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Evaluating solid phase (micro-) extraction tools to analyze freely ionizable and permanently charged cationic surfactants

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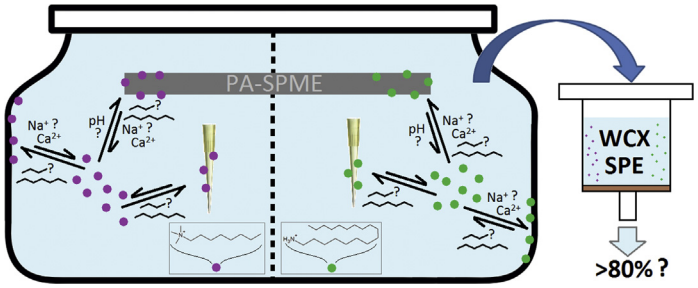
HIGHLIGHTS

- An SPE method to measure 32 amine based cationic surfactants is proposed.
- Sorption of cationic surfactants to pipette tips and glassware is quantified.
- Charged compounds adsorb to and neutral compounds absorb into PA-SPME fibers.
- pH-dependency of sorption of cationic surfactants to PA-SPME fibers is explored.
- PA-SPME shows pH-dependency even for quaternary ammonium surfactants.

GRAPHICAL ABSTRACT



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ABSTRACT

Working with and analysis of cationic surfactants can be problematic since aqueous concentrations are difficult to control, both when taking environmental aqueous samples as well as performing laboratory work with spiked concentrations. For a selection of 32 amine based cationic surfactants (including C8- to C18-alkylamines, C14-dialkyldimethylammonium, C8-tetraalkylammonium, benzalkonium and pyridinium compounds), the extraction from aqueous samples was studied in detail. Aqueous concentrations were determined using solid phase extraction (SPE; 3 mL/60 mg Oasis WCX-SPE cartridges) with recoveries of ≥80% for 30 compounds, and ≥90% for 16 compounds. Sorption to glassware was evaluated in 120 mL flasks, 40 mL vials and 1.5 mL autosampler vials, using 15 mM NaCl, where the glass binding of simple primary amines and quaternary ammonium compounds increased with alkyl chain length. Sorption to the outside of pipette tips (≤20% of total amount in solution) when sampling aqueous solutions may interfere with accurate measurements. Polyacrylate solid phase microextraction (PA-SPME) fibers with two coating thicknesses (7 and 35 μm) were tested as potential extraction devices. The uptake kinetics, pH-dependence and influence of ionic strength on sorption to PA fibers were studied. Changing medium from 100 mM Na^+ to 10 mM Ca^{2+} decreases K_{fw} with one order of magnitude. Results indicate that for PA-SPME neutral amines are absorbed rather than adsorbed, although the exact sorption mechanism remains to be elucidated. Further research remains necessary to establish a definitive applicability domain for PA-SPME. However, results indicate that alkyl chain lengths ≥14 carbon atoms and multiple alkyl chains become problematic. A calibration curve should always be measured together with the samples. In conclusion, it seems that for amine based surfactants PA-SPME does not provide the

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reliability and reproducibility necessary for precise sorption experiments, specifically for alkyl chain lengths beyond 12 carbon atoms.

1. Introduction

Cationic surfactants are commercially important compounds with diverse applications in industrial and household preparations such as detergents, preservatives, antiseptics, fabric softeners, and personal care products [1,2]. The combination of a positively charged head group and one or more hydrophobic alkyl chains gives cationic surfactants their amphiphilic properties. It is well know that these cationic surfactants have a strong sorption affinity to different kinds of surfaces [3], and they are acknowledged as emerging contaminants in sewage sludge and sediments [4]. In environmental risk assessment, sorption is an important parameter that has an effect on the distribution of a compound among different compartments in the environment, including the aqueous phase, soil, sediment and biota. Within the aqueous phase itself, sorption to dissolved organic matter may affect the bioavailability, bioaccumulation and effects on biota [5]. Particularly for strongly sorbing cationic surfactants, bioavailability is an important feature in risk assessment [3,6].

Within the context of bioavailability, the concept is that only freely dissolved molecules can cross biomembranes, and only the freely dissolved external concentration (C_{free}) will equilibrate with the internal tissue concentrations to exert (adverse) effects [7–9]. Solid-phase microextraction (SPME) is broadly used to measure the C_{free} of polar and non-polar analytes in a range of different matrices [10–13]. More recently, polyacrylate (PA) SPME has also been applied to sample quaternary ammonium based cationic surfactants [14,15]. PA-coated SPME fibers have sufficient cation exchange capacity (CEC) to effectively adsorb several nitrogen-based cationic surfactants to the fiber surface, whereas the CEC is low enough to prevent depletive extraction in most samples [5,15]. PA-SPME has specific benefits when dealing with environmental samples: (i) the SPME coating is in direct equilibrium with C_{free}, (ii) the small fiber volume (extraction phase) leads to selective isolation of analytes, resulting in relatively clean samples which can be analyzed without matrix effects, (iii) pH-modification of samples is not required for quantitative purposes since PA-SPME has sufficient affinity for positively charged species and can be calibrated at the required sample pH, (iv) the fiber structure eliminates problems related to typical sample clean-up steps using SPE or filter cartridges, such as solid phase clogging with suspensions and breakthrough volume with voluminous samples [16]. Thin film SPME (TFME) is a relatively new technique that has also been applied to sample cationic surfactants [17]. A detailed optimization of the TFME procedure was presented, including the evaluation of matrix effects [17]. TFME is mostly a depletive extraction technique, while for some situations non-depletive sampling might be preferable. Liquid-phase microextraction (LPME) has also been suggested for analysis of cationic surfactants, but preparation of LPME is more time consuming and the applicability is less versatile [18]. PA-SPME opens the possibility of non-depletive sampling and can also be applied offline, for instance during toxicity testing or when sampling multiple phases in a closed system (anaerobic sediment, aerobic sediment, supernatant). However, the sorption coefficient to the PA-SPME fiber has to be carefully calibrated for each cationic surfactant in every medium of interest.

The main aim of this manuscript was to elucidate the challenges and limitations when using PA-SPME to sample the C_{free} of a wide range of cationic surfactants, thereby determining the boundaries of the applicability domain. Cationic surfactants were selected based on structural diversity and environmental relevance. Whereas previous studies with PA-SPME were limited to permanently charged quaternary ammonium compounds (QACs), the current study also included primary, secondary and tertiary amines, as well as several other types of QACs. Ionizable amines were included specifically as they exist partly as ionized and neutral species, depending on the pH, which may affect their affinity for PA-SPME [14,19].

It is well known that working with – and analysis of – cationic surfactants can be problematic, in the sense that aqueous concentrations are difficult to control. Losses can be expected from accumulation on gas-liquid or liquid-solid interfaces, and adsorption to negatively charged surfaces such as glassware, dissolved organic matter, clay particles, and biomolecules [5,15]. Significant binding to glassware and other laboratory equipment can be expected [5], as well as sorption to PTFE lined septa and surfaces [20,21]. Furthermore, the efficiency of electrospray ionization frequently employed with MS/MS analyses can be influenced by surfactants in a concentration-dependent matter [22].

In order to more easily determine and confirm aqueous concentrations in SPME calibration studies and adsorptive studies with laboratory equipment, this study tested the performance of a weak cation exchange solid phase extraction (WCX-SPE) cartridge for a wide range of cationic surfactants. In addition, sorption losses to glass vials and pipette tips was studied to assess flaws in experimental procedures and to design special methods to sample cationic surfactants most adequately. Sorption to glass was measured with five primary alkylamines (chain length range $C_{10\text{-}18}$) and five quaternary alkyltrimethylammonium compounds (chain length range $C_{10\text{-}18}$). Sorption was expected to increase with increasing chain length [23], which makes working with the longest chain cationics extremely challenging. Therefore, one of the objectives was to identify the boundaries for application of SPE and PA-SPME with respect to longer alkyl chain isomers.

Combining findings regarding glass binding and SPE, the recovery of WCX-SPE was measured for all test chemicals. WCX-SPE was then used to measure aqueous concentrations when calibrating PA-SPME fibers in different matrices. Calibration under different conditions opens the possibility to determine fiber-water sorption affinity (K_{fw}) as a function of exposure time, analyte concentration, pH or ionic composition, and reproducibility of the PA-SPME batch applied. Measuring K_{fw} of structural homologues could also lead to better understanding of the contribution of molecular structure to K_{fw} for PA-SPME fibers. The conclusions presented could guide future studies on the use of PA-SPME in environmental and toxicological studies for (hydrophobic) cationic surfactants.

2. Materials and methods

2.1. Selection of chemicals

An overview of the 32 selected compounds is given in Table 1. In their simplest form, these amines contain one alkyl chain (primary amines “P10, P12, P14, P16, P18”), and in addition one (secondary

Table 1
Overview of test chemicals.

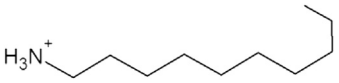
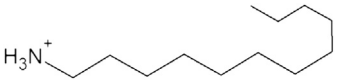
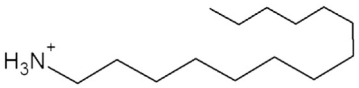
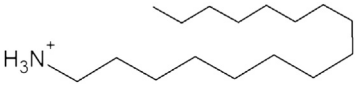
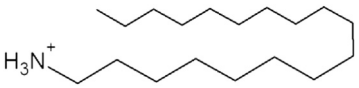
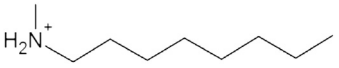
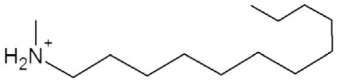
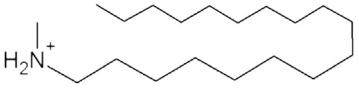
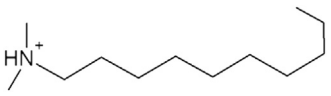
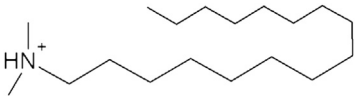
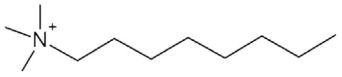
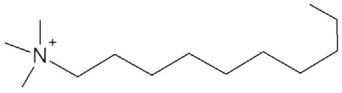
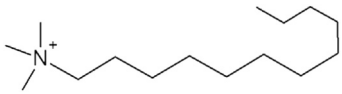
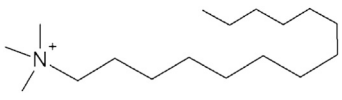
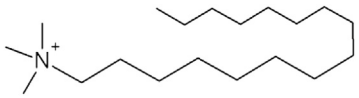
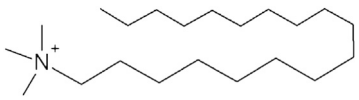
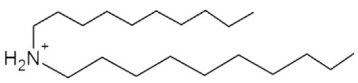
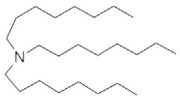
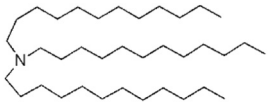
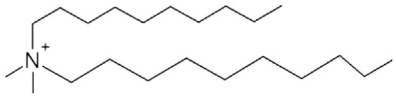
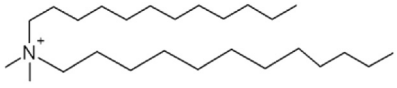
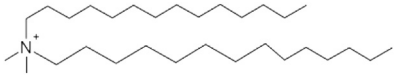
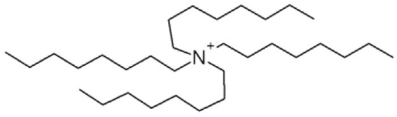
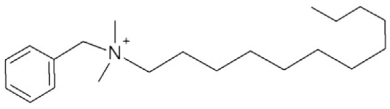
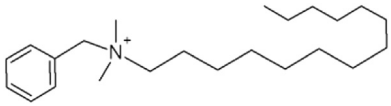
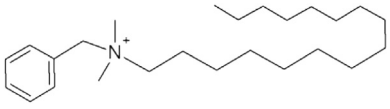
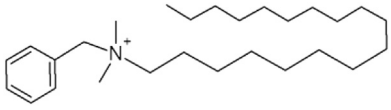
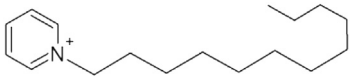
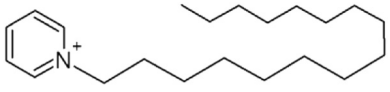
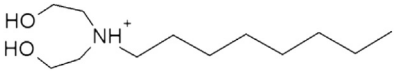
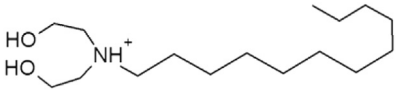
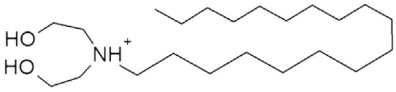
Chemical name	Code	Molecular structure
Decylamine	P10	
Dodecylamine	P12	
Tetradecylamine	P14	
Hexadecylamine	P16	
Octadecylamine	P18	
N −methyl-1-octanamine	S8	
N-methyl-1-dodecanamine	S12	
N-methyl-1-octadecanamine	S18	
N,N-dimethyl-1-decanamine	T10	
N,N-dimethyl-1-hexadecanamine	T16	
N,N,N-trimethyl-1-octanaminium bromide	Q8	
N,N,N-trimethyl-1-decanaminium bromide	Q10	
N,N,N-trimethyl-1-dodecanaminium chloride	Q12	
N,N,N-trimethyl-1-tetradecanaminium chloride	Q14	
N,N,N-trimethyl-1-hexadecanaminium chloride	Q16	
N,N,N-trimethyl-1-octadecanaminium chloride	Q18	

Table 1 (*continued*)

Chemical name	Code	Molecular structure
N-decyl-1-decanamine	S2-C10	
N,N-dioctyloctan-1-amine	T3-C8	
N,N-didodecyldodecan-1-amine	T3-C12	
N,N-didecyl-N,N-dimethylammonium bromide	Q2-C10	
N,N-didodecyl-N,N-dimethylammonium bromide	Q2-C12	
N,N-ditetradecyl-N,N-dimethylammonium bromide	Q2-C14	
N,N,N-trioctyl-1-octanaminium bromide	Q4-C8	
N,N-dimethyl-N-dodecylbenzylaminium chloride	BAQ12	
N,N-dimethyl-N-tetradecylbenzylaminium hloride	BAQ14	
N,N-dimethyl-N-hexadecylbenzylaminium chloride	BAQ16	
N,N-dimethyl-N-octadecylbenzylaminium chloride	BAQ18	
1-N-dodecylpyridinium chloride monohydrate	PYR12	
1-N-hexadecylpyridinium chloride monohydrate	PYR16	
N,N-bis(2-hydroxyethyl)octylamine	2EtOH-T8	
N,N-bis(2-hydroxyethyl)dodecylamine	2EtOH-T12	
N,N-bis(2-hydroxyethyl)octadecylamine	2EtOH-T18	

amines "S10, S12, S18"), two (tertiary amines "T10, T16") or three (quaternary ammonium "Q10, Q12, Q14, Q16, Q18") methyl groups. Tertiary diethanolamines ("2EtOH-T8,-T12,-T18"), benzalkonium ("BAQ-12,-14,-16,-18") and pyridinium ("PYR12,-16") compounds were added because of their environmental significance, and to evaluate the influence of more complex functional groups on sorption behavior. Amines with multiple alkyl chains were also included; secondary dialkylamine "S2-C10", tertiary trialkylamines ("T3-C8, T3-C12"), quaternary dialkyldimethylammonium ("Q2-C10, Q2-C12, Q2-C14") and tetraalkylammonium ("Q4-C8"). These amines with multiple alkyl chains are more hydrophobic than most single chain surfactants and constitute a challenge from an experimental and analytical perspective, because of their relatively stronger adsorptive properties. Amines with two long alkyl chains are widely used in various applications [24,25], and it is of specific interest to determine how the second alkyl chain influences sorption in comparison to single chain surfactants.

2.2. Chemicals and other materials

The molecular structures, suppliers, purities and physico-chemical properties of the 32 amine based cationic surfactants are listed in the supporting information (Table S1). Buffer salts and other salts were of analytical grade and were obtained from Merck (Darmstadt, Germany), except for $CaCl_2$ which was obtained from Sigma-Aldrich (Zwijndrecht, The Netherlands). Trifluoroacetic acid (TFA) and formic acid (FA) were also obtained from Sigma-Aldrich. All aqueous solutions were prepared using MilliQ ultrapure water (>18.2 MΩ·cm-1, Millipore, Amsterdam, The Netherlands). Methanol (analytical grade) was obtained from BioSolve (Valkenswaard, The Netherlands). Aqueous concentrations of surfactants were determined using solid phase extraction (SPE), utilizing 3 mL/60 mg OASIS weak cation-exchange cartridges (WCX-SPE), obtained from Waters (Etten-Leur, The Netherlands). The 7 μm and 35 μm coated solid phase micro-extraction (SPME) fibers were obtained from Polymicro Technologies (Phoenix, AZ, USA). Both 7 μm and 35 μm PA-coated SPME fiber were ordered as one custom made stretch of 1000 m, which was divided over five 200 m batches. All fibers used in the work reported in this manuscript were cut from the same 200 m batch, which was a different batch than those applied in studies by Wang et al. and Chen et al. [14,15,26].

2.3. Overview of experiments

SPE recovery was determined using two different aqueous media compositions: unbuffered 10 mM $CaCl_2$ solution and Dutch Standard Water (DSW). DSW has a pH of 8.2–8.4 and contains 1.36 mM Ca^{2+} and 0.73 mM Mg^{2+} as most important cations [27]. The 10 mM $CaCl_2$ solution is the OECD-guideline recommended medium for sorption experiments [28], while DSW approximates the general ionic composition of hard (Dutch) freshwater and has been applied as such in ecotoxicological experiments [27]. If SPE recovery would not be negatively impacted by 10 mM of divalent Ca^{2+} cations, we expected WCX-SPE to be effective for most common testing media. Sorption to glassware was initially evaluated in 15 mM NaCl, following up on previous glass binding experiments [15]. Because of the lower suppression of the glass surface potential in medium of 15 mM NaCl compared to 10 mM $CaCl_2$ [28], DSW, and phosphate buffered saline (PBS), 15 mM NaCl was regarded as a medium where glass binding is most prominent. In these other media, higher ionic strength and/or divalent cations are expected to reduce glass binding of cationic surfactants. If glass binding has negligible impact on PA-SPME calibration in 15 mM NaCl medium, we pose that glass binding will not be an issue in other commonly applied test media. Sorption to pipette tips was studied only in 10 mM $CaCl_2$. Sorption studies with 7 μm and 35 μm PA fibers always applied 10 mM $CaCl_2$, as one of the future applications of PA-SPME could be in standardized soil sorption studies with cationic surfactants. In PA-SPME calibration experiments with ionizable amines the medium was always buffered with BES (N,N-Bis(2-hydroxyethyl)-2-aminoethanesulfonic acid, Sigma-Aldrich, Zwijndrecht, The Netherlands) at pH 6.5, to ensure that >99.95% of the surfactant molecules (with $pK_a > 10$) were in the charged form. The pH-dependent affinity for PA-SPME fibers was studied for P12 and Q12 using phosphate and carbonate buffers, with an ionic strength of 100 mM Na^+.

2.4. Determination of SPE recovery for cationic surfactants

Recovery upon elution from WCX-SPE cartridges (Waters, Etten-Leur, The Netherlands) was determined for the full set of test compounds. The method for this was adapted from Chen et al. [15]. The 3 cc 60 mg Cartridges were conditioned with 1 mL of MeOH, pre-equilibrated with 1 mL of MilliQ and equilibrated with 2 mL of DSW or 10 mM $CaCl_2$. The test medium used in the equilibration phase was spiked while still retained on top of the SPE layer in the cartridge, using 50 μL of a MeOH stock solution. This was followed immediately by transfer of an additional 2 mL of medium into the cartridge, dispersing the methanol stock solution throughout the sample. Spiking was done on an analytical scale to quantify the amount of stock solution added precisely. This spiking method was chosen to avoid binding of test compound to glassware and pipette tips. Through the addition of 4 mL medium in total, test concentrations of 6 and 120 nM were simulated. Following sample loading, each cartridge was washed two times with 3 mL of MilliQ and one time with 3 mL of MilliQ acidified with 0.5% TFA, bringing the WCX material into a neutral form. Finally, cationic analytes were eluted using 3 mL of acidic eluent mixture (90% MeOH, 10% MilliQ, 0.1% TFA v/v), with the final volume being weighed. This procedure was carried out in triplicate for each concentration and matrix. Controls were prepared in quadruplicate by spiking 3 mL acidic eluent mixture directly with 50 μL of stock solution, again on an analytical scale.

2.5. Sorption of cationic surfactants to glassware and pipette tips

Glass binding was measured by adding, in triplicate, 200 μL of stock solution (in MeOH) to either a clear glass 40 mL vial (Supelco 27181, supplied by Sigma-Aldrich, Zwijndrecht, The Netherlands) or an amber glass 120 mL flask (Supelco 23234, supplied by Sigma-Aldrich, Zwijndrecht, The Netherlands). In addition, 1.5 mL short thread autosampler vials (Grace, Discovery Sciences) were tested. Vials were then filled to the top (in order to minimize headspace) with 15 mM NaCl solution. Control vials were instead filled to the top with MeOH; glass binding was not expected in 100% organic solvent. The final nominal concentration in all vials was approximately 4 μM. All vials were then placed on roller mixers for 24 h in a darkened, climate controlled room (20 ± 1 °C). Roller mixers (Stuart Roller Mixer SRT9, set at 33 rpm) were used, as horizontal and orbital shakers may cause foaming, decreasing the freely dissolved concentration. After this a 3 mL aliquot of the samples in 15 mM NaCl was extracted from 40 mL vials or to 120 mL flasks using the SPE method that was validated previously. The pipette tip used to sample a 3 mL aliquot in a single draw from the 40 mL vial or 120 mL flask was flushed with the acidic 90/10 eluent used for the SPE step, in order to extract any compound that might have adsorbed to the inside of the pipette tip. HPLC vials were transferred directly to the LC-MS/MS autosampler. Control vials were sampled without SPE and served as a 100% control where no glass

binding was expected, which was verified by mass balance calculation. Subsequently, glass vials containing 15 mM NaCl solution were emptied using a Pasteur pipette connected to a vacuum pump, with less than 40 μL of the original solution (<0.1%) remaining in all cases. In order to extract any remaining compound from the glassware, 3 mL of the acidic 90/10 eluent was added to the emptied vials prior to placing them back on the roller mixer for several minutes. Glass binding was then evaluated by (i) direct comparison of aqueous samples with MeOH samples, and (ii) evaluation of the amount of compound extracted from glassware. In addition, sorption to the outside of pipette tips was assessed in a separate experiment. Without drawing up the aqueous solution, pipette tips were submerged by approximately 1 cm for 10 s in 1.5 mL vials containing a surfactant solution. After wiping off any drops of aqueous solution on the outside of the pipette tip, the tip was emerged in acidic eluent solution to extract cationic surfactant bound to the outside of the pipette tip.

2.6. Measuring of SPME uptake profiles and sorption isotherms with 7 μm and 35 μm PA fiber

Sorption measurements to the PA-SPME fibers for a broad variety of surfactants were primarily executed using 10 mM $CaCl_2$ medium, buffered at pH 6.5 with 100 μM BES. Experiments focusing on pH dependency of sorption isotherms were performed by using different phosphate and carbonate buffers to produce media with the desired pH, all with buffer strength of 10 mM and no additional salts added. Kinetic uptake profiles into the PA-SPME fibers were determined for P12 and Q12, based on 10 mM $CaCl_2$ medium where possible and using alternative media for higher pH levels. Fibers were exposed in clear glass 40 mL vials with aluminum lined septa, placed on a roller mixer in a dark and climate controlled (20 ± 1 °C) room. The 7 μm PA-SPME fibers were cut to 50 ± 0.2 mm and 35 μm PA-coated SPME fibers to 40 ± 0.2 mm, using a bundle of SPME fibers packed in a stretch of folded aluminum foil and a laser guided paper cutter. Customizable fiber length is one of the advantages when using a 200 m stretch of SPME fiber instead of prefabricated fibers on a solid support. Exposure duration was 4 days unless noted otherwise. Following exposure, fibers were blotted dry, gently wiped along a wet tissue and subsequently cut into ~1 cm pieces that were collected in a single autosampler vial. Fibers were desorbed in a weighed volume of the acidic eluent mixture for at least 60 min, vortexed for 10 s, and stored at 4 °C until analysis. The volume of eluent added was based on the expected C_{fiber}, upper and lower detection limits, and practical limitations. If necessary, eluent was further diluted before analysis. The aqueous concentration at the time of SPME sampling was determined following SPE clearance of inorganic medium salts, or direct injection of the salt medium to the LC-column. Direct injection of medium was done by pipetting a 200 μL aliquot from the test vial into an autosampler vial already containing 600 μL of eluent, rinsing the pipette tip five times with the eluent inside the autosampler vial to wash out any compound stuck to the inside of the pipette tip. These direct aqueous samples were analyzed using a solvent switch, in order to divert poorly-retaining inorganic salts to the waste outlet, before switching to a steep gradient that introduced the surfactant into the MS (see below). SPE eluted aqueous samples were analyzed using an isocratic HPLC method with shorter run time.

2.7. Chemical analysis

Each compound was tested and analyzed separately, removing the need for complex chromatographic techniques to separate mixtures to allow for simple and fast chromatographic analysis. Two Kinetex XB-C18 columns (Phenomenex, Torrance, USA) were used, which were end-capped with trimethylsilyl and additional isobutyl groups at the base of the C18 chain. Core-shell columns were used because of their relatively low operating pressure and reduced band broadening when analyzing surfactants [29]. The specific placement of isobutyl sidechains helped to diminish peak tailing, which is otherwise expected when analyzing cationic surfactants using a silica-based stationary phase. A Kinetex 2.6 μm, 100 Å 50 mm × 2.1 mm column was used with a flow rate of 200 μL/min for clean samples; i.e. SPE samples or fiber extracts. A similar column with larger particles (5 μm) was used for gradient analysis, as the increased particle size allowed for a higher flow rate (350 μL/min) with decreased backpressure. Mobile phase was a mixture of A (MilliQ water with 0.1% formic acid) and B (MeOH with 0.1% formic acid). Clean samples were analyzed using an isocratic flow of A and B; information on percentages of A and B for each compound is listed in the supporting information (Table S3). Aqueous samples of P12 and Q12 were analyzed using a gradient of A and B, starting with 95% A for 2.5 min which was then increased to 95% B over 1 min using a convex gradient, after which the flow was kept at 95% B for 2.2 min to be instantly changed back to 95% A to equilibrate the column for the next injection. During the first 2.5 min of the run analytes were effectively trapped on the column, allowing for dissolved salts to be washed off the column and be diverted to waste by using a solvent switch. LC-MS/MS settings are listed in the Supporting Information (Table S2).

2.8. Data analysis

All data was analyzed using GraphPad Prism 6 for Windows (version 6.07).

3. Results and discussion

3.1. Performance of analytical equipment

Replicate sampling was used in all experiments, preferably with triplicate samples and duplicate or triplicate fibers. For PA-SPME samples, deviations between replicates of ≤20% were regarded as acceptable for surfactants [15,30]. For aqueous samples and standards, deviations between replicates of ≤10% were regarded as acceptable. Calibration standards were also subject to replicate injections. Quality of calibration data was assessed by back-calculation, where a deviation of ≤10% was deemed acceptable. For most compounds the LC-MS/MS performed best between concentrations of 5 nM and 20 μM, roughly four orders of magnitude. Since aqueous samples were always diluted four times with the acidic eluent mixture, the effective LOQ for aqueous samples was approximately 20 nM.

3.2. SPE recovery for cationic surfactants

As shown in Fig. 1, Oasis WCX-SPE columns displayed a recovery ≥80% in all cases, and ≥90% for 16 of the 30 compounds tested. We thereby show that this SPE protocol can be confidently used to extract, retain, and elute all cationic surfactants tested from aqueous samples (see Fig. 1), ranging from C8 to C18 alkylamines, including, C14-dialkyldimethylammonium, C8-tetraalkylammonium, and benzalkonium and pyridinium compounds. The mixed-mode retention mechanism ensures favorable interaction between cationic surfactant and Oasis WCX sorbent when flushing the cartridge with water or even solvent at alkaline pH, because both ionic and hydrophobic interactions retain the surfactants, as well as when flushing with acidified water because then hydrophobic interactions with the neutralized WCX material still retain the surfactants. Elution is easily

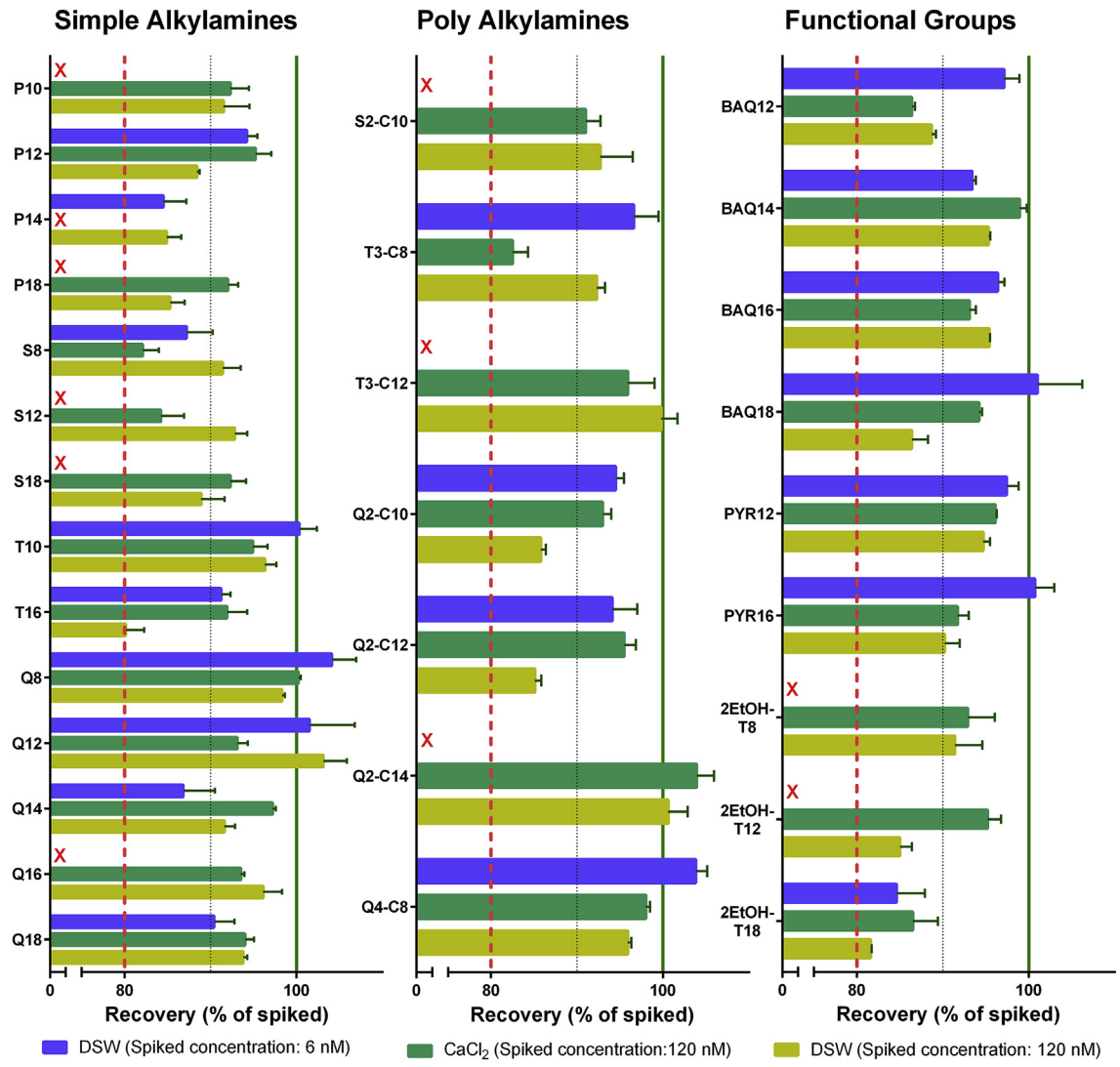


Fig. 1. SPE recovery for a broad series of cationic surfactants. Determined in DSW and 10 mM $CaCl_2$. Red X indicates a compound has not been tested with this medium or at this concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

achieved for even the more hydrophobic cationic surfactants when using acidified solvent, which diminishes both ionic and hydrophobic interactions. Strong retention of analyte when flushing with acidified water is important, as (inorganic) cations that might be retained on the cartridge could cause artefacts if they are injected into the MS/MS. This WCX material should also be effective for complex technical cationic surfactant mixtures and environmental samples, as long as the ion-exchange capacity of the WCX material is not exceeded. There seems to be no correlation between alkyl chain length and extraction recovery; as long as the analyte is sufficiently hydrophobic a sample can be flushed without breakthrough losses for cleanup at pH > 5 and the all analytes can be fully eluted using a strongly acidic solvent mixture. This is likely due to the nature of the WCX solid phase, which combines hydrophobic interactions with ionizable carboxylic acid groups.

3.3. Sorption of cationic surfactants to glassware and pipette tips

The extent of glass binding of simple primary amines increased considerably with alkyl chain length above a certain minimum length, as shown in Fig. 2. Using the data obtained with glassware extractions, for example, for pH 6 buffered solutions with 15 mM NaCl as electrolyte for P10 less than 10% loss to the glass of 1.5 mL autosampler vials was determined, while more than 50% of the total spiked amount was sorbed to glass for P12 amines (in the ~0.3 μM spiked group), which increased up to >80% for primary amines with longer alkyl chains. Direct comparison of aqueous samples with MeOH samples were generally in good agreement and lead to comparable estimates of extent of glass binding. This warrants against testing or storing such hydrophobic cationic surfactants in aqueous solution in such small glass vials without careful measurement, as the actually dissolved concentrations may be several factors lower than nominal(ly intended) concentrations. Overall losses from the dissolved phase to glass surface in 40 and 120 mL flasks is markedly lower than in autosampler vials due to the lower area/volume ratio, but fractions lost to the glass surface were still >40% for P16 and P18. Results for the 1.5 mL autosampler vials also indicate a minor concentration dependency, with lower relative losses at higher spiked concentrations. The results for P18 seem somewhat counterintuitive, because at 0.3 μM the relative losses for P16 are higher than for P18 (Fig. 2).

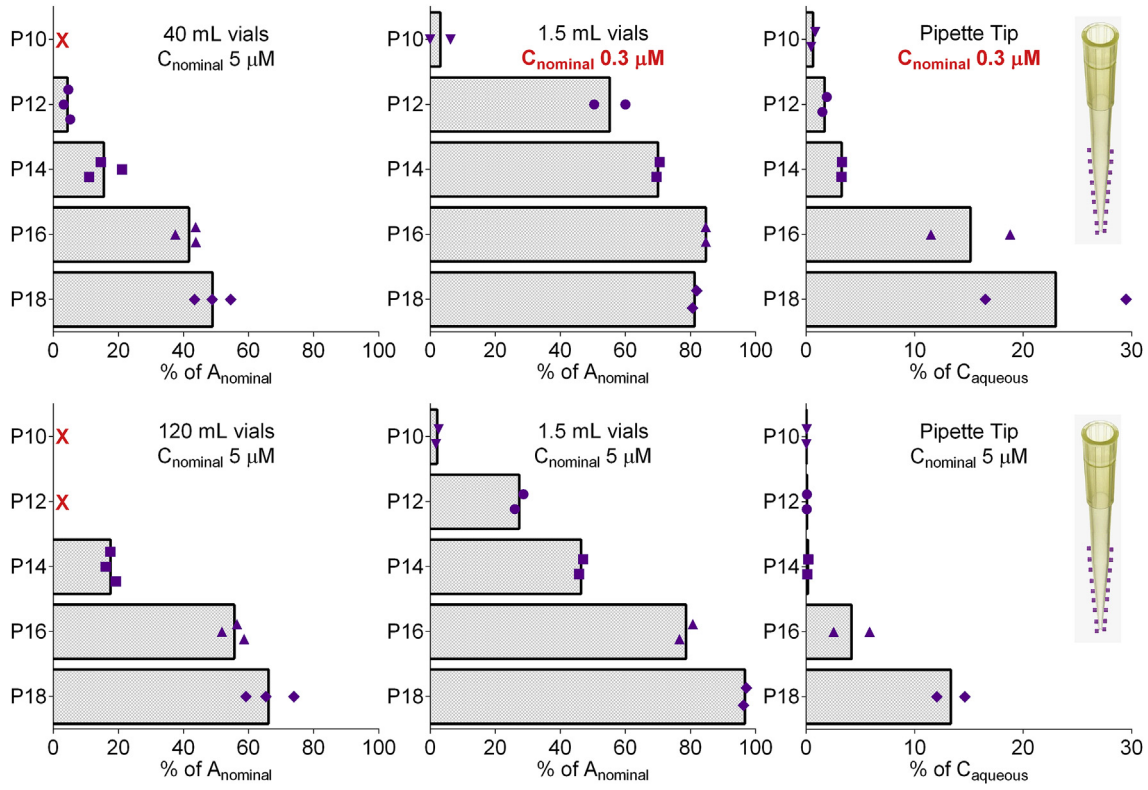


Fig. 2. Glass binding and pipette tip binding for a series of primary amines. Determined in 10 mM $CaCl_2$. Red X indicates this compound has not been tested in this specific vial. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Significant binding of surfactant to the outside of 200 µL polypropylene (PP) pipette tips, which were dipped into aqueous solution, may lead to overestimation of the actually dissolved concentration when this amount is co-extracted upon releasing the pipetted sample into a vial filled with solvent. As shown in Fig. 2, compared to glass surface binding, PP tip binding was significant only at higher alkyl chain lengths, and showed a more pronounced concentration dependency; considerably stronger at lower concentrations. For primary amines P10, P12 and P14, PP tip binding does not seem to be a significant artefact when sampling, but for P16 and P18 in 1.5 mL vials more than 20% of the total amount in aqueous solution (thus, excluding the glass sorbed fraction) can be sorbed to the outside of the tip, which may cause a strongly confounding increase in sampled surfactant. P10 is the only compound with insignificant sorption in all instances. For P12 and P14 sorption to glassware is increased, but sorption to pipette tips is still negligible. P16 and P18 have significant sorption losses to both PP tips and glass in all experiments. At pH 6.5, it is unlikely that sorption to glassware is influenced by the neutral form (<0.1%).

Sorption to glassware was generally lower for quaternary amines (see Fig. 3), when compared with primary amines with equal alkyl chain length. Differences are especially obvious for 120 mL and 40 mL glass vials, where quaternary amines have approximately two times smaller adsorbed fractions. This does contradict sorption trends for several aluminosilicate clays, where quaternary ammonium displayed higher affinities than analogue primary amines [31,32]. Sorption to 1.5 mL vials is roughly comparable with primary amines, with some slight differences for the shorter alkyl chain lengths. Binding to PP tips is much lower for quaternary amines than analogue primary amines. There is virtually no significant sorption to PP tips at 5 µM, except for Q18. Sorption is stronger at 0.3 µM, though, but is still only significant for the longer alkyl chain lengths of ≥Q16.

Previous studies indicated that sorption of cationic surfactants to kaolinite increases with alkyl chain length [23]. Moreover, decreases in C_{free} due to sorption to a surface (e.g. glass) is often more substantial at lower concentrations because the surface sorption sites may become saturated at relatively high concentrations. This can significantly decrease C_{free} in aqueous samples, hampering mass balance based calculations. In studies with an additional sorbent phase such as sediment or humic substances, glass binding might pose less of a challenge, if other sorption phase(s) are dominant by volume or affinity. Glass binding is hypothesized to be highest in solutions containing monovalent electrolytes with low salinity, whereas increases in salinity and presence of divalent cations lead to lower glass binding [33–35]. In addition, with glass adsorption being nonlinear this leads to concentration-dependent losses that are enhanced as analyte concentrations decrease.

3.4. Sorption of cationic surfactants to PA fiber

Initial sorption experiments were carried out on a large set of simple cationic surfactants of varying alkyl chain lengths. In contrast to previous publications from our lab on PA-SPME with quaternary ammonium compounds, however, for most compounds relatively large variability (>1 order of magnitude) within and between experiments was found (see supporting information, Figs. S1–S5). These effects seemed to increase with number of alkyl chains as well as alkyl chain length. Together, these results indicate that reproducibility of the PA-SPME taken from this batch of fiber material becomes too low, and uncertainty becomes too high, for accurate determination of C_{free} by passive sampling for compounds

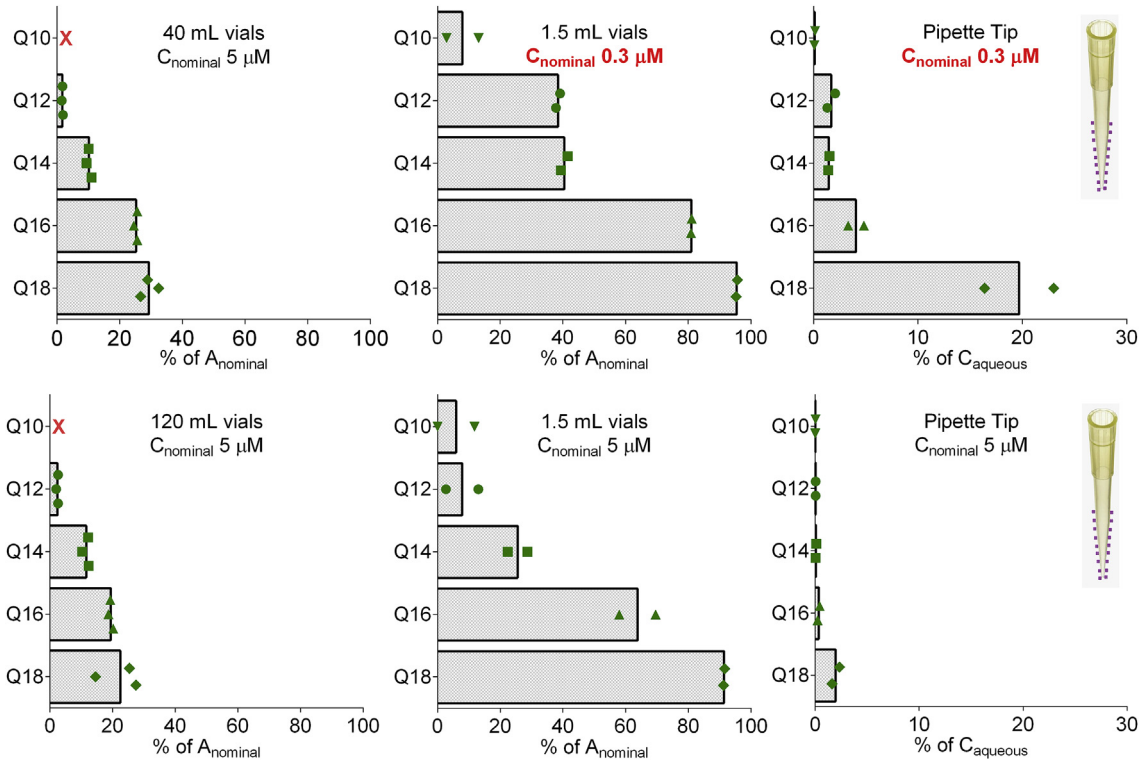


Fig. 3. Glass binding and pipette tip binding for a series of quaternary amines. Determined in 10 mM $CaCl_2$. Red X indicates this compound has not been tested in this specific vial. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with more than one alkyl chain or an alkyl chain length ≥14 carbon atoms. Similar findings of unfavorable sorption behavior of the current batch of 7 µm PA-SPME for anionic surfactants, compared to an older 7 µm PA-SPME batch [36,37], were reported in one of our labs other recent studies [38]. As a partial solution, it is strongly advisable to perform a calibration and the full experiment with SPME fibers cut from one length of fiber, to rule out effects of variability in coating thickness along the length of a batch of fiber. Results of these more controlled experiments are presented in Figs. 4–6. Combining these findings with previous research

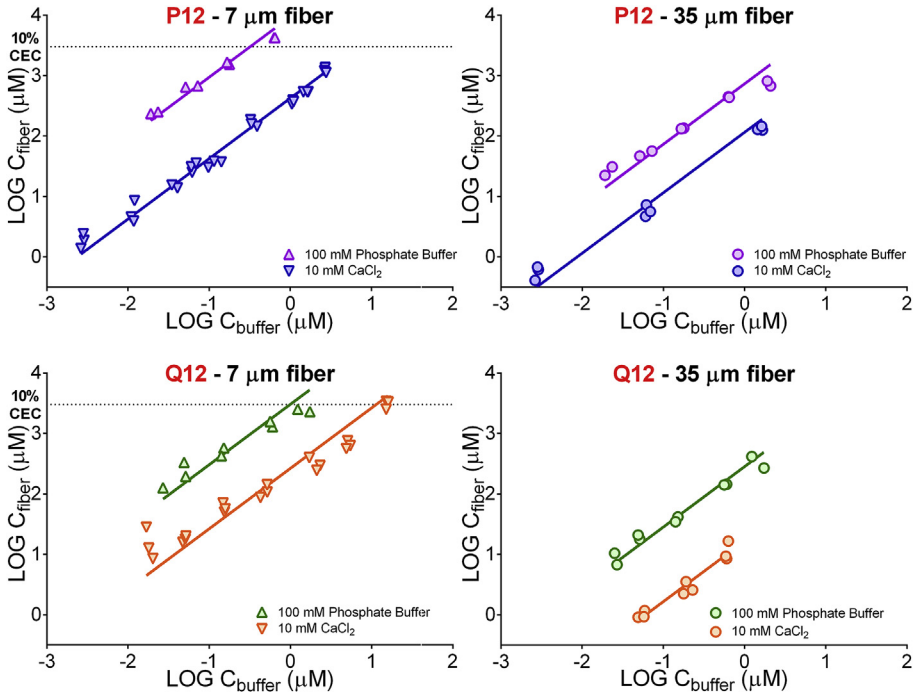


Fig. 4. Influence of medium composition on fiber affinity. Higher fiber affinity is seen for 100 mM Na^+ in all cases. Fixed slope of 1.0 in all graphs.

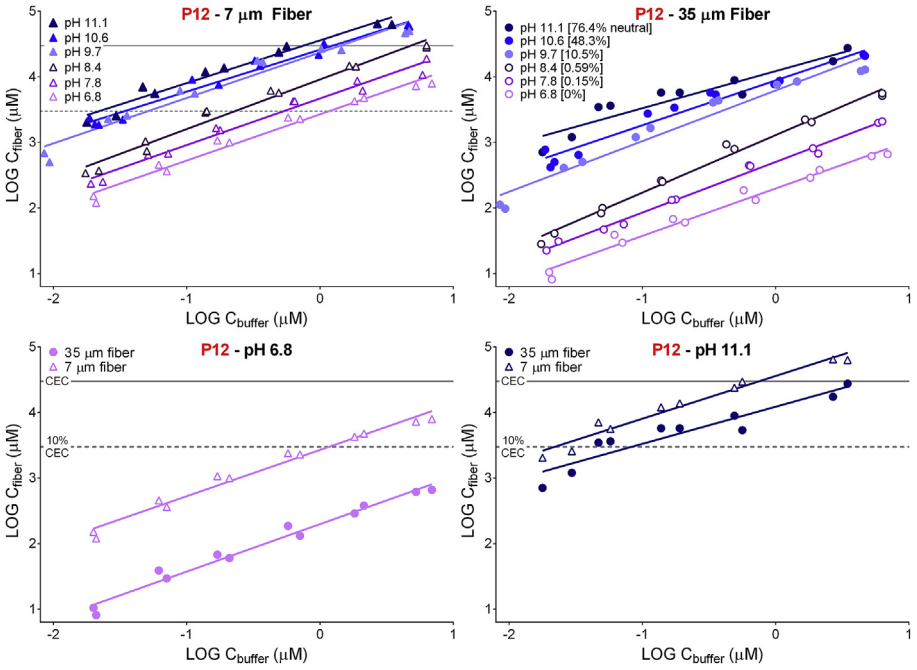


Fig. 5. Influence of medium pH on fiber sorption for P12, determined in 100 mM Na^+.

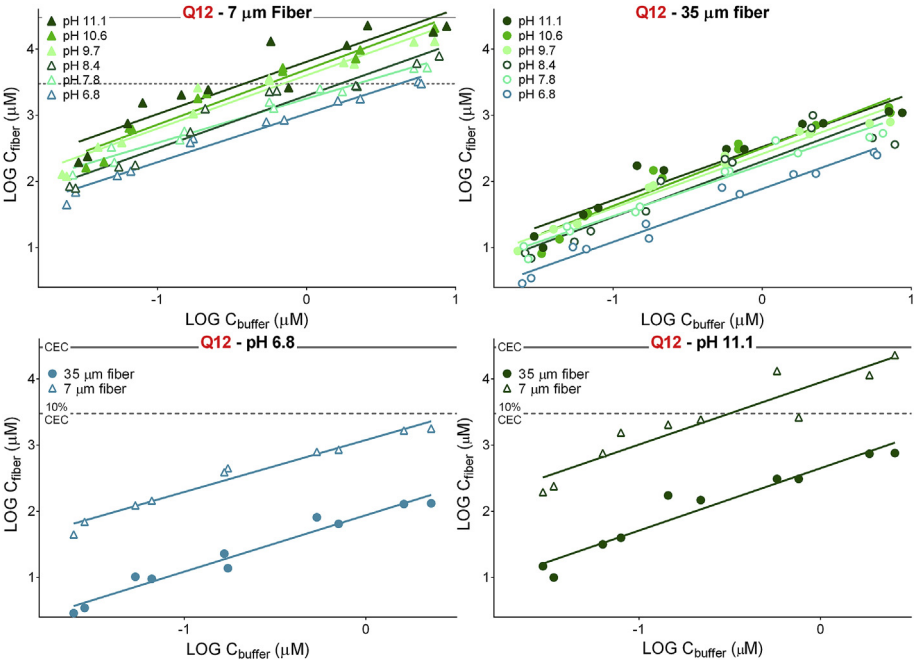


Fig. 6. Influence of medium pH on fiber sorption for Q12, determined in 100 mM Na^+.

[15,26,39], it is difficult to establish a definitive applicability domain for PA-SPME, while the exact sorption mechanism of PA-SPME remains to be elucidated [15,19,38]. Nor did it seem feasible anymore to systematically determine structural trends in K_{fw} for cationic surfactants on 7 µm PA-SPME, and define a K_{fw} QSAR, as was one of our key intentions with the current study. It was decided that detailed PA-SPME experiments in this manuscript were limited to one ionizable and one permanently charged C_{12}-chain cationic surfactant.

3.5. Uptake kinetics with 7 and 35 µm PA-SPME fibers, for the ionizable P12 and permanently charged Q12

Combining K_{fw} calibration samples with each experiment, uptake kinetics of two relatively short chain length surfactants onto PA-SPME fibers of two different polymer thicknesses, 7 and 35 µm, were measured: an ionizable primary amine (P12) and quaternary ammonium compound (Q12). Kinetics for Q12 were determined only at pH 6.5; results are presented in SI-Fig. S6. Both fiber coatings reach >90% of equilibrium in less than 6 h. Overnight exposure is

therefore sufficient for sampling of Q12. Kinetics for P12 were determined at pH 6.5 and pH 11.1 (Figs. S7 and S8), to assess kinetics of both the ionic and the neutral form (pK_a P12 ~10.5). Both PA-coatings reach equilibrium at pH 6.5 fast enough to render overnight exposure is suitable to measure P12 under standard conditions. The neutral form of P12 needs more time to reach equilibrium, an effect that is correlated with coating thickness, which is a strong indication that the neutral form is absorbed into the PA polymer rather than adsorbed to the (charged) PA-surface (groups). At pH 11.1, >90% of equilibrium is reached in approximately 10 h for the 7 μm fiber, while the 35 μm fiber needs 23 h. Also of note is the more than one order of magnitude increase in K_{fw} of P12 between pH 6.5 and 11.1, for both PA-coatings. In theory, both fiber types are suitable to sample P12 at alkaline pH, although implementation of the PA coating at alkaline pH should be subject to additional testing.

3.6. Effect of ionic composition and pH on PA-SPME calibration curves

The effect of ionic composition of exposure medium on fiber uptake was measured for P12 and Q12 in two exposure media: 100 mM phosphate buffer (pH 7.8 ± 0.1) and 10 mM $CaCl_2$ buffered with 1 mM BES (pH 7.5 ± 0.1). Results are presented in Fig. 4. Switching medium from 100 mM Na^+ to 10 mM Ca^{2+} leads to an order of magnitude decrease in K_{fw}. This effect seems to be similar for P12 and Q12 and between fiber types, leading to the hypothesis that the higher competition of Ca^{2+} with cationic surfactants (in comparison with Na^+) for cation exchange sites, and in more detail, the much stronger reduction of the surface potential by divalent cations that attracts the organic cations near the charged surface, are the principal causes [15].

Effects of pH on PA-SPME calibration isotherms are presented in Figs. 5 and 6 for P12 and Q12, respectively. The associated Freundlich coefficients and K_{fw} are presented in Tables S4 and S5, respectively. As expected based on the results of kinetic experiments, partitioning of the ionizable amine P12 to both PA-fiber coatings is highly pH-dependent (Fig. 5), with a higher affinity of the neutral amine species compared to the protonated form. This effect is more pronounced in 35 μm coating, likely due to the lower cation-exchange capacity of the 35 μm PA coating (Haftka et al. [19]) compared to the 7 μm PA coating, as suggested by Chen et al. [15]. When results for 7 and 35 μm PA-coatings are plotted together in Fig. 5D, it becomes obvious that K_{fw} is much more similar at pH 11.1. This further supports the hypothesis that the neutral amine fraction is absorbed into the fiber coating, a process that is unlikely to be impacted by differences in cation exchange capacity, and which can be corrected for by using concentration units per volume of coating. Assuming that the cationic amine has a maximum affinity at pH 6.8, the increase in affinity to the fiber with higher pH can be assumed to be due to the neutral fraction, and a pK_a may be fitted to the data.

The sorption affinity of the permanent cation Q12 to PA fibers, however, showed a minor but distinct influence of medium pH above pH 6.8 (Fig. 6), with about 0.8 log units for 7 μm fiber and 0.5 log units for the 35 μm fiber. This suggests that the number of ion-exchange groups on the PA material surface may not be constant, and not only have a fixed pK_a of approximately 5, as assumed by Chen et al. [15], but surface acid groups with pK_a values between pH 6–10 likely exist. As a result, it is not possible to accurately derive the pK_a value of P12 from the PA fiber isotherm data. Also, this stresses the need to always perform a calibration study in the exact same media as applied in test samples.

These ionic composition tests and pH series implicate that quaternary ammonium surfactants, as well as the cationic form of ionizable surfactants, have at least an order of magnitude higher affinity for the 7 μm PA fiber compared to the 35 μm PA fiber, as shown for the Q12 sorption isotherm differences at both pH 6.5 and pH 11. This corresponds to measured differences between these two PA-coatings reported previously for other cationic organic compounds [40], using different PA-fiber batches. This was assumed to be the result of a higher density of cation exchange sites on the surface of the 7 μm PA fiber. Cation exchange capacity (CEC) for the 7 μm fiber was determined in earlier work using Ba^{2+}/Ca^{2+} substitution [15]. The CEC value of ~20 mmol/L corresponds with the maximum C_{fiber} of quaternary ammonium surfactants below their respective CMC. The ion exchange groups are presumably unpolymerized carboxylic acids originating from the polyacrylate or polymethacrylate used to produce the fiber coating. In earlier work by Chen et al. the sorption affinity of quaternary ammonium surfactants was shown to increase in the pH range of 2–6, but did not differ between pH 6 and 8 [15]. These results led to the hypothesis that ion exchange sites dominate the sorption process of cationic surfactants to the PA fiber, i.e. sole interaction of hydrophobic alkyl chains with the PA surface is not a significant contributor. The decreasing affinity between pH 6 and 8 corresponds with the expected pK_a of carboxylic acids (4–6), which are also important cation exchange sites in humic acids and the Oasis WCX-SPE cartridge. Based on this hypothesis, it was expected that the CEC of the 7 μm PA fiber would remain constant at pH ≥ 6.0, and that cationic surfactants would therefore have a constant affinity throughout the alkaline pH range. However, experimental results in this work have shown that this was not entirely the case.

4. Conclusions

The data presented in this publication on significant sorption to the outside of polypropylene pipette tip and various glassware, as well as irreproducible or highly scattered SPME sorption isotherms, show that analytically justified experiments with hydrophobic cationic surfactants are challenging. Sorption to glass becomes significant for surfactants with a carbon chain length above 10 carbon atoms. Sorption to glass surface may be as high as 90% of the total added amount of C18 cationic surfactants, rendering ten times lower dissolved concentration than intended. Using pipette tips to sample hydrophobic cationic surfactants from aqueous solution, on the other hand, may substantially overestimate the amount of surfactant sampled from the medium when flushing the pipette tip in solvent (to make sure that the amount sorbed to the inside of the tip is included). Unwanted effects due to sorption are lower but can still be significant for quaternary ammonium surfactants. However, cationic surfactants with a diversity of structures, including multiple alkyl chains and functional groups and ionizable as well as permanently charged compounds, can be efficiently extracted from an aqueous phase with a weak cation exchange solid phase extraction (WCX-SPE) column. Extraction efficiencies were above 90% for almost all chemicals. An overview of glassware sorption and recoveries of primary amine and quaternary ammonium surfactants is presented in Tables 2 and 3, respectively.

SPME is not a universal solution to measure cationic surfactants. There are certain specific issues beyond what was expected beforehand. The ultimate goal of this work was to lay down an applicability domain for PA-SPME in the context of sampling cationic surfactants. Although it proved to be difficult to establish detailed boundaries for such an applicability domain, the results indicate that alkyl chain lengths longer than 14 carbon atoms and the presence of multiple alkyl chains are highly likely to give irreproducible measurements. If PA-SPME is employed a calibration curve should always be measured together with the samples, using the same medium and batch of fiber. Although the PA-SPME

Table 2
Overview for linear primary alkylamine surfactants of SPE recoveries, losses to glass ware and pipette tips, and extraction efficiency of PA-SPME fibers. Values between brackets are standard deviations.

Cationic surfactant		P10	P12	P14	P16	P18
Intrinsic SPE recovery (SD)	10 mM CaCl2; 120 nM	n.d.	95% (3.2)	n.d.	n.d.	92% (2.1)
	DSW; 120 nM	92% (5.2)	88% (0.5)	85% (2.9)	n.d.	85% (2.9)
	DSW; 6 nM	n.d.	94% (2.1)	85% (4.6)	n.d.	n.d.
Glass binding in autosampler vial	0.3 μM	3.2% (3.2)	55% (4.8)	70% (0.5)	85% (0.0)	81% (0.7)
(loss in 1.5 mL 10 mM $CaCl_2$)	5 μM	2.2% (0.4)	27% (1.4)	46% (0.6)	79% (2.1)	97% (0.5)
Glass binding in 40 mL vial	5 μM	n.d.	4.3% (0.8)	16% (4.2)	42% (2.9)	49% (4.5)
(loss in 40 mL 10 mM $CaCl_2$)						
Glass binding in 120 mL vial	5 μM	n.d.	n.d.	18% (1.3)	56% (2.8)	66% (6.0)
(loss in 120 mL 10 mM $CaCl_2$)						
Binding to pipette tip (loss relative to total dissolved amount in 1.5 mL 10 mM $CaCl_2$)	0.3 μM	0.6% (0.2)	1.7% (0.2)	3.3% (0.0)	15% (3.7)	23% (6.5)
	5 μM	0% (0.0)	0.1% (0.0)	0.1% (0.1)	4.2% (1.7)	13% (1.3)
Extraction efficiency (1 cm 7 μm fiber in 10 mL)	pH 6.8	n.d.	0.69%	n.d.	n.d.	n.d.
relative to dissolved amount	pH 11.1	n.d.	8.5%	n.d.	n.d.	n.d.
Extraction efficiency (1 cm 35 μm fiber in 10 mL)	pH 6.8	n.d.	0.31%	n.d.	n.d.	n.d.
relative to dissolved amount	pH 11.1	n.d.	16%	n.d.	n.d.	n.d.

Table 3
Overview for linear quaternary alkyltrimethylammonium surfactants of SPE recoveries, losses to glass ware and pipette tips, and extraction efficiency of PA-SPME fibers. Values between brackets are standard deviations.

Cationic surfactant		Q10	Q12	Q14	Q16	Q18
Intrinsic SPE recovery (SD)	10 mM CaCl2; 120 nM	n.d.	93% (2.1)	97% (0.7)	94% (0.8)	94% (1.9)
	DSW; 120 nM	n.d.	103% (4.8)	92% (2.1)	96% (3.8)	94% (0.8)
	DSW; 6 nM	n.d.	102% (9.1)	87% (6.4)	n.d.	90% (4.1)
Glass binding in autosampler vial	0.3 μM	8.0% (5.1)	38% (0.7)	40% (1.1)	81% (0.1)	96% (0.2)
(loss in 1.5 mL 10 mM $CaCl_2$)	5 μM	3.9% (8.0)	7.9% (5.2)	26% (3.2)	64% (5.8)	91% (0.2)
Glass binding in 40 mL vial	5 μM	n.d.	1.7% (0.2)	10% (0.7)	25% (0.5)	29% (2.3)
(loss in 40 mL 10 mM $CaCl_2$)						
Glass binding in 120 mL vial	5 μM	n.d.	2.4% (0.3)	12% (0.9)	19% (0.6)	23% (5.7)
(loss in 120 mL 10 mM $CaCl_2$)						
Binding to pipette tip (loss relative to total dissolved amount in 1.5 mL 10 mM $CaCl_2$)	0.3 μM	0.1% (0.0)	1.7% (0.4)	1.5% (0.1)	4.1% (0.8)	20% (3.3)
	5 μM	0% (0.0)	0% (0.0)	0.1% (0.0)	0.3% (0.1)	2.0% (0.4)
Extraction efficiency (1 cm 7 μm fiber in 10 mL) relative to dissolved amount	pH 6.8	n.d.	0.31%	n.d.	n.d.	n.d.
	pH 11.1	n.d.	2.2%	n.d.	n.d.	n.d.
Extraction efficiency (1 cm 35 μm fiber in 10 mL) relative to dissolved amount	pH 6.8	n.d.	0.14%	n.d.	n.d.	n.d.
	pH 11.1	n.d.	0.69%	n.d.	n.d.	n.d.

calibration isotherms are confirmed to be near linear for low, environmentally relevant concentrations (Fig. 4), the PA-SPME calibration curves become more non-linear at high concentrations, which approach the CEC of the polymer (Figs. 5–6) [15]. Toxic effects of cationic surfactants in sediments have been observed at sorbed concentrations approximating 15% of the CEC of the sorbent [6], and the proportionally high freely dissolved concentrations in such systems are likely to be in the non-linear SPME calibration range. Unfortunately, this further hampers accurate use of PA-SPME for toxicity testing in the presence of mitigating sorbent [5]. At present, it seems that the PA-SPME material of the currently available batch does not provide enough reliability and reproducibility to warrant use for precise experiments on the environmental fate of cationic surfactants, especially with alkyl chain lengths beyond 12 carbon atoms.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.aca.2017.11.051.

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