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

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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).

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## 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 non-ionic 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

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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.

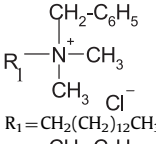
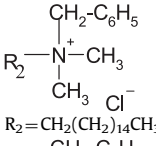
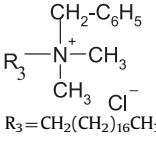
## 2. Experimental

### 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:<br>• eyes<br>• skin<br>• respiratory tract | Rats: $LD_{50}$ = 400 mg/kg (oral)<br>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)<br>Algae: $EC_{50}$ = 0.07 mg/L (72 h)<br>Fish: $LC_{50}$ = 0.31 mg/L (96 h)<br>Rabbit: $LD_{50}$ = 150 mg/kg |

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