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Determination of atmospheric organosulfates using HILIC chromatography with MS detection

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Abstract

Measurements of organosulfates in ambient aerosols provide insight to the extent of secondary organic aerosol (SOA) formation from mixtures of biogenic gases and anthropogenic pollutants. Organosulfates have, however, proved analytically challenging to measure. This study presents a sensitive new analytical method for the quantification of organosulfates based upon ultra-performance liquid chromatography with negative electrospray ionization mass spectrometry (UPLC-ESI-MS/MS). The separation is based upon hydrophilic interaction liquid chromatography (HILIC) with an amide stationary phase that provides excellent retention of carboxy-organosulfates and methyltetrol-derived organosulfates. The method is validated using six model compounds: methyl sulfate, ethyl sulfate, benzyl sulfate, hydroxyacetone sulfate, lactic acid sulfate, and glycolic acid sulfate. A straightforward protocol for preparation of highly pure organosulfate potassium salts for use as quantification standards is presented. This highly efficient method of separating and quantifying organosulfates is used to evaluate the efficiency and precision of two methods of ambient $PM_{2.5}$ sample extraction. Spike recoveries averaged $98 \pm 8\,\%$ for extraction by sonication and $98 \pm 10\,\%$ for extraction by rotary-shaking. Sonication was determined to be the superior method for its better precision. Analysis of ambient $PM_{2.5}$ samples collected 10–11 July 2013 in Centreville, AL, USA during the Southeast Atmosphere Study (SAS) confirms the presence of hydroxyacetone sulfate in ambient aerosol for the first time. Glycolic acid sulfate was the most abundant compound measured (ranging 8–14 $\mathrm{ng\,m^{-3}}$), followed by hydroxyl acetone sulfate (2.7–5.8 $\mathrm{ng\,m^{-3}}$) and lactic acid sulfate (1.4–2.9 $\mathrm{ng\,m^{-3}}$). Trace amounts of methyl sulfate were detected, while ethyl sulfate and benzyl sulfate were not detected. Future research will focus on the development of additional organosulfates standards, expansion of this UPLC-MS/MS to include more target molecules, and the application of this method to assess temporal variations in organosulfates in ambient environments.

1 Introduction

On a large scale, particulate matter (PM) in the atmosphere impacts the earth's radiative balance directly by scattering and absorbing solar radiation (Jacobson et al., 2000) and indirectly by acting as cloud condensation nuclei (CCN) (Novakov and Penner, 1993). PM also contributes to negative human health outcomes, such as cardiovascular and respiratory diseases (Davidson et al., 2005). Knowledge of the chemical composition of PM can aid in the identification of PM sources and better management of air resources. Secondary organic aerosol (SOA) is formed in the atmosphere by reactions of gaseous precursors that yield products that partition to the particle phase. It remains one of the most poorly understood PM sources (Foley et al., 2010), in part because of its chemical complexity and the fact that it forms in complex environmental mixtures.

Atmospheric organosulfates are SOA compounds that contain a characteristic sulfate ester functional group ($R-O-SO_3^-$). It has been suggested that they are a significant component of fine particulate organic matter (Frossard et al., 2011; Hawkins et al., 2010; Shakya and Peltier, 2013; Stone et al., 2012; Surratt et al., 2008; Tolocka and Turpin, 2012). Laboratory chamber experiments have demonstrated that SOA formed from biogenic volatile organic compounds (BVOCs, e.g. isoprene, 2-methyl-3-buten-2-ol [MBO], monoterpenes, and sesquiterpenes) in the presence of oxidants and sulfuric acid, contain a large organosulfate component (Chan et al., 2011; Iinuma et al., 2009; Surratt et al., 2007b; Zhang et al., 2012a, b, 2014).

Due to the atmospheric abundance of organosulfates and their importance in SOA formation, analytical methods have been developed to detect them in ambient aerosol by Fourier transform infrared spectroscopy (FTIR) (Hawkins et al., 2010; Maria et al., 2003), in-situ single particle mass spectrometry (Farmer et al., 2010; Froyd et al., 2010), and capillary electrophoresis (CE) and liquid chromatography (LC) coupled with negative electrospray ionization ((−)ESI) mass spectrometry (MS) (Olson et al., 2011; Surratt et al., 2008; Yassine et al., 2012). ESI MS is especially sensitive to the detection of organosulfates in the negative mode, because these compounds carry a negative charge (Romero and Oehme, 2005; Surratt et al., 2007a). High-resolution MS may be used to determine organosulfate exact masses, chemical formulas, structural characteristics, and abundance (Altieri et al., 2008; Laskin et al., 2009; Pratt et al., 2013; Shalamzari et al., 2013; Staudt et al., 2014; Surratt et al., 2008; Tao et al., 2014; Zhao et al., 2013). A major limitation in the quantification and speciation of organosulfates is the glaring lack of authentic quantification standards.

Chemical identification and quantification of organosulfates requires the analytical separation of target analytes from the inorganic aerosol matrix and from each other. Organosulfates are strongly acidic (Guthrie, 1978) and are consequently anionic and non-volatile in the environment. Hence, they cannot be separated using gas chromatographic techniques and must be approached using a condensed-phase separation process (e.g. liquid chromatography (LC) or capillary electrophoresis). Prior studies have applied reversed-phase LC to aqueous atmospheric samples that range from water-soluble and methanol-extractable aerosol components to fogwater (Cappiello et al., 2003; Stone et al., 2012; Surratt et al., 2008). Reversed-phase separations that rely upon a non-polar stationary phase and polar mobile phase are successful in retaining higher-molecular weight, monoterpene-derived nitro-oxy organosulfates (e.g. $C_{10}H_{16}NSO_7^-$) (Gao et al., 2006; Surratt et al., 2007a) and aromatic organosulfates (e.g. $C_7H_7SO_4^-$) (Kundu et al., 2010; Staudt et al., 2014). However, this mode of LC separation is not optimized for lower-molecular weight and highly polar organosulfates; for example glycolic acid sulfate ($C_2H_3O_6S^-$) and 2-methyltetrol sulfate ($C_5H_{11}O_7S^-$) are retained less than 2.5 min and co-elute with numerous other organosulfates, small organic acids, polyols, and inorganic sulfate (Stone et al., 2012). Co-elution of analytes with other compounds may lead to negative biases in their ESI response due to competition for ionization (Reemtsma and These, 2003). Other modes of LC separation, such as hydrophilic interaction liquid chromatography (HILIC), are specifically designed to retain molecules with ionic and polar functional groups (Hemstrom and Irgum, 2006). HILIC chromatography has previously been shown to retain hydroxycarboxylic acid organosulfates, such as glycolic acid sulfate and lactic acid sulfate, which are among the most abundant atmospheric organosulfates quantified to date (Olson et al., 2011).

The objective of this study was to develop an accurate and sensitive method of quantifying highly-polar atmospherically-relevant organosulfates using HILIC chromatography for separation and tandem mass spectrometry for detection. Used in concert with commercially available and laboratory-prepared pure standards of the organosulfates, this combination enables the facile separation, identification, and quantification of all manner of small samples of highly polar, ionic, and nonvolatile organosulfates collected from the atmosphere. This method provides a means of assessing the efficiency of extracting organosulfates from fine particulate matter deposited on filters and for accurately measuring organosulfates in ambient aerosol.

This study presents the development and validation of a new analytical method to separate highly-polar and ionic organosulfates by ultra-performance liquid chromatography (UPLC) using an HILIC stationary phase modified with amide functional groups. Organosulfates with aromatic, keto-, hydroxyl-, and carboxyl- functional groups are quantified with triple quadrupole mass spectrometric detection (TQD) against calibration curves prepared from commercially-available or synthesized standards. In addition to quantifying these compounds, the new method is shown to be efficient in the separation of other major organosulfates present in the southeastern United States, for which standards are not yet available. A highly efficient sample preparation protocol for the extraction and pre-concentration of organosulfates from fine particulate matter ($PM_{2.5}$) samples is reported, and the extraction efficiencies of ultra-sonication and rotary shaking are compared. Also reported here are the first measurements of hydroxyacetone sulfate in ambient $PM_{2.5}$, from samples that were collected in Centreville, Alabama during the Southeast Oxidant and Aerosol Study (SOAS).

2 Materials and methods

2.1 Chemicals, reagents, and general methods

Six organosulfate standards were used in method development, two of which were commercially-available: methyl sulfate (sodium methyl sulfate, 99 %, Acros Organics) and ethyl sulfate (sodium ethyl sulfate, Sigma-Aldrich). Lactic acid sulfate was prepared according to Olson et al. (2011). Benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate were synthesized as described below. Acetonitrile (ACN) was purchased from Fisher Scientific (Optima™ LC/MS grade) and ultrapure-water was prepared on-site (Thermo, BARNSTED EasyPure-II; 18.2 MΩ resistivity). All other reagents and solvents were obtained from FisherAcros and used without further purification. Elemental Analysis was conducted by Atlantic Microlabs in Norcross, GA and NMR spectra were collected on a Bruker ARX-400 NMR spectrometer with a 5 mm broadband probe.

High-resolution MS analysis in the negative (–)ESI mode was performed on a micrOTOF spectrometer (Bruker Daltonics). The ESI conditions used include capillary voltage 2.6 kV (benzyl sulfate) and 2.8 kV (for other 5 standards), sample cone voltage 15 V (benzyl sulfate), 30 V (methyl sulfate, ethyl sulfate, lactic acid sulfate and glycolic acid sulfate) and 35 V (hydroxyacetone sulfate), desolvation temperature 350 °C, source temperature 110 °C, cone gas flow rate 30 L h^{-1}, desolvation gas flow rates of 550–650 L h^{-1}. Data were collected from a mass range 40 to 400 with V geometry in reflectron mode. Signals below a threshold level (set at 5–18 % of the relative abundance) were filtered out. A small peptide (Val-Tyr-Val, m/z 378.2029, Sigma-Aldrich) was used for lock mass correction.

2.2 General procedure for the synthesis of organosulfates

Each sulfate ester standard was synthesized using a general method derived from that of Hoff et al. (2001). To synthesize a sulfate ester, 1 molar equivalent (eq) of the appropriate alcohol was added with stirring to 15 mL of dry pyridine in a round bottom flask under nitrogen. To that clear, colorless mixture, slightly more than 1 eq of pyridine sulfur trioxide complex was added at once and the resulting cloudy white mixture was stirred for 8 h, after which the solution was clear. The pyridine was removed via distillation under vacuum, and the resulting clear oil (the pyridinium salt of the ester), varying in color from colorless to slight yellow, was converted to the potassium form. The conversion to the potassium salt and the crystallization procedures varied among the esters.

2.2.1 Benzyl sulfate, potassium salt

To synthesize the potassium salt of benzyl sulfate, once the pyridine solvent had been removed via distillation under vacuum, the resulting clear yellow oil was dissolved in approximately 10 mL of distilled water and titrated with 1 M KOH until the pH was above 11. Then, 50 mL of ethanol (neat) was added to the remaining aqueous solution. The resulting solution (approximately 75 % ethanol) was heated to boil and quickly vacuum filtered to remove a small amount of stark white precipitate that gave no proton or carbon NMR spectrum when analyzed. The mother liquor was then placed in a freezer (–5 °C) overnight. Potassium benzyl sulfate formed in the mother liquor as colorless needles that were collected by vacuum filtration and rinsed with cold 90 % ethanol. The needles proved to be analytically pure benzyl sulfate. Yield: 1.648 g (75 %); 1 H NMR (400 MHz, DMSO-d6): $\delta\,\mathrm{ppm}^{-1}$ 4.84 (s, 2 H); 7.25–7.41 (m, 5 H). 13C-NMR (400 MHz, DMSO-d6): $\delta\,\mathrm{ppm}^{-1}$ 8.45; 56.01; 67.54; 127.42; 127.59; 128.13; 137.56. HR-MS ((–)ESI) m/z (relative intensity, %): 187.0072 (81.75, $C_7H_7SO_4^-$), 95.9497 (100.00), 80.9636 (15.74). Analysis calculated for $C_7H_7SO_4^-K^+$: C 37.15, H 3.12, S 14.17. Found: C 36.64, H 2.93, S 14.10.

2.2.2 Hydroxyacetone sulfate, potassium salt

The isolation of the potassium salt of hydroxyacetone sulfate was accomplished using Dowex 50WX8-200 cation exchange resin that had been charged with potassium ions. The exchange was conducted by making a slurry with the pyridinium salt of the ester dissolved in water and approximately 80 equivalents of resin, using appropriate water to maintain a slurry. After filtration, the water was removed via rotary evaporation under vacuum at no more than 40 °C, and the resulting white solid was recrystallized from a boiling 80 % ethanol solution, including a hot filtration step as in the synthesis of benzyl sulfate. The potassium salt of hydroxyacetone sulfate formed as colorless needles that were collected by vacuum filtration and rinsed with cold 90 % ethanol. The needles proved to be analytically pure hydroxyacetone sulfate. Yield: 35 %; 1 H NMR (400 MHz, DMSO-d6): δ ppm^{-1} 2.10 (s, 3 H); 4.26 (s, 2 H). 13C-NMR (400 MHz, DMSO-d6): δ ppm^{-1} 26.47; 71.05; 206.39. HR-MS ((–)ESI) m/z (relative intensity, %): 152.9836 (21.94, $C_3H_5SO_5^-$), 96.9564 (96.86), 80.9609 (50.19), 79.9533 (100.00). Analysis calculated for $C_3H_5SO_5^-K^+$: C 18.74, H 2.62, S 16.68. Found: C 18.57, H 2.55, S 16.79.

2.2.3 Glycolic acid sulfate, potassium salt

The isolation of the potassium salt of glycolic acid sulfate was conducted in a similar manner to that of hydroxyacetone sulfate, except that after filtering off the cation exchange resin and rinsing, the water was reduced to about 10 mL via rotary evaporation at 40 °C, and then titrated to pH 2 using 3 M HCl, before enough ethanol was added to make an 80 % ethanol solution. The product was then crystallized from the boiling ethanolic solution as in the previous syntheses. The potassium salt of glycolic acid sulfate formed as colorless needles that were collected by vacuum filtration and rinsed with cold 90 % ethanol. The needles gave NMR and mass spectra consistent with glycolic acid sulfate, and gave elemental analysis results fitting approximately 50 % protonation of the carboxylic acid moiety. Yield: 45 %; 1 H NMR (400 MHz, DMSO-d6): δ ppm^{-1} 4.54 (s). 13C-NMR (400 MHz, DMSO-d6): δ ppm^{-1} 63.59; 172.20. HR-MS ((–)ESI) m/z (relative intensity, %): 154.9650 (10.00, $C_2H_3SO_6^-$), 96.9588 (100.00), 75.0076 (30.50). Analysis calculated for $C_2H_{2.5}SO_6^-K_{1.5}^+$: C 11.27, H 1.18, S 15.04. Found: C 11.58, H 1.18, S 15.13.

2.3 Collection of $PM_{2.5}$ in Centreville, AL

$PM_{2.5}$ was collected at the Southeastern Aerosol Research and Characterization (SEARCH) network site in Centreville, Alabama (CTR) from 1 June to 15 July 2013 during the SOAS field study. Sample collection followed the daytime (08:00–19:00) and nighttime (20:00–07:00) schedule. A medium-volume sampler (URG Corporation) was used to collect particles with aerodynamic diameter of 2.5 µm by way of a Teflon-coated aluminum cyclone operating at 92 Lpm. $PM_{2.5}$ was collected on quartz fiber filters (90 mm diameter, Pall Life Sciences) were pre-baked at 550 °C for 18 h to remove organic material. Pre-and post-sampling flow rates were measured with a calibrated rotameter. All filters were handled using clean-techniques, which included storage of filters in plastic petri dishes lined with pre-cleaned aluminum foil and manipulation with pre-cleaned stainless steel forceps. Post-sampling, filters were stored frozen in the dark. One field blank was collected for every five samples.

2.4 PM sample extraction and preparation

Sub-samples of $PM_{2.5}$ filter samples and field blanks (totaling 15 cm^2) were obtained using standardized filter punches of known area. These sub-samples were submerged in 10.0 mL of acetonitrile and ultra-pure water (95 : 5, by volume) and extracted for 20 min by ultra-sonication (60 sonics min^{-1}, 5510, Branson) or an orbital shaker (125 rpm, VWR). Extracts were filtered through polypropylene membrane syringe filters (0.45 µm pore size). Filtrates were reduced in volume to 500 µL under ultra-high purity nitrogen gas (5 psi) at 50 °C using an evaporation system (TurboVap® LV, Caliper Life Sciences) and then to a final volume of 100 µL using a micro-scale nitrogen evaporation system (Reacti-Therm III TS-18824 and Reacti-Vap I 18825, Thermo Scientific). To test the efficiency of extraction by sonication and rotary shaking, a series of quality control samples were extracted by each method. These quality control samples consisted of 4 laboratory blanks (of 5.3 cm^2 quartz fiber filters) and 7 spiked samples, for which standards were spiked on to blank quartz fiber filters to achieve a final concentration of 100 $\mu g L^{-1}$.

2.5 Separation and detection of organosulfates

Organosulfates were separated using an UPLC (equipped with quaternary pump, autosampler, and thermostatted column compartment, ACQUITY UPLC, Waters, Milford, USA). The separation was optimized using a bridged ethylene hybrid (BEH) amide column (2.1 mm × 100 mm, 1.7 µm particle size; AQUITY UPLC, Waters) equipped with a pre-column. The column was maintained at 35 °C and the mobile phase flow rate was 0.5 $mL min^{-1}$. A 5 µL injection volume was used for quantitative analysis of samples and standards. The optimized mobile phase A (organic) consisted of ammonium acetate buffer (10 mM, pH 9) in acetonitrile and ultra-pure water (95 : 5, by volume) and mobile phase B (aqueous) consisted of ammonium acetate buffer (10 mM, pH 9) in ultra-pure water. A solvent gradient was used to elute the analytes: mobile phase A was maintained at 100 % for 2 min, then decreased to 85 % from 2 to 4 min and held constant until 11 min, which was sufficient to elute the analytes. To re-equilibrate the column prior to the next injection, the solvent program was returned to 100 % mobile phase A from 11 to 11.5 min and was held constant until 14 min. The wash solvent (needle wash) consisted of acetonitrile and water (80 : 20, v/v).

Organosulfates were detected by a TQD MS (ACQUITY, Waters) equipped with an ESI source in the negative ion mode. The detector operated in multiple reaction monitoring (MRM) mode, in which the molecular ion was selected in the first quadrupole, fragmented in the second quadrupole and product ions were selected in the third quadrupole. Optimized MS conditions (cone voltages and collision energies) used for each authentic standard transition are provided in Table 1. Other ESI conditions include a capillary voltage of 2.7 kV, source temperature of 150 °C, desolvation temperature of 450 °C, cone gas (N_2) flow rate at 100 $L h^{-1}$, desolvation gas (N_2) flow rate at 900 $L h^{-1}$

and collision gas (N_2) flow rate at 0.05 mL min^{-1}. All data were acquired and processed using MassLynx software (version 4.1). The linear range of each authentic standard was determined using a series of standard solutions at 0.5, 1.0, 25.0, 50.0, 100.0, 300.0 and 500.0 µg L^{-1} that were prepared in organic mobile phase. Reproducibility of the MS method was determined based on seven replicate injections of the 100.0 µg L^{-1} solution. The limit of detection (3 × SD) and the limit of quantification (10 × SD) were obtained from multiple injections ($n = 10$) of 25.0 µg L^{-1} solution.

3 Results and discussion

3.1 MS/MS fragmentation and optimization

Product ion spectra given by methyl sulfate, ethyl sulfate, hydroxyacetone sulfate, lactic acid sulfate, and glycolic acid sulfate under applied (–)ESI conditions are shown in Fig. 1. Formulas were assigned to precursor and product ions using high-resolution MS/MS. Major fragment ions included the sulfite radical ($SO_3^-\bullet$ at m/z 80) that forms from the homolytic cleavage of an O-S bond, the sulfate radical ($SO_4^-\bullet$ at m/z 96) that forms from the homolytic cleavage of a C-O bond, the bisulfite anion (HSO_3^- at m/z 81) that forms from the heterolytic cleavage of the S-O bond, and the bisulfate anion (HSO_4^- at m/z 97) that is postulated to form via a cyclic syn-elimination pathway (Attygalle et al., 2001). Notably, the bisulfate anion is absent in the MS/MS spectrum of methyl sulfate, because there is no C2 position from which a hydrogen may be abstracted. Glycolic acid sulfate and lactic acid sulfate spectra contain glycolate ($C_2H_3O_3^-$, m/z 75) and methyl glycolate ions ($C_3H_5O_3^-$, m/z 89), respectively, which form from the heterolytic cleavage of O-S bond and are resonance stabilized. The MS/MS fragmentation of benzyl sulfate is discussed elsewhere (Attygalle et al., 2001; Kundu et al., 2013).

The MS/MS method was optimized for the detection of each analyte. The source conditions (collision energy and cone voltage) used in MRM are given in Table 1. Two transitions were optimized for each analyte, except for ethyl sulfate and lactic acid sulfate that relied solely on 125 > 97 and 169 > 97 transitions, respectively. For quantitative analysis of compounds with two transitions, the corresponding signals were summed.

3.2 HILIC separation

Analytes were separated on a BEH amide column that retains extremely polar compounds. In HILIC chromatography, water in the mobile phase is adsorbed to the stationary phase, forming a hydrophilic layer (Strege, 1998) into which polar compounds in the organic mobile phase partition (Alpert, 2007). The delocalization of the amide nitrogen electrons to the carbonyl oxygen imparts a partial positive charge on the nitrogen atom, promoting strong dipolar interactions. Polar analytes are eluted from the column as the aqueous fraction of the mobile phase increases (Grumbach et al., 2004, 2008).

Under the optimized conditions that provided the best resolution of analytes, the aqueous portion of the mobile phase increased 5–20 % and eluted the six organosulfate standards within 8 min (Table 1 and Fig. 2). The mobile phase was buffered to pH 9 with 10 mM ammonium acetate to maintain a consistent charge state on the stationary phase and analytes. However, the actual pH of the mobile phase may be 1 pH unit closer to neutral due to the high organic content of the mobile phase (Canals et al., 2001; Espinosa et al., 2000). A slightly basic pH was selected to completely deprotonate carboxylic acids groups in glycolic acid sulfate and lactic acid sulfate. At pH values greater than 5, silanol groups in the stationary phase are similarly deprotonated, increasing the thickness of the adsorbed hydrophilic layer, and increasing retention of polar compounds (Jandera, 2008). The buffer is maintained at a relatively high ionic strength, compensating for repulsion between the anionic silanol groups and organosulfates, by providing ammonium ions to pair with silanol groups (McCalley, 2007; Storton et al., 2010).

The charge state of organosulfates plays a key role in their retention on the BEH amide column. At pH 9, glycolic acid sulfate and lactic acid sulfate are fully deprotonated; each carry a −2 charge, and are retained 7.84 and 7.57 min, respectively. Singly-charged organosulfates – methyl sulfate, ethyl sulfate, benzyl sulfate, and hydroxyacetone sulfate – elute within the window of 0.58–0.88 min, and are baseline-resolved.

The UPLC method is also efficient at resolving other organosulfates present in atmospheric aerosols that are expected to have high atmospheric abundances due to their strong MS signals. As shown in Fig. 3a, six methyltetrol sulfate isomers derived from isoprene epoxide (IEPOX) (Gomez-Gonzalez et al., 2008; Surratt et al., 2008) with a precursor ion of m/z 215 ($C_5H_{11}O_7S^-$) are baseline resolved. The separation of these isomers by this method is superior to reversed phase chromatography, in which these IEPOX-derived organosulfate isomers co-elute in two peaks (Stone et al., 2012). The resolution of individual IEPOX-derived organosulfate isomers is significant, because their separation will support future quantification of individual isoprene SOA products that may prove useful in elucidating different organosulfates formation pathways (Surratt et al., 2010) and because IEPOX-derived organosulfates have generated the greatest organosulfates signals in prior field studies (Froyd et al., 2010; Lin et al., 2013). Two additional organosulfates derived from isoprene, with precursor ions of m/z 213 ($C_5H_9O_7S^-$) and m/z 211 ($C_5H_7O_7S^-$) (Gomez-Gonzalez et al., 2008; Surratt et al., 2008) shown in Fig. 3b and c, respectively, were retained although not fully resolved by this method. Future study should target improving resolution and ultimately identifying and quantifying these two compounds.

3.3 Method validation

The goal of method development was to develop a robust and sensitive protocol for the quantification of organosulfates in ambient aerosol. Optimized UPLC and MS/MS conditions were applied to a series of authentic organosulfate standards, and produced highly linear calibration curves ($R^2 \geq 0.995$), as shown in Table 1. The linearity requirement was met for methyl sulfate and ethyl sulfate across concentration ranges of 25.0–500 µg L^{-1}, and for all other compounds across 25.0–300 µg L^{-1}. LOD and LOQ ranged

1.9–3.9 and 6.3–13.2 µg L^{-1}, respectively. The relative standard deviation (RSD) was 2.5–3.0 % for the first four compounds to elute, and increased to 16 % for glycolic acid sulfate and 6 % for lactic acid sulfate, which were retained longer on the column.

3.4 Optimization of extraction

It has been previously shown that methanol converts carboxy-organosulfates to methyl esters and should be avoided in quantitative analysis of organosulfates (Olson et al., 2011). Instead, ACN and water (95 : 5, by volume) were used as the extracting solvent in this study. Two methods of extracting organosulfates from the filters were investigated: the commonly used methods of sonication (Gao et al., 2006; Surratt et al., 2007a) and rotary shaking. Extraction by sonication has previously been associated with negative artifacts, due to the formation of hydroxyl radicals and heat, which can degrade certain organic compounds (Mutzel et al., 2013; Riesz et al., 1985). Rotary shaking, on the other hand, is considered to be a milder method of extraction that is not subject to these potential problems.

Extraction by sonication and rotary shaking were both tested, and were both found to be efficient and reproducible methods for extracting organosulfates from filters. The results of seven replicate extractions of the six organosulfates in a standard solution are shown in Fig. 4. Overall, spike recoveries for sonication ranged 83–121 % and averaged (±SD) 98 ± 8 % and for rotary shaking ranged 79–122 % and averaged 98 ± 10 %. Both methods were found to be accurate within 100 ± 15 % for 95th percentile values and did not introduce artifacts into extraction. Sonication had the advantage of better precision with narrower ranges of results and lower RSD. Consequently, sonication was selected for the extraction of ambient aerosol samples from filter media.

3.5 Application to ambient aerosol

Concentrations of organosulfates quantified in ambient $PM_{2.5}$ from Centreville, AL are provided in Table 2. Glycolic acid sulfate was the most abundant compound measured, with 10–11 July daytime and nighttime concentrations of 14 ± 2 and 8 ± 1 ng m^{-3}, respectively. Hydroxyacetone sulfate, quantified for the first time in this study, was the second-most abundant compound measured at levels of 5.8 ± 0.2 and 2.7 ± 0.1 ng m^{-3}, respectively. Lactic acid sulfate and methyl sulfate were observed at lower concentrations, and benzyl sulfate and ethyl sulfate were not detected. These results are in agreement with those of Olsen et al. (2011) who report glycolic acid sulfate concentrations in the range of 1.9–11.3 ng m^{-3} across six locations, lactic acid concentrations in the range of 0.4–3.8 ng m^{-3}, and a 3-fold or greater enhancement of glycolic acid sulfate relative to lactic acid sulfate.

4 Conclusions

A UPLC-MS/MS method for the quantification of atmospheric organosulfates was developed and validated for the purpose of evaluating the ambient concentrations of a variety of lower-molecular-weight organosulfates containing alkyl, benzyl, hydroxyl, carbonyl and carboxy functional groups. In addition to resolving the six model compounds used in method validation, the HILIC separation holds promise for the separation of a range of isoprene-derived organosulfates. In comparing two procedures for the preparation of filter samples for organosulfates quantification, both sonication or rotary shaking were proven to be efficient, with sonication providing better precision. Initial measurements indicate that hydroxyacetone sulfate is relatively abundant in $PM_{2.5}$, compared to the measured organosulfates. HILIC chromatography is a promising analytical technique for the separation of organosulfates from one another and the complex aerosol matrix. When coupled with authentic standard development and highly-sensitive MS/MS detection, it provides an improve technique for the quantification and speciation of atmospheric organosulfates. Improved measurements of this class of compounds will advance the understanding of SOA precursors and formation mechanisms.

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Table 1. Mass spectrometry parameters for MRM transitions of UPLC-MS/MS, linearity, squared correlation coefficient (R^2), limit of detection (LOD), limit of quantification (LOQ), and relative SD (RSD) of 7 replicate standard injections. For compounds with more than one transition, MRM signals were summed prior to quantification.

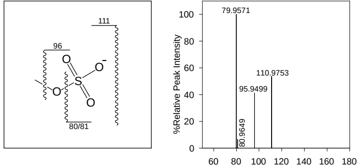
Compound	Precursor ion and m/z		Product ion and m/z		Cone voltage (V)	Collision energy (eV)	Retention time (min)	Linear range ($\mu g L^{-1}$)	R^2	LOD ($\mu g L^{-1}$)	LOQ ($\mu g L^{-1}$)	RSD (%)
Methyl sulfate	$CH_3SO_4^-$	111	$SO_3^{-\cdot}$ $SO_4^{-\cdot}$	80 96	36	18 14	0.88 ± 0.03	25.0–500.0	0.998	2.6	8.6	2.9
Ethyl sulfate	$C_2H_5SO_4^-$	125	HSO_4^-	97	26	12	0.78 ± 0.03	25.0–500.0	0.998	3.4	11.2	2.5
Benzyl sulfate	$C_7H_7SO_4^-$	187	HSO_3^- $SO_4^{-\cdot}$	81 96	42	18 20	0.58 ± 0.02	25.0–300.0	0.995	3.9	13.2	3.0
Hydroxy-acetone sulfate	$C_3H_5SO_5^-$	153	$SO_3^{-\cdot}$ HSO_4^-	80 97	32	18 20	0.66 ± 0.02	25.0–300.0	0.996	2.6	8.7	3.0
Lactic acid sulfate	$C_3H_5SO_6^-$	169	HSO_4^-	97	28	16	7.57 ± 0.02	25.0–300.0	0.995	3.9	13.0	5.9
Glycolic acid sulfate	$C_2H_3SO_6^-$	155	$C_2H_3O_3^-$ HSO_4^-	75 97	26	18 14	7.84 ± 0.01	25.0–300.0	0.998	1.9	6.3	15.6

Table 2. Ambient concentrations of organosulfates with analytical uncertainties (ng m^{-3}) measured in PM$_{2.5}$ from Centreville, AL in 2013.

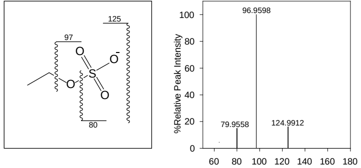
Compound	10 Jul – Day (08:00–19:00)	10–11 Jul – Night (20:00–07:00)
Methyl sulfate	0.70 ± 0.05	0.34 ± 0.04
Ethyl sulfate	BDL*	BDL*
Benzyl sulfate	BDL*	BDL*
Hydroxyacetone sulfate	5.8 ± 0.2	2.7 ± 0.1
Glycolic acid sulfate	14 ± 2	8 ± 1
Lactic acid sulfate	2.9 ± 0.2	1.4 ± 0.1

* BDL – below detection limit.

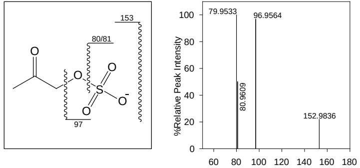
A) Structure and product ion spectrum of methyl sulfate



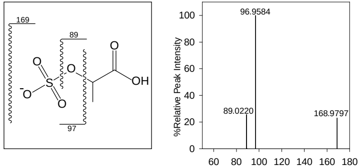
B) Structure and product ion spectrum of ethyl sulfate



C) Structure and product ion spectrum of hydroxyacetone sulfate



D) Structure and product ion spectrum of lactic acid sulfate



E) Structure and product ion spectrum of glycolic acid sulfate

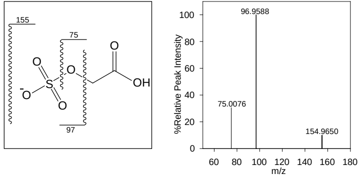


Figure 1. Production spectra of organosulfates standards generated by Q-ToF MS/MS of a directly infused standard solution.

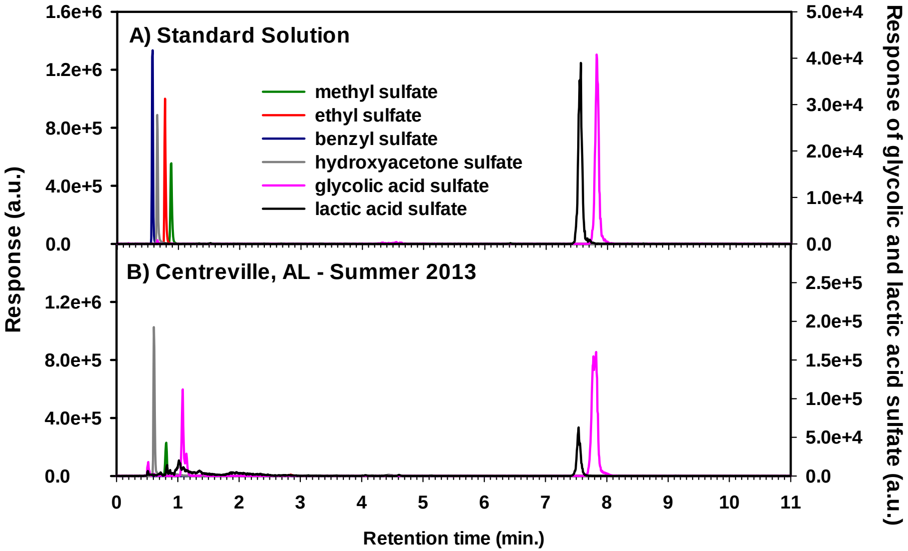


Figure 2. MRM chromatograms of **(a)** a mixed standard containing six organosulfates at 100 µg L^{-1} and **(b)** an ambient aerosol sample. Responses of glycolic acid sulfate (GAS) and lactic acid sulfate (LAS) are shown on the right axis.

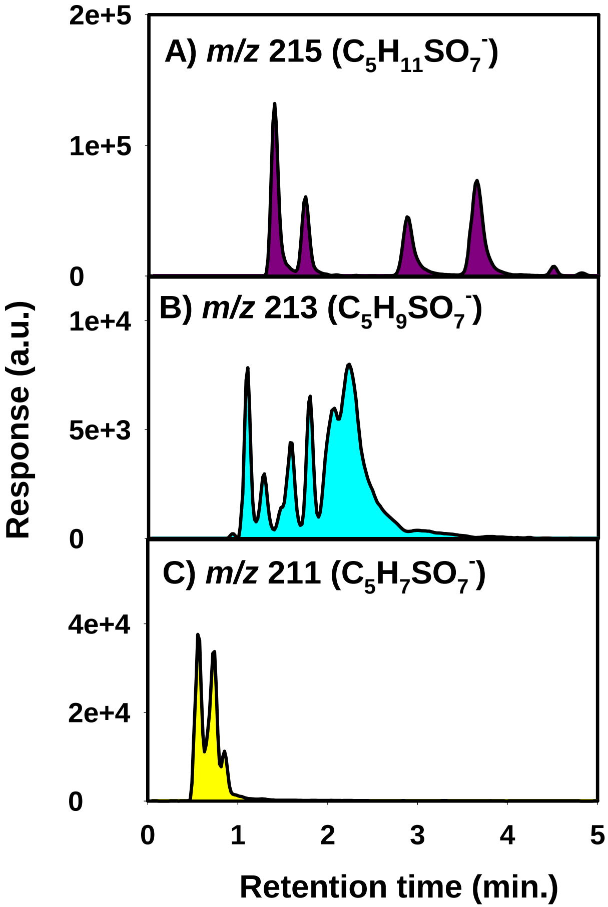


Figure 3. Extractedion chromatograms of isoprene-derived organosulfates qualitatively identified in an ambient aerosol sample collected in Centreville, AL on 10 July 2013 during the daytime (08:00–19:00).

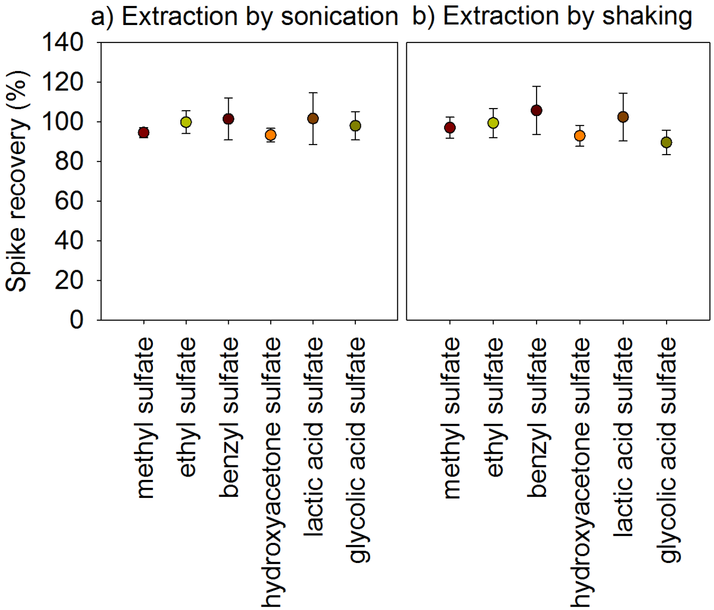


Figure 4. Comparison of spike recovery samples ($n = 7$ each) extracted by **(a)** sonication and **(b)** rotary shaking.