Talanta 116 (2013) 210–216

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A solid phase extraction–ion chromatography with conductivity detection procedure for determining cationic surfactants in surface water samples

Ewa Olkowska*, Żaneta Polkowska, Jacek Namieśnik

Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology (GUT), G. Narutowicza 11/12, 80-233 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 17 October 2012
Received in revised form
20 April 2013
Accepted 24 April 2013
Available online 16 May 2013

Keywords:
Cationic surfactants
Solid phase extraction
Ion chromatography-conductivity detection
Surface water samples

ABSTRACT

A new analytical procedure for the simultaneous determination of individual cationic surfactants (alkyl benzyl dimethyl ammonium chlorides) in surface water samples has been developed. We describe this methodology for the first time: it involves the application of solid phase extraction (SPE—for sample preparation) coupled with ion chromatography-conductivity detection (IC-CD—for the final determination). Mean recoveries of analytes between 79% and 93%, and overall method quantification limits in the range from 0.0018 to 0.038 μg/mL for surface water and CRM samples were achieved. The methodology was applied to the determination of individual alkyl benzyl quaternary ammonium compounds in environmental samples (reservoir water) and enables their presence in such types of waters to be confirmed. In addition, it is a simpler, less time-consuming, labour-intensive, avoiding use of toxic chloroform and significantly less expensive methodology than previously described approaches (liquid–liquid extraction coupled with liquid chromatography–mass spectrometry).

1. Introduction

Because of their specific physicochemical properties, surfactants (Surface Active Agents—SAAs) are used in many areas of human activity. Consequence, SAAs or their biodegradation products are systematically emitted into the environment. To date, research has focused on determining levels of anionic and nonionic surfactants in different parts of the environment. Hence, there is a need to extend this field of research to include cationic SAAs.

Analysis of literature data shows that surfactants can impact on living organisms in different ways. Cationic compounds, in particular, exhibit specific properties that may prevent (or retard) growth or cause mortality in different micro-organisms (bacteria, yeasts, and fungi) [1]. This means that their antibacterial and antifungal properties could be put to use during the storage of cosmetic and household products. Moreover, with their positive charge, cationic compounds have a strong affinity for negatively charged surfaces and are thus frequently applied as fabric softeners or disinfectants [2]. On the other hand, the occupational or endemic exposure of humans to SAAs may cause irritation or burns to the skin, eyes and respiratory system [3–7]. In this context, it becomes necessary to develop analytical procedures enabling the simultaneous qualitative and quantitative determination of different types of surfactants in environmental samples.

The analysis of SAAs involves a number of different problems arising from the specificity of this type of sample matrix and analytes (the presence of contaminants, low levels of surfactants, their diverse chemical structure, the amphiphilic nature of molecules, limited access to standard solutions and reference materials). Attempts to solve these problems involve the use of suitable extraction techniques during the preparation of environmental samples for analysis.

Known analytical procedures for determining cationic surfactants in liquid environmental samples at the sample preparation

---

Abbreviations: ACN, acetonitrile; ATAC, trimethyl ammonium compounds; BDMA, benzyl dimethyl ammonium compounds; C_{12}BDMA, dodecyl benzyl dimethyl ammonium chloride; C_{14}BDMA, tetradecyl benzyl dimethyl ammonium chloride; C_{16}BDMA, hexadecyl benzyl dimethyl ammonium chloride; CRM, certified reference material; CTAB, hexadecyl-trimethyl-ammonium bromide; DEEDMAC, diethyl ester dimethyl ammonium compounds; DTDMAC, ditallow dimethyl ammonium compounds; DTAB, dodecyl-trimethyl ammonium bromide; DEQ, diesterquaternary; EC_{50}, effective concentration; FA, formic acid; HPLC, high performance liquid chromatography; HPB, 1-hexadecyl-pyridinium bromide; IC-CD, ion chromatography-conductivity detection; LC_{50}, lethal concentration; LC–MS, liquid chromatography–mass spectrometry; LC–MS–MS, liquid chromatography–tandem mass spectrometry; LD_{50}, lethal dose; LLE, liquid–liquid extraction; MDL, method limit detection; MQL, method limit quantification; MH/AF, Mixed Hemimicelle/Admicelle Formation; N-C_{12}P, N-dodecylpyridinium chloride; RSD, relative standard deviation; SAAs, surface active agents; SD, standard deviation; SDS, dodecyl sodium sulphate; SPE, solid phase extraction; TBAB, tetrabutyl-ammonium bromide; TMA, dialkyl dimethyl ammonium compounds;
TPB, 1-tetradecylpyridinium bromide; QACs, quaternary ammonium compounds; UV, ultra-violet

* Corresponding author. Tel.: +48 58 347 21 10.
E-mail address: ewaolkow@wp.pl (E. Olkowska).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.04.083

stage require the use of a traditional technique: liquid–liquid extraction (LLE). In this technique, an organic solvent (chloroform) is added to samples and analytes are transferred from the aqueous to the organic layer. During the isolation of analytes with LLE, there may be some difficulties in phase separation. Eliminating this problem involves the use of reagents to form hydrophobic ion pairs. LLE is regarded as the most effective technique for isolating cationic surface active agents from liquid samples [2].

However, LLE requires an extensive clean-up stage (time-consuming and labour-intensive) and involves the use of toxic solvents (undesirable effects on living organisms). For these reasons, this traditional approach has to be replaced by other, more effective, simpler and environmentally friendlier analytical techniques.

These demands can be satisfied by solid-phase extraction (SPE). So far, SPE has been used only a few times for isolating cationic surfactants from environmental samples (mainly in combination with LC–MS techniques at the final determination stage) [2,8–11]. The use of LC–MS involves the adsorption of cationic analytes from water samples on the surface of an appropriate sorbent (e.g. octadecyl-bonded silica [2], SDS hemimicelle-alumina [9,10], modified polystyrene-divinylbenzene [8,11], poly(methacrylic acid-co-ethylene dimethacrylate) (MAA-co-EDMA) monolith as on-line SPE [12]). The sorbent is then flushed with mixtures of solvents (e.g. acetonitrile, deionized water) to remove the majority of contaminants. Finally, the analytes are eluted from the sorbent with an appropriate mixture of solvents (acetonitrile, methanol, acetic acid, water, and ammonium formate buffer).

In routine environmental analysis spectrophotometric techniques are used to determine the total concentration of cationic surfactants in extracts. This has several advantages: it enables the quick and simple determination of analyte concentrations and the use of simple equipment. The main drawbacks of this approach, however, are the impossibility of determining individual compounds and the influence of co-extracted contaminants on the analytical results [13].

A solution to this analytical problem is feasible if chromatographic techniques are used for the final determination. The literature makes no mention of GC being used for separating cationic SAAs contained in solvent extracts. At present, liquid chromatography (LC) is the most commonly used technique for analysing different classes of surfactants (including cationic compounds) in extracts of environmental samples. LC can be coupled with the following types of detectors for determining single cationic analytes in extracts: ultra-violet (UV) [10], conductometric (CD) [14,15], mass spectrometry (MS) [9,11], tandem mass spectrometry (MS–MS) [2,8].

This study describes a new analytical procedure for determining several cationic compounds in environmental samples (surface water). This novel methodology includes the application of SPE for sample preparation, and ion chromatography coupled with conductivity detection (SPE–IC-CD) for the final determination. So far, SPE has been used only a few times for isolating cationic surfactants from environmental samples, mainly from sea water or waste water. Application of SPE techniques gives possibility to elimination of toxic chloroform from sample preparation stage to analysis of cationic surfactants in environmental samples. In turn, IC-CD has been applied to the determination of cationic surfactants only in cosmetics and detergents. We have attempted to use this technique in environmental analysis. With this methodology, trace concentrations of cationic surfactants in liquid samples can be determined quickly and easily. In comparison with LC–MS, IC-CD is cheaper solution, while maintaining sufficient selectivity and sensitivity.

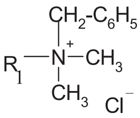
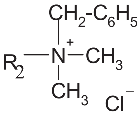
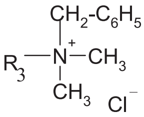
2. Experimental

2.1. Chemicals

All the organic and inorganic chemical reagents used for sample preparation or final determination were supplied by Merck (Frankfurt/Main, Germany). The ultra pure water (18 MΩ/cm) used during analysis was obtained from a Milli-Q system by EMD Millipore Corporation (Billerica, USA). Water certified reference material (CRM) delivered by Sigma-Aldrich (St. Louis, USA) was applied during developing of analytical procedure.

Quaternary ammonium compounds (QACs)—benzalkonium chlorides—were used in this study. Dodecyl benzyl dimethyl ammonium chloride (C_{12}BDMA, purity ≥99%), tetradecyl benzyl dimethyl ammonium chloride (C_{14}BDMA, purity ≥99%)), hexadecyl benzyl dimethyl ammonium chloride (C_{16}BDMA, purity not given) were purchased from Sigma-Aldrich. The chemical structure of the QACs assessed and information about their toxic effects on different organisms are listed in Table 1 [3–7].

Table 1
Basic information about the properties of analytes from the group of surfactants [3–7].

Analyte	Molecular formula and weight [g/mol]	Chemical structure	Potential health effects on humans	Toxic effects on animals
Dodecyl benzyl dimethyl ammonium chloride (C_{12}BDMA)	$C_{21}H_{38}NCl$ 339	 $R_1=CH_2(CH_2)_{12}CH_3$	Causes burns to: • eyes • skin • respiratory tract	Rats: $LD_{50}=400$ mg/kg (oral) Very toxic to aquatic organisms
Tetradecyl benzyl dimethyl ammonium chloride (C_{14}BDMA)	$C_{23}H_{42}NCl$ 368	 $R_2=CH_2(CH_2)_{14}CH_3$		Mouse: $LD_{50}=18$ mg/kg
Hexadecyl benzyl dimethyl ammonium chloride (C_{16}BDMA)	$C_{25}H_{46}NCl$ 396	 $R_3=CH_2(CH_2)_{16}CH_3$		*Daphnia magna*: $EC_{50}=0.02$ mg/L (48 h) Algae: $EC_{50}=0.07$ mg/L (72 h) Fish: $LC_{50}=0.31$ mg/L (96 h) Rabbit: $LD_{50}=150$ mg/kg

Stock solutions of individual cationic surfactants were prepared in deionized water (concentration of analytes 1000 mg/L). Working solutions were obtained by successive dilutions of the stock solution. Before use, all the sample solutions were stored in the dark at a temperature of 5 °C.

2.2. *Preparation of glassware and fine laboratory equipment*

The procedure for cleaning the glassware and laboratory equipment required for the preparation of samples for analysis included the following steps: rinsing with cold and then hot tap water, next with deionized water, then rinsing in distilled water in an ultrasonic bath for 15 min and finally rinsing with methanol. Next, the glassware was dried in an oven at about 100 °C. The syringe used for injecting standard solutions and extracts to the HPLC column was flushed with a portion of deionized water before each use (activity performed by an autosampler).

2.3. *The sample preparation stage*

The methodologies used to date for determining levels of cationic surfactants require the LLE isolation of analytes during the sample preparation step, which implies the use of a toxic extractant such as chloroform [2]. An attempt was therefore made to develop a methodology in which this toxic reagent could be replaced by SPE for preparing extracts.

Extraction cartridges containing three different types of sorbents: polymerically bonded octadecyl phase (Discovery® DSC-18, 500 mg, 6 mL, Supelco, Bellefonte, PA); polymeric reversed phase (Strata-X, 500 mg, 6 mL, Phenomenex, Macclesfield, USA) and polymeric strong cation phase (Strata-X-C, 500 mg, 6 mL, Phenomenex, Macclesfield, USA) were used to isolate QACs from surface water samples based on literature review [10,11,13].

In this study, two different mixtures of solvents were investigated as eluants of analytes from the sorbent (based on literature data and previous research [10,11,13] and producer's recommendations). During the optimisation of the SPE apparatus, 1 and 10 μg/mL of QACs standard solutions were utilised as model solutions. This enabled the recovery of cationic surfactant analytes under different conditions to be calculated. The sample preparation procedure for chromatographic analysis was the same for each model solution but, as already mentioned, three types of cartridges and two different mixtures for analyte elution were applied (see Table 2). During the preparation of each sample three fractions of eluting agent were collected ("fraction I"—2 mL, "fraction II"—6.5 mL and "fraction III"—2 mL), which were denoted as a "mixture I for the elution of analytes" or "mixture II for the elution of analytes". All extract samples obtained with use of solid phase extraction technique were evaporated to dryness under a stream of nitrogen, and then the dry residue was dissolved in water (up to 1 mL with ultra pure water).

Table 2
Conditions for isolating analytes from model solutions of cationic surfactants.

Types of sorbent in cartridges	Discovery® DSC-18	Strata-X	Strata-X-C
Concentration of analytes in model solution	1|10 μg/mL		
Number of repetitions	3		
Stages of extraction			
Conditioning of sorbent	5 mL ACN; 10 mL H_2O		
Sample loading—volume of sample	200 mL		
Washing of sorbent	10 mL · H_2O+CH_3COOH (10%)		
Elution of analytes	[a] [b]	[a] [b]	[a] [b]
Evaporation of extract under a gentle nitrogen stream			
Dissolution of the dry residues in deionized water (1 mL)			

[a] Mixture I for the elution of analytes—8.5 mL A:B (9:1), where A: ACN $+CH_3COOH$ (10%), and B: H_2O+CH_3COOH (10%).

[b] Mixture II for the elution of analytes—8.5 mL A:B:C (20:15:65), where A: ACN $+H_2O$ (7:3), B: 0.1 M HCOOH, and C: H_2O.

In the case of isolation of the analytes using the liquid–liquid extraction to sample was added 8 mL of acidified chloroform in a separatory funnel. Then, the organic layer was evaporated to dryness under a mild stream of nitrogen and the dry residue was dissolved in chloroform. After clean-up stage (with use of ultra pure water) and phase separation, the chloroform layer was again evaporated to dryness under a nitrogen and the dry residue was dissolved in deionized water [2].

2.4. *Apparatus*

After the sample preparation stage, solvent extracts were analysed with a ICS 3000 system equipped with a gradient pump, a conductivity cell and a CSRS 300 suppressor (Dionex, Sunnyvale, California, USA). The analytes were separated on an Acclaim Surfactant column (2.1 × 150 mm, 5 μm, polar-embedded stationary phase) and all injections were performed automatically using an AS autosampler apparatus (Dionex, Sunnyvale, California, USA).

All chromatographic analysis were performed under the conditions reported in [14,16] with some modifications: mobile phase flow rate through the column—0.25 mL/min; volume of sample injection —10 μL; flow rate of external medium (ultra pure water) to regeneration of suppressor—1.5 mL/min, current settings for suppression: 11 mA, temperature during separation and detection—35 °C.

The mobile phase consisted of three solvent: acetonitrile, formic acid, and water as: (A) pure water, (B) 100 mM FA and (C) mixture of ACN:H_2O (7:3, v-v). A linear gradient was used starting with 65% of A and 20% of mixture C. The percentage of A was reduced from 65% to 35% in 10 min, and the final conditions were maintained for 10 min. During chromatographic analysis percentage of B was constant (15%). Between each sample the chromatographic column was allowed to equilibrate at the initial conditions for 7 min.

The data were evaluated using Chromeleon® 6.8 software (Dionex, Sunnyvale, California, USA) and were further analysed using Microsoft® Excel (Microsoft Corporation, Redmond, Washington, USA).

3. Results and discussion

3.1. *Sample preparation*

The first step in the determination of cationic surfactants in liquid environmental samples involved selecting the SPE conditions with use of standard solutions (1 mg/L and 10 mg/L). To define the elution profiles using different types of column sorbents (*Discovery*® DSC-18, *Strata-X*, *Strata-C-X*), different combinations of solvents and additives were used for analyte elution. The elution profiles of the surfactants obtained using these columns took a similar course (see 2 (see Supplementary materials: Table S1). Most of the quaternary ammonium compounds were eluted from the sorbent in "fraction II" (average more than 39%). The experimental volume of elution mixture (8.5 mL) was enough to remove analytes from sorbent.

The recovery of surfactant analytes was calculated on the basis of the results of analyses of extract samples obtained at the modelling stage (see Table 3). They can be the basis for the following statements: the use of extraction columns filled with polymeric sorbent (*Strata-X)* and application of mixture of ACN:water:CH_3COOH in an appropriate ratio (referred as "mixture I for the elution of analytes") allow to achieve recovery of compounds from 74% to 127% (RSD = 1.5–15%). This sorbent contains N-vinylpyrrolidone, whose occurrence provides multiple modes of retention mechanisms for stronger interaction

Table 3
Recovery of cationic surfactants (calculated on the basis of analyses of solvent extracts obtained from analyte isolation carried out under different conditions, $n=3$).

Type of sorbent	Discovery® DSC-18	Strata-X	Strata-X-C	Discovery® DSC-18	Strata-X	Strata-X-C
Mixture of solvents used for elution	Mixture I—8.5 mL A:B (9:1) A: ACN+CH_3COOH (10%) B: H_2O+CH_3COOH (10%)			Mixture II – 8.5 mL A:B:C (20:15:65) A: ACN+H_2O (7:3) B: 0.1 M HCOOH C: H_2O		
Analytes	**Recovery of analytes [%]**					
C_{12}BDMA	34–75	74–115	n.d.–7	n.d.	2.3–20	1.5–19
RSD	21%	12%	1.8%	–	4.5%	3.4
C_{14}BDMA	26–46	89–127	7.8–45	n.d.–47	4.8–41	4.8–29
RSD	10%	15%	14%	24%	28%	3.7
C_{16}BDMA	37–62	90–91	7.7–84	37–49	3.7–31	2.2–24
RSD	14%	1.5%	45%	3.7%	8.9%	9.8%

n.d.—not detected.

between analytes and sorbent (e.g. hydrophobic interactions, hydrogen bonding) [17].

Therefore, further research aimed to isolate analytes from the group of cationic surfactants from environmental samples, it was decided to use column containing that type of sorbent and mentioned mixture of solvents used during the elution stage. The solvents extracts of real samples were prepared according to the scheme of the developed analytical procedure, which is shown in Fig. 1.

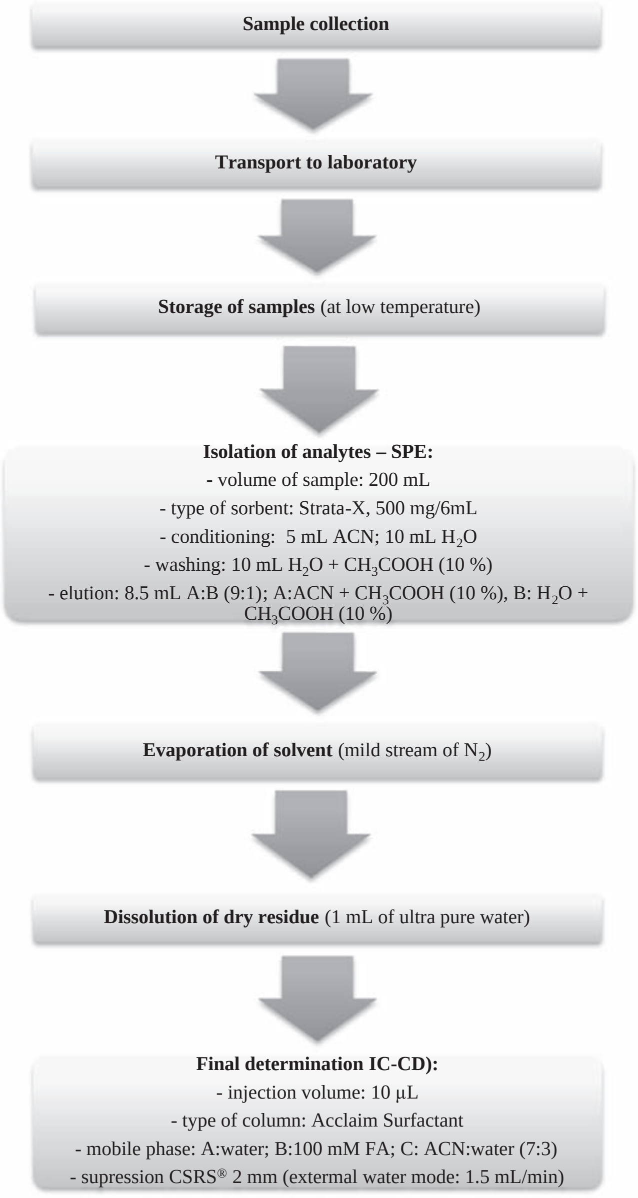
3.2. Final determination

Appropriated extracts samples were analysed with use of ion chromatographer coupled with conductivity detector. Application of reversed-phase columns (e.g. C18) for analyses of cationic SAA causes difficulties due to presence of free silanol groups (peaks are not sharp and symmetrical). Acclaim Surfactant columns based on novel mixed mode phase (reversed, anion-exchange, hydrogen-bonding retention mechanisms) allow for deactivation of free silanols against positively charged analytes. This resulted in better peak shapes under similar conditions. Moreover, Acclaim Surfactant columns can be used during analysis of different types of surface active agents, which will decrease cost of analysis [14,16].

The external standard method was used for the final determination of cationic surfactants. Standard solutions containing known concentrations of target analytes and also extracts containing unknown concentrations of these analytes were analysed chromatographically. The retention time (qualitative analysis) and peak area (quantitative analysis) of the chromatograms were compared [15,18,19]. Fig. 2 shows a chromatogram of a solvent extract obtained using SPE technique for isolation of analytes and IC-CD technique at final determination stage.

3.3. Analytical characteristics

The analytical procedures applied to the determination of individual surface active agents in environmental samples with various matrix compositions should be validated against certified reference materials, but unfortunately there are no such materials available in the market [13,20]. As a consequence, the validation of the proposed analytical methodologies is not a simple matter. In this study, to evaluate the completeness of analyte isolation from samples, these were extracted twice. Moreover, the recoveries of surfactants from the liquid samples obtained under the proposed conditions (using SPE) were compared to those obtained with LLE [20,21]. During the analysis of solvent extracts, procedural blanks (containing Milli-Q water) were prepared for every six samples to check the instrumental background. Duplicate samples and calibration check standards were run after every five samples to assure the precision of each run [22]. In this research the linearity, detection limits and analyte recovery of the proposed procedure were estimated.



Sample collection

Transport to laboratory

Storage of samples (at low temperature)

Isolation of analytes – SPE:
- volume of sample: 200 mL
- type of sorbent: Strata-X, 500 mg/6mL
- conditioning: 5 mL ACN; 10 mL H_2O
- washing: 10 mL H_2O + CH_3COOH (10 %)
- elution: 8.5 mL A:B (9:1); A:ACN + CH_3COOH (10 %), B: H_2O + CH_3COOH (10 %)

Evaporation of solvent (mild stream of N_2)

Dissolution of dry residue (1 mL of ultra pure water)

Final determination IC-CD):
- injection volume: 10 µL
- type of column: Acclaim Surfactant
- mobile phase: A:water; B:100 mM FA; C: ACN:water (7:3)
- supression CSRS® 2 mm (external water mode: 1.5 mL/min)

Fig. 1. Scheme of the proposed analytical procedure.

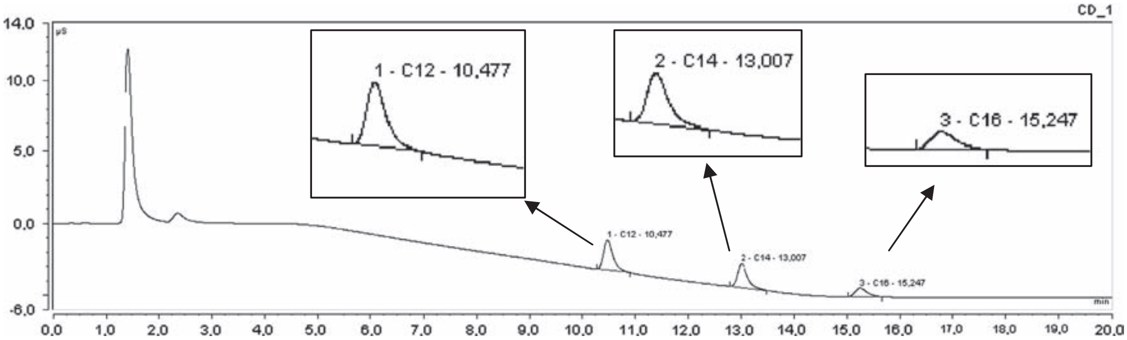


Fig. 2. Chromatogram obtained for a solvent extract containing three cationic surfactants (C12—dodecyl benzyl dimethyl ammonium chloride; C14—tetradecyl benzyl dimethyl ammonium chloride; and C16—hexadecyl benzyl dimethyl ammonium chloride) prepared using SPE and analysed with application of IC-CD technique.

Table 4
Parameters of the analytical methodology developed in this work ($n=3$).

Analytes	Retention time t_R [min]	Regression coefficients (r)	Slope standard deviations (RSD_b, %]	Linearity [%]	MDL [µg/mL]
C_{12}BDMA	10.47	0.9993	0.14	99.58	0.0143
C_{14}BDMA	13.01	0.9989	0.23	99.24	0.0258
C_{16}BDMA	15.25	0.9983	0.24	99.61	0.0345

Table 5
Contents of cationic surfactants determined in surface water and CRM samples ($n=3$).

Analyte	$MDL_{surface\ water}$ [µg/mL]	Sites of sample collection 1	2	3	4	5	**6:** CRM
C_{12}BDMA	0.0188	0.0854 ± 0.0091	n.q.	n.q.	0.0996 ± 0.0043	0.0728 ± 0.0014	n.d
C_{14}BDMA	0.0286	0.071 ± 0.011	n.d.	0.157 ± 0.014	n.q.	n.d	n.q
C_{16}BDMA	0.0377	n.d.	n.d.	0.174 ± 0.011	0.243 ± 0.012	n.q	0.0382 ± 0.0045
$\Sigma C_{12}+C_{14}+C_{16}$BDMA	–	0.156 ± 0.023	n.q.	0.331 ± 0.023	0.342 ± 0.014	0.0728 ± 0.0014	0.0056 ± 0.0010
Sum of cationic SAA obtained by spectrophotometric technique	0.05	0.188 ± 0.042	n.d.	0.392 ± 0.029	0.368 ± 0.054	0.0945 ± 0.0081	0.0102 ± 0.0011

n.d.—not detected; n.q.—not quantified but detected.

Calibration curves were plotted for concentrations from 0.01 to 100 µg/mL (in this range they were linear ($r \geq 0.998$) (Table 4) on the basis of the analysis of external standard solutions of selected cationic surfactants; each time they were analysed in triplicate.

Then the method detection limit (MDL) was determined for surfactants in the water samples based on three replicates of measurement (Table 5). MDL was calculated using the equation $LOD=3.3SD/b$ (b is the slope of the calibration curve; SD is the standard deviation of the curve). The method quantification limit was calculated as $MQL=3MDL$. The MDLs for C_{12}BDMA; C_{14}BDMA and C_{16}BDMA were at following levels 0.0143; 0.0258 and 0.0345 µg/mL, respectively. It may therefore be inferred that the analytical procedure postulated here is suitable for determining concentrations of cationic surfactants in liquid environmental samples (e.g. surface waters).

3.4. Method application

In order to assess the usefulness of this new analytical procedure, tests were carried out to compare the effectiveness of the two extraction techniques used to isolate analytes from surface water samples. These were taken from five different sites in the city of Gdańsk) and additionally, the accuracy of proposed protocol was evaluated using water certified reference material. Series of samples was prepared (three each using LLE and SPE) with and without the addition of a solution of standard. The procedure for preparing real samples for analysis using SPE technique is shown in Fig. 1. Next, every solvent extract samples were evaporated to dryness in a mild stream of nitrogen and the dry residue dissolved in deionized water (1 mL). The extracts prepared in this way were subjected to chromatographic analysis. These conditions of QACs isolation from environmental samples were chosen based on results of modelling stage. The conditions for isolating analytes using LLE were chosen on the basis of earlier work done at a different centre [2] and they are presented in Section 2.3, The sample preparation stage.

The recoveries of analytes (selected cationic surfactants) from the test samples (marked from 1 to 5) and certified reference material (marked as CRM) using LLE and SPE are shown in the histogram below (Fig. 3). The smallest recovery (LLE: 7–60%; and SPE: 53–93%) was obtained for the analyte C_{12}BDMA (dodecyl benzyl dimethyl ammonium chloride), the highest (LLE: 48–112%; and SPE: 67–112%) for C_{16}BDMA (hexadecyl benzyl dimethyl ammonium chloride). The recovery of C_{14}BDMA (tetradecyl benzyl dimethyl ammonium chloride) ranges from 72% to 99% for solid phase extraction and from 10 to 119 for liquid–liquid extraction. Comparison of the average recoveries (79–93%) of the surfactants shows that SPE may be the more effective technique for separating analytes from liquid environmental samples; the mean standard deviation of the recovery of the various compounds is from 7 to 12. For liquid–liquid extraction technique the mean standard deviation of analytes recovery's was calculated in range from 11 to 30.

With SPE, highly toxic solvents like chloroform can be eliminated from the sample preparation step. The procedure proposed here is therefore environmentally friendlier than the earlier approaches (e.g. LLE). Moreover, the separation of target analytes from environmental samples is quicker with SPE than with LLE, and so a greater number of determinations can be performed in a shorter time. Neither technique requires specialist equipment nor need specially qualified laboratory staff, but SPE does lend itself to automation, which means that analytical results can be obtained more quickly and for a smaller financial outlay.

Fig. 4 shows a chromatogram of a solvent extract obtained using SPE for sample preparation. Cationic surfactants were found in all the environmental samples analysed (see Table 5). The levels of these compounds were determined below the $MDL_{surface\ water}$ up to 0.243 µg/mL. The total content of cationic compounds in surface water samples ranged from 0.0725 ± 0.0014 to 0.342 ± 0.014 µg/mL. The samples were contaminated chiefly by C12 chain benzalkonium chloride (C_{12}BDMA), because their concentration in every sample was higher than $MDL_{surface\ water}$ (more than 0.0188 µg/mL).

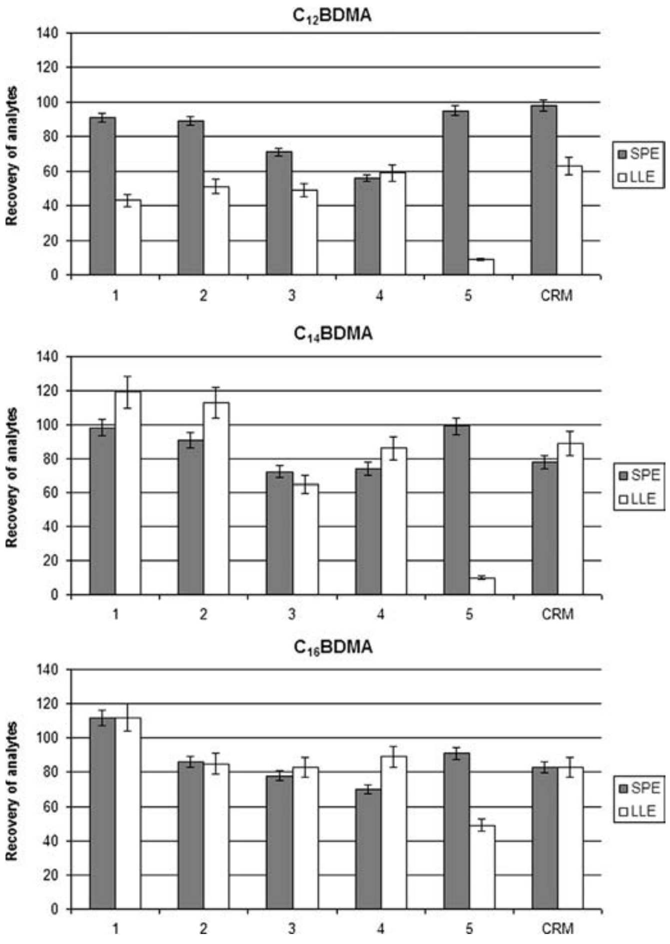


Fig. 3. Recoveries of surfactant analytes from real samples using two different extraction techniques.

Table 6 lists the methodological characteristics of analytical procedure for determining cationic surfactants in water samples; it includes the new procedure postulated in this paper.

4. Conclusion

The various application and the specific properties of surfactants (including their toxicity towards living organisms) cause the need to investigate their environmental fate, especially as they migrate freely between the atmosphere, water, sediments, soils and living organisms. In this context, it becomes imperative to develop analytical procedures enabling the simultaneous qualitative and quantitative determination of different types of surfactants in environmental samples.

However, analysis of the literature data shows that research carried out to date has tended to focus on determining levels of contamination of various compartments of the environment by anionic and non-ionic surfactants. That is why we have developed a new methodology to determine concentrations of cationic quaternary ammonium compounds in water samples with high levels of selectivity and repeatability. In addition, this new methodology is simple in execution, less time-consuming and eliminates the need for toxic reagents like chloroform at the sample preparation stage (like LLE coupled with LC–MS). These aspects show that the analytical approach we are proposing complies with the concept of sustainable development and hence with the principles of green analytical chemistry.

In this study, at sample preparation stage (SPE) were applied extraction columns filled with polymeric sorbent (*Strata-X)* and 8.5 mL mixture of ACN:water:CH_3COOH in an appropriate ratio (for elution of analytes from sorbent). This combination allows to achieve recovery of cationic compounds from 74% to 127% (RSD = 1.5–15%). This is the first time that SPE has been coupled with ion chromatography and conductometric detection (SPE–IC-CD) to determine cationic surfactants in environmental samples (surface waters). Proposed analytical protocol allows for significantly less expensive analysis of environmental samples than procedures which involve application of mass spectrometry technique at final determination stage (e.g. equipment cost).

In all analysed surface water samples were found compounds from the group of cationic surfactants (below the $MDL_{surface\ water}$ up to 0.243 µg/mL). The total concentration of quaternary ammonium

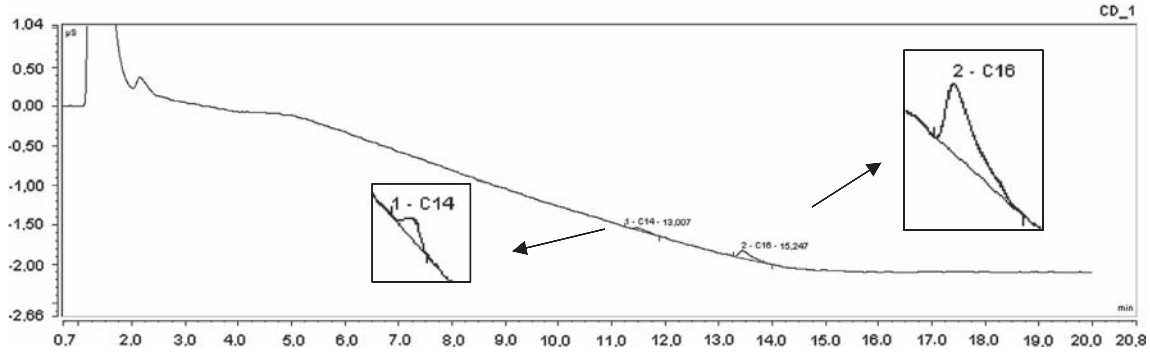


Fig. 4. Chromatogram of a solvent extract of real water samples prepared using SPE and analysed with application of IC-CD technique (C12—dodecyl benzyl dimethyl ammonium chloride; C14—tetradecyl benzyl dimethyl ammonium chloride; and C16—hexadecyl benzyl dimethyl ammonium chloride).

Table 6
Methodological characteristics of analytical procedures for determining surfactants in water samples.

Analytes	Type of sample	Sample preparation	Recovery of analytes	Separation and quantification	MDL [μg/L]	References
$C_{10–18}$ TMA $C_{12–18}$ BDMA $C_{10–16}$ ATAC	Surface water Waste water	LLE	80–99%	LC–MS–MS	0.004–0.019	[2]
DTDMAC DEEDMAC DEQ	Sea water	LLE	95–97%	LC–MS	Not given (< 0.11)	[23]
$C_{12–16}$ BDMA N-C_{12}P	Waste water River water	SPE–MH/AF	~75%	LC–MS	~0.004	[9]
$C_{12–16}$ BDMA	Waste water River water	SPE–MH/AF	95–106%	LC-UV	800–1200	[10]
C_{12} TMA C_{12} BDMA	Sea water	SPE	80–105%	LC–MS	0.6–0.3	[11]
$C_{12–16}$ BDMA CTAB, DTAB, TBAB, TPB, HPB	Waste water Lake water Pond water	On-line SPE	80–115%	LC–MS	0.015–0.024	[12]
$C_{12–16}$ BDMA	Surface water	SPE	79–87%	IC-CD	14–34	Proposed analytical procedure

compounds in investigated samples ranged from 0.0725 ± 0.0014 up to 0.342 ± 0.014 μg/mL. Research confirms that pollution of aquatic environment has become a significant problem.

Further studies will be carried out to assess the possible use of this procedure for the qualitative and quantitative determination of cationic surfactants in a wide variety of environmental samples.

Acknowledgements

E. Olkowska would like to thank the National Science Centre (Poland) for financial support (Decision no. DEC-2012/05/N/ST4/01995).

This research work was co-financed by the European Commission in the frame of the European Social Fund, by the European Social Fund, the State Budget and the Pomorskie Voivodeship Budget according to the Operational Programme Human Capital, Priority VIII, Action 8.2, Under-action 8.2.2: 'Regional Innovative Strategy' within the system project of the Pomorskie Voivodeship “InnoDoktorant—Scholarships for Ph.D. students, Vth edition”.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.04.083.

References

[1] S.A. Ostroumov, Biological Effects of Surfactants, CRC Press/Taylor & Francis Group, Boca Raton, 2005.
[2] E. Martınez-Carballo, C. Gonzaez-Barreiro, A. Sitka, N. Kreuzinger, S. Scharf, O. Gans, Environ. Pollut. 145 (2007) 489–496.
[3] J. Marhold, Prehled Prumyslove Toxikologie; Organicke Latky, Avicenum, Prague, 1986.
[4] 〈http://chem.sis.nlm.nih.gov/chemidplus/jsp/common/Toxicity.jsp〉.
[5] 〈http://www.chemcas.com/msds/cas/msds8/122-18-9.asp〉.
[6] 〈http://www.sigmaaldrich.com〉.
[7] J.L. Schardein, Antimicrobial Agents. Chemically Induced Birth Defects, Marcel Dekker, New York, 1993.
[8] I. Ferrer, E.T. Furlong, Environ. Sci. Technol. 35 (2001) 2583–2588.
[9] R. Merino, S. Rubio, D. Pérez-Bendito, Anal. Chem. 75 (2003) 6799–6806.
[10] N. Luque, F. Merino, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 1094 (2005) 17–23.
[11] P. Bassarab, D. Williams, J.R. Dean, E. Ludkin, J.J. Perry, J. Chromatogr. A 1218 (2011) 673–677.
[12] X.-T. Peng, Z.-G. Shi, Y.-Q. Feng, J. Chromatogr. A 1218 (2011) 3588–3594.
[13] E. Olkowska, Ż. Polkowska, J. Namieśnik, Chem. Rev. 111 (2011) 5667–5700.
[14] 〈http://www.dionex.com/en-us/products/columns/lc/specialty/acclaim-surfactant/lp-71771.html〉.
[15] L.M. Nair, R. Saari-Nordhaus, J. Chromatogr. A 804 (1998) 233–239.
[16] 〈http://www.dionex.com/en-us/webdocs/87422-PO-HPLC-Surfactant-Analysis-08July10-LPN2525-1.pdf〉.
[17] 〈https://phenomenex.blob.core.windows.net/documents/e62d67d8-eef5-42f0-b829-4e188661ab57.pdf〉.
[18] A.D. McNaught, A. Wilkinson, IUPAC Compendium of Chemical Terminology, Royal Society of Chemistry, Cambridge, 1997.
[19] T.E. Beesley, B. Buglio, Quantitative Chromatographic Analysis, CRC Press/Taylor & Francis Group, Boca Raton, 2000.
[20] E. Cortazar, L. Bartolomé, A. Delgado, N. Etxebarria, L.A. Ferńandez, A. Usobiaga, O. Zuloaga, Anal. Chim. Acta 534 (2005) 247–254.
[21] S.L.R. Ellison, M. Rosslein, A. Williams, CITAC/Eurachem: Quantifying Uncertainty in Analytical Measurement, 2nd ed., 2002 on-line book.
[22] J. Bao, W. Liu, L. Liu, Y. Jin, X. Ran, Z. Zhang, Chemosphere 80 (2009) 123–130.
[23] M. Radke, T. Behrends, J. Förster, R. Herrmann, Anal. Chem. 71 (1999) 5362–5366.