, Linear alkylbenzene sulfonates; AESs, alkyl ethoxysulfates; PFOS, perfluorooctanesulfonic acid; PFOA, perfluorooctanoic acid; SLES, sodium lauryl ether sulfate; PFCAs, Perfluorinated carboxylic acids; n.g., not given.

Previous studies have shown the effective use of ion-pairing reagents for determination of anions using ESI-MS in the positive mode [4,5,9,72]. In this work, the application of these reagents was studied for the determination of anionic surfactants. Also, one of the main purposes of this work was to use a triple quadrupole for PIESI-MS and evaluate its sensitivity as ion trap instrumentation has been used predominantly in previous applications.

3.1. System Optimization

Initial optimization studies were performed using the dicationic reagent $C_3(tpr)_2$ and bromide, iodide, and benzoate anions at $10 \mu\text{g L}^{-1}$. Different flow rate values of 100, 250, 500, and $1000 \mu\text{L min}^{-1}$ were tested and a value of $250 \mu\text{L min}^{-1}$ was chosen, because it provided higher intensity signals. Higher flow rates did not significantly improve the sensitivity of the method; in fact, a decrease in analyte response was observed. The syringe pump flow rate (dicationic reagent) was also studied and values of 10, 20, 50, 75, and $100 \mu\text{L min}^{-1}$ were tested. A value of $75 \mu\text{L min}^{-1}$ was chosen since an increase in the signal was observed until that value. Furthermore, this flow rate was chosen as a compromise to reduce reagent waste. The ratio between water and methanol for sample introduction was also studied and ratios of 0:100; 25:75; 50:50; 75:25, and 100:0 were tested. The signal intensity increased with the increase in MeOH percentage. A ratio of 25% H_2O / 75% MeOH was found to provide the best sensitivity. Sample injection volumes of 5, 10, 20, and $40 \mu\text{L}$ were studied. A higher injection volume was chosen as it is possible to reach lower limits of detection based on absolute amount of analyte introduced, thus increasing the sensitivity of the method.

3.2. Limits of Detection for General Anions

In order to determine the method sensitivity, the LODs for the anions I^- , Br^- , and BzO^- were determined and compared with those described in previous literature (Table 4). Experiments were performed using four different dicationic ion-pairing reagents in the Scan, SIM, and SRM modes. The monoisotopic mass was used to calculate the mass-to-charge ratio of the complex that was monitored in the SIM mode. For the SRM mode, the fragmentation

pathways for the reagents $C_3(\text{tpr})_2$, $C_5(\text{Bpyr})_2$, and MeImC_9 have been previously proposed [5,12]. The fragments correspond to a cleavage of the $C_\alpha\text{-N}$ bond in $C_5(\text{Bpyr})_2$ and the $C_\alpha\text{-C}_\beta$ bond in $C_3(\text{tpr})_2$ and ButImC_{12} . The MeImC_9 reagent forms a $[\text{M-H}]^+$ species by losing a C_2 hydrogen on one imidazole ring upon fragmentation.

Table 4. LODs obtained for the anions using the developed method and the different dicationic ion-pairing reagents.

This work (pg)						Literature (pg)	
Reagent	Analyte	SIM mass	Q1 Scan	Q3 SIM	SRM m/z 187.2	SIM [6]	
$C_3(\text{tpr})_2$	Br^-	443.2	4.6	1.3	6.4	120	
	I^-	489.2	24	28	17	1.1	
	BzO^-	483.3	20	13	1.6	130	
						SIM [72]	
	Analyte	SIM mass	Q1 Scan	Q3 SIM	SRM m/z 140	SRM m/z 196	SRM m/z 278
$C_5(\text{Bpyr})_2$	Br^-	405.2	11	2.8	11	43	10
	I^-	451.2	54	5.6	35	-	-
	BzO^-	445.35	110	55	31	20	-
						SIM [5]	
	Analyte	SIM mass	Q1 Scan	Q3 SIM	SRM m/z 207	SRM m/z 289	SRM [5]
MeImC_9	Br^-	417.1	18	2.8	8.1	10	60
	I^-	371.1	3.0	5.7	29	10	6.0
	BzO^-	413.2	130	15	120	21	390
						SIM [5]	
	Analyte	SIM mass	Q1 Scan	Q3 SIM	SRM m/z 291		
ButImC_{12}	Br^-	497.3	7.7	0.93	2.6		
	I^-	543.3	77	30	1.9		
	BzO^-	537.4	68	16	75		

Different LODs were obtained for the same anion using different dications, which indicated that the choice of ion-pairing reagent has an influence on the sensitivity of the method. The reagent $C_3(\text{tpr})_2$ gave lower LODs for the tested anions in all modes when compared to the $C_5(\text{Bpyr})_2$ and MeImC_9 reagents, which indicated that this reagent provided a more sensitive method than the other two. When compared to the ButImC_{12} , the $C_3(\text{tpr})_2$ reagent gave similar LOD values. In fact, some LODs were lower with the ButImC_{12} reagent. As expected, some LODs were lower using the SRM, presumably due to a reduction in noise. However, many

LODs obtained using the SRM mode were the same or higher than the ones obtained using the SIM mode. According to Soukup-Hein et al. [5], this could be due to the presence of other unknown (neutral) fragmentation pathways that reduce the amount of the fragment being monitored.

When compared to values presented in previous literature, using the same dicationic ion-pairing reagents, lower LODs were obtained in this work for all anions except for iodide using the $C_3(\text{tpr})_2$ and $C_5(\text{Bpyr})_2$ reagents. These results could be explained by the fact that different instruments were used. In this work, a triple quadrupole was used, whereas previously for PIESI-MS [5,6,72], a linear ion trap was used. When comparing a triple quadrupole to an ion trap with identical ion source emittances, the triple quadrupole device provides an order of magnitude better LOQ for quantitation experiments than an ion trap, primarily due to integration effects and a significant reduction in noise. Triple quadrupoles offer better performance for SRM experiments for target compound quantitation. These results demonstrate that the developed method is generally more sensitive than the ones previously described in the literature.

The LODs for the presented anions were also determined using a next generation Shimadzu LCMS 8050. The manufacturer claims that this equipment is more sensitive than the Shimadzu LCMS 8040 used primarily in this work. One main difference is that the LCMS 8050 uses a heated ion source, which can enhance electrospray droplet desolvation and ionization efficiency. The previously optimized conditions were used to make a comparison. Some of the LODs obtained using the Shimadzu LC-MS 8050 were as much as ten-fold lower than those obtained on the 8040 instrument. As an example, the LODs for bromide using the $C_3(\text{tpr})_2$ reagent were 1.26 pg and 0.203 pg for the 8040 and 8050 models, respectively. Some of the other LODs obtained were similar and no significant improvement was observed.

3.3. LOD for anionic surfactants

After determining the LODs for the anions and comparing them to previously reported values (Table 4), the LODs for the anionic surfactants were determined using the same four dicationic reagents. The values obtained are presented in Table 5.

Table 5. LODs obtained for the anionic surfactants using the developed method and the different dicationic ion-pairing reagents.

		This work (pg)			
Reagent	Analyte	SIM mass	Q3 SIM	SRM m/z 187.2	
C ₃ (tpr) ₂	SDS	627.5	3.3	4.0	
	SA	645.5	35	54	
	DBS	687.5	37	110	
	PFOS	861.4	55	37	
	PFOA	775.3	4.5	10	
	Analyte	SIM mass	Q3 SIM	SRM m/z 140	SRM m/z 196
C ₅ (Bpyr) ₂	SDS	589.5	2.4	-	7.3
	SA	609.6	37	-	210
	DBS	649.5	220	510	520
	PFOS	823.3	6.3	11	16
	PFOA	737.3	6.2	19	2.8
	Analyte	SIM mass	Q3 SIM	SRM m/z 207	SRM m/z 289
MeImC ₉	SDS	555.2	12	29	55
	SA	573.4	170	170	-
	DBS	615.4	79	150	85
	PFOS	789.2	2.7	5.6	54
	PFOA	703.2	0.68	12	5.0
	Analyte	SIM mass	Q3 SIM	SRM m/z 291	SRM m/z 415
ButImC ₁₂	SDS	681.5	18	34	28
	SA	699.7	180	90	54
	DBS	741.5	65	280	310
	PFOS	915.4	3.6	1.7	-
	PFOA	829.4	6.8	10	8.6

The best LOD values were 2.4, 35, 37, 1.7, and 0.68 pg for SDS, SA, DBS, PFOS, and PFOA, respectively. Compared to the available literature values presented in Table 3, the values obtained in this study are lower. When compared to the methods that use LC/MS/MS, this work is in the same approximately ng L^{-1} range. So, the developed PIESI method is a simple but sensitive alternative method for anionic surfactant determination. In fact, a major enhancement was not expected as surfactants are already surface active and responsive in ESI-MS. Analytes with a higher surface activity exhibit greater desorption characteristics, which will increase signal intensity [73].

3.4. Solid-Phase Extraction Recovery Study

For matrix interference elimination, solid-phase extraction was performed according to the procedure described in the Experimental section. In order to evaluate its efficacy, recovery studies were performed by spiking LC-MS water and tap water with the anionic surfactants in a concentration range of $0.1 - 5 \mu\text{g L}^{-1}$ (Figure 1). Different surfactant concentrations were used due to the different LODs for each analyte. Recovery percentages were in the range between 87-97% for LC-MS water and 95-109% for tap water which indicates a good recovery for anionic surfactants in different water matrices at the $\mu\text{g L}^{-1}$ levels.

Figure 1, here please

3.5. Application to Water Samples

After developing a sensitive method for anionic surfactants determination, it was applied for the determination of these compounds in different water samples (Table 6). These water samples were: A) tap water; B) water collected from a drinking fountain at the University; C) and D) different brands of bottled drinking water; E) water boiled in a used non-stick pan; F) water boiled in a microwavable plastic box; G) wastewater; H) water placed in a new (not used)

non-stick pan; I) water boiled in a new (not used) non-stick pan, and J) water boiled in the same new, but intentionally scratched, non-stick pan.

For the MS determination, the SIM mode was used since no significant improvement in the sensitivity was generally observed for the surfactants using the SRM mode. As previously explained, the $C_3(tpr)_2$ reagent was chosen as it provided lower LODs.

Table 6. Application of the developed method for anionic surfactants determination in water samples using the $C_3(tpr)_2$ reagent and the SIM mode. Values are presented \pm one standard deviation ($n = 3$).

Samples	SDS $\mu\text{g L}^{-1}$	SA $\mu\text{g L}^{-1}$	DBS $\mu\text{g L}^{-1}$	PFOA $\mu\text{g L}^{-1}$	PFOS $\mu\text{g L}^{-1}$
A	2.51 ± 0.02	42.2 ± 0.4	14.2 ± 0.2	0.069 ± 0.005	<LOD
B	1.26 ± 0.02	10.0 ± 0.3	1.5 ± 0.2	$0.33_2 \pm 0.01_4$	<LOD
C	0.57 ± 0.04	21.5 ± 0.1	0.6 ± 0.2	<LOD	<LOD
D	0.530 ± 0.004	43.8 ± 0.5	<LOD	<LOD	1.19 ± 0.02
E	68.9 ± 0.3	35.4 ± 0.5	172 ± 5	0.210 ± 0.005	0.59 ± 0.07
F	0.813 ± 0.003	11.3 ± 0.3	<LOD	0.613 ± 0.003	<LOD
G	17.4 ± 0.4	10.7 ± 0.7	16.8 ± 0.5	3.57 ± 0.02	1.05 ± 0.01
H	<LOD	3.3 ± 0.9	8 ± 1	<LOD	<LOD
I	<LOD	4.6 ± 0.8	14 ± 2	<LOD	<LOD
J	$3.9_9 \pm 0.9_7$	42.9 ± 0.2	12.5 ± 0.9	0.30 ± 0.03	0.2 ± 0.1

Anionic surfactants were found in all the water samples and the highest concentrations were obtained for the wastewater samples. A study was performed where water was boiled before and after a non-stick pan was scratched to test for possible release of PFOA (samples I and J). Before scratching the pan, no value of PFOA was detected, while after scratching the pan, $0.30 \pm 0.03 \mu\text{g L}^{-1}$ were found. The concentration of SDS and SA also increased after scratching the pan. In fact, Bradley et al. [74] previously showed the release of SA from non-stick coating. However, these compounds may not be part of the coating formulation. It was explained that some compounds may be present due to the coatings “picking up” these substances when the articles were packaged and transported. This could explain the presence of SDS and SA after scratching the pan. The developed method is a sensible method for the determination of anionic surfactants at the sub-pg level. To assess recovery, LC-MS water and tap water were spiked with the anionic surfactants and values with an average (\pm one standard deviation) of $98 \pm 8\%$ for LC-MS water and of $103 \pm 7\%$ for tap water were obtained. The

repeatability of the method was assessed by calculating the relative standard deviation, RSD% ($\mu\text{g L}^{-1} \pm \text{SD}$) obtained by the mean of seven consecutive injections of standard solutions: 5% (0.81 ± 0.04) for DBS, 8% (6.0 ± 0.5) for PFOS, 4% (0.63 ± 0.02) for PFOA, 14% (0.40 ± 0.05) for SDS, and 10% (4.5 ± 0.4) for SA.

Accepted manuscript

4. Conclusions

In this work a paired ion electrospray ionization tandem mass spectrometry method (PIESI-MS) was developed for determination of anionic surfactants. This method proved to be a very sensitive and simple method for the determination of anionic surfactants at the ng L^{-1} (sub-pg) level. In fact, these surfactants were detected in all the tested water samples and reached the highest levels in the wastewater samples. In January 2009, the EPA's Office of Water established a provisional health advisory (PHA) of $0.2 \mu\text{g L}^{-1}$ for PFOS and $0.4 \mu\text{g L}^{-1}$ for PFOA in drinking water. However, a PFOS value of $1.2 \mu\text{g L}^{-1}$ was found in a bottled drinking water which is of concern due to the health risks that this compound may cause to humans. The release of PFOA from Teflon coating of a non-stick pan was also detected which indicates that these pans can be a source of exposure by fluorinated compounds to humans.

The time consuming step of this method is the SPE procedure as it is not an automatic procedure. The automation of this step would be an advantage as it would decrease the time necessary for this procedure and would also reduce human error. For further applications, the method could be used for the determination of other anionic surfactants. Also, to potentially remove the need for SPE in samples that are not overly complex, the PIESI-MS could be coupled to HPLC for analyte separation prior to PIESI-MS.

Acknowledgements

Support for this work was provided by the National Science Foundation (CHE-0846310). I.C. Santos thanks Fundação para a Ciência e a Tecnologia (FCT, Portugal) and Fundo Social Europeu (FSE) for the grant SFRH/BD/76012/2011. This work was supported by European Union FEDER funds through COMPETE and by National Funds from FCT through project PEst-OE/EQB/LA0016/2013. Instrumentation support from Shimadzu Scientific Instruments, Inc. is also acknowledged.

References

- [1] R.F. Straub, R.D. Voyksner, Negative ion formation in electrospray mass spectrometry, *J. Am. Soc. Mass Spectrom.* 7 (1996) 578-587.
- [2] G. Wang, R.B. Cole, Effects of solvent and counterion on ion pairing and observed charge states of diquatamary ammonium salts in electrospray ionization mass spectrometry, *J. Am. Soc. Mass Spectrom.* 4 (1993) 1050-1058.
- [3] N.B. Cech, C.G. Enke, Practical implications of some recent studies in electrospray ionization fundamentals, *Mass Spec. Rev.* 20 (2001) 362-387.
- [4] P.K. Martinelango, J.L. Anderson, P.K. Dasgupta, D.W. Armstrong, R.S. Al-Horr, R.W. Slingsby, Gas-phase ion association provides increased selectivity and sensitivity for measuring perchlorate by mass spectrometry, *Anal. Chem.* 77 (2005) 4829-4835.
- [5] R.J. Soukup-Hein, J.W. Remsburg, P.K. Dasgupta, D.W. Armstrong, A general, positive ion mode ESI-MS approach for the analysis of singly charged inorganic and organic anions using a dicationic reagent, *Anal. Chem.* 79 (2007) 7346-7352.
- [6] Z.S. Breitbach, E. Wanigasekara, E. Dodbiba, K.A. Schug, D.W. Armstrong, Mechanisms of ESI-MS selectivity and sensitivity enhancements when detecting anions in the positive mode using cationic pairing agents, *Anal. Chem.* 82 (2010) 9066-9073.
- [7] R.J. Soukup-Hein, J.W. Remsburg, Z.S. Breitbach, P.S. Sharma, T. Payagala, E. Wanigasekara, J. Huang, D.W. Armstrong, Evaluating the use of tricationic reagents for the detection of doubly charged anions in the positive mode by ESI-MS, *Anal. Chem.* 80 (2008) 2612-2616.
- [8] Z.S. Breitbach, M.M. Warnke, E. Wanigasekara, X. Zhang, D.W. Armstrong, Evaluation of flexible linear tricationic salts as gas-phase ion-pairing reagents for the detection of divalent anions in positive mode ESI-MS, *Anal. Chem.* 80 (2008) 8828-8834.
- [9] C. Xu, H. Guo, Z.S. Breitbach, D.W. Armstrong, Mechanism and sensitivity of anion detection using rationally designed unsymmetrical dications in paired ion electrospray ionization mass spectrometry, *Anal. Chem.* 86 (2014) 2665-2672.

- [10] E. Dodbiba, C. Xu, E. Wanigasekara, D.W. Armstrong, Sensitive analysis of metal cations in positive ion mode electrospray ionization mass spectrometry using commercial chelating agents and cationic ion-pairing reagents, *Rapid Commun. Mass Spectrom.* 26 (2012) 1005-1013.
- [11] C. Xu, E. Dodbiba, N.L.T. Padivitage, Z.S. Breitbach, D.W. Armstrong, Metal cation detection in positive ion mode electrospray ionization mass spectrometry using a tetracationic salt as a gas-phase ion-pairing agent: Evaluation of the effect of chelating agents on detection sensitivity, *Rapid Commun. Mass Spectrom.* 26 (2012) 2885-2896.
- [12] C. Xu, D.W. Armstrong, High-performance liquid chromatography with paired ion electrospray ionization (PIESI) tandem mass spectrometry for the highly sensitive determination of acidic pesticides in water, *Anal. Chim. Acta* 792 (2013) 1-9.
- [13] Y.R. Bazel, I.P. Antal, V.M. Lavra, Zh.A. Kormosh, Methods for the determination of anionic surfactants, *J. Anal. Chem.* 69 (2014) 211-236.
- [14] S.D. Richardson, T.A. Ternes, Water Analysis: Emerging contaminants and current issues, *Anal. Chem.* 86 (2014) 2813-2848.
- [15] D. Trudel, L. Horowitz, M. Wormuth, M. Scheringer, I.T. Cousins, K. Hungerbühler, Estimating consumer exposure to PFOS and PFOA, *Risk Anal.* 28 (2008) 251-269.
- [16] F.M. Hekster, R.W.P.M. Laane, P. Voogt, Environmental and toxicity effects of perfluoroalkylated substances, *Rev. Environ. Contam. T.* 179 (2003) 99-121.
- [17] United States Environmental Protection Agency. Perfluorooctanoic Acid (PFOA) and Fluorinated Telomers. Retrieved February 22th, 2015, from <http://www.epa.gov/oppt/pfoa/pubs/pfoainfo.html#pfos>
- [18] United States Environmental Protection Agency. Long-Chain Perfluoroalkyl Carboxylate (LCPFAC) Chemicals. Retrieved February 22th, 2015, from <http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html>
- [19] D.C. Harris, *Quantitative Chemical Analysis* 8^{ed} (2011).
- [20] N. Dürüst, S. Naç, N. Ünal, Quantitative determination of anionic surfactants using optical sensors with microtiter plate reader, *Sensors Actuat. B* 203 (2014) 181-186.

- [21] L. Ciofi, C. Ancillotti, U. Chiuminatto, D. Fibbi, L. Checchini, S. Orlandini, M. Del Bubba, Liquid chromatographic-tandem mass spectrometric method for the simultaneous determination of alkylphenols polyethoxylates, alkylphenoxy carboxylates and alkylphenols in wastewater and surface-water, *J. Chromatogr. A* 1362 (2014) 75-88.
- [22] X.H. Lin, S.F.Y. Li, Determination of organic pollutants in municipal reverse osmosis concentrate by electrospray ionization-quadrupole time-of-flight tandem mass spectrometry and photocatalytic degradation methods, *Desalination* 344 (2014) 206-211.
- [23] O. Galović, M. Samardžić, S. Petrušić, M. Sak-Bosnar, A new sensing material for the potentiometric determination of anionic surfactants in commercial products, *Int. J. Electrochem. Sci.* 9 (2014) 3802-3818.
- [24] X.-L. Wei, Z.-H. Mo, Modified magnetite nanoparticles for colorimetric sensing of anionic surfactants in water, *Micro Nano Lett.* 9 (2014) 239-242.
- [25] Z. Tong, Y. Chunli, W. Bo, Z. Wei, Determination of seven sodium alkyl sulphates in environmental water by ion-pair chromatography with suppressed conductivity detection, *LC GC Europe* 27 (2014) 68-75.
- [26] O.S. Arvaniti, A.G. Asimakopoulos, M.E. Dasenaki, E.I. Ventouri, A.S. Stasinakis, N.S. Thomaidis, Simultaneous determination of eighteen perfluorinated compounds in dissolved and particulate phases of wastewater, and in sewage sludge by liquid chromatography-tandem mass spectrometry, *Anal. Methods* 6 (2014) 1341-1349.
- [27] B. Wyrwas, A. Zgoła-Grześkowiak, Continuous flow methylene blue active substances method for the determination of anionic surfactants in river water and biodegradation test samples, *J. Surfact. Deterg.* 17 (2014) 191-198.
- [28] L. Ripoll-Seguer, M. Beneito-Cambra, J.M. Herrero-Martínez, E.F. Simó-Alfonso, G. Ramis-Ramos, Determination of non-ionic and anionic surfactants in industrial products by separation on a weak ion-exchanger, derivatization and liquid chromatography, *J. Chromatogr. A* 1320 (2013) 66-71.
- [29] B. Oliver-Rodríguez, A. Zafra-Gómez, F.J. Camino-Sánchez, J.E. Conde-González, J.P. Pérez-Trujillo, J.L. Vilchez, Multi-residue method for the analysis of commonly used

commercial surfactants, homologues and ethoxymers, in marine sediments by liquid chromatography-electrospray mass spectrometry, *Microchem. J.* 110 (2013) 158-168.

[30] C. Fernández-Ramos, O. Ballesteros, A. Zafra-Gómez, R. Blanc, A. Navalón, J.L. Vílchez, Determination of alcohol sulfates and alcohol ethoxysulfates in wastewater samples by liquid chromatography tandem mass spectrometry, *Microchem. J.* 106 (2013) 180-185.

[31] F. Pena-Pereira, R.M.B.O. Duarte, T. Trindade, A.C. Duarte, Determination of anionic surface active agents using silica coated magnetite nanoparticles modified with cationic surfactant aggregates, *J. Chromatogr. A* 1299 (2013) 25-32.

[32] C. Draghici, D. Coman, M. Sica, C. Dima, Method validation and uncertainty estimation for anionic surfactants determination from municipal wastewaters, *Rev. Roum. Chim.* 58 (2013) 711-716.

[33] S.A. Dolenko, Sorption-photometric method for determination of sodium dodecyl sulfate with methylene blue in the presence of non-ionic surfactant, *J. Water Chem. Technol.* 35 (2013) 117-121.

[34] C. Kubwabo, I. Kosarac, K. Lalonde, Determination of selected perfluorinated compounds and polyfluoroalkyl phosphate surfactants in human milk, *Chemosphere* 91 (2013) 771-777.

[35] S. Devi, M.C. Chattopadhyaya, Determination of sodium dodecyl sulfate in toothpastes by a PVC matrix membrane sensor, *J. Surfact. Deterg.* 16 (2013) 391-396.

[36] R.M. Baena-Nogueras, E. González-Mazo, P.A. Lara-Martín, Determination and occurrence of secondary alkane sulfonates (SAS) in aquatic environments, *Environ. Pollut.* 176 (2013) 151-157.

[37] J. Martín, D. Camacho-Muñoz, J.L. Santos, I. Aparicio, E. Alonso, Determination of priority pollutants in aqueous samples by dispersive liquid-liquid microextraction, *Anal. Chim. Acta* 773 (2013) 60-67.

[38] J.-M. Kim, J.-M. Park, K.-T. Kim, K.-W. Moon, S.-J. Park, D.-W. Shin, M.-H. Kim, J.-M. Kim, Analysis of dish detergent in anionic and nonionic surfactants by HPLC, *Food Eng. Prog.* 17 (2013) 137-142.

- [39] A.C. Pereira, F.R.P. Rocha, A multicommuted flow system with liquid-liquid microextraction for determination of anionic surfactants in freshwaters, *Anal. Methods* 5 (2013) 2104-2109.
- [40] B. Chen, S. Wang, Q. Zhang, Y. Huang, Highly stable magnetic multiwalled carbon nanotube composites for solid-phase extraction of linear alkylbenzene sulfonates in environmental water samples prior to high-performance liquid chromatography analysis, *Analyst* 137 (2012) 1232-1240.
- [41] C. Fernández-Ramos, O. Ballesteros, R. Blanc, A. Zafra-Gómez, I. Jiménez-Díaz, A. Navalón, J.L. Vílchez, Determination of alcohol sulfates in wastewater treatment plant influents and effluents by gas chromatography-mass spectrometry, *Talanta* 98 (2012) 166-171.
- [42] H. Chen, C. Zhang, J. Han, Y. Yu, P. Zhang, PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments, *Environ. Pollut.* 170 (2012) 26-31.
- [43] Y. Zhang, W. Meng, C. Guo, J. Xu, T. Yu, W. Fan, L. Li, Determination and partitioning behavior of perfluoroalkyl carboxylic acids and perfluorooctanesulfonate in water and sediment from Dianchi Lake, China, *Chemosphere* 88 (2012) 1292-1299.
- [44] W.-L. Liu, Y.-C. Ko, B.-H. Hwang, Z.-G. Li, T.C.-C. Yang, M.-R. Lee, Determination of perfluorocarboxylic acids in water by ion-pair dispersive liquid-liquid microextraction and gas chromatography-tandem mass spectrometry with injection port derivatization, *Anal. Chim. Acta* 726 (2012) 28-34.
- [45] Q. Ma, G.-C. Xi, C. Wang, H. Bai, Q. Zhang, H.-W. Xi, Z.-M. Wang, L.-H. Guo, Comprehensive two-dimensional separation for the analysis of alkylphenol ethoxylates employing hydrophilic interaction chromatography coupled with ion mobility-mass spectrometry, *Int. J. Mass Spectrom.* 315 (2012) 31-39.
- [46] J. Falandysz, P. Rostkowski, G. Jarzyńska, J. J. Falandysz, S. Taniyasu, N. Yamashita, Determination of perfluorinated alkylated substances in sediments and sediment core from the Gulf of Gdańsk, Baltic Sea, *J. Environ. Sci. Health, Part A* 47 (2012) 428-434.

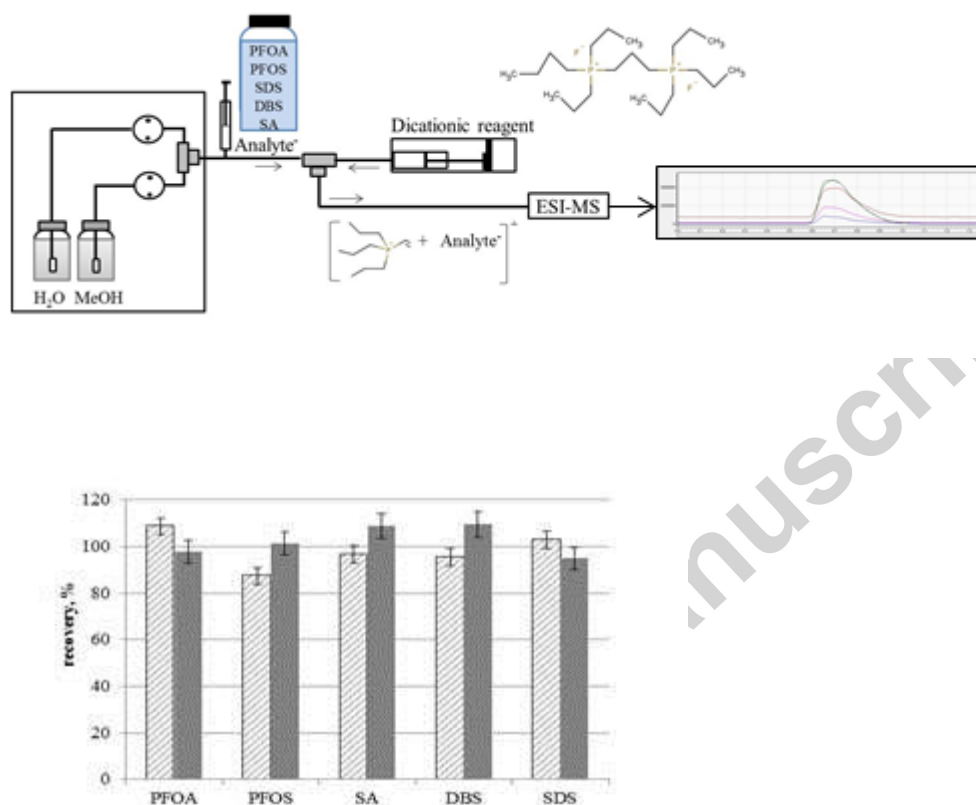
- [47] Y. Cheng, H.-M. Chen, W. Chen, Y. Cui, X.-J. Li, D.-D. Chen, S.-J. Li, W.-L. Yu, X. Zhou, Determination of perfluorooctane sulfonates (PFOS) in four chemical materials by HPLC/MS/MS, *Adv. Mat. Res.* 554-556 (2012) 1872-1879.
- [48] A.I. García-Valcárcel, E. Miguel, J.L. Tadeo, Determination of ten perfluorinated compounds in sludge amended soil by ultrasonic extraction and liquid chromatography-tandem mass spectrometry, *Anal. Methods* 4 (2012) 2462-2468.
- [49] D. Madunić-Čačić, M. Sak-Bosnar, R. Matešić-Puač, M. Samardžić, Potentiometric determination of anionic surfactants in formulations containing cocoamidopropyl betaine, *Int. J. Electrochem. Sci.* 7 (2012) 875-885.
- [50] Y.-C. Chang, W.-L. Chen, F.-Y. Bai, P.-C. Chen, G.-S. Wang, C.-Y. Chen, Determination of perfluorinated chemicals in food and drinking water using high-flow solid-phase extraction and ultra-high performance liquid chromatography/tandem mass spectrometry, *Anal. Bioanal. Chem.* 402 (2012) 1315-1325.
- [51] E. Villaverde-de-Sáa, J.B. Quintana, R. Rodil, R. Ferrero-Refojos, E. Rubí, R. Cela, Determination of perfluorinated compounds in mollusks by matrix solid-phase dispersion and liquid chromatography–tandem mass spectrometry, *Anal. Bioanal. Chem.* 402 (2012) 509-518.
- [52] M. Trojanowicz, L. Wójcik, J. Musijowski, M. Koc, E. Poboży, E. Król, New analytical methods developed for determination of perfluorinated surfactants in waters and wastes, *Croat. Chem. Acta* 84 (2011) 439-446.
- [53] E. Poboży, E. Król, L. Wójcik, M. Wachowicz, M. Trojanowicz, HPLC determination of perfluorinated carboxylic acids with fluorescence detection, *Microchim. Acta* 172 (2011) 409-417.
- [54] H. Yoo, J.W. Washington, T.M. Jenkins, J.J. Ellington, Quantitative determination of perfluorochemicals and fluorotelomer alcohols in plants from biosolid-amended fields using LC/MS/MS and GC/MS, *Environ. Sci. Technol.* 45 (2011) 7985-7990.
- [55] S. Somnam, P. Novichai, J. Jakmunee, K. Grudpan, An economical ultrasonic-assisted extraction for the spectrophotometric determination of anionic surfactants, *Maejo Int. J. Sci. Technol.* 5 (2011) 426-435.

- [56] Y. Yokoyama, E. Tai, H. Sato, Spectrometric determination of anionic surfactants in environmental waters based on anisole extraction of their bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) ion pairs, *Anal. Sci.* 27 (2011) 845-849.
- [57] C. Sun, H. Sun, Y. Lai, J. Zhang, Z. Cai, Liquid chromatography/Mass spectrometry method for determination of perfluorooctane sulfonyl fluoride upon derivatization with benzylamine, *Anal. Chem.* 83 (2011) 5822-5826.
- [58] L.A. Rodríguez- Bravo, M. Palomar-Pardavé1, S. Corona-Avendaño, M. Romero-Romo, H. Herrera-Hernández, M.T. Ramírez-Silva, R. Escarela-Pérez, Electrochemical and SPR characterization of a polypyrrole-modified carbon paste electrode useful for the potentiostatic quantification of surfactants, *Int. J. Electrochem. Sci.* 6 (2011) 2730-2745.
- [59] V. Gomez, L. Ferreres, E. Pocurull, F. Borrull, Determination of non-ionic and anionic surfactants in environmental water matrices, *Talanta* 84 (2011) 859-866.
- [60] P. Guo, Z. Guan, W. Wang, B. Chen, Y. Huang, Determination of linear alkylbenzene sulfonates by ion-pair solid-phase extraction and high-performance liquid chromatography, *Talanta* 84 (2011) 587-592.
- [61] S. Cantarero, A. Zafra-Gómez, O. Ballesteros, A. Navalón, J.L. Vílchez, C. Verge, J.A. De Ferrer, Matrix effect study in the determination of linear alkylbenzene sulfonates in sewage sludge samples, *Environ. Toxicol. Chem.* 30 (2011) 813-818.
- [62] J. Hu, J. Yu, S. Tanaka, S. Fujii, Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water environment of Singapore, *Water Air Soil Pollut.* 216 (2011) 179-191.
- [63] C.A. Huset, M.A. Barlaz, D.F. Barofsky, J.A. Field, Quantitative determination of fluorochemicals in municipal landfill leachates, *Chemosphere* 82 (2011) 1380-1386.
- [64] S. Ullah, T. Alsberg, U. Berger, Simultaneous determination of perfluoroalkyl phosphonates, carboxylates, and sulfonates in drinking water, *J. Chromatogr. A* 1218 (2011) 6388-6395.
- [65] Z. Moldovan, V. Avram, O. Marincas, P. Petrov, T. Ternes, The determination of the linear alkylbenzene sulfonate isomers in water samples by gas-chromatography/mass spectrometry, *J. Chromatogr. A* 1218 (2011) 343-349.

- [66] L. Yu, M. Wu, W. Dong, J. Jin, X. Zhang, Reverse flow injection analysis of trace amounts of anionic surfactants in seawater without liquid-liquid extraction, *Soil Water Res.* 6 (2011) 198-204.
- [67] Y.-I. Feng, W.-Q. Tang, R.-Y. Zeng, Fluorimetric method to determine trace anionic surfactants using a novel triazene reagent, *Adv. Mater. Res.* 233-235 (2011) 1370-1374.
- [68] J. Hu, J. Yu, An LC-MS-MS method for the determination of perfluorinated surfactants in environmental matrices, *Chromatographia* 72 (2010) 411-416.
- [69] S. Nakayama, M.J. Strynar, J.L. Reiner, A.D. Delinsky, A.B. Lindstrom, Determination of perfluorinated compounds in the upper Mississippi river basin, *Environ. Sci. Technol.* 44 (2010) 4103-4109.
- [70] W. Wang, B. Chen, Y. Huang, J. Cao, Evaluation of eggshell membrane-based bio-adsorbent for solid-phase extraction of linear alkylbenzene sulfonates coupled with high-performance liquid chromatography, *J. Chromatogr. A* 1217 (2010) 5659-5664.
- [71] S.A. Dolenko, E.Y. Alekseenko, N.F. Kuschevskaya, Sorption-photometric determination of anionic surfactants in water, *J. Anal. Chem.* 65 (2010) 229-233.
- [72] J.W. Remsburg, R.J. Soukup-Hein, J.A. Crank, Z.S. Breitbach, T. Payagala, D.W. Armstrong, Evaluation of dicationic reagents for their use in detection of anions using positive ion mode ESI-MS via gas phase ion association, *J. Am. Soc. Mass Spectrom.* 19 (2008) 261-269.
- [73] K. Tang, R.D. Smith, Physical/chemical separations in the break-up of highly charged droplets from electrosprays, *J. Am. Soc. Mass Spectrom.* 12 (2001) 343-347.
- [74] E.L. Bradley, W.A. Read, L. Castle, Investigation into the migration potential of coating materials from cookware products, *Food Addit. Contam.* 24 (2007) 326-335.

Figure Captions

Fig. 1. Recovery percentages obtained for spiked LC-MS water (striped bar): 0.50; 2.0; 5.0; 1.0 and 0.10 $\mu\text{g L}^{-1}$ of PFOA, PFOS, SA, DBS and SDS, respectively and tap water (full bar): 0.50; 2.0; 5.0; 1.0; 5.0 $\mu\text{g L}^{-1}$ of PFOA, PFOS, SA, DBS and SDS, respectively.



Highlights:

- A paired ion electrospray ionization (PIESI) tandem mass spectrometry method for anionic surfactants;
- A triple quadrupole was for the first time used for PIESI;
- Water samples such as wastewater, cooking, tap, and bottled drinking water were analyzed;
- Literature review for the methods published between 2010 and 2015 determining anionic surfactants.