



# Development of a multiple-class analytical method based on the use of synthetic matrices for the simultaneous determination of commonly used commercial surfactants in wastewater by liquid chromatography-tandem mass spectrometry



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## ABSTRACT

Discharges of surfactants from wastewater treatment plants are often considered as the principal vector of pollution into the environment. The analysis of complex matrices, such as urban wastewater, suspended solids and biological sludge requires careful preparation of the sample to obtain a sensitive, selective and reproducible analysis. A simple, fast, effective and multi-residue method based on the SPE (water) and QuEChERS (solid matrices) approaches using synthetic matrices for validation and quantification, has been developed for the determination of 16 surfactants in wastewater, suspended solids and biological sludge.

This work resulted in an innovative method that was validated to detect and assess several classes of surfactants such as quaternary ammonium compounds, betains, alkylphenols and their ethoxylated or sulfated derivatives in urban wastewater and solid matrices. The optimised extraction method exhibited recoveries comprised between 83% and 120% for all the tested compounds in the dissolved matrix and between 50% and 109% for particulate matrix. The limits of quantification of all compounds were comprised between 0.1 and 1.0 µg/L for dissolved matrix and between 2 and 1000 ng/g (dry weight) in particulate matrix. Linearity was assessed for all compounds within the [LOQ–250LOQ] range. Confidence intervals were also computed in real matrices with less than 15% margin of error for all studied surfactants. This work has confirmed, first and foremost, that surfactants are indeed highly concentrated in urban wastewater. As expected, linear alkylbenzene sulfonates were present at significant concentrations (up to 1–2 mg/L). In addition, although biological processing results in significant removal of the total pollution, the residual concentrations at output of WWTP remain significant (up to 100 µg/L).

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## 1. Introduction

Over the last decades, a significant number of studies have focused on several categories of man-made compounds classified as “emerging pollutants”. Among recently reported contaminants, surfactants are of particular concern due to their ubiquity and their large scale application [1,2]. These compounds can be classified, according to their charge, into four main families, namely, anionic, cationic, non-ionic and zwitterionic [1–4]. Linear alkylbenzene sul-

fonates (LAS), alkyl ethoxy sulfates (AES), alkylphenol ethoxylates (APEO), and quaternary ammonium compounds are the commonly used commercial surfactants. LAS are the most widely used synthetic anionic surfactants. They have been extensively employed over the last decades with an estimated worldwide consumption of 18.2 million tons in 2003 compared with 9, 4.5, 1.7, 0.5, 0.1 and 2.4 million tons of soap, anionic, non-ionic, cationic, amphoteric and other surfactants, respectively [1]. Surfactants are widely used for both industrial and household applications, with over 3 million tons per year consumed in Western Europe [5]. Synthetic surfactants comprise a broad group of chemicals that are designed to exhibit cleaning or solubilizing properties and are included in the formulation of personal care products, pesticides and pharmaceu-

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tics [2]. Surfactants consist of a polar head group (either charged or uncharged) and a nonpolar hydrocarbon functional group and, therefore, combine both hydrophobic and hydrophilic properties.

Once used, surfactants enter aquatic environments via treated or untreated discharges, where they are often measured at significant concentrations [6] despite their high removal efficiencies (between 85% and 99.9%) in wastewater treatment plants (WWTPs) [7–9]. Few measurements of surfactants in sewage effluents have been undertaken. Surfactant concentrations of up to 872  $\mu\text{g/L}$  for LAS [7] and from 0.9 to 964  $\mu\text{g/L}$  for alkylphenol polyethoxylates [8,10,11] have been reported worldwide. As opposed to the paucity of studies in urban environments, a considerable number of studies have underlined the presence of LAS [3,12–14] and nonylphenol ethoxylates [10,12,15–17] in surface waters all around the world, with values between <50 and >1000  $\mu\text{g/L}$  and between <0.1 and 100  $\mu\text{g/L}$ , respectively.

Although LAS and APEO have been recognized to be easily biodegradable by aerobic processes, much of the load into wastewater treatment plants is associated with suspended solids, despite their high solubility, due to their hydrophobic character (the log  $K_{ow}$  values of LAS homologues are in the 1.94–3.42 range) [9,18].

The usual methods used to quantify detergents in environmental matrices are ultrasonic extraction [19] and accelerated solvent extraction [20,21] for solid matrices and liquid-liquid extraction [22–25] and solid phase extraction [26–30] for liquid matrices. As an alternative for surfactant extraction from environmental samples, QuEChERS is considered a quick, easy, cheap, effective, rugged, safe, multiclass and multi-residue analytical approach. This method presents many advantages. Among them are high recovery rates, rapid extraction and decreased solvent consumption [31].

The major difficulties in the development of a quantitative method for ubiquitous substances such as detergents are the absence of certified reference materials and the lack of availability of real matrix-free samples of the targeted contaminants. To overcome this analytical issue, one possibility is to implement synthetic matrices whose nature is closer to that of real matrices.

The purpose of the current work was to use synthetic matrices to develop a selective, sensitive and trustworthy analytical method, based on solid phase extraction/quick, easy, cheap effective, rugged and safe (SPE/QuEChERS) pretreatment followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) quantification, for the detection of 16 multiple-class surfactants in both municipal wastewater and sludge. The selected surfactants include benzotriazole, Comperlan 100, cetyl betain, Triton X-100 (Fig. S1), benzalkonium chlorides (BDDAC and BDTAC), Stepanquat GA 90, lauryl pyridinium chloride, Incromine SD, sodium 2-ethylhexyl sulfate, sodium dodecyl sulfate, sulfonic acid (LAS C<sub>10-13</sub>) and Texapon N 701 S. To our knowledge, the development of such a multi-class approach for surfactants analysis has never been proposed or published. Moreover, the use of synthetic matrices adapted to the nature of each of the investigated samples is new.

## 2. Experimental section

### 2.1. Chemical and materials

All solvents (LC quality) were purchased from Sigma-Aldrich (Saint-Quentin Fallavier, France) and ammonium acetate from VWR (Fontenay-sous-Bois, France). SPE columns Cunax2 (3 cc, 200 mg), ECDVB (6 cc, 500 mg) and SSBCX (3 cc, 200 mg) were supplied by UCT (Bristol, PA, USA), SPE columns Oasis HLB (6 cc, 200 mg) by Waters (Guyancourt, France), SPE columns Florisil (3 cc, 500 mg) by Sigma-Aldrich (Saint-Quentin Fallavier, France) and SPE columns Strata-XL (3 cc, 100 mg) by Phenomenex (Le-Pecq, France). The commercial surfactant mixtures containing benzalko-

nium chloride, cetyl betain, lauryl pyridinium, sodium 2-ethylhexyl sulfate, Triton X-100 and sodium dodecyl sulfate were supplied by Sigma-Aldrich, Stepanquat GA 90 by Stepan Company (Chassieu, France), Texapon N 701 S and benzotriazole by BASF (Lyon, France), Incromine SD by Crodarom SAS (Chanac, France), Comperlan 100 by Cognis (Boussens, France) and the LAS C<sub>10-13</sub> mixture by Marseille soap company (Marseille, France). Stock solutions of the surfactants (200 mg/L) were prepared in pure water/LC grade methanol (50/50; v/v) and stored at 4 °C in the dark. Pure water was obtained from a MilliQ® A10 water purification system from Millipore (St. Quentin en Yvelines, France).

QuEChERS citrate-buffering salts were purchased from Agilent Technologies (Massy, France). Each buffer contained 4 g of anhydrous magnesium sulfate, 1 g of sodium citrate, 0.5 g of sodium hydrogen citrate sesquihydrate and 1 g of sodium chloride.

### 2.2. Optimized analytical extraction

#### 2.2.1. Dissolved fraction

An SPE procedure was developed and optimized for extraction and preconcentration of surfactants from wastewater filtered with a pore size of 0.7  $\mu\text{m}$ . Under the optimized final conditions, the extraction was performed using a Cunax2 (3 cc, 200 mg). The cartridge was conditioned with 8 mL of methanol (MeOH), 4 mL of pure water and 4 mL of phosphate buffer (0.1 M at pH = 6). Then, the samples (100 mL for raw materials and 200 mL for treated waters) were loaded onto the cartridge. After the sample loading and prior to elution, the cartridges were washed with 5 mL of phosphate buffer and then dried under vacuum for 10 min. The analytes were eluted with a two-step elution process: first, 2  $\times$  5 mL of ACN, followed by 2  $\times$  5 mL ACN with 5% of  $\text{NH}_4\text{OH}$ . The extracts were evaporated to dryness at 45 °C under a gentle stream of nitrogen and finally reconstituted to 1 mL in a mixture, ACN/ $\text{H}_2\text{O}$  (65/35; v/v). The two extracts were combined into one vial and stored at –20 °C prior to analysis.

#### 2.2.2. Particulate fraction

A QuEChERS extraction protocol was developed and optimized for extraction of the target contaminants from sludge and suspended solids. Under the optimized final conditions, the extraction was carried out using citrate-buffering salts and purified using the SPE protocol previously detailed for the dissolved fraction extraction. Before the QuEChERS procedure, sludge and total suspended solids were lyophilized, crushed and homogenized. Then, 500 mg of homogenized sludge was transferred into a 50 mL propylene tube. Volumes of 10 mL of ACN and 6 mL of water were added to the tube, and the mixture was shaken for 20 s with a vortex device (Vortex Fischer Scientific FB15013 TopMix). After shaking, 3 mL of heptane was added. The mixture was then swirled on the vortex mixer for an additional 40 s. The citrate-buffering salts were then added and the tube was immediately manually shaken for 20 s and swirled on the vortex mixer for 40 s. After centrifugation at 10,000 rpm for 5 min (Sigma Laboratory Centrifuges 3K30H, Fisher Bioblock Scientific), 4 mL of the ACN layer was transferred into a 10 mL glass tube. A volume of 0.5 mL of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was added to the QuEChERS tube and the mixture was shaken for 20 s with a vortex device. After centrifugation at 10,000 rpm for 5 min, 4 mL of the ACN layer was combined with the first 4 mL of ACN. The combined volume of ACN were transferred into 150 mL of deionized water and purified following the dissolved fraction extraction protocol.

### 2.3. LC-MS/MS analysis

An ABSciex (Les Ulis, France) API-3200 QTRAP triple quadrupole MS/MS with electrospray ionization (ESI) coupled to an Agilent (Massy, France) 1200 LC (quaternary pump) was used. ABSciex Ana-

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