Video Article

Extraction and Characterization of Surfactants from Atmospheric Aerosols

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Abstract

Surface-active compounds, or surfactants, present in atmospheric aerosols are expected to play important roles in the formation of liquid water clouds in the Earth’s atmosphere, a central process in meteorology, hydrology, and for the climate system. But because specific extraction and characterization of these compounds have been lacking for decades, very little is known on their identity, properties, mode of action and origins, thus preventing the full understanding of cloud formation and its potential links with the Earth's ecosystems.

In this paper we present recently developed methods for 1) the targeted extraction of all the surfactants from atmospheric aerosol samples and for the determination of 2) their absolute concentrations in the aerosol phase and 3) their static surface tension curves in water, including their Critical Micelle Concentration (CMC). These methods have been validated with 9 references surfactants, including anionic, cationic and non-ionic ones. Examples of results are presented for surfactants found in fine aerosol particles (diameter <1 μm) collected at a coastal site in Croatia and suggestions for future improvements and other characterizations than those presented are discussed.

Video Link

The video component of this article can be found at https://www.jove.com/video/55622/

Introduction

Clouds are essential in the Earth’s atmosphere, for the hydrology of most environments and ecosystems, and for the climate system. But some aspects of their formation mechanisms are still not understood, in particular the contributions of the chemical compounds present in the aerosol particles that act as condensation nuclei. Theory predicts that surface-active compounds, or surfactants, present in aerosol particles should strongly enhance cloud droplet formation by lowering their surface tension, thus their formation energy. But these effects have remained elusive to observation for decades and the role of surfactants on cloud formation is currently denied by a large part of the atmospheric community and ignored in all cloud investigations and atmospheric and climate models.

One reason for the lack of understanding of the role of aerosol surfactants in cloud formation has been the absence of method to isolate and characterize them. Unlike samples from other environments, the analysis of atmospheric samples faces recurring challenges such as very small sample volume and mass (here, typically between 10 and 100 μg) and chemical complexity (mixtures of salts, minerals, and numerous organics). To overcome these challenges and improve the understanding of aerosol surfactants some methods have been recently developed by our group to 1) extract specifically these compounds from atmospheric aerosol samples, 2) determine their absolute concentrations in the aerosol phase and 3) determine their surface tension curves in water, including their Critical Micelle Concentration (CMC), the concentration at which the surfactants are saturated at the surface and start to form micelles in the bulk. The latest versions of these methods are presented in this paper.

Further improvements and other types of characterizations, that could be used in complement to those presented, will be discussed. Recent applications of these methods have already shown how such analyses can improve the understanding of the role of surfactants in cloud formation, by evidencing this role itself, determining the surfactant concentrations in atmospheric aerosols and mode of action in cloud droplet formation, evidencing their biogenic origin, and explaining their lack of observation by classical instruments.
Protocol

1. Prepare the Material for the Protocol as Listed in Table 1

| Material | Preparation/Washing |
|----------|---------------------|
| **Consumables** (plastic syringes, needles, 4-mL vials, Pasteur pipettes, micropipette tips) | To be used directly without pre-treatment and discarded after use. |
| **Reusable glassware** (beakers for ultrapure water; 15, 30, and 60 mL bottles with corks; tubes for solid phase extraction (SPE); and magnetic stirring bars) | Wash with ethanol (only for the vials used for the colorimetric method). Rinse sequentially with tap water, ethanol, tap water, and ultrapure water. Fill the glass vials and beaker containing the corks, magnetic stirrers, and SPE tubes with ultrapure water and place them in an ultrasonic bath for 15 min. Remove the water and rinse with ultrapure water. Dry the glassware in air at room temperature. Once dried, close all bottles and store them under cover to avoid dust collection. To avoid contamination, use distinct glassware for the water extraction and the colorimetric method. |
| **Tweezers and scissors** | Wash with ethanol and then ultrapure water. Dry with compressed air. |
| **Glass Petri dishes and lids** | Wash with tap water and a brush and then with ethanol. Rinse with tap water and then ultrapure water. Dry in air at room temperature. Once dried, close the boxes and store them under cover to avoid dust collection. |
| **SPE vacuum manifold** | Wash with ethanol and then ultrapure water. Dry with compressed air. |
| **Quartz cuvette (for UV-Vis analysis)** | Wash with ethanol and rinse with tap water and then ultrapure water. Dry with compressed air. |

Table 1: List of material and glassware used for the protocol, including their preparation and washing.

2. Handling of the Aerosol Samples

NOTE: The extraction method presented here has been developed for atmospheric aerosol samples collected on Quartz fiber filters of a total weight of at least 8 µg. The method for collecting aerosol samples on filters in the atmosphere will not be explained here but numerous descriptions can be found in the literature, such as references 2,3,4,5,6 Only the following steps are underlined.

1. Number each individual filter. **NOTE:** throughout the entire protocol the filters should be manipulated with clean tweezers and held by their edge.
2. Pre-condition the filters and aluminum foils or glass Petri dishes before sampling by baking them at 773 K for 6 h.
3. Pre-weigh, under controlled temperature and humidity conditions, the filters using a microbalance having a precision of at least 1 µg, to determine pre-sample weight.
4. Take blank samples regularly at the beginning, during, and at the end of the sampling period, by placing a filter on the filter holder of the sampler but keeping the pump off for the same duration as for the actual sample collection (e.g. if the sample collection lasts 24 h, the blank filter should be left in the sampler, with the pump off, for 24 h). Analyze these blanks with the same protocol as for the actual samples.
5. As soon as possible after sampling, pack the filters in containers (backed aluminum foils or glass Petri dishes) and store them in a freezer at -18 °C (255 K) until analysis.
6. Leave the filters to equilibrate in a desiccator for 24 h prior to weighing. Determine each sample volume (collected aerosol mass on filters) by weighing it after sampling (and subtract pre-sampling weight) under the same controlled temperature and relative humidity as during pre-weighing.

3. Extraction of Surfactants from Aerosol Samples

1. Water extraction
1. Immerse the filter samples in ultrapure water for 2 h at 279 ± 1 K in glass Petri dishes, close the lid and shake the Petri dishes while holding them flat, about every 30 min. 

NOTE: 47-mm filters are immersed in 7 mL and 150-mm ones in 35 mL. With 120 mm glass Petri dishes, the 150 mm filters need to be cut in four pieces with clean scissors before to be placed in the dish.

2. Clean a syringe filters (0.4 µm PVD) with 3 x 1 mL ultrapure water.

3. Filter the solution obtained in step 3.1.1 with the clean syringe filter and place it in a pre-weighted 60 mL glass bottle. Rinse the Petri dish with 5 mL of ultrapure water, filter the water with the syringe filter and add it to the solution in the 60 mL glass bottle. Then weigh the 60 mL glass bottle containing the solution to determine the volume of filtered water and the surfactant concentration in step 4.4.5.

2. **SPE (Solid Phase Extraction) extraction**

1. Attach the SPE silica based C18 cartridges (see Materials List for details about the cartridges) onto the SPE vacuum manifold, which is itself connected to a pump.

2. Wash the cartridges by flowing 6 mL of acetonitrile with a flow rate at 1 mL/min and applying a vacuum with the pump. Repeat with 6 mL of ultrapure water. Stop the pump to maintain the water level high enough and keep the cartridge wet.

3. Flow the sample obtained in step 3.1.3 through the SPE cartridge at a rate of less than 1 mL/min.

4. Flow 1 mL ultrapure water though the cartridge for cleaning and dry the cartridge by applying a stronger vacuum on the SPE set-up.

5. Elute the surfactant fraction absorbed on the column by flowing 4 mL of acetonitrile through it at a flow rate of less than 1 mL/min.

1. Evaporate the obtained acetonitrile solution with a flux of N2 to obtain a dry surfactant extract and re-dissolve the dry extract in 60 µL of ultrapure water.

NOTE: The 60 µL extracts obtained from this method can then be used as parent solution for various characterizations of the surfactants.

3. **Determination of the extraction efficiencies**

NOTE: The efficiencies of the extraction method for different types of surfactants need to be determined for the determination of their absolute concentrations in Section 4. For this, the following protocol needs to be applied to reference surfactants such as, for instance, sodium dodecyl sulfate (SDS), dioctyl sulfosuccinate sodium (AOT), benzyltetradecyl dimethylammonium (zephiramine), cetyltrimethyl ammonium chloride (CTAC), (1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol (see Materials List), polyethylene glycol dodecyl ether (see Materials List), surfactin, rhamnolipid, or L-α-phosphatidylcholine.

1. Spike the reference aqueous standard solutions (10⁻⁸ to 10⁻⁴ moles of surfactants in 1 mL ultrapure water) on clean quartz filters (grammage 0.85 g m⁻²) with a micropipette. In parallel, add the same amount of these solutions directly in vials as “initial solutions”.

2. Dry the filters (placed in Petri dishes) in a desiccator for 24 h and extract the filters with surfactants according to the protocol in Section 3.1-3.2.

3. Measure the concentration of the reference compounds in the initial (solutions of references in vials from step 3.3.1) and extracted solutions (from step 3.3.2) with the methods described in Section 4. The extraction efficiencies are determined as the ratio of these concentrations.

NOTE: Typically, in this work, for SDS and AOT (anionic surfactants), this efficiency was found to be 65 ± 10%, for zephiramine and CTAC (cationic surfactants), it was 20 ± 5%, and for (1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (see Materials List), Polyethylene glycol dodecyl ether (see Materials List), Surfactin, Rhamnolipid, and L-α-Phosphatidylcholine (non-ionic surfactants) it was 90 ± 10%.

4. **Extraction of the total surfactant fraction in samples**

NOTE: To verify that the proposed extraction method removes all the surfactants present in the analyzed samples (i.e. all the compounds lowering their surface tension), the following test can be performed.

1. Measure the surface tension (see Section 5) of a known solution of reference compound (or of a sample extract) after the first extraction (step 3.1.3). It should be around 50 mN m⁻¹.

2. Measure the surface tension of the solution left after the second extraction steps, in step 3.2.3. This value should be close to 72.8 ± 1 mN m⁻¹, the one of pure water, showing that most or all the surface-active compounds present in the samples have been removed by the extraction.

4. **Determination of Surfactant Aerosol-phase Concentrations**

NOTE: A colorimetric technique has been chosen for the determination of aerosol-phase surfactant concentrations, which provides absolute concentrations and has adequate sensitivity for surfactants in environmental samples. But it requires to measure separately the concentrations of anionic, cationic and non-ionic surfactants because different reagents have to be used for each surfactant type. All the solutions for the following protocol must be prepared with micropipettes for accuracy and all the reactions must be performed in glass vials.

1. **Colorimetric titration of anionic surfactants**

1. Prepare a solution of acetate buffer in water at pH = 5 (sodium acetate solution 0.2 M / acetic acid solution 0.2 M, 70/30 in volume) with a volume of at least n 200 µL, where n is the number of samples to be analyzed.

2. Prepare a solution of EDTA 0.1 M with a volume of at least n x 100 µL, where n is the number of samples to be analyzed.

3. Prepare a solution of sodium sulfate 1 M in water with a volume of at least n x 500 µL, where n is the number of samples to be analyzed.

4. Prepare a solution of ethyl violet (C₁₁H₂₁N₂O₂) 0.49 g L⁻¹ in water with a volume of at least n x 200 µL, where n is the number of samples to be analyzed.

5. If starting from the 60 µL sample extracts obtained in Section 3, dilute them to 10 mL with ultrapure water using micropipettes in a 60 mL glass bottle with a lid. Otherwise, take 10 mL of sample and add 200 µL of acetate buffer solution, 100 µL of the EDTA solution, 500 µL of the sodium sulfate solution and 200 µL of the ethyl violet solution using micropipettes.

6. Add 2.5 mL of toluene to the solution with a micropipette, a magnetic stir bar, and stir for 1 h at 500 rpm.
7. Leave the aqueous and organic phases to set for about 10 min. Once they are separated, remove the toluene phase (upper phase) with a Pasteur glass pipette to perform the UV-vis analysis (see Section 4.4).

2. Colorimetric titration of cationic surfactants
   1. Prepare a solution of acetate buffer in water at pH = 5 (sodium acetate solution 0.2 M/acetic acid solution 0.2 M, 70/30 in volume) with a volume of at least n x 1 mL, where n is the number of samples to be analyzed.
   2. Prepare a solution of disulfine blue (C27H12N2O6S2) at 2.58 g L\(^{-1}\) in a 90:10 water/ethanol mixture (diluting the dye first with the volume of water and then adding the volume of ethanol), with a volume of at least n x 500 µL, where n is the number of samples to be analyzed.
   3. Place 10 mL of sample in a 30 mL glass bottle with a lid and add 1 mL of the acetate buffer solution and 500 µL of the disulfine blue solution using micropipettes.
   4. Add 2.5 mL of chloroform with a micropipette, a magnetic stir bar, and stir for 1 h at 500 rpm.
   5. After leaving the aqueous and organic phases to separate for about 10 min, remove the chloroform (lower phase) with a syringe to perform the UV-Vis absorption analysis (see Section 4.4).

3. Colorimetric titration of non-ionic surfactants
   NOTE: For the titration of non-ionic surfactants, it was not possible to identify a dye reacting with all non-ionic surfactants, but cobalt thiocyanate (Co(NCS)\(_2\)) was chosen as it reacts with the widest range of compounds.\(^{(1,19)}\)
   1. Prepare a solution of cobalt thiocyanate by mixing n x 0.62 g of ammonium thiocyanate and n x 0.28 g cobalt nitrate hexahydrate in n x 1 mL water, where n is the number of samples to be analyzed.
   2. Place 3 mL of sample in a 15 mL glass bottle with a lid and add 1 mL of the cobalt thiocyanate solution with a micropipette.
   3. Add 2 mL of chloroform with a micropipette, a magnetic stir bar, and stir for 1 h at 500 rpm.
   4. After leaving the aqueous and organic phases to separate for about 10 min, remove the chloroform (lower phase), using a syringe to perform the UV-Vis absorption analysis (see Section 4.4).

4. Calibration curves and quantification by UV-Vis spectroscopy
   1. Establish a calibration curve (absorbance vs concentration curves) for anionic surfactants by measuring the absorbance at 612 nm of series of known solutions of a reference compound, such as SDS or AOT.
      NOTE: Typically 12 solutions with concentrations between 0 and 5 µM (and including some repetitions) should be used to establish the curve.
      A unique calibration curve should be obtained with both anionic compounds (SDS and AOT) with a slope of ε = 0.37 ± 0.02 µM cm\(^{-1}\) and a detection limit of 0.054 µM, for all anionic surfactants.
   2. Establish a calibration curve for cationic surfactants by a similar approach, but measuring the absorbance at 628 nm and using reference compounds such as Zephiramine or CTAC.
      NOTE: the slope should be ε = 0.35 ± 0.05 µM cm\(^{-1}\) and the detection limit 0.059 µM, for all cationic surfactants.
   3. Establish a calibration curve for non-ionic surfactants by a similar approach, but for a range of concentration of 0 to 20 µM, measuring the absorbance at 317 nm, and using Polyethylene glycol dodecyl ether (see Materials List) as reference compound.
   4. To determine the concentrations of surfactant-dye complex in the organic solutions obtained in Section 4.1, 4.2 and 4.3, place ~1.5-2 mL of these solutions in a 1 cm quartz cell and measure its absorbance at 612, 628 and 317 nm, respectively, with an UV-Vis Spectrophotometer. Prior to each solution measurement, take a blank of the organic solvent (toluene for anionic surfactant method and chloroform for cationic and non-ionic surfactants methods)
      NOTE: Unlike for anionic and cationic surfactants, using cobalt thiocyanate as dye will give different calibration curves with different non-ionic surfactants. Using polyethylene glycol dodecyl ether, as suggested here, will underestimate the concentrations of most non-ionic surfactants, thus ensuring that the errors on the measurements are always of the same sign, i.e. underestimate actual concentrations. The slope using polyethylene glycol dodecyl ether as reference should give a slope of ε = 0.013 ± 0.001 µM cm\(^{-1}\) and a detection limit of 0.3 µM.
   5. Determine the total surfactant concentration in each sample as the sum of the concentrations of anionic, cationic, and non-ionic surfactants measured separately\(^{(6)}\) and after correcting each concentration by the extracted volume efficiency from step 3.1.3 and by the respective extraction efficiency determined in step 3.3.
      NOTE: The overall uncertainties in these total concentrations is estimated to 33%, mostly because of the uncertainties on the non-ionic surfactant concentrations.
   6. Determine the average surfactant concentrations in the aerosol sample by multiplying the concentration obtained for the extract by the ratio of the aerosol sample volume to the extract volume (60 µL).

5. Determination of the Surfactant Absolute Surface Tension Curves in Water
   1. Surface tension measurements by hanging drop tensiometry
      NOTE: For aerosol samples, surface tension measurements are best made with the hanging droplet method, as this is the method requiring the smallest sample volume (for details about the tensiometer, see Materials List). Although such measurements are performed on droplets of diameters between 1.4 and 2.4 mm, experiments have shown that the surface tension measured is identical to that of micron-size droplets containing the same surfactant concentration.\(^{(10,20)}\) Throughout the measurements, the temperature must be constant to at least ± 3 K, and the droplet volume should be monitored continuously to rule out evaporation effects. Each droplet must be left to equilibrate (the surface tension value does not vary any more) before to make a measurement and each measurement should be repeated 3 to 5 times.
      1. Start the tensiometer camera and software (see Materials List for references). Calibrate the tensiometer by measuring the surface tension of droplets of ultrapure water, following the protocol in steps 5.1.2-5.1.5 below.
2. Fill a 1 mL syringe with a Ø 0.30 mm needle (for σ <45 mN m\(^{-1}\)) or a Ø 0.51 mm (for σ >45 mN m\(^{-1}\)) needle with the surfactant solution obtained in step 3.2.6 and place it on the tensiometer, making sure that the needle tip is in the camera field.

3. Produce a droplet of diameter between 1 and 3 mm at the tip of the needle by pushing the piston.

4. Take a picture or a video of the droplet before it falls with the software.

5. Run the analysis function of the software to fit the droplet shape to the Young-Laplace equation and obtain a surface tension value. A noted above, this operation should be repeated several times for the same droplet until the surface tension does not vary any more, to ensure that the surfactants have reached equilibrium in the droplet.

NOTE: the overall uncertainties on these surface tension measurements are typically of ± (0.3-1.0) mN m\(^{-1}\).

2. Complete surface tension curves and CMC
   1. Measure the surface tension of the initial extract, obtained in step 3.2.6, following the protocol in 5.1.
   2. Measure the total surfactant concentration in the same extract, following the protocols in Section 4. This concentration and surface tension of this extract will provide the starting point of the curve.
   3. To plot the remainder of the curve, dilute the extract by a factor 2 by adding ultrapure water with a micropipette. Measure the surface tension of the diluted solution.
   4. Repeat step 5.2.2 until the solution has reached (or is close to) the surface tension of pure water (72.8 ± 1 mN m\(^{-1}\)). The surface tension values and dilution factors for each of these diluted solutions will provide the points defining the surface tension curve.
   5. Determine the average concentration of surfactant in the initial aerosol sample by multiplying the concentration in the extract by the ratio of the extract to sample volume.
   NOTE: As the aerosol sample volume is usually smaller than the 60 µL extract, the aerosol surfactant concentration is usually larger than the extract concentration, thus the furthest point on the x-axis of the curve.

6. Plot the surface tension curve (Figure 2). For this, place the first point corresponding to the conditions in the aerosol (x axis = surfactant concentration in the aerosol sample determined at step 5.2.5; y-axis = minimum surface tension measured in the 60 µL extract solution at step 5.2.1). Then place the second point corresponding to the 60 µL extract of step 5.2.1 (x-axis = surfactant concentration in the 60 µL extract; y-axis = minimum surface tension measured in the 60 µL extract solution). Then place the third point corresponding to the diluted aerosol extract of step 5.2.2 (x axis = surfactant concentration in the 120 µL diluted extract solution = concentration in the 60 µL extract solution divided by a factor of 2; y-axis: minimum surface tension measured in the 120 µL extract solution), and so on until the last measured surface tension (step 5.2.3)

7. Once the surface tension curve established, determine the CMC graphically by determining the intersection between the sharp slope and the minimum surface tension level (see Figure 2).
   NOTE: Only if the surfactant concentration in the extract is significantly above the CMC (above the sharp transition on the curve) the value of the CMC and of the minimum surface tension can be determined accurately. But if this concentration is lower than the CMC, the exact value of the CMC can not be determined and the surface tension of the extract will only give an upper limit of the one of the sample.

Representative Results

Note: Before being applied to atmospheric samples, all the protocols presented in this section have been tested with 9 reference surfactants and the surface tension curves, minimum surface tensions, and CMCs obtained were in excellent agreement with the literature.\(^{21,22}\)

1. Concentrations

   Fine aerosols (<1 µm in diameter, or “PM1”) samples were collected on Quartz fiber filters at the coastal site of Rogoznica, Croatia in February 2015. These samples were handled and extracted as described in Sections 2 and 3, respectively, of this manuscript. The concentrations for anionic, cationic and non-ionic surfactants and the total surfactant concentration in the aerosol sample volume, C\(_{surf,p}\) (M), were measured according to Section 4. The results are presented in Figure 1, and evidence the dominance of anionic and non-ionic surfactants among the surfactants measured.

2. Surface Tension of Sample and Surface Tension Curve for Extracted Surfactants

   Combining surface tension measurements as described in Section 5, and the concentration measurements, resulted in absolute surface tension curves for the same samples, as shown in Figure 2. These curves indicate the surfactant concentration in the aerosol sample and the surface tension of these samples ("σ\(_{min}\)" and allow to determine graphically the CMC values (Figure 2).
Discussion

In the protocol, all the critical steps have been detailed. They include the collection of the aerosols on filters, the extraction of surfactants from them (using a double extraction: a water extraction followed by a SPE extraction) and the analysis of the extracts (surface tension and concentration measurements).

For the whole method, a quality control has been made 1) by the application of the extraction and analysis method on blank filters (deviation <5 mN m⁻¹ compared with ultrapure water on the surface tension and absorbance under the detection limit for the colorimetric method), 2) by determining the extraction efficiency and their uncertainties including the reproducibility/repeatability, the % of extracted surfactants in a given range of concentration, 3) by checking the potential interferents on the colorimetric method, i.e. by checking that the method detects only the
targeted type of surfactant (anionic, cationic and non-ionic) and do not see the others as fully detailed in references\textsuperscript{4,6} by checking potential interferents from the aerosol extracts (inorganic salts, small acids) on the colorimetric method as fully detailed in reference\textsuperscript{6}.

To our knowledge, the extraction method for surfactants from atmospheric samples presented in this article is currently the most selective one in atmospheric chemistry. In particular it is much more selective than the simple water extractions performed in the past for the investigation of these compounds.\textsuperscript{11,23,24} The second extraction step is important as it has been shown to remove ionic components, such as inorganic salts and small organic acids, that are in large concentrations in the aerosol samples and interfere with the concentration measurements.\textsuperscript{5} This extraction method has also been shown to remove all the surfactants present in the samples, at the surface and in the bulk. The resulting extracts are thus concentrated enough to allow for accurate characterizations of these compounds.

However, in addition to surfactants, it is possible that other non-polar or mildly polar compounds are extracted from the atmospheric aerosols. For instance, “Humic-like Substances” (HULIS), that are usually extracted by similar methods\textsuperscript{25} and, depending on the sampling region, could be present in the extracts. These compounds are only mildly surfactant compared to the surfactants characterized in our samples,\textsuperscript{26,27,28} thus should not contribute significantly to the surface tension or CMC measured. However, they are polyacids and could interfere with the anionic concentration measurements. In the future, their contribution to the surfactant concentrations (i.e. whether or not they react with ethyl violet, the dye used to titrate anionic surfactants) will need to be determined. If their contribution is significant, extra steps could be added to the extraction method, to eliminate for instance all the compounds that are active in the UV-Vis or by fluorescence, which would include HULIS but not surfactants.

So far, no other method for the measurement of the surface tension of aerosols and of the surface tension curve for aerosol surfactants than the one presented in this manuscript is available. The hanging droplet technique is recommended for these measurements as it is the only one requiring sample volumes consistent with atmospheric samples. Optical techniques, measuring directly the surface tension on micron-size particles without any extraction, are being developed.\textsuperscript{10,20,29} So far, they are only applicable to laboratory-produced particles but could potentially someday be applied to atmospheric ones.

The colorimetric method presented in this work for the measurement of surfactant concentration has been applied previously to atmospheric aerosol samples\textsuperscript{13,14,30} but only to water extracts and not to double extracts, as in our method. This is an important difference as, as underlined above, the second extraction step removes compounds such as inorganic salts and small organic acids, which interfere with the concentration measurements.\textsuperscript{6}

An electrochemical technique, initially developed for seawater and larger aqueous samples, has also been used to measure the concentration of surfactants in atmospheric aerosols.\textsuperscript{10,32} This method is relative, i.e. the surfactant concentrations obtained depend on the reference compounds chosen and assume that the detection sensitivity of all surfactants is identical. The detection limit reported for this technique is 0.02 mg L\textsuperscript{-1} when using tetra-octylphenolethoxylate as reference, thus 0.03 μM, and comparable to the detection limit of about 0.05 μM for anionic and cationic surfactants by the colorimetric method. But because of the uncertainties in the determination of the non-ionic and total surfactant concentrations with the colorimetric method, it would be interesting to compare both methods (inter-calibration).

A few points in the presented methods could be further improved.

Another dye than cobalt thiocyanate that would detect all non-ionic surfactants and wit the same sensitivity would be very useful and reduce the main source of uncertainties in the current concentration measurements.

The extraction efficiency for cationic surfactants, currently estimated to 20%, could also be improved, as these compounds are often at the detection limit in atmospheric samples. This could be done, for instance, by using a specific SPE column.

The extractions and titration conditions could be further improved. For instance, using in parallel three different SPE set-ups, each optimized for a class of surfactants, could improve the extraction efficiency, and improve the quality of the procedure (less contamination risks). The optimum sorbent density of the SPE cartridge for the sample mass to be analyzed could also been determined. The conditions for the titration reactions (pH, additives) could also be further optimized, to further improve the sensitivity of the concentration measurements, i.e. lower the detection limits.

Additional tests or steps could be added to the extraction protocol to exclude the non-surfactant compounds that might have been extracted. For instance, the potential presence of HULIS in the samples could be investigated by optical techniques (UV-Vis or fluorescence).

Further modifications, while not improving the quality of the analysis itself, would bring more information on atmospheric surfactants, such as applying the present method to different size-fractions (i.e. sub-populations) of the aerosol rather than on all the particles collected, as presented here. Other types of analyses could also be applied to the extracts such as, LC/HR MS, tandem MS, or NMR to determine the chemical structure of the surfactants or UV-Vis absorbance, fluorescence, or polarimetry, to indicate the presence of highly-conjugated or chiral compounds in the extracts.

Disclosures

The authors have nothing to disclose.

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