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A multi-family offline SPE LC-MS/MS analytical method for anionic, cationic and non-ionic surfactants quantification in surface water

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Abstract

Of the large number of emerging pollutants discharged from wastewaters into surface waters, surfactants are among those with the highest concentrations. However, few monitoring in river waters of these substances have already been performed and only on a few families, mostly anionic.

This work aimed to develop a multi-family analytical strategy suitable for the quantification of low concentrations of surfactant in surface waters. Twelve families of surfactants, anionic, cationic and non-ionic were selected. Their quantification by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) and their extraction by SPE were optimized by comparing different retention mechanisms. The best performances were obtained with a C18 grafted silica LC column and a hydrophilic-lipophilic balanced (HLB) polymeric SPE cartridge. The final analytical method was validated and applied for the quantification of surfactants in 36 river water samples. Method limits of quantification (LQ), intra and inter days precision and trueness were evaluated. With LQ between 15 and 485 ng/L, and trueness over 80%, this method was suitable for monitoring surfactants in surface water. Application on French river water samples revealed the presence of anionic, cationic and non-ionic surfactants with median concentrations from 24 ng/L for octylphenol ethoxylates (OPEO), up to 4.6 µg/L regarding linear alkylbenzene sulfonates (LAS).

Keywords

Anionic surfactant; cationic surfactant; non-ionic surfactant; surface water; SPE; LC-MS/MS;

1. Introduction

Technological innovations in analytical chemistry, in particular mass spectrometry, and improved knowledge of man-made chemicals [1] (ECHA 2019) have led to questions about the presence of micropollutants in river water. Among this wide variety of pollutants, surfactants are among the most largely used and produced. For example, linear alkylbenzene sulfonates (LAS) are widely used in various detergent formulations, including liquid and powder detergents, dishwashing liquids and tablets, car washes and hard surface cleaners. Industrial detergents and cleaners also often contain them, which implies contaminations even in analytical instruments and materials [2]. Consequently, their concentrations in wastewater treatment plant (WWTP) influents and effluents are among the highest [3]. There is a very large number of surfactant molecules. Amphiphilic, they are often classified according to the ionic charge of their polar function, anionic, cationic or non-ionic.

Among this diversity of substances, previous studies only addressed a limited number of homologues or isomers and most of monitorings were carried out in wastewaters [4]. Only a few have been monitored in surface waters: the anionic surfactants, LAS [5], alkylethersulfate (AES) and alkylsulfate (AS) [6], the non-ionic alkylphenol ethoxylates (APEO) [7], and the cationic benzalkonium chloride (BAC) [2] and dialkyldimethyl ammonium chloride (DDAC) [8]. Conversely, triethanolamine esterquat (TEAQ) are the most produced and/or imported cationic surfactants in Europe with more than 100,000 tons per year [1] (ECHA 2019) but no data about their occurrence in the aquatic environment is available in the literature. There is therefore a lack of knowledge about the presence of surfactants in receiving environments. One of the analytical difficulties that could partly explain this absence of data is the lack of analytical

standards, which are essential for method development, validation then quantification. Indeed, surfactants are often a mixture of homologues or isomers.

Due to the large number of surfactants and low concentrations in the environment [6], analysis in surface waters needs multi-residue and sensitive analytical strategies. Existing analytical protocols for surfactants in surface waters were mostly based on solid phase extraction (SPE) followed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) [9]. They generally focused on only one type of surfactant, anionic [6, 10-13], cationic [8, 14] or non-ionic [15-18]. Very few analytical methods were developed and validated for more than one type of surfactant. Lara-Martin et al. [5] and Gomez and al. [19] developed methods for the simultaneous analysis of anionic and non-ionic surfactants in waters, respectively using C18 grafted silica and hydrophilic-lipophilic balanced (HLB) polymeric SPE cartridges. This latter cartridge was also used by Li et al. [2] to extract anionic and cationic surfactants. Finally, Bergé et al.[20] optimized an analytical method that allowed the quantification of the three types of surfactants, based on SPE with a solid phase that combines aminopropyl and C8 grafted silica. Nevertheless, this method was applied to WW and not to surface water.

Within this context, the aim of this study was to develop one multi-families method to extract and analyse cationic, anionic and non-ionic surfactants in surface waters. Twelve different families of surfactants were targeted including some substances that have not been analysed previously in the aquatic environment. Different kinds of LC columns and SPE cartridges were compared in order to reach the best sensitivity. Special care to avoid contamination issues was undertaken at all stages of the analysis. Finally, the optimized analytical method was validated and applied to 36 river water samples.

2. Materials and methods

2.1 Target compounds, chemicals and materials

The molecules targeted in this study include 9 anionic, 7 non-ionic and 9 cationic surfactants, making a total of 25 individual substances which represents 12 families of surfactants (Table S1). The anionic surfactants targeted in this study belong to three families: linear alkylbenzene sulfonate (LAS), alkylethersulfate (AES) and alkylsulfate (AS). Non-ionic surfactants belong to three families: octylphenol ethoxylate (OPEO), cocamides and surfynol. The cationic and amphoteric surfactants targeted in this study belong to five families: benzalkonium chloride (BAC), dialkyldimethyl ammonium chloride (DDAC), alkylpyridinium, triethanolamine esterquat (TEAQ) and amidoamines. Finally, one amphoteric surfactant belong to alkylbetaines.

The suppliers of standards are reported in Table S2. Five of these standards (in grey in Table S2) consist of mixture of homologues or isomers. Of these, the BAC-C₁₂ and C₁₄ standard was characterised by the supplier as containing 64.9% and 31.2% BAC-C₁₂ and C₁₄ respectively. The compositions of the other four analytical standards (LAS C₁₀-C₁₃, laureth sulfate (C₁₂EO₀₋₂S), OPEO and TEAQ) were not provided by the supplier. Consequently, as already reported [4, 17], the relative percentages of isomers or homologues were estimated by LC-MS. Standard solutions were analyzed by LC-MS and individual isomer or homologue concentrations were deduced from the areas of each, making the approximation that all isomers or homologues have identical response factors (Table S2). The surrogate standards, which are deuterated compounds, Benzyltrimethyldecylammonium-d₅ Chloride (BDDA-d₅), Hexadecylpyridinium-d₅ Bromide (HexPyr-d₅) and Sodium Dodecyl-d₂₅ Sulfate (SDS-d₂₅), were supplied by CDN isotopes (purity > 98%). Individual stock standard and surrogate standard solutions were prepared at a concentration of 200 mg/L, by dissolving 2 mg in 10 mL of methanol/water 50/50. After preparation, standards were stored in the dark at 4°C. A mixture of these standards at 10

mg/L, prepared in methanol/water 50/50, stored at 4°C was stable for three months. Diluted working standard solutions were prepared regularly and stored at 4°C.

The suppliers of the reagents were: LC-MS grade formic acid and ammonium acetate (Biosolve-chemicals, Dieuze, France), LC-MS grade water (Fisher Chemical, Geel, Belgium), methanol and acetonitrile (Honeywell, Seelze, Germany), ammonium hydroxide (Merck KGaA, Saint Louis, USA). MilliQ water was produced by a Millipore filtration system. Mineral water packaged in glass bottles was supplied by Evian® (Evian-les-Bains, France). Binder-free glass fiber filters, 0.7 µm pore size, diameter 142 mm were supplied by Merck Millipore Ltd. (Carrigtwohill, Ireland). Glass fiber filters, field sample vials and glass tubes were calcined for 15 hours at 450°C before use.

2.2 Solid Phase Extraction

Solid Phase Extractions (SPE) were carried out with an automatic extractor AutoTrace™ 280 (Thermo Fisher Scientific, Waltham, MA, USA). Three different SPE cartridges were tested: Oasis™ HLB (Waters®, Milford, USA), 6 mL, 150 mg, Strata-C18-E™ (Phenomenex®, Torrance, USA), 3 mL, 200 mg, and Cunax2™ (United Chemical Technologies®, Bristol, USA) 3 mL, 200 mg. For SPE optimization, Each sample consisted of mineral water spiked with all standards at approximately 1 µg/L and each experiment was performed in triplicates. Conditioning, loading and elution protocols were based on Bergé et al. [20] and were as follows: first, the SPE cartridge was conditioned with 8 mL of methanol, 4 mL of LC-MS grade water and 4 mL of 0.1 M phosphate buffer (pH=6). The phosphate buffer was composed of 13 mL of 1M K₂HPO₄ and 87 mL of 1M KH₂PO₄ per liter. Then, after the percolation of 250 mL of sample at 10 mL/min, the cartridge was rinsed with 5 mL of phosphate buffer and dried under nitrogen stream for 5 min. Finally, two elution steps were done: a first one with 2 times 5 mL

of acetonitrile, recovered in a first calcined tube, and a second one with 2 times 5 mL of a mixture of 95/5 acetonitrile and a 25% solution of ammonium hydroxide NH_4OH , recovered in a second calcined tube. Improved recoveries using a second elution step with NH_4OH have already been demonstrated by Bergé et al. 2016 [20]. The extracts obtained after SPE were recombined and evaporated to dryness at 40°C under nitrogen stream and then stored at -18°C . Before LC-MS/MS analysis, the extract was reconstituted in $800\ \mu\text{L}$ of the injection solvent, which was a mixture of acetonitrile, mineral water and a 25% NH_4OH solution, 30/65/5 (v/v/v).

2.3 Liquid chromatography instrument and conditions

An Agilent 1290 Infinity liquid chromatograph system (Agilent Technologies, Avondale, USA) was used for the chromatographic separation. Two LC methods were compared: one based on hydrophobic and anionic exchange interactions, referenced as RP/anion.exch and the second, only based on hydrophobic interaction. For both methods, the injection volume was $40\ \mu\text{L}$ and the injection solvent was a mixture of acetonitrile, water and a 25% ammonium hydroxide (NH_4OH) with the respective proportions of 30%, 65% and 5% (25% NH_4OH solution). NH_4OH was added in the injection solvent to prevent the cationic surfactants from adhering to the silanol moieties of the glass tubes. The RP/anion.exch method was based on previous work [20]. The column was an Acclaim Surfactant Plus $3.0\ \mu\text{m}$ (150×3) mm (Thermo Fisher Scientific, Waltham, MA, USA), the flow rate set at $900\ \mu\text{L}/\text{min}$ and temperature oven at 30°C , aqueous phase (A) was LC-MS grade water at 5 mM ammonium acetate and 0.1% formic acid and organic phase (B) acetonitrile at 5 mM ammonium acetate. In the second method, the column was a Poroshell 120 C18 (Agilent) $1.9\ \mu\text{m}$ (50×2.1) mm, the flow rate set at $500\ \mu\text{L}/\text{min}$ and temperature oven at 40°C , aqueous phase (A) was LC-MS grade water at 0.1% formic acid for positive ESI and at 1 mM ammonium acetate for negative ESI, and organic phase (B) methanol. The mobile phase gradients are summarized in Tables S3 and S4.

2.4 Tandem mass spectrometry instrument and parameters

The MS/MS instrument was a 3200 QTrap (Sciex, Foster City, USA) triple quadrupole mass spectrometer, used with electrospray (ESI) ionization. To optimize MS/MS parameters, solutions at 1 mg/L of each compound in a water/methanol mixture (50/50) with 10 mM NH₄Ac for the negative ESI and 10 mM NH₄Ac and 0.1% formic acid for the positive ESI, were prepared and infused, one by one, at 10 μL/min in the mass spectrometer.

The 1st stage of optimization consisted of determining in which ionization mode, positive or negative, the response factor of each molecule was the highest and which ion was the most abundant (parent ion) and optimize the declustering potential (DP) (Table 1).

The 2nd stage of optimization consisted of choosing the m/z of at least 2 fragments (product ions) that appeared the most intense, for each molecule, and optimize their collision energy (CE). The multiple reaction monitoring (MRM) mode was used to achieve the quantitative analysis of the target compounds. Two MRM transitions, parent ion > product ion, were monitored for each target compound: the most sensitive one, for quantification (MRM1), and the least sensitive one for confirmation (MRM2) (Table 1). Finally, the source temperatures were also optimized and finally set to 450 and 500°C, for negative and positive ionization modes respectively.

2.5 Validation and application

Spiked mineral water was employed to perform the validation of the analytical method. A loading sample volume of 400 mL was used for the optimized Oasis HLB SPE protocol. In the case of no contamination of method blank (i.e., signal to noise (S/N) signal < 10), method limits of quantification (LQ) were determined as the analyte concentration that produced a peak signal of 10 times the background noise from the chromatogram. In the opposite case (i.e., S/N > 10 in method blanks), LQ were determined so that they were 2 times higher than the peak area of the

method blank. LQ were finally validated according to the French standard NF T90-210 [21] (AFNOR 2009). Intra and inter days precisions and trueness experiments were performed using spiked mineral water at LQ and at 10 times LQ. Linearity was evaluated between LQ and 10 times LQ. To determine the trueness, 6 mineral water spiked at LQ and 6 at 10 times LQ were extracted and analyzed according to the optimized protocol, and quantified with matrix-matched calibration. The recovery percentage between the expected and the obtained concentrations was finally calculated.

River water samples (n=36) were collected on French territory as part of a national campaign on emerging pollutants carried out in 2018 and 2019, called EMNAT. They were delivered to the laboratory within 24 hrs in coolers maintained at 4°C, and used to assess the suitability of the validated method for the characterisation of traces in surface water. Protocol was the following: after filtration with a calcined glass fiber filter, 450 mL of sample were transferred to a 500 mL glass vial, previously calcined at 450°C for 15 hrs. Then, after spiking the sample with 2.25 mL of a solution of deuterated compounds (BDDA-d5 (100 µg/L), HexPyr-d5 (1000 µg/L), SDS-d25) (1000 µg/L)), the optimized SPE method was performed with a loading volume of 400 mL. Finally, the reconstituted extract was analysed by LC-MS/MS, and surfactants were quantified using matrix-matched calibration with mineral water packaged in glass bottles as the reference matrix. Extractions of the samples were performed the day of reception and analysis of the extracts were done in the month following their sampling. Between each sample, the channels of the SPE system were cleaned with 10 mL of methanol, then 10 mL of a solvent mixture (LC-MS grade water, isopropanol, acetonitrile, methanol 25/25/25/25 with 1% formic acid) and finally 10 mL of mineral water. Each sample was spiked with three surrogate standards, BDDA-d5, HexPyr-d5 in positive ESI and SDS-d25 in negative ESI, in order to monitor the quality of extraction and analysis. Surfactants were identified thanks to a

S/N > 10 for MRM 1, S/N > 3 for MRM2 and the concordance of retention time and MRM ratio (Table 1) in the sample with those of the corresponding standard.

3. Results and discussion

3.1 Liquid chromatography optimization

The objective of this step was to find the optimal chromatographic conditions that allowed the quantification of all target compounds using a minimum of analytical methods. As the physico-chemical properties of the molecules already required them to be analysed in two ionisation modes, in positive mode and in negative mode, the aim was to optimize two chromatographic methods, one for positively charged compounds and one for negatively charged compounds.

As surfactants have both hydrophobic and ionic functions, they can create both hydrophobic and ionic interactions with the stationary phases of the LC column. We choose to compare two LC methods, which involved two types of column: C18 grafted silica, which is the most commonly used phase, and a phase that combines hydrophobic interactions and anionic exchanges (RP/anion.exch), specially designed for the analysis of surfactants [20]. Figures 1 and 2 compare the chromatograms obtained with the two methods, respectively in positive and negative modes. Overall, there is a very clear difference in asymmetry and peak width. Indeed, peaks were sharper and presented a more Gaussian shape with the C18 column. However, the RP/anion exch. column provided a better resolution than the C18 column. Several parameters, which are mainly related to the size and stationary phase of the column, can explain this result. Indeed, on the one hand, the C18 column has a smaller internal diameter, 2.1 mm as opposed to 3 mm for the RP/anion.exch column. Smaller diameter columns are operated at lower flow rates than larger columns. This allows both a reduction in solvent consumption and also an increase in sensitivity in ESI-MS, the efficiency of ESI sources being much higher with lower

flow rates [22]. On the other hand, two main parameters of the stationary phases explain the differences observed: the interactions involved and the particle size. The binding energies of the ionic interactions (100 - 350 kJ/mol) are higher than those of the hydrophobic interactions (5 - 10 kJ/mol), which may explain the tailing of the peaks obtained with the RP/anion.exch column. In addition, the particle size of the RP/anion.exch column is 3 μm , compared to 1.9 μm for the C18 column, i.e. corresponding to UHPLC conditions. This last parameter is probably the most critical since the efficiency of an LC column is inversely proportional to the particle diameter [23]. Consequently, we choose the method with the C18 column for the remainder of this study. Retention times of the targeted surfactants are presented in Table 1.

3.2 Solid Phase Extraction optimization

As for LC, surfactants can both create hydrophobic or ionic interactions with the phases of SPE cartridges. In this work, three types of phases were tested: the first one is a polymeric phase combining hydrophobic and hydrophilic groups, Oasis HLB, which is one of the most used SPE phase. It results from the polymerisation of two monomers: a lipophilic, divinylbenzene and a hydrophilic, N-vinylpyrrolidone (DVB-NVP) (Table S5). It presents several advantages: its benzene functions allow interactions π - π with the phenyl of the surfactants and, as a polymeric phase, it has a greater load-bearing capacity and does not deteriorate during the drying steps. As C18 grafted silica phases have also been frequently selected in the literature for the extraction of surfactants, we selected Strata-C18-E, which is composed of endcapped C18 grafted silica, which allows the reduction of residual silanols. Finally, the 3rd evaluated phase is composed of C8 grafted silica and aminopropyl and combines hydrophobic interactions and anionic exchanges (Cunax2).

Figure 3A shows the extraction recoveries of the anionic surfactants performed with the three types of SPE cartridges. The three families of surfactants show different trends: regarding alkylsulfates (EHS and SDS), the recoveries of the 3 cartridges were very similar, with a slight decrease, less than 10%, in the case of Strata-C18-E. For LAS C10 to C13, the Cunax2 cartridge gave the best recoveries, which is probably linked to the presence of anionic exchange sites that allow better retention of these compounds. After the Cunax2 cartridge, the Oasis HLB provided the best recovery for LAS C10 and C11, whereas it was the Strata-C18-E for LAS C12 and C13. Lower extraction yields with the Oasis HLB for LAS C12 and C13 have also been reported by Lara-Martin [5]. This difference can be explained by the longer alkyl chain length of LAS C12 and C13, which allowed higher retention with C18 chains. However, the recoveries between these two cartridges remained comparable. Finally, considering laureth sulphates ($C_{12}EO_{1-2}S$), Cunax2 gave the best results, followed by Oasis HLB and finally Strata-C18-E, with a 20% loss between Strata-C18-E and Cunax2. Overall, Cunax2 showed the best recoveries for all anionic surfactants, as reported by Bergé et al. [20]. However, the Oasis HLB and Strata-C18-E cartridges also allowed good retention of these compounds since the losses observed were less than 25%, which is in line with the literature.

Figure 3B show the recoveries of non-ionic surfactants obtained with the three types of SPE cartridges. Overall, as for anionic surfactants, except for TMDD, the three solid phases gave similar recoveries, with differences between the cartridges lower than 20%. Slightly higher recoveries are nevertheless observed with Strata-C18-E. These observations are consistent with the study of DeArmond and DiGoregorio [17], in which DVB-NVP, C18 and C8 solid phases were compared for NPEO and OPEO extraction. Regarding TMDD, recoveries about 2 times lower were obtained with Cunax2. This may be related to the fact that TMDD does not contain a long alkyl chain, unlike other non-ionic surfactants. It is therefore likely that the C8 alkyl chain of Cunax2 is not hydrophobic enough to retain these compounds.

Results for cationic surfactants were much more contrasted (Figure 3C). Overall, the Oasis HLB cartridge gave the highest recoveries and Strata-C18-E the lowest ones. For BAC-C₁₂, the average recovery was higher with the C18 phase but the repeatability was poor, as for the zwitterionic surfactant cetylbetaine. For other cationic surfactants, the recovery of Strata-C18-E was significantly lower than the other two phases with almost 0% recovery for TEAQ-C₁₆ and SADP-DMA. The recovery obtained with Cunax2 was lower but fairly close to that obtained for Oasis HLB. As Oasis HLB is the most reported cartridge for cationic surfactant extraction [14], these observations are consistent with the literature.

In summary, the optimal cartridge was different for each type of surfactant: Cunax2 for anionic surfactants, Strata-C18-E for non-ionic surfactants and Oasis HLB for cationic surfactants. The objective of extracting all 27 substances in a single step therefore required finding the best compromise. In our case, even if it was not optimum for LAS, it was finally the Oasis HLB SPE cartridge that globally allowed the most efficient extraction of all the targeted surfactants and therefore was selected. Finally, supplementary experiments with Oasis HLB were performed to determine if the lower recoveries of OPEO and cationic surfactants were from lack of retention or incomplete elution. These showed that the elution was incomplete but the addition of elution steps was tested and did not increase the recoveries.

3.3 Blank contamination

Surfactants are widely used and can be present in air, water, organic solvents or plastics. It is recognised that one of the major problems in trace analysis of micropollutants is possible contamination at every stage of the analytical procedure, from sampling and sample preparation to chromatographic analysis, which often leads to false positive or overestimated results [24]. It is sometimes impossible to eliminate this contamination but, at least, it is important to ensure

that it is stable and to decrease it so that contamination-related concentrations are negligible compared to expected concentrations in real samples.

During the optimization of the LC-MS/MS method, we observed the presence of some of the targeted molecules in the injection solvent used to perform the instrument blanks. In order to limit this contamination, we first tested solvents and salts (acetonitrile and NH_4OH) from different suppliers, but these experiments did not allow to reduce the contamination. Then we tested different waters: water from a MilliQ filtration system, LC-MS grade water, and finally mineral water packaged in glass bottles. Figure 4 shows the signal to noise (S/N) ratios of surfactants, with S/N greater than 10, in the instrument blanks prepared with MilliQ and mineral water. The three types of surfactants, non-ionic, anionic and cationic, presented instrument blank contamination. The use of mineral water drastically reduced contamination linked to the injection solvent, especially regarding OPEOs. LC-MS grade water gave intermediate contaminations between MilliQ water and mineral water. Even if S/N ratios of instrument blanks were lower, they remained high for some molecules, between 15 for DDAC- C_{10} and 75 for SDS. Corresponding concentrations in mineral water instrument blanks, estimated with external calibration, are presented in Table S6. While blank contaminations related to LAS and APEOs have already been referenced [2, 25], little or no data exist for SDS, BACs, DDACs and TEAQ.

After the impact of the injection solvent, the second source of contamination studied was the filtration step. To reduce it, calcination of the glass fibre filters can be a good solution, as reported by Loyo-Rosales et al [15]. Figure S1 shows the areas normalized to 100 of the method blanks prepared with mineral water (i.e. including the SPE step) carried out without filtration and with filtration using a filter without pre-treatment and a filter previously calcined at 450°C for 8 hours. For non-ionic and cationic surfactants, the calcination was relatively efficient with a decrease in peak areas between 40% for BAC- C_{14} and 90% for DDAC- C_{10} . In addition, the

areas of TEAQ-C₁₆ and DDAC-C₁₀ in the method blanks were the same without filtration and with filter calcination. With decreases of less than 30%, calcination was less effective regarding anionic surfactants. Only the TMDD contamination did not decrease. Nevertheless, thanks to the use of mineral water in the injection solvent and the filter calcination, stability of method blank contamination was obtained. Method blank concentrations were estimated based on method blank signal to noise and are reported in Table 2.

3.4 Method validation

Validation is an essential step of the life cycle of an analytical method [26]. It allows identifying the limits of the method, its field of application, and recovery characteristics. Performances of the method (trueness and repeatability) enable to determine the uncertainties in the measurements. We therefore thoroughly evaluated the optimised analysis method in terms of sensitivity, linearity, trueness, repeatability and intermediate precision (inter days), using mineral water packaged in glass bottles as the reference matrix (Tables 2 and 3).

Method limits of quantification (LQ) were all lower than 1 µg/L (Table 2). They were ranged between 15 ng/L (LAS C10) and 485 ng/L (SDS). LQ of LAS C11 and C12, C₁₂EO₁₋₂S, SDS and TEAQ were above 100 ng/L not because of a lack of sensitivity but due to residual contamination of method blanks. Although our method was multi-family and therefore required some compromises, the LQ obtained were comparable or even lower than those in the literature. Only those of the quaternary ammoniums BAC-C₁₂ and C₁₄ and DDAC-C₁₀ were higher than those of the work of Ostman et al. [14] but the method developed in this article was specific to cationic surfactants. Absolute extraction recoveries, evaluated at five times LQ, were above 75% for anionic surfactants and between 56 and 78% for non-ionic surfactants (Table 2). They were lower for cationic surfactants, between 36 and 56%, and more particularly for TEAQ with

recoveries comprised between 36 and 38%. This could be explained by the both cationic and hydrophobic nature of TEAQ which may not be fully eluted from SPE cartridges.

In order to take into account contamination brought by the analytical protocol and the lowest recoveries, matrix-matched calibration was chosen using mineral water packaged in glass bottles as the reference matrix. Linearity range and determination coefficients obtained with this strategy are presented in Table 3. All determination coefficients were more than 0.99. In addition, for each analyte, the deviation of back calculated concentration from true concentration, using the calibration curve, was monitored for each calibration point and was always inferior to 20%. Trueness was evaluated at the LQ and at ten times LQ levels (see section 2.5). In both cases, trueness was above 80%, showing that matrix-matched calibration was effective in correcting for lower cationic surfactant recoveries. Repeatability and intermediate precision over 3 days were also assessed at these two concentration levels. The coefficients of variation (CV) were between 8 and 25% and between 4 and 29% for repeatability and intermediate precision respectively. TEAQ were the compounds with the most variability, for two possible reasons: high and variable levels of blank contamination and low response factors in mass spectrometry. Overall, these validation data were satisfactory, and the method was validated.

3.5 Application to field samples

The validated analytical method was applied to 36 river water samples, collected throughout France in 2018. The surfactants were quantified using a matrix-matched calibration with the standards being spiked mineral water (packaged in doped glass bottles) that had undergone the entire analytical protocol. Twelve method blanks were extracted along with the samples and injected in the same LC-MS/MS sequences to ensure that the signals of the substances in the blanks were below the corresponding LQ. The MRM of the surrogate standards were monitored

at each injection and the coefficients of variation of their areas in field samples were 18, 25 and 27% respectively for BDDA-d5, HexPyr-d5 and SDS-d25. These areas were compared to those of the calibration standards and method blanks to monitor the quality of extraction and analysis in real samples. This comparison showed a signal suppression for BDDA-d5 and a signal increase for HexPyr-d5 and SDS-d25. However, these matrix effects were less than 25%, and were therefore still acceptable.

The number of positive samples, quantification frequencies and median concentrations of the targeted surfactants are summarised in Table 4. Anionic (LAS, AES, AS), cationic (DDAC-C₁₀ and LaurPyr) and non-ionic (OP₇₋₁₁EO, TMDD) surfactants were quantified. Eight substances were never quantified, comprising mainly cationic surfactants and the zwitterionic surfactant cetylbetaine. This is consistent with the literature which shows that cationic surfactants are predominantly present in the particular phase of environmental matrices [27]. The non-ionic surfactants OPEOs and CMEA were quantified in less than 5% of the samples. On the other hand, TMDD was quantified in 25% of the samples with a median concentration of 347 ng/L. This compound has so far been investigated in only 2 studies [18, 28], and reported at mean concentrations of about 500 ng/L, which is in accordance with our study. Finally, anionic surfactants were the most frequently quantified, and at the highest concentrations, especially LAS. Indeed, the frequencies of quantification of LAS-C₁₀ to C₁₃ were greater than 90%, and their median concentrations were between 0.71 and 4.6 µg/L. This finding is coherent with previous monitoring in Spain [10] and Malaysia [11]. Although LAS are well eliminated by WWTP, the concentrations in the effluents are still significant, leading to pseudo-persistence in the environment [29, 30]. These results therefore show that the analytical method developed is well suited to the analysis of surfactants in surface waters.

4. Conclusion

An offline SPE LC-MS/MS was successfully developed for the analysis of anionic, non-ionic and cationic surfactants, with only one extraction and two LC injections. This last point could be further improved by using only one separation with polarity switching. As these compounds have many areas of application and are used in high tonnages, contaminations of instrument and method blanks were investigated and taken into account for the determination of LQ. Nevertheless, analytical recoveries were adequate for the analysis of surfactants in river water, with LQ between 15 and 485 ng/L. The application of this method on samples collected in France showed a strong presence of anionic surfactants, especially LAS. The analytical method developed in this work will therefore be useful for future monitoring of surfactants. Moreover, this method, which shows good recoveries for anionic, non-ionic and cationic surfactants, may be easily adapted to other surfactants.

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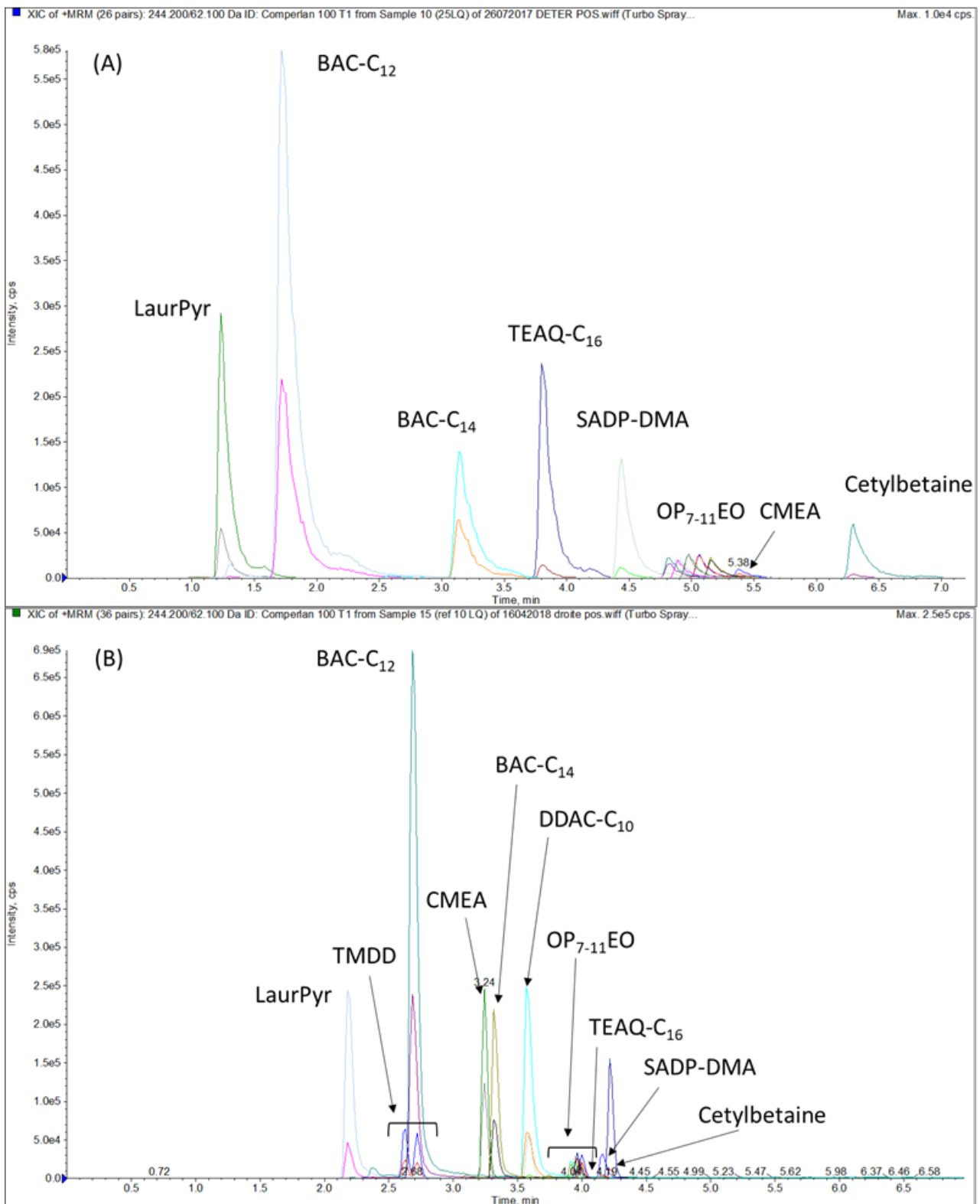


Figure 1: Chromatograms in positive ESI with columns (A) RP/anion.exch and (B) C18.

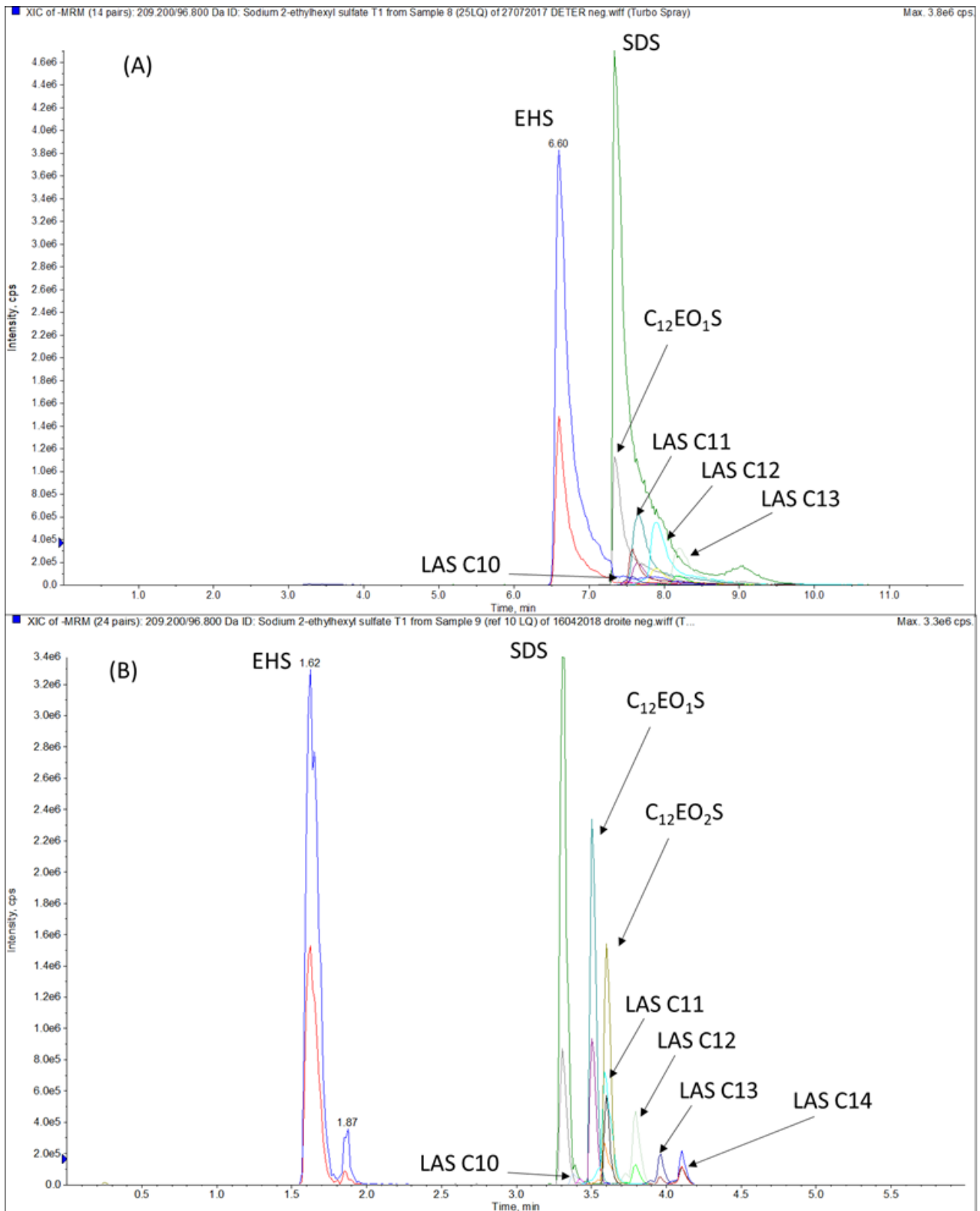


Figure 2: Chromatograms in negative ESI with columns (A) RP/anion.exch and (B) C18

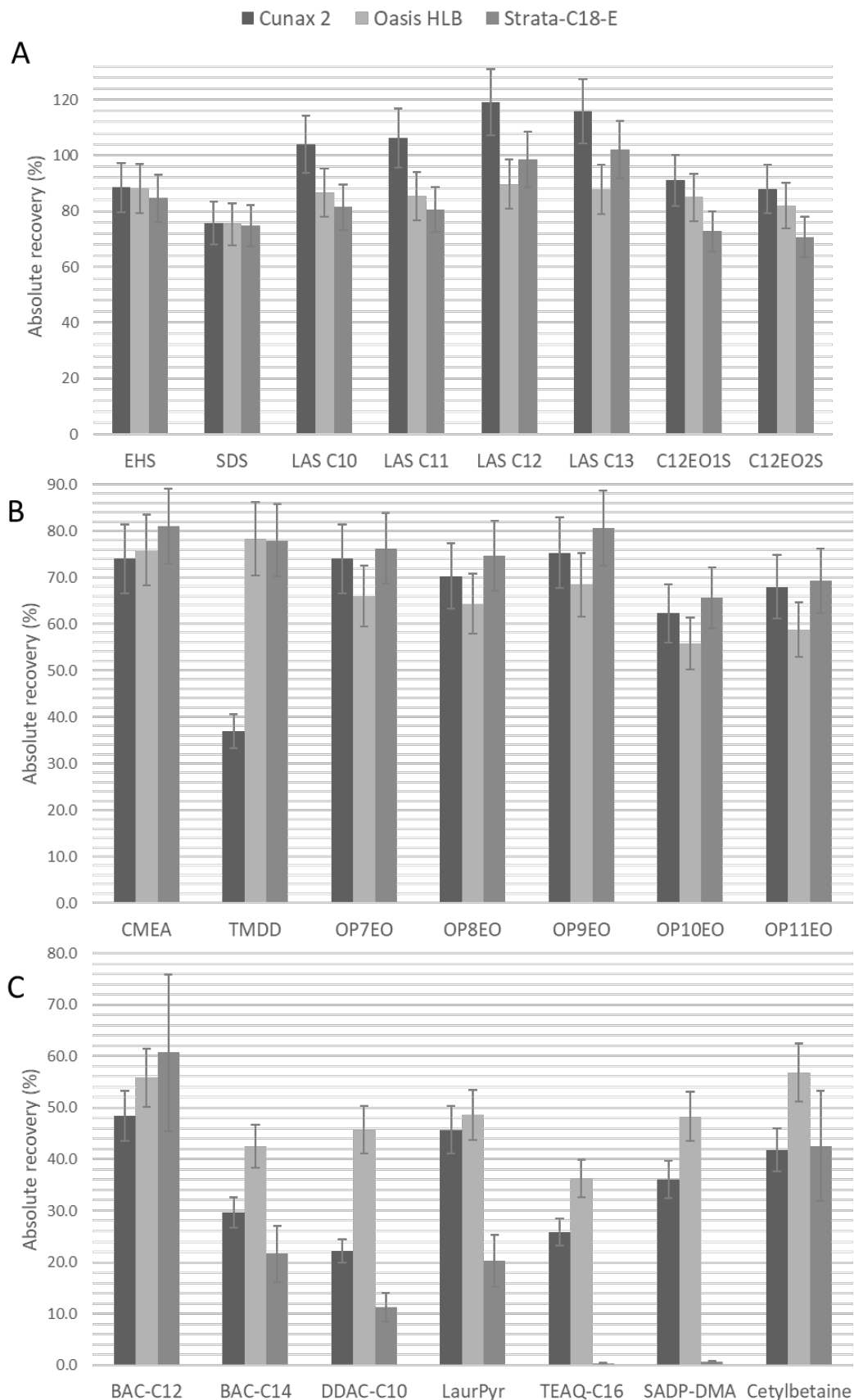


Figure 3: Absolute extraction recoveries for three SPE cartridges for (A) Anionic, (B) non-ionic and (C) cationic surfactants (n = 3)

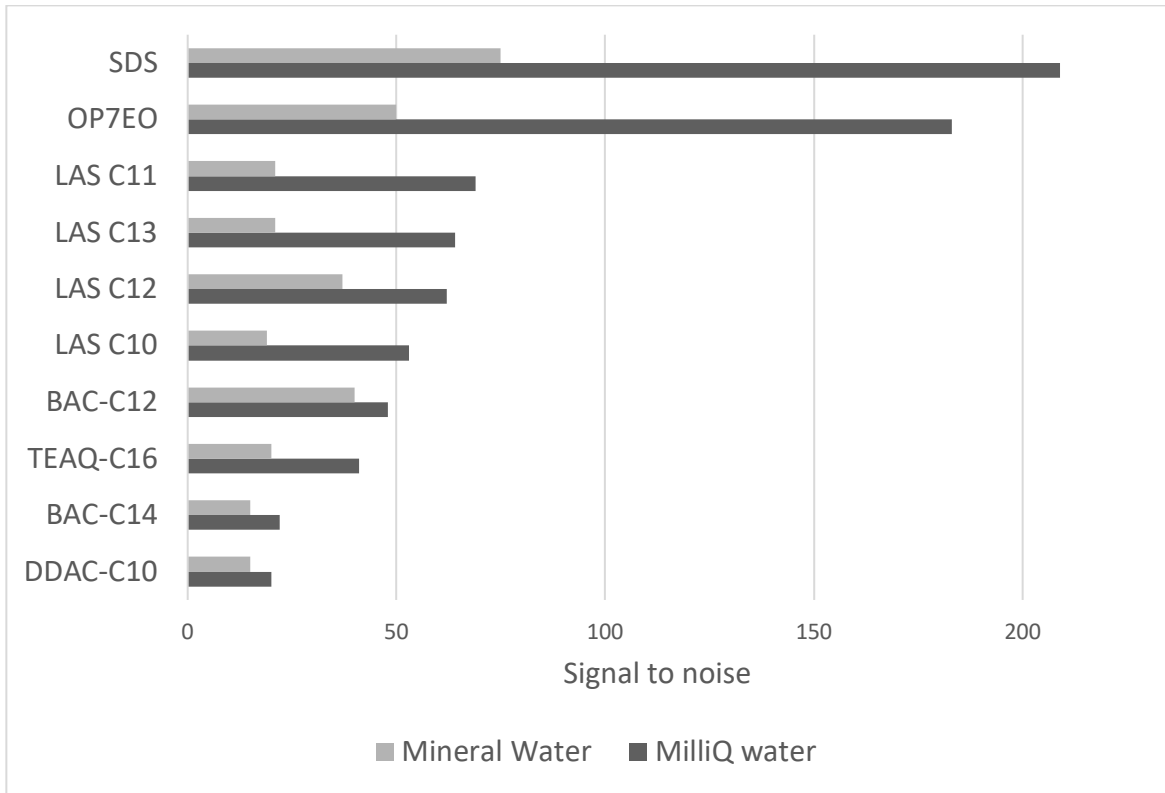


Figure 4: Signal to noise ratios of instrument blanks prepared with mineral and MilliQ water (substances with S/N greater than 10 in instrument blanks)

Table 1: Formula, retention times (t_R) and MS/MS parameters of the targeted surfactants

Name	Formula	t_R (min)	Parent Ion (m/z)	Ion formed	DP (V)	Product Ion 1 (m/z)	CE (V)	Product Ion 2 (m/z)	CE (V)	MRM ratio
<i>Negative ESI</i>										
LAS C10	C ₁₆ H ₂₅ O ₃ S	3.35	297	[M] ⁻	-75	119	-62	183	-38	2.43
LAS C11	C ₁₇ H ₂₇ O ₃ S	3.57	311	[M] ⁻	-80	183	-48	119	-68	3.22
LAS C12	C ₁₈ H ₂₉ O ₃ S	3.77	325	[M] ⁻	-85	183	-48	119	-70	3.81
LAS C13	C ₁₉ H ₃₁ O ₃ S	3.94	339	[M] ⁻	-95	183	-50	119	-72	4.04
LAS C14	C ₂₀ H ₃₃ O ₃ S	4.09	353	[M] ⁻	-70	183	-50	119	-76	5.37
C ₁₂ EO ₁ S	C ₁₄ H ₂₉ O ₅ S	3.49	309	[M] ⁻	-60	97	-44	80	-78	0.97
C ₁₂ EO ₂ S	C ₁₆ H ₃₃ O ₆ S	3.58	353	[M] ⁻	-65	97	-48	80	-88	3.34
SDS	C ₁₂ H ₂₅ O ₄ S	3.29	265	[M] ⁻	-65	97	-36	80	-82	6.30
EHS	C ₈ H ₁₇ O ₄ S	1.60	209	[M] ⁻	-55	97	-32	80	-60	3.37
<i>Positive ESI</i>										
OP ₇ EO	C ₂₈ H ₅₀ O ₈	3.87	532	[M+NH ₄] ⁺	46	89	41	133	33	1.19
OP ₈ EO	C ₃₀ H ₅₄ O ₉	3.90	576	[M+NH ₄] ⁺	51	89	47	133	33	1.40
OP ₉ EO	C ₃₂ H ₅₈ O ₁₀	3.92	620	[M+NH ₄] ⁺	61	89	51	133	37	1.51
OP ₁₀ EO	C ₃₄ H ₆₂ O ₁₁	3.93	664	[M+NH ₄] ⁺	61	89	51	133	37	1.42
OP ₁₁ EO	C ₃₆ H ₆₆ O ₁₂	3.95	708	[M+NH ₄] ⁺	66	89	51	133	41	1.77
CMEA	C ₁₄ H ₂₉ NO ₂	3.21	244	[M+H] ⁺	31	62	35	57	35	2.22
TMDD	C ₁₄ H ₂₆ O ₂	2.58	369	[M+NH ₄] ⁺	46	324	31	57	57	2.99
BAC-C ₁₂	C ₂₁ H ₃₈ N	2.78	244	[M] ⁺	11	191	11	153	11	3.45
BAC-C ₁₄	C ₂₃ H ₄₂ N	3.40	304	[M] ⁺	51	91	45	212	27	3.34
BAC-C ₁₆	C ₂₅ H ₄₆ N	3.88	332	[M] ⁺	46	91	49	240	29	4.34
BAC-C ₁₈	C ₂₇ H ₅₀ N	4.33	360	[M] ⁺	86	268	31	91	59	2.69
DDAC-C ₁₀	C ₂₂ H ₄₈ N	3.62	388	[M] ⁺	56	91	53	58	65	16.6
LaurPyr	C ₁₇ H ₃₀ N	2.25	326	[M] ⁺	20	186	186	57	55	5.78
TEAQ-C ₁₆	C ₂₃ H ₄₈ NO ₄	3.80	248	[M] ⁺	66	80	33	57	37	12.0
TEAQ-C ₁₈	C ₂₅ H ₅₀ NO ₄	3.93	402	[M] ⁺	56	283	31	57	65	5.24
TEAQ-C ₁₈ sat.	C ₂₅ H ₅₂ NO ₄	4.26	428	[M] ⁺	36	309	29	55	65	6.85
SADP-DMA	C ₂₃ H ₄₈ N ₂ O	4.36	430	[M+H] ⁺	46	311	35	57	73	10.8
Cetylbetaine	C ₂₀ H ₄₁ NO ₂	4.21	328	[M+H] ⁺	66	104	31	85	35	11.8

TEAQ-C₁₈ sat. : saturated TEAQ-C₁₈

Table 2: Method limits of quantification (LQ) compared to the literature, estimated method blank concentration and absolute extraction recoveries

Substance	Method LQ (µg/L)	Literature LQ (µg/L)	Ref.	Method blank concentration (µg/L)	Absolute extraction recovery (%) at 5*LQ
LAS C10	0.015	1.6	[4]	0.005	86.7
LAS C11	0.113	1.6	[4]	0.015	85.4
LAS C12	0.101	1.6	[4]	0.01	89.7
LAS C13	0.072	1.6	[4]	0.005	87.8
LAS C14	0.12	1.6	[4]	S/N <10	78.2
C ₁₂ EO ₁ S	0.43	0.1	[4]	0.143	85.0
C ₁₂ EO ₂ S	0.34	0.1	[4]	0.113	82.0
SDS	0.485	0.5	[13]	0.162	75.3
EHS	0.05	0.5	[13]	0.002	88.2
OP ₇ EO	0.02	0.05	[17]	0.0016	66.0
OP ₈ EO	0.02	0.05	[17]	0.0016	64.3
OP ₉ EO	0.02	0.05	[17]	0.0016	68.4
OP ₁₀ EO	0.02	0.05	[17]	0.0016	55.8
OP ₁₁ EO	0.02	0.05	[17]	0.0016	58.7
CMEA	0.1	0.1	[20]	S/N <10	75.8
TMDD	0.1	0.03	[18]	0.01	78.3
BAC-C ₁₂	0.06	0.01	[14]	0.006	55.8
BAC-C ₁₄	0.04	0.01	[14]	0.01	42.5
DDAC-C ₁₀	0.05	0.005	[14]	0.01	45.7
LaurPyr	0.03	ND		S/N <10	48.6
TEAQ-C ₁₆	0.28	5.0	[20]	0.016	36.2
TEAQ-C ₁₈	0.152	ND		0.007	38.0
TEAQ-C ₁₈ sat.	0.06	ND		0.016	35.5
SADP-DMA	0.05	0.2	[20]	S/N <10	48.3
Cetylbetaine	0.1	0.1	[20]	S/N <10	56.8

TEAQ-C₁₈ sat. : saturated TEAQ-C₁₈

ND: No Data

Table 3: Linearity range and their determination coefficient (R²), trueness, and intra and inter-days precision

Substance	Linearity range (µg/L)	R ²	Trueness (%) at LQ (n = 6)	Intra-day precision CV (%) at LQ (n = 6)	Inter-day precision CV (%) at LQ (3 days) (n = 6)	Trueness (%) at 10*LQ (n = 6)	Intra-day precision CV (%) at 10*LQ (n = 6)	Inter-day precision CV (%) at 10*LQ (3 days) (n = 6)
LAS C10	0.015 - 0.15	0.998	103	15	18	113	9.8	8.3
LAS C11	0.113 - 1.13	0.999	97	12	31	116	8.4	7.0
LAS C12	0.101 - 1.01	0.997	117	16	14	103	8.6	9.7
LAS C13	0.072 - 0.72	0.990	98	8	17	86	15	17
LAS C14	0.12 - 1.2	0.990	101	10	28	120	9.6	11
C ₁₂ EO ₁ S	0.43 - 4.3	0.990	113	15	20	117	2.8	4.1
C ₁₂ EO ₂ S	0.34 - 3.4	0.990	85	18	20	81	3.6	4.3
SDS	0.485 - 4.85	0.990	114	20	26	80	3.6	7.6
EHS	0.05 - 0.5	0.996	107	19	26	96	2.7	2.8
OP ₇ EO	0.02 - 0.2	0.995	106	15	18	107	5.7	5.3
OP ₈ EO	0.02 - 0.2	0.995	115	13	22	103	8.2	6.8
OP ₉ EO	0.02 - 0.2	0.995	113	12	20	115	7.3	5.6
OP ₁₀ EO	0.02 - 0.2	0.993	120	12	21	110	7.3	6.2
OP ₁₁ EO	0.02 - 0.2	0.996	120	12	21	88	7.7	6.9
CMEA	0.1 - 1.0	0.999	120	10	15	110	4.1	5.1
TMDD	0.1 - 0.6	0.998	103	12	18	115	4.5	17
BAC-C ₁₂	0.06 - 0.3	0.993	98	16	25	119	3.2	5.2
BAC-C ₁₄	0.04 - 0.4	0.994	88	17	25	111	3.2	7.0
DDAC-C ₁₀	0.05 - 0.5	0.990	112	12	28	109	5.0	14
LaurPyr	0.03 - 0.3	0.993	92	11	27	109	2.3	2.8
TEAQ-C ₁₆	0.28 - 1.4	0.993	92	15	15	87	22	27
TEAQ-C ₁₈	0.152 - 0.76	0.997	109	20	16	84	25	28
TEAQ-C ₁₈ s	0.06 - 0.3	0.990	103	18	23	82	17	29
SADP-DMA	0.05 - 0.25	0.991	99	14	21	115	21	26
Cetylbetaine	0.1 - 1	0.999	105	10	18	101	4.9	6.0

TEAQ-C₁₈ s: saturated TEAQ-C₁₈

Table 4: Quantification frequency and median concentration of the targeted surfactants in 36 river waters sampled in France in 2018

Substance	Number of positive samples (n=36)	Quantification frequency (%)	Median concentration (µg/L)
LAS C10	34	94	0.714
LAS C11	35	97	4.63
LAS C12	35	97	3.81
LAS C13	33	92	2.36
LAS C14	0	0	<LQ
C ₁₂ EO ₁ S	3	8	1.14
C ₁₂ EO ₂ S	1	3	0.898
SDS	3	8	0.480
EHS	9	25	0.140
OP ₇ EO	1	3	0.024
OP ₈ EO	1	3	0.024
OP ₉ EO	1	3	0.024
OP ₁₀ EO	1	3	0.024
OP ₁₁ EO	1	3	0.024
CMEA	1	3	0.254
TMDD	9	25	0.347
BAC-C ₁₂	0	0	<LQ
BAC-C ₁₄	0	0	<LQ
DDAC-C ₁₀	1	3	0.074
LaurPyr	1	3	0.043
TEAQ-C ₁₆	0	0	<LQ
TEAQ-C ₁₈	0	0	<LQ
TEAQ-C ₁₈ sat.	0	0	<LQ
SADP-DMA	0	0	<LQ
Cetylbetaine	0	0	<LQ