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Development and application of a quantification method for water soluble organosulfates in atmospheric aerosols[☆]

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ABSTRACT

In recent years, organosulfates have been found as a significant component of secondary organic aerosols from both smog chamber experiments and field measurements. In this study, an indirect method was developed to estimate organosulfates in aerosol particles as a whole based on their sulfate functional group. A series of experiments were conducted to optimize and validate the method, and it was then applied to quantify organosulfates in the aerosol samples collected at three sampling characteristic sites in Shenzhen, with one close to a power plant (PP), one at a heavy traffic intersection (HTI), and one on the campus of Harbin Institute of Technology Shenzhen graduate school (HITSZ). On average, the mass concentrations of organic sulfur (S_{org}) were 1.98, 1.11, 0.25 μgS m^{-3} in PP, HTI and HITSZ respectively. The lower bounds of mass concentrations of organosuflates ($OM_{s\text{-}related}$) were 6.86, 3.85 and 0.86 μg m^{-3} and the upper bounds of mass concentrations of organosulfates were 23.05, 12.93 and 2.90 μg m^{-3} in PP, HTI and HITSZ respectively. This indicates that primary emissions from coal burning and automobile exhaust can promote the secondary formation of organosulfates in the atmosphere. Overall, the mass concentrations observed in this work were higher than those reported by previous studies.

1. Introduction

Chamber studies have evidenced the generation of organosulfates during the processes of secondary organic aerosol formation from oxidation of biogenic and aromatic VOCs, such as α-pinene (Surratt et al., 2007, 2008; Ma et al., 2014), β-pinene (Iinuma et al., 2007a; Surratt et al., 2008; Ma et al., 2014), isoprene (Surratt et al., 2007, 2008, 2010; Perri et al., 2010; McNeill et al., 2012; Ma et al., 2014), toluene (Stone et al., 2012; Kundu et al., 2013), PAHs (Riva et al., 2015) and C_{10}-C_{12} alkanes (Riva et al., 2016). Up to date, over a hundred of different structures of organosulfates have been found in aerosols from both chamber experiments and ambient atmosphere. Researchers recently have started to look into the abundance of organosulfates in ambient aerosols at different locations worldwide. Organosulfates were found in the range of 0.05 ng m^{-3} and 2 μg m^{-3} in the aerosols collected from some Asia countries (Stone et al., 2012; Kundu et al., 2013; Ma et al., 2014; Huang et al., 2015), 1 ng m^{-3} to 3.1 μg m^{-3} in some places in Europe (Surratt et al., 2008; Claeys et al., 2010; Kristensen and Glasius, 2011), and 0.6 ng m^{-3} to 0.35 μg m^{-3} in the United States (Surratt et al., 2008; Chan et al., 2010; Olson et al., 2011; Worton et al., 2011; Tolocka and Turpin, 2012; Zhang et al., 2012b; Lin et al., 2013; Shakya and Peltier, 2013). A large variation appeared in the reported concentrations of organosulfates. This may be due to site-specific factors such as the composition of air pollutants and atmospheric conditions, etc. However, different measurement methods used by various research groups could also introduce the discrepancy in the estimation of organosulfates.

Current methods applied for the quantification of organosulfates in chamber-generated and ambient aerosols basically can be categorized into two groups: direct and indirect approaches. The direct measurements are mainly based on a variety of mass spectrometry (MS) techniques (Surratt et al., 2007; Iinuma et al., 2009; Chan et al., 2011; Hatch et al., 2011; Pavlovic and Hopke, 2012; Wang et al., 2012; Zhang et al., 2012a, 2016, 2012b). Individual organosulfate species are identified using characteristic fragmentation ion, i.e. bisulfate anion (HSO_4^-) signal at m/z 97 for aliphatic

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organosulfates (Stone et al., 2012), and the sulfite radical ($\bullet SO_3^-$, m/z 80) and the sulfate radical ($\bullet SO_4^-$, m/z 96) for aromatic organosulfates (Staudt et al., 2014). However, given the diversity and trace levels of organosulfates in ambient aerosols, a complete characterization of all organosulfates at molecular level is still challenging even with the most sophisticated MS. Another direct measurement of organosulfates is conducted using FTIR based on the absorbance of organosulfate functional groups (-$COSO_3$-) at 876 cm^{-1} (Hawkins et al., 2010). However, such quantification may be interfered by the absorbance of HSO_4^- and CO_3^{2-}. Moreover, the relative low sensitivity of FTIR quantification sometimes may overlook the existence of certain amount of organosulfates. Indirect methods have also been developed and applied to the measurement of organosulfates in ambient aerosol particles. Lukács et al. (2009) proposed to estimate the content of organic sulfate by subtracting the inorganic sulfate mass concentration measured by ion chromatography (IC) from the total sulfur mass concentration measured by X-ray fluorescence (XRF) spectroscopy. They converted the content of organic sulfate to the carbon content in organosulfates using the average molar ratio of carbon to sulfur of the identified organosulfates reported in literature. Tolocka and Turpin (2012) used the similar method to determine the inorganic sulfate and total sulfur mass concentrations in ambient aerosols. Differently, during the process of estimating upper bounds on the contribution of organosulfates to the organic aerosols, they converted the calculated values of organic sulfate to the organosulfate mass concentrations based on the molecular weight ratio of organosulfates (156 and 334 u for low and high MW assumption respectively) to sulfate.

In this work, we propose a method for the estimation of organosulfates in aerosols as a whole based on their sulfate functional group. The sulfate group in organosulfates is released when the water extracts of atmospheric aerosol samples are treated under a harsh dissociation condition developed in this study. The mass concentrations of sulfate ion before and after dissociation are measured by IC as those of inorganic sulfate (IS) and total sulfate (TS), respectively. The mass concentrations of organic sulfate (OS), that is the sulfate in organosulfates, are estimated as a difference between TS and IS. The resulting OS is then converted to the mass concentrations of organic sulfur (S_{org}, $\mu gS\ m^{-3}$) and to the carbon content in organosulfates ($OC_{s\text{-}related}$) or the mass concentrations of organosulfates ($OM_{s\text{-}related}$) to quantitatively assess the abundance of organosulfates in the ambient air. This approach is applied to analyzing the $PM_{2.5}$ samples collected at three locations with different environmental characteristics in Shenzhen for the S_{org}, $OC_{s\text{-}related}$ and $OM_{s\text{-}related}$. The measured S_{org} as well as the estimated $OC_{s\text{-}related}$ and $OM_{s\text{-}related}$ are compared not only within the different sampling locations in this study but also to the prior ambient measurement results reported in literature.

2. Materials and methods

2.1. Materials and device

All the reagents employed were of analytical grade. Sodium sulfate, Sodium hydroxide and hydrochloric acid were from Sigma-Aldrich. Sodium dodecyl sulfate (SDS), a surrogate standard for organosulfates used in this method, was also purchased from Sigma-Aldrich. All aqueous solutions were prepared in high purity water. A middle volume $PM_{2.5}$ sampler (KC-6120, Laoying) was applied to collect field samples with a pre-baked quartz fiber filter (Φ90, Millipore). The measurement for IS and TS was performed with a Dionex ICS 3000 ion chromatography (IC) system. Separations were carried out on a DionexIonPac AS11-HC anion analytical column (2 × 250 mm) located after a DionexIonPac AG11-HC guard column (2 × 50 mm). The conductivity of the eluent was suppressed with a Dionex ASRS4mm suppressor.

2.2. IC analysis of sulfate

Sodium sulfate was used as a surrogate compound for the quantification of sulfate group in IS and TS using IC. Sodium hydroxide solution (0.1 mol/L) was used as the eluent, and it was stored under N_2 atmosphere and prepared daily. The gradient elution used in this work was as follows: 0~10 min, 10% NaOH:90% H_2O; 10~14 min, linear change from 10% NaOH:90% H_2O to 45% NaOH:55% H_2O; 14~19 min, 45% NaOH:55% H_2O; 19~25 min, 10% NaOH:90% H_2O. The flow rate of the eluent remained constant at 0.25 mL min^{-1}. The retention time of SO_4^{2-} was 19 min under those operating conditions. All samples were analyzed in duplicate.

The calibration curve for quantifying IS and TS in ambient samples was constructed based on the peak area (Y-axis) versus the concentration of sulfate functional group (X-axis) using sodium sulfate. A linear calibration curve with sulfate concentration ranging from 50 to 600 ppb was obtained with R^2 of 0.999. The RSD values varied between 1.45 and 11.35% with an average of 5.93%. The Method Detection Limit (MDL) for sulfate was determined by measuring 21 blanks in the same way as the standards (Skoog et al., 2007). The resulting data were treated statistically to obtain the mean blank absorbance $\overline{S}_{bl}$ and the standard deviation s_{bl}. The minimum distinguishable absorbance S_m was taken as the sum of the mean blank absorbance $\overline{S}_{bl}$ plus a multiple k of the standard deviation of the blanks (Equation (1)). The slope of the standard curve was used to convert S_m to C_m, which was the MDL calculated by Equation (2). The MDL was 13.88 ppb.

$$S_m = \overline{S}_{bl} + 3s_{bl} \tag{1}$$

$$C_m = \frac{S_m - \overline{S}_{bl}}{m} \tag{2}$$

Where, S_m——minimum distinguishable absorbance;
s_{bl}——standard deviation of the blanks;
$\overline{S}_{bl}$——mean blank absorbance;
m——slope of the standard curve;
C_m——MDL (ppb).

2.3. Aerosol sampling

The aerosol samples were collected simultaneously from three sites between Dec. 21 and Dec. 24 2014 in Shenzhen (113°46′-114°37′E, 22°27′-22°52′N), with one close to a power plant (PP), one at a heavy traffic intersection (HTI), and one on the campus of Harbin Institute of Technology Shenzhen graduate school (HITSZ). PP, as one of the largest coal-fired power plants in Shenzhen, is subjected to heavy SO_2 emission. HTI sampling site is a very busy intersection with slow moving traffic of trucks, buses and cars and thus is exposed to heavy traffic pollution. HITSZ is a suburban site relatively far from the nearest commercial center and less affected by pollution sources. Three samples were collected on each site, and sampling started at 9:00 a.m. and lasted for 24 h. The fine particles were sampled on pre-baked quartz fiber filters using a middle volume $PM_{2.5}$ sampler at a flow rate of 100 L min^{-1}. All samples were collected on 10 m high and transferred back to our laboratory in a cooler and stored in a freezer at −20 °C until analysis. One half of the quartz filter was ultrasonically extracted twice with 10 mL of ultrapure water for 20 min each time. The extracts were stored at 4 °C in a refrigerator before analysis.

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