Characterization of seawater and aerosol particle surfactants using solid phase extraction and mass spectrometry

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ABSTRACT

Surface-active organic molecules (surfactants) may influence the ability of an aerosol particle to act as a cloud condensation nuclei by reducing its surface tension. One source of organic mass in aerosol particles, which may also contain surfactants, is bubble bursting on the sea surface. In order to directly compare these molecules in the ocean and aerosol particles, we developed a method using multiple solid phase extractions and high resolution mass spectrometry to characterize surface active organic molecules in both. This method has extraction efficiencies greater than 85%, 75%, and 60% for anionic, cationic, and nonionic surfactant standards, respectively. In this study, we demonstrate the presence of three ionic classes of surface active organics in atmospheric aerosol particles and estuarine water from Skidaway Island, GA. With this extraction method, organic molecules from both estuarine water and atmospheric aerosol particles significantly reduced surface tension of pure water (surface tension depression of ˜ 18 mN/m) and had high ratios of hydrogen to carbon (H/C) and low ratios of oxygen to carbon (O/C), indicative of surfactants. While previous work has observed a larger fraction of anionic surface active organics in seawater and marine aerosol particles, here we show cationic surface active organics may make up a large fraction of the total surface active molecules in estuarine water (43%–47%).

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Introduction

Surface-active compounds partition to interfaces and reduce the free energy of surfaces and interfaces. Surfactants are surface-active organic compounds that contain both hydrophobic and hydrophilic ends and contribute to a large reduction in surface tension when in solution (Kronberg et al., 2014). In atmospheric aerosol particles, surfactants can influence particle growth (Frossard et al., 2018) and change their potential to act as cloud condensation nuclei (Petters and Petters, 2016; Ruehl et al., 2016). One source of surfactants in atmospheric aerosol particles is through emission from the sea surface as a fraction of primary marine aerosol particles produced from bubble bursting (Blanchard, 1964). The sources, chemical composition, and concentration of the organics, specifically surfactants, in primary marine aerosol particles have not been well constrained (Gantt and Meskhidze, 2013).

The surfactant production processes and their chemical, as well as physical, transformations at the sea surface are still unclear (Kurata et al., 2016). In seawater, surfactants are scavenged on rising bubbles and transported to the sea surface. There, they modulate the surface tension of bubbles, contributing to foam and bubble rafts (Wurl et al., 2011). Surfac-

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tants may also play a role in seawater bubble bursting and the emission of sea spray aerosol particles (Frossard et al., 2019b; Lewis and Schwartz, 2004). The influence of surfactants on these systems depends on their concentrations and properties, such as chemical composition and molecular structure (e.g. Modini et al., 2013; Sellegri et al., 2006). To determine the influence of seawater surfactants on the chemical and physical properties of atmospheric aerosol particles, surfactant chemical properties need to be characterized in both.

The sources and composition of surfactants in atmospheric aerosol particles and seawater remain largely unexplored. Often, the presence of surfactants is inferred by measuring a surface tension depression compared to that of pure water. Surface tension depression has been observed for organic mass extracted from aerosol particles (Capel et al., 1990; Cavalli et al., 2004; Facchini et al., 2000) and for seawater directly (Long et al., 2014), implying the presence of surfactants in these systems. Past studies used electrochemical methods to measure the total concentration of surfactants in extracts of aerosol particles (Frka et al., 2012; Kroflic et al., 2018), atmospheric precipitation (Cosovic et al., 2007; Leko et al., 2004), and the sea surface microlayer (Frka et al., 2009; Wurl et al., 2009). Electrochemical methods provide total surfactant concentration, expressed as the equivalent concentration of a standard surfactant, but do not allow for the speciation of surfactants.

Other studies have used colorimetry and ultraviolet–visible (UV-Vis) spectroscopy to characterize surfactants by their ionic states and measure the concentrations of each. These methods mainly focus on the total concentrations of each ionic class including anionic, cationic, and/or nonionic surfactants in aerosol particles (Jaafar et al., 2018; Roslan et al., 2010), the sea surface microlayer (Huang et al., 2015; Roslan et al., 2010; Shaharom et al., 2018), estuarine water (Huang et al., 2015), seawater (Shaharom et al., 2018), and atmospheric precipitation (Olkowska et al., 2014). Recent work combined colorimetry and UV-Vis spectroscopy with solid phase extraction to separate and quantify anionic, cationic, and nonionic surfactants from aerosol particles (Gérard et al., 2016; Nozière et al., 2017; Frossard et al., 2019a) and sub-surface seawater (Frossard et al., 2019a).

Mass spectrometry is a valuable tool in identifying the composition of dissolved organic matter in seawater (e.g. Dittmar et al., 2008; Morales-Cid et al., 2009). Also using mass spectrometry, some anionic surfactants have been tentatively characterized in marine aerosol particles (Cochran et al., 2016), and fatty acid coatings have been observed on aerosol particles (e.g. Tervahattu et al., 2002). However, there has been limited work identifying specific surfactants produced from natural sources in the ocean and linking their properties to those of aerosol particle surfactants.

Recent measurements of surfactants both in sea spray aerosol particles and in sub-surface seawater using colorimetry and UV-Vis spectroscopy found the largest fraction of surfactants to be anionic but did not characterize the molecular formula or structure of the surfactants (Frossard et al., 2019a). The compositions of cationic and nonionic surfactants have not been investigated, and past work has focused on identifying anionic surfactants or on total surfactant concentrations. The sparse identification and quantification of cationic surfactants in aerosol particles and marine waters may be due

to a lack of a specific procedure for their targeted separation from these matrices.

In this work, we present an optimized method for extracting three surfactant classes from both aerosol particle and marine water samples and quantifying them using mass spectrometry. We used high resolution mass spectrometry to characterize the extracted organics and confirmed the presence of surfactants with tensiometry. The hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios of the extracted organic compounds from the aerosol particles and estuarine water are compared to each other and to those of the surfactant standards.
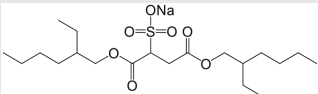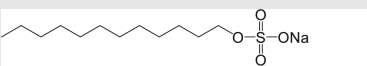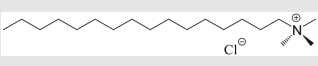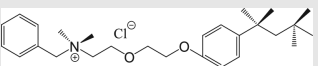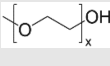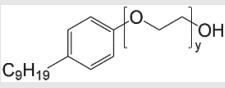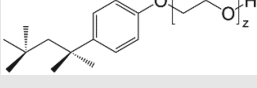
1. Methods

Solutions of standard surfactants as well as model seawater and model aerosol particle extracts, consisting of mixtures of standard salts, organics, and surfactants, were used to test the efficiencies of multiple solid phase extraction cartridges for surfactant extraction and separation from these sample types. Surfactants were characterized with mass spectrometry, and the interference of salt and organics in the extraction and characterization steps were investigated. The resulting method was then applied to samples of ambient estuarine water and atmospheric aerosol particles.

1.1. Standard solutions

For the surfactant standards, we used anionic surfactants sodium dodecyl sulfate (SDS) and dioctyl sulfosuccinate sodium (AOT), cationic surfactants cetyltrimethylammonium chloride (CTAC) and Hyamine 1622, and nonionic surfactants Triton X-100, Tergitol np-40, and polyethylene glycol methyl ether (mPEG) (all from MilliporeSigma). The anionic and cationic surfactant standards have single molecular weights and monoisotopic identifying mass-to-charges within a mass spectrum (**Table 1, Fig. S1**). The nonionic surfactant standards have a range of masses, represented by an average molecular weight for each (**Table 1**). An identifying ion mass-to-charge was selected for the nonionic surfactant standards based on the signal to noise of the peaks in the spectra (**Table 1, Fig. S1**). These surfactant standards vary widely in critical micelle concentrations, chemical formulas, molecular weights, and structures (**Table 1**). Some of the standards contain functional groups similar to those in the classes of major anionic organics identified in generated sea spray aerosol particles, including sulfates, alkyl chains, and alkyl benzenes (Cochran et al., 2016), while others contain amine, ether, and alcohol functional groups.

Standard solutions were prepared in 100 mL volumes for each surfactant ionic class and consisted of 500 nM each of SDS and AOT for anionic surfactants; 800 nM and 2 μM of Hyamine and CTAC, respectively, for cationic surfactants; and 1 μM, 1 μM, and 2 μM of mPEG, Triton X-100, and Tergitol np-40, respectively, for nonionic surfactants. Model seawater solutions were prepared with all of the surfactants at the concentrations listed and 35 g/L of artificial sea salt (comprising 55.5% chloride, 30.5% sodium, 7.4% sulfate, 3.6% magnesium, 1.1% potassium, 1.1% calcium, and <0.8% other salt ions; Milli-

Table 1 – Extraction efficiencies (%) for standard surfactants and salt mixtures using the selected Envi18-0.5g (anionic and nonionic surfactants) and EnviCarb (cationic surfactants) solid phase extraction cartridges (median and range[a] for each extraction efficiency are shown).

Standard surfactant	Surfactant structure	Surfactant Class	Counter Ion	Molecular Weight (g/mol)	Identifying ion peak in mass spectrum (Da)	No Sea Salt[b]	0.002 g/L Sea Salt[c]	35.0 g/L Sea Salt[b]
Dioctyl Sodium Sulfosuccinate (AOT)		Anionic	Na$^+$	444.56	421.2	99.7 (1.3)	91.1 (3.2)	99.8 (2.6)
Sodium Dodecyl Sulfate (SDS)		Anionic	Na$^+$	288.38	264.9	85.1 (4.7)	76.6 (1.6)	82.5 (2.0)
Cetyltrimethyl ammonium (CTAC)		Cationic	Cl$^-$	320.00	284.2	77.3 (2.7)	65.2 (2.1)	76.7 (0.1)
Hyamine 1622		Cationic	Cl$^-$	448.08	412.2	84.1 (2.3)	75.4 (2.7)	74.9 (2.9)
Polyethylene glycol methyl ether (mPEG)		Nonionic	N/A	550 average[d]	490.4	73.3 (8.1)	64.5 (3.4)	70.1 (1.2)
Tergitol NP-40		Nonionic	N/A	1960 average[e]	634.8	62.8 (1.3)	61.4 (2.4)	63.2 (0.6)
Triton X-100		Nonionic	N/A	625 average[f]	620.5	82.7 (1.1)	47.0 (0.2)	68.1 (3.1)

[a] Range is given as the maximum value minus the minimum value.
[b] Total volume of 100 mL to mimic volumes of seawater samples.
[c] Total volume of 10 mL and surfactant concentrations one order of magnitude less to mimic volumes and concentrations of aerosol particle samples.
[d] Average x ranges from 11-12; a single m/z value was selected as the identifying ion peak from the observed range of peaks (**Fig. S1**).
[e] Average y ranges from 39-40; Tergitol is triply charged when ionized, and a single m/z value was selected as the identifying ion peak from the observed range of peaks (**Fig. S1**).
[f] Average z ranges from 9-10; a single m/z value was selected as the identifying ion peak from the observed range of peaks (**Fig. S1**).

poreSigma). Model solutions of aerosol particle extracts were prepared as 10 mL solutions containing 0.002 g/L of sea salt and surfactant concentrations one order of magnitude lower than those in the model seawater. Standard blanks of both 10 mL and 100 mL of ultrapure (18.2 mega-ohm•cm) water were used to account for background signal from the extraction methods.

1.2. Method to separate surfactants

To mimic extractions from ambient samples, standard solutions and blanks were filtered with 0.45 µm polyethersulfone membrane syringe filters (VWR) and transferred to precleaned and preweighed glass bottles. The filtered solutions were then processed through reversed-phase solid phase extraction (SPE) cartridges (Frossard et al., 2019a; Gérard et al., 2016; Nozière et al., 2017) at a flow rate of 1 mL/min using a vacuum pump and extraction manifold (SPE cartridge details are described in Section 1.4). The SPE cartridges were conditioned with 6 mL of acetonitrile and rinsed with 12 mL of ultrapure water. After processing, the sample bottles were rinsed with 2 mL of 0.1% triethylamine (TEA) in ultrapure water which was then processed through the SPE cartridge. A final wash of 10 mL of 0.1% TEA in ultrapure water was used to rinse the SPE cartridge of remaining salts and other potential interferents, and the cartridges were dried by continuing the vacuum. The collected organic compounds were eluted from the sorbent material of the SPE cartridge using 4 mL of acetonitrile into a precleaned vial. The acetonitrile was then evaporated using dry nitrogen gas (99.998% purity, Airgas), leaving the dried organic compounds in the vial.

1.3. Mass spectrometric analysis of extracted surfactants

Following the SPE cartridge extraction and drying, samples were rehydrated using 1 mL of a 1:1 methanol to water mixture and diluted to the initial concentrations of the solutions.

The reference standards Genistein (MilliporeSigma) and Reserpine (SCIEX) were added at concentrations of 5 µM each to each rehydrated solution. Genistein and Reserpine have reference peaks at 268.9 and 609.2 m/z in the negative and positive electrospray ionization (ESI) modes, respectively. Aliquots of 0.1 mL of each solution were removed for analysis, and 1 mM ammonium acetate (MilliporeSigma) was added to increase the signal of nonionic surfactants (Kebarle, 2000). In the presence of ammonium acetate, the nonionic standard surfactants preferentially ionized through the ammonium addition in the positive ionization mode (Sterling et al., 2010). With the addition of ammonium acetate, we were able to observe the ionization of nonionic surfactants at lower concentrations.

The surfactant extracts were analyzed using an electrospray ionization ion trap mass spectrometer (ESI-IT-MS; Esquire 3000, Bruker, USA) at the Proteomics and Mass Spectrometry Facility at the University of Georgia. The samples were introduced into the ESI through loop injection, with a carrier solution of methanol at a flow rate of 6.12 µL/min. The ESI was operated in both positive and negative ionization modes simultaneously, with a capillary voltage of 3.75 kV. Spectra were acquired in the range of 200–1000 Da. The instrument accumulated a target of 30,000 ions and 20,000 ions within the ion trap per scan for the positive and negative ionizations, respectively. Samples were injected 2 or 3 times per sample, with 10 min between injections to ensure any organics in the lines were fully eluted. Mass-to-charges with signal to noise greater than 5 were evaluated. Spectra from the multiple injections were compared to ensure consistency before averaging. The corresponding blank spectra (for 10 mL or 100 mL) were subtracted from the standard spectra prior to further quantification.

The surfactants of each class and the reference standards were ionized with mass spectrometry to determine the observable concentration limits. **Fig. S1** shows example mass spectra of the standard surfactants, using the determined concentrations. For the nonionic surfactant standards, which all contain mixtures of m/z values, peaks at 490.4, 620.5, and 634.8 m/z were used to determine the concentration of mPEG, Triton X-10, and Tergitol np-40, respectively (**Table 1**).

Calibration curves were measured using the peak area of the surfactant standards each at six different concentrations, compared to the peak area of the reference standard for each type (**Fig. S2**). Similar calibration curves were produced using the peak intensity of the surfactant standards compared to the reference standard, for comparison. The average R^2 values of the linear fits to the anionic, cationic, and nonionic surfactants were 0.978, 0.982, and 0.961, respectively.

1.4. Analyses of SPE cartridges and quantification of extraction efficiencies

The extraction method was tested using four different SPE cartridge types to determine the most efficient cartridge for each type of surfactant. The cartridges tested include Hypersep C18 (0.5 g bed weight, Thermo Scientific, referred to as Hypersep); Envi18 C18 (0.5 g and 1 g bed weights, MilliporeSigma, referred to as Envi18-0.5g and Envi18-1g, respectively); and Envi-Carb graphitized carbon (0.5 g bed weight, MilliporeSigma, referred to as EnviCarb) cartridges. The extraction efficiency of each surfactant (and surfactant class) was quantified for each cartridge type using the extraction method described in the previous section.

Two or more surfactant standards were analyzed for each ionic type. The standard surfactants were mixed in solution, and a calibration curve was calculated based on the peak intensities and peak areas of the standard surfactants compared to a reference compound using ESI-IT-MS. The extraction efficiencies were calculated by using the linear fits from the calibration curves for each of the surfactants to determine the concentration (**Fig. S2**) and comparing that concentration to the initial concentration in the sample, prior to extraction (Eq. 1).

$$E = \frac{C_c}{C_i} * 100\% \tag{1}$$

Extraction efficiency (E) was calculated as the concentration of surfactant calculated from the calibration curve after extraction (C_c) divided by the initial concentration in the sample prior to extraction (C_i).

1.5. Aerosol particle and estuarine water collection

Aerosol particles and estuarine water were collected at Skidaway Institute of Oceanography, Skidaway Island, GA, in May and June 2018. Ambient atmospheric aerosol particles were dried with a diffusion drier and collected on aluminum substrates in an 8-stage micro-orifice uniform deposition impactor (MOUDI; Model 100, MSP, USA) (Marple et al., 1991). The aluminum substrates were baked at 500 °C for 4 hr prior to sampling to remove organic matter (Nie et al., 2010). Particles were sampled for 23 hr at a flow rate of 30 L/min. After sampling, substrates were stored in sterile glass vials, frozen, and transported to the laboratory for analysis.

To extract the aerosol particles in solution, substrates were vortexed for 5 min in 5 mL of ultrapure water and stored at 4 °C for 15 hr (Frossard et al., 2019b; Keene et al., 2017; Nozière et al., 2017; Gérard et al., 2016). Then, the vials were vortexed for an additional 5 min, and the solutions were transferred to clean vials. The substrates were rinsed with an additional 5 mL of ultrapure water and vortexed before sitting for 30 min. The solution was transferred to the vial containing the initial extract, resulting in volumes of 10 mL for each aluminum substrate extraction. A quartz fiber filter was used as a back-up filter in the last MOUDI stage. Particles were extracted in a similar procedure from the back-up filter but were not analyzed in this study. Here, we show results for particles collected in the 560 nm to 1000 nm and 1.8 to 3.2 µm size bins on June 4, 2018.

Estuarine water at a depth of ~15 cm was collected in volumes of ~18 L in precleaned 20 L Teflon-lined, high-density polyethylene (HDPE) carboys. The carboys were frozen and transferred to the laboratory for analysis. Prior to extraction, the water was thawed at room temperature for 72 hr and inverted slowly to mix. 100 mL samples were transferred to precleaned amber glass bottles for filtering and extraction. We present results for estuarine water collected at the Skidaway Institute of Oceanography dock on June 1, 2018.

Blank samples were collected for both the estuarine water and the aerosol particle samples. For estuarine water blanks, precleaned amber glass bottles were filled with 100 mL ultrapure water and handled the same as the estuarine water. For the aerosol particle blanks, aluminum substrates were loaded in the MOUDI, which was connected in line with the inlet and vacuum pump and sat for 1 min with no air flow. Substrates for the blanks were handled the same as for the samples, and a corresponding blank substrate was collected for each MOUDI stage. The 560 nm to 1000 nm and 1.8 to 3.2 µm size bin blanks were used in this study.

1.6.   *Mass spectrometric analyses of aerosol particle and estuarine water extracts*
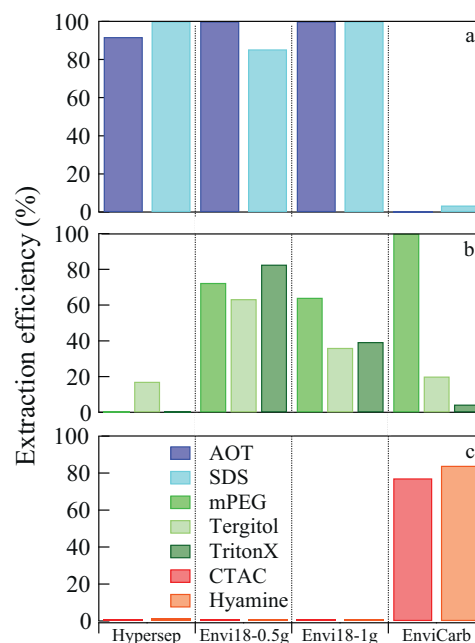
Extracted aerosol particles and estuarine water were filtered and processed through the SPE cartridges, as described for the standard solutions. These extracts were first analyzed with the ES-IT-MS, using the same procedure and instrument parameters as the standard solutions. The mass spectrum of the corresponding blank sample was subtracted from each sample mass spectrum. Major organic peaks were initially selected as those with signal to noise greater than 10 and further compared to the background spectra to ensure no overlap. The concentrations of surfactants in the estuarine water samples were calculated by assuming the organic compounds in the mass spectra were extracted and ionized similarly to each surfactant standards. The area for each individual peak and the standard calibration curves were used to calculate an estimated concentration range for each mass spectral peak.

Additional analyses were done using an electrospray ionization quadrupole time of flight mass spectrometer (ESI-Q-TOF-MS; Impact II, Bruker, USA). This instrument has high resolution and high mass accuracy, which contributes to the assignment of specific formulas to the ion peaks. The surfactant extracts were injected using a loop injection, with a flow rate of 1.33 µL/min. The ESI was operated in positive and negative ionization modes, consecutively, with a capillary voltage of 4 kV. Spectra were acquired in the range of 50–1500 Da. Samples were injected 2 or 3 times for reproducibility.

The resulting high resolution and high mass accuracy spectra were processed to assign chemical formulas to the peaks using the formula calculation software (DataAnalysis, Bruker). Calculations were done with C_{0-50}, H_{0-100}, O_{0-20}, N_{0-20}, S_{0-4}, and P_{0-4}. Potential formula identifications were further constrained by comparing theoretical and observed isotope peak ratios. The mass errors between observed m/z and theoretical m/z values were limited to less than 6 ppm. Final formula assignments limited the mass errors while ensuring isotope peak ratio matches. In the positive ESI mode, masses were assigned assuming ionization through protonation $[M + H]^+$, ammonium addition $[M + NH_4]^+$, or the loss of a counterion $[M - X]^+$. In the negative ESI mode, masses were assigned assuming ionization through deprotonation $[M - H]^-$ or the loss of a counterion $[M - Y]^-$.

1.7.   *Surface tension of estuarine water and extracts*

The surface tensions of estuarine water samples were measured using a pendant drop tensiometer (OCA 15EC, Data-

Fig. 1 – Extraction efficiencies for (a) anionic, (b) nonionic, and (c) cationic surfactants in pure water containing all seven surfactants (100 mL) for each of the four SPE cartridges. The uncertainties are within ± 5% for all surfactants.

physics, Germany) (Frossard et al., 2019a; Gérard et al., 2016) prior to filtering and extraction. Surface tension devoid of organics was calculated using the salinity of the estuarine water and the temperature of the water at the time of the measurement (Frossard et al., 2019a; von Boguslawski and Krümmel, 1907). Surface tension depression was calculated as the difference between the calculated surface tension devoid of organics and the measured surface tension of the solution (Frossard et al., 2019a). Additionally, the surface tension of the surfactant extracts from the estuarine water, dissolved in 40 µL of ultrapure water, were measured (Frossard et al., 2019a).

2.   Results of method development for standard surfactants

2.1.   *Extraction efficiencies of standard surfactants*

To determine the extraction efficiency of each cartridge type, the standard solutions containing the surfactants from each class were extracted with the four SPE extraction cartridges. The extraction efficiencies were calculated using Eq. 1 and are shown for each cartridge and surfactant standard in **Fig. 1**. Anionic surfactants were extracted at the highest efficiency across all three C18 cartridges (Hypersep, Envi18-0.5g, and Envi18-1g). The highest extraction efficiency for the anionic surfactants was found using the Envi18-1g cartridge, which collected both anionic surfactants at nearly 100% efficiency (**Fig. 1**). The nonionic surfactants were collected using both the Envi18-0.5g and Envi18-1g cartridges at higher efficien-

cies than with the Hypersep cartridge (**Fig. 1**). The extraction efficiency of nonionic surfactants was above 60% for all three nonionic surfactants using the Envi18-0.5g cartridge. The lower extraction efficiency of the nonionic surfactants compared to previous studies may be due to the capability of the nonionic organics to ionize through ESI (Banerjee and Mazumdar, 2012; Kebarle, 2000). Cationic surfactants were not extracted at detectable concentrations using the Hypersep, Envi18-0.5g, or Envi18-1g cartridges. Using the EnviCarb cartridge, the cationic surfactants were extracted with greater than 75% extraction efficiency. The variability in extraction efficiencies across the different surfactant standards (**Fig. 1**) may be due to the differences in their molecular structures (**Table 1**) (Gérard et al., 2016).

Based on these results, the most efficient method for extracting the three different surfactant types from seawater and aerosol particles is to use two extractions, one with the Envi18-0.5g cartridges for anionic and nonionic surfactants and one with the EnviCarb cartridges for cationic surfactants. Together, these cartridges give total extraction efficiencies of greater than 85%, 75%, and 60% for anionic, cationic, and nonionic surfactants, respectively.

Because the Envi18-0.5g cartridge does not retain cationic surfactants (**Fig. 1**), the extraction of the three types of surfactants can be done in series, if sample volumes are limited, starting first with the extraction of anionic and nonionic surfactants in the Envi18-0.5g cartridge and followed by the extraction of cationic surfactants in the EnviCarb cartridge. With this method, there is also the potential for nonionic surfactants not retained in the Envi18-0.5g cartridge to be retained in the EnviCarb cartridge, depending on their structure and affinity for the cartridge. For larger available sample volumes (i.e. bulk seawater), parallel samples can be done instead to reduce the potential for sample error using the SPE extractions in series.

2.2. Extraction efficiencies of surfactants in solutions with interferents

Using these cartridges, we quantified the effects of potential interferents in seawater and aerosol particles on the extraction efficiencies of the surfactants. Extraction efficiencies were calculated for the same surfactant standards, using an addition of 35 g/L sea salt to each solution (**Table 1**). **Table 1** shows standard surfactants in 100 mL samples retain high extraction efficiencies with the added salt. Extraction efficiencies of surfactants may be reduced with the addition of high concentration of salts due to a change in the surfactant solubility and thus retention in the solid phase due to changes in confirmation (Kruger et al., 2011) or the formation of ion pairs between the salt ions and the oppositely charged surfactants, in place of the pairs formed with the surfactant counterions (**Table 1**). However, **Table 1** shows that the addition of salt did not drastically reduce the extraction efficiency of the standard surfactants. Additionally, **Table 1** demonstrates that the wash steps included in this procedure (0.1% TEA in ultrapure water) are sufficient in removing high concentrations of salt from the SPE cartridges, which have the potential to interfere with ionization of the surfactants in the mass spectrometer. If there was an increase in surfactant solubility and a cor-

responding decrease in surfactant retention on the cartridge from the addition of the salt, the TEA wash step would not influence the extraction efficiencies and they would remain low.
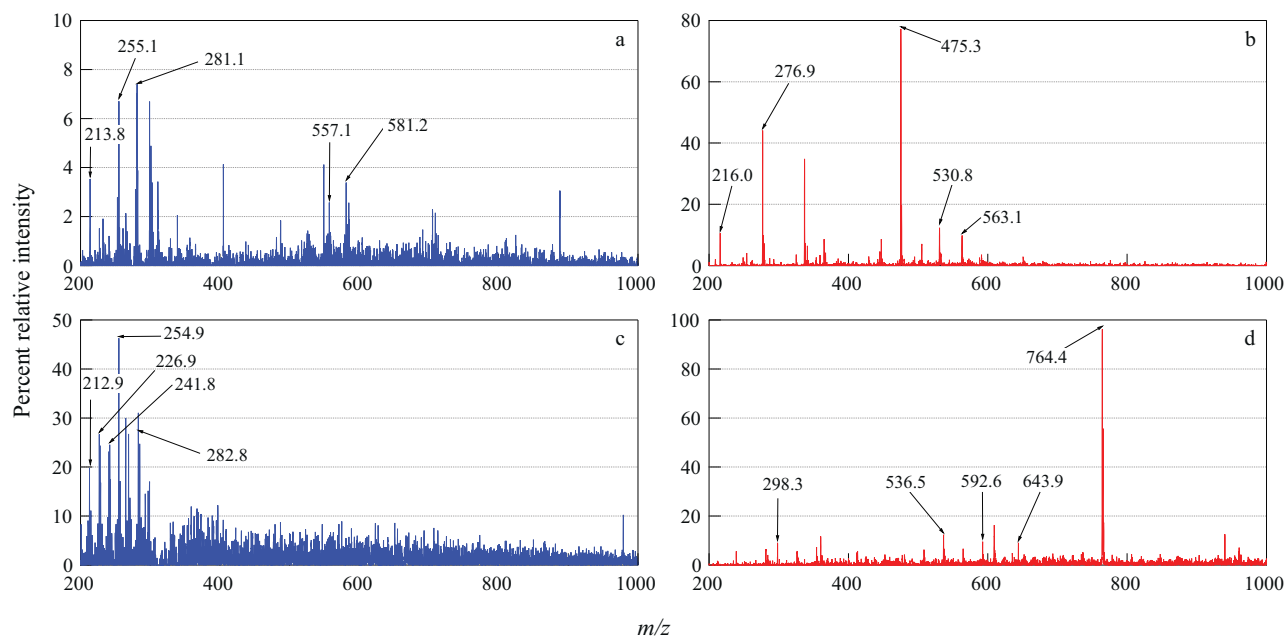
Table 1 also includes the extraction efficiencies of 10 mL standards containing 0.002 g/L of sea salt and surfactants at concentrations an order of magnitude lower than those in the 100 mL standards. Extraction efficiency decreased by less than 12% for all of the standard surfactants when salt was added, except for Triton X-100, which had a 36% decrease. The order of magnitude lower concentrations of surfactants in these model aerosol extract solutions may have a larger influence on the extraction efficiency than the presence of salt. The 100 mL standard solutions maintained high extraction efficiencies even though they contained higher mass ratios of salt to surfactants than the 10 mL standard solutions. Thus, a smaller dilution factor in preparation for the mass spectrometric analysis could be used instead to obtain better signal for samples containing low concentrations.

Extraction efficiencies were also calculated with the addition of a small organic compound, glucose, to measure the influence of a non-surfactant organic on the extraction efficiency of the surfactant standards. Overall, the addition of glucose (MilliporeSigma) at 1 µM (similar to concentrations observed in seawater (Vaccaro et al., 1968)) reduced the extraction efficiencies of the standard surfactants by 8% and 14% for the anionic and nonionic surfactants, respectively. The biggest difference in extraction efficiency was observed for the cationic samples, which had an apparent decrease in extraction efficiency to about 50%. This apparent decrease in extraction efficiency may be due to ionization competition between the glucose and cationic surfactants in the mass spectrometer. Because this concentration of glucose is similar to concentrations observed in seawater, this decrease in extraction efficiency can be considered an upper bound. To reduce this interference, samples can be extracted in series, such that most of the smaller organics are extracted with the anionic and nonionic surfactants instead of with the cationic surfactants.

2.3. Method developed for surfactant extraction and characterization

We applied the extraction method using Envi18-0.5g and EnviCarb cartridges to the samples collected from Skidaway Institute of Oceanography. Samples of 100 mL of estuarine water were extracted through each cartridge in parallel. Extracts were rehydrated using methanol and water with the corresponding additions of the reference standards for the positive and negative modes to quantify the concentrations of surfactants. This quantification assumes that surfactants in ambient water samples were extracted and ionized similar to the standard surfactants. Aerosol particles collected using the MOUDI sampler were extracted from the aluminum substrates using the method in Section 1.5. The resulting 10 mL samples were processed first through the Envi18-0.5g cartridges to extract the anionic and nonionic surfactants. The fraction of the sample that passed through the cartridge without being retained was collected and then processed through the EnviCarb cartridge to retain the cationic surfactants. This order is based on the very low extraction efficiency of the cationic surfactant standards in the Envi18-0.5g (**Fig. 1,**

Fig. 2 – Mass spectra of organics extracted using SPE cartridges from aerosol particles (a and b) and estuarine water samples (c and d). Mass spectra are shown for the negative (a and c) and positive (b and d) ionization modes. The negative spectra correspond to extracts from the Envi18-0.5g cartridge, targeting anionic and nonionic surfactants. The positive spectra correspond to extracts from the EnviCarb cartridge, targeting cationic surfactants. Major peaks of interest are listed for each.

Section 3.1). The aerosol particle surfactant extracts were prepared for mass spectral analyses the same way as the water samples. Results from the characterization of the aerosol particle and estuarine water extracts using ESI-IT-MS and ESI-Q-TOF-MS are presented in the following Section 2.1.

3.   Surfactants in aerosol particles and estuarine water

3.1.   *Quantification of surfactants using ESI-IT-MS*
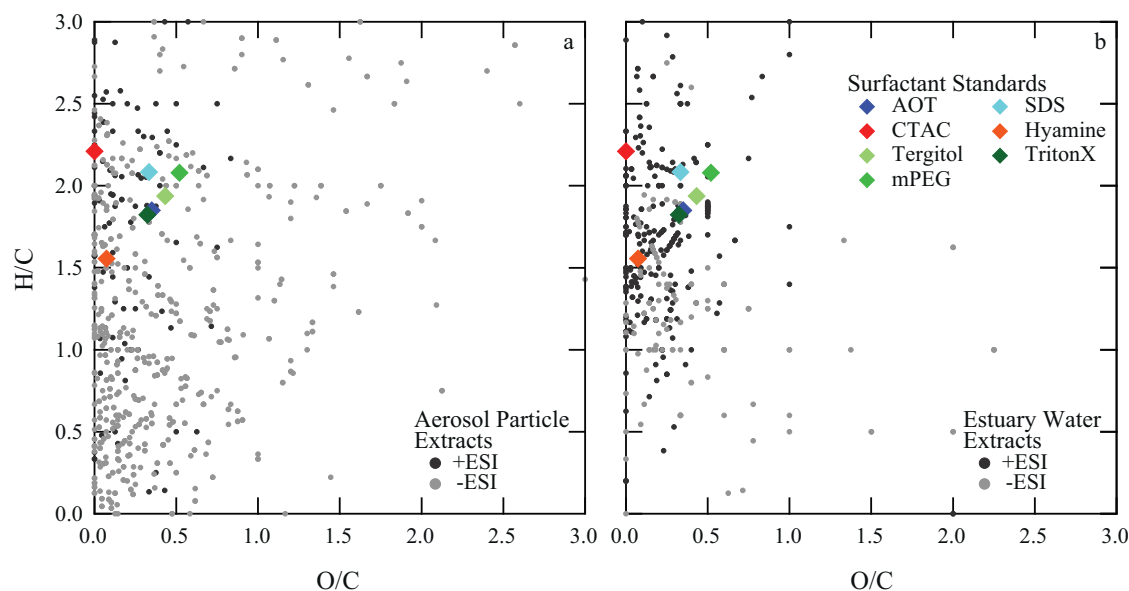
Organic and surfactant compounds were extracted from aerosol particle and estuarine water samples collected at Skidaway Institute of Oceanography. Clear signals representing large organics and/or surfactants are shown in the spectra of both sample types for the negative and positive ionization modes (**Fig. 2**). The positive ionization spectra (**Fig. 2b** and **2d**) include organics extracted with the EnviCarb cartridge, which had the highest extraction efficiencies for cationic surfactants, suggesting that the organics identified in those spectra are likely cationic. The negative ionization spectra (**Fig. 2a** and **2c**) represent organics extracted with the Envi18-0.5g cartridge, which had the highest extraction efficiencies for nonionic and anionic surfactants, suggesting these are a mixture of anionic and nonionic surfactants.

In the estuarine water, the major signal peaks are 298.3, 536.5, 592.6, 643.9, and 764.4 *m/z* from the positive ionization (EnviCarb cartridge extraction, **Fig. 2d**) and 212.9, 226.9, 241.8, 254.9, and 282.8 *m/z* from the negative ionization (Envi18-0.5g cartridge extraction, **Fig. 2c**). Using the concentrations calculated from the cationic calibration curves for each of the major

signal peaks in the positive ionization mode, concentrations of individual signals, assumed to be cationic surfactants, ranged from 0.02 to 1.3 µM. The signal and resulting concentration at 764.4 *m/z* were significantly higher than that of the other peaks, suggesting a different ionization efficiency for that signal, and thus, it is not included in the concentration total. The resulting total cationic surfactant concentration in estuarine water ranges from 0.21 to 0.66 µM. The concentrations calculated from the anionic calibrations curves for each of the major signals in the mass spectrum of the negative ionization mode range from 0.02 and 0.18 µM, with a total anionic concentration in the range of 0.27 to 0.76 µM.

These concentrations can be considered lower bounds on the actual concentrations of these species in the estuarine water, since smaller organic compounds are present in estuarine water and may reduce the extraction and/or ionization efficiency of the surfactants (Section 2.2). With a calculated presence of small organic compounds, such as glucose, the total concentrations could be as high as 0.32 to 0.95 µM for cationic surfactants and 0.29 to 0.83 µM for anionic and nonionic surfactants.

The concentration of total organics assumed to be surfactants from the estuarine water, in the range of 0.48 to 1.42 µM, are comparable to total surfactant concentrations previously measured in seawater (<0.03 to 0.52 µM; Frossard et al., 2019a). That study found more than 85% of the surfactant mass to be anionic, with no presence of cationic surfactants (Frossard et al., 2019a). The higher concentration of cationic surfactants in the estuarine water, compared to that study, can be attributed to the targeted extraction of cationic surfactants and the associated high extraction efficiency in this

Fig. 3 – Van Krevelen diagrams of aerosol particle (a) and estuarine water (b) surfactant-like organics extracted using both the Envi18-0.5g (negative ionization mode, -ESI) and the EnviCarb (positive ionization mode, +ESI) cartridges. The H/C and O/C ratios of the surfactant standards are included in both panels as diamond markers.

study. Here, cationic surfactants make up 43% to 47% of the total surfactant concentration.

The aerosol particle mass spectra followed similar trends to those from the estuarine water samples, with higher signal-to-noise in the positive ionization mode (EnviCarb cartridge extraction), compared to the negative ionization mode (Envi18-0.5g cartridge extraction). The major signal peaks from the positive ionization mode are 216.0, 276.9, 475.3, 530.8, and 563.1 m/z (**Fig. 2b**), and those from the negative ionization mode are 213.8, 255.1, 281.1, 557.1, and 581.2 m/z (**Fig. 2a**).

The major signal peaks in the aerosol particle extractions are different from those in the estuarine water samples, for both the positive and negative ionization modes. This suggests different organics are present in the aerosol particle and estuarine water, which may be due to differences in sources of organics or in differences in processing. Additionally, given the low resolution of the ESI-IT-MS analyses, some of the ion peaks present in **Fig. 2** may represent non-surfactant organic molecules. Further analyses with high resolution mass spectrometry were completed to investigate the presence of surfactants in these organic extracts.

3.2. Characterization of surfactants using ESI-Q-TOF-MS

Aerosol particle and estuarine water extracts were analyzed using ESI-Q-TOF-MS, and the measured formulas were used to calculate the associated O/C and H/C ratios for each. These ratios are used to group chemical formulas based on functional groups (Osterholz et al., 2016; Waggoner et al., 2017). Surfactants generally have low O/C ratios (< 0.5) and high H/C ratios (> 1.5), as demonstrated by the ratios of surfactant standards in this study (**Fig. 3**) and those tentatively identified in previous work (Cochran et al., 2016).

Fig. 3 shows the van Krevelen diagrams of the molecules characterized from the aerosol particle and estuarine water extracts. These include molecules extracted using the EnviCarb cartridges and the Envi18-0.5g cartridges, with each ionized in both the positive and negative ESI modes. Cationic, anionic, and nonionic molecules were present in the extracts from the aerosol particles and estuarine water. Additionally, the H/C and O/C ratios from both the positive and negative ESI modes are similar suggesting that the overall formula of the cationic and anionic/nonionic molecules contain similar functional groups and organic classes.

Both the aerosol particle and estuarine water extracts have low O/C ratios and high H/C ratios, consistent with the surfactant standards (**Fig. 3**). The estuarine water extracts contain H/C ratios clustered mainly around 1 to 2, with an overall average H/C ratio of 1.55. There is a larger spread in the H/C ratios of the aerosol particles with an overall average H/C ratio of 1.24. For both extract types, the O/C ratios were low, generally falling in the range of 0 to 1, with the majority less than 0.5. Additionally, the aerosol particle extracts have more formulas with O/C ratios greater than 1, with an average O/C ratio of 0.41, whereas the estuarine water extracts had an average O/C ratio of 0.29. The difference between these ratios indicates that the molecules in the aerosol particle extracts were more oxidized than those in the estuarine water extracts. This may be a result of atmospheric processing of the aerosol particle extracts, including reactions with other atmospheric species or photochemical reactions. Alternatively, this may be indicative of different sources of molecules in the aerosol particle and the estuarine water extracts.

The O/C and H/C ratios of the aerosol particle and estuarine water extracts are similar to the O/C and H/C ratios found in previous mass spectrometry measurements of generated sea spray aerosol particles, using negative ionization

(Cochran et al., 2016). The formulas for the ions they identified had low O/C ratios and high H/C ratios (Cochran et al., 2016), similar to the formulas observed in this study and in surfactant standards. Additionally, the formulas identified here include those similar to fatty acids, both saturated ($C_XH_{2X}O_2$) and unsaturated ($C_XH_{2X-2,4,6}O_2$), with high H/C and low O/C ratios, consistent with the formulas identified by Cochran et al. (2016) to be surfactants.

To confirm the surfactant-like nature of the organics characterized in this study, surface tension measurements were also used. Surface tension measurements of the estuarine water, prior to surfactant extraction, indicate a surface tension depression of 1.85 mN/m compared to the calculated surface tension, devoid of organics, at the measured salinity. This is similar to surface tension depressions measured in previous studies of bulk seawater from different regions, which were attributed to the presence of seawater surfactants (Frossard et al., 2019a; Long et al., 2014). The surface tension depression in the estuarine water samples also indicates the presence of surfactants in these samples.

Additionally, the surface tension of the surfactant extract dissolved in 40 μL of water was 53.4 mN/m. This surface tension was measured after extraction of a duplicate sample using the Hypersep cartridge. Thus, the extract may not have included all of the surfactants extracted by the more efficient Envi18-0.5g cartridge and likely did not include cationic surfactants extracted by the EnviCarb cartridge, which were included in the mass spectrometric analyses. Even without the cationic surfactants and with the lower extraction efficiency, the surface tension of the extract is much less than that of pure water (72 mN/m), indicating the presence of surfactants in the extract. This large surface tension depression is similar to that of previous measurements of the surface tension of surfactants extracted from seawater (Frossard et al., 2019a) and atmospheric aerosol particles (Gérard et al., 2016). These surface tension measurements add further support to the characterization of the extracted organics as surfactants.

The organic compounds from atmospheric aerosol particles and estuarine water samples extracted with this two cartridge solid phase extraction method and observed with mass spectrometry likely have surfactant-like properties. The surface tension depression and the H/C and O/C signatures of the extracted organics are consistent with those of organics previously tentatively identified as surfactants (Cochran et al., 2016).

4.   Conclusions

In this study, we demonstrate an optimized method for extracting and characterizing anionic, cationic, and nonionic surfactants from seawater and atmospheric aerosol particles. By combining two solid phase extractions, using Envi18-0.5g cartridges to target anionic and nonionic surfactants and EnviCarb cartridges to target cationic surfactants, this method achieves extraction efficiencies greater than 85%, 75%, and 60% for anionic, cationic, and nonionic surfactant standards, respectively.

Organic compounds extracted with these two solid phase extractions from estuarine water and atmospheric aerosol particles collected at Skidaway Island, GA were identified to be surfactant-like. The organic compounds extracted from both sample types significantly reduced the surface tension of water and had H/C and O/C ratios indicative of aliphatic-rich molecules. Together, these compounds, observed in both the positive and negative ESI modes after extractions targeting cationic and anionic/nonionic organics, respectively, are consistent with compounds previously identified as surfactants (Frossard et al., 2019a; Cochran et al., 2016).

While previous work has focused on the anionic fraction of surfactant-like compounds in seawater and marine aerosol particles (Frossard et al., 2019a; Cochran et al., 2016), this study shows the presence of surfactant-like material from the three ionic classes in both estuarine water and atmospheric aerosol particles. In estuarine water, total cationic surfactant concentrations were measured in the range of 0.21 to 0.66 μM, making up 43% to 47% of the total measured surfactant mass.

This method can be applied to measure the molecular formula and estimated concentration ranges of anionic, cationic, and nonionic surfactant-like compounds in seawater and aerosol particle samples. Future work using this method can be done to identify the structure of surfactants from both extractions, using the high resolution mass spectra. These structures can be compared to identify potential changes due to atmospheric aging of aerosol particles or the emission of primary marine aerosol particles from seawater.

Acknowledgements

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2021.01.026.

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