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Evaluation of a Sequential Spot Sampler (S3) for time-resolved measurement of PM$_{2.5}$ sulfate and nitrate through lab and field measurements

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AMTD
8, 10611–10633, 2015

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a Sequential Spot
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Abstract

The Sequential Spot Sampler (S3), a newly developed instrument to collect aerosols for time resolved chemical composition measurements, was evaluated in the laboratory and field for the measurement of particulate sulfate and nitrate. The S3 uses a multi-temperature condensation growth tube to grow individual aerosols to droplets which are then deposited as a $\sim 1\,mm$ diameter dry spot at the end of the growth tube on a $100\,\mu L$ well of a multi-well plate. The well plate advances automatically to provide a sequence of time-resolved samples. The collected aerosols are subsequently analyzed in the laboratory. The sample is concentrated during the collection process and the laboratory extraction and analysis steps can be automated. The well plate, as received from the field, is placed onto a needle-based autosampler that adds liquid for sample extraction and injects sample extract from each well onto an ion chromatograph for analysis. Laboratory evaluation for sulfate and nitrate ions showed that PEEK used as well plate material does not contribute any artifacts; a 60 min extraction procedure leads to the recovery of sulfate and nitrate from the dry spots at above 95 % extraction efficiency; and samples stored frozen and analyzed up to 23 months later show less than a 10 % change in sulfate and nitrate concentrations. In a month long field study conducted in Southern California, two S3s were deployed alongside a URG denuder/filter-pack and a Particle-Into-Liquid Sampler combined with an Ion Chromatograph (PILS-IC). Collocated S3 sampler concentrations compared by linear regression show good agreement with $r^2 = 0.99$ and slope = 0.99 (± 0.004) $\mu g\,m^{-3}$ for sulfate and $r^2 = 0.99$ and slope = 1.0 (± 0.006) $\mu g\,m^{-3}$ for nitrate. When compared to the URG denuder/filter-pack and the PILS-IC, the S3 sulfate and nitrate concentrations yielded correlations above 0.84 for the square of the correlation coefficient and regression slopes close to one.

1 Introduction

Atmospheric aerosols have important local, regional and global impacts. To understand the extent and nature of these effects, time-resolved observations of aerosol chemical composition are needed. Many different semi-continuous and online methods of measurement have been explored to address this need. Various instruments using aerosol mass spectrometry have been developed in recent years (e.g., Jayne et al., 2000; Allan et al., 2003; Drewnick et al., 2003; Jimenez et al., 2003; Takegawa et al., 2005) to make direct online measurements of particle chemical composition. These include single-particle measurements (e.g., Prather et al., 1994; Noble et al., 1996) and measurements of submicron, non-refractory aerosols (e.g., Canagaratna et al., 2007; Hings et al., 2007; Ng et al., 2011; Budisulistiorini et al., 2014). Several other semi-continuous methods have also been developed, including the Particle-Into-Liquid Sampler coupled with an Ion Chromatograph (PILS-IC), which can grow and collect aerosol particles into a flowing liquid stream and utilize an IC for the analysis (Orsini et al., 2003; Weber et al., 2001), the Monitor for AeRosols and Gases in ambient Air (MARGA) which uses steam capture and IC analysis of aerosols and trace gases (Schaap et al., 2011; Makkonen et al., 2012), the humidified impaction with flash volatilization method, developed by Stolzenburg et al. (2003) and used by Wittig et al. (2004), the Ambient Ion Monitor-Ion Chromatograph (AIM-IC) which has been characterized and used by Markovic et al. (2012) for the measurement of water-soluble chemical composition of atmospheric fine particulate matter, and the Gas Particle Ion Chromatography (GPIC) system developed by Dionex (Godri et al., 2009). Most of these systems provide very useful information about aerosol composition with time resolutions of several minutes or better. However, because these instruments locate the analytical measurement component (e.g., an IC or a mass spectrometer) in the field, they carry significant capital cost, have a large footprint, and work best with a highly skilled field operator. These factors have so far limited the use of such approaches in large measurement networks, where cost, space, and operator time are critical considerations.

A more common and cost effective approach for aerosol composition measurement in aerosol networks is to collect the samples in the field, then analyze them at a central laboratory location. This approach has been used for decades to measure aerosol composition in monitoring networks around the world (e.g., Chow et al., 1994). These off-line aerosol measurement systems often require the collection of aerosols on filters. Extraction of the filters usually involves sonicating them in a liquid (e.g., ultrapure water), then filtering the liquid, relocating it into a different vessel and analyzing it. Filter collections in the field are relatively inexpensive, as long as sample frequency is modest, but once in the laboratory they are labor intensive and subject to possible contamination during operator handling. Another disadvantage to this approach is the need for collection of large air volumes to ensure sufficient sensitivity for analyte measurement in filter extracts (usually several ml or greater in volume) only a small fraction of which is typically analyzed. As a consequence of the large air sampling volumes required and the inconvenience of making frequent filter changes in the field, filter sampling is typically conducted with sample durations of 24 h or longer. In addition, for network monitoring purposes, samples are usually only collected once a week, every three days or every 6th day. A higher time resolution (at least hourly samples) for the measurement of aerosol chemical composition is an important tool in addressing the impact of aerosols on the environment (Shaap et al., 2011). In order to provide convenient and higher time resolution field collection of aerosols in a manner suitable for automated post-collection analysis at a centralized laboratory, the Sequential Spot Sampler (S3) was developed.

The development and function of the S3 have been discussed in detail by Eiguren-Fernandez et al. (2014). The S3 uses the water-based condensation growth technique developed by Hering et al. (2014) to grow fine particles into micrometer sized droplets. The droplets are deposited as dry, ~ 1 mm diameter spot at the bottom of a 100 μL well on a multi-well plate. The well plate advances in accordance with an operator-selected schedule to provide as many as 23 sequential samples. Well plates can be exchanged after all wells are used, or earlier, by the operator. At the conclusion of sampling, the

plate is transferred into a clean Petri dish, sealed, and transferred to the laboratory where it is stored in a freezer until analyzed.

This sample collection method facilitates the automation of laboratory aerosol sample extraction and analysis. The well plate is placed on a customized tray in a needle-based, commercial autosampler. The autosampler handles the addition of solution, sample extraction and injection onto a chromatograph such that the entire plate may be analyzed without user intervention. The small volume of a well ($\sim 100\,\mu L$) allows the deposited aerosol to be efficiently extracted, keeping extract concentrations higher to provide sufficient analytical sensitivity for short sampling times.

The suitability of the choice of well plate material, sample storage and extraction processes and the integrity of the collected samples over time were investigated in the laboratory and the results are presented here. After the completion of these tests, the S3 was deployed at a site in Southern California to test its capability for accurate hourly aerosol composition measurements. The field site was chosen to present the S3 with a broad range of aerosol concentrations. During this field measurement two S3 systems were operated side-by-side for comparison. Measurements using the S3 samplers were also compared with two well-established reference methods: a PILS-IC system and a URG denuder/filter-pack sampler. The overall field performance of the S3 during the field campaign is summarized, including quantification of sampler precision and accuracy.

2   Methods

2.1   The Sequential Spot Sampler (S3)

The S3 (Eiguren-Fernandez et al., 2014) consists of a 3-stage (conditioner, initiator, and moderator) water condensation growth tube followed by a single-jet impactor collector. It operates at a flow rate of $1.0–1.5\,L\,min^{-1}$. The first and third stages, measuring 154 mm (first stage) and 100 mm (third stage) in length, are cooled to provide wetted

walls at 2–5 °C and 10–12 °C, respectively. The walls of the 73 mm long second stage are actively heated to 32–35 °C and wetted. This approach provides sufficient supersaturation to activate particles in the nanometer size range, but reduces the temperature and dew point of the exiting flow to below 16 °C, as described by Hering et al. (2014). A diagram of the S3 is presented in Fig. 1. Particles as small as 8 nm grow through water condensation to form 1–3 µm droplets, which are collected by impaction as a concentrated spot at the bottom of a 6 mm diameter, 3 mm deep well within a multi-well plate. The active well, which is the well situated directly under the impaction jet from the growth tube, is heated slightly. This evaporates the water from the droplets during collection to form a dry spot. The well plate contains 24 wells and advances automatically to give a sequence of time resolved samples. Except for the active well, the wells are kept at ambient temperature and are covered by a Teflon lid.

At the conclusion of a sequence of samples, the well plate is removed from the S3 sampler, placed in a sealed petri dish, stored cold, and returned to the laboratory for analysis. The laboratory analyses are done in an automated fashion using a needle-based autosampler such as the Dionex AS or the PAL CTC (both of which have been used in the S3 development and testing). The well plate is simply placed on the autosampler, the autosampler adds liquid (e.g., water, eluent) to the active well and then after the required extraction period, injects the extracted sample into a multi-port valve, from where it is transferred onto an IC. The autosampler is programmed such that the soaking period overlaps with the analysis of the previously extracted sample. Thus the complete set of samples from the well plate may be analyzed in no more time than required for the chromatography and without operator intervention. During the analyses for this study, the soaking time was 60 min and the IC analysis time, 30 min.

2.2 Laboratory evaluation

Laboratory studies were conducted to test the efficiency and suitability of well plates for use with the S3 system for the analysis of sulfate and nitrate. Initial well plate material tests were conducted using acrylonitrile-butadiene-styrene (ABS), high density

polyethylene (HDPE), ultra-high molecular weight polyethylene (UHMWP), and poly ether ether ketone (PEEK) to test for sample extraction efficiency and sample stability over time. A combined seven anion standard from Dionex (Sunnyvale, CA) was used as a surrogate sample for testing purposes.

PEEK (McMaster Carr, Elmhurst, IL) was chosen to manufacture well plates for further S3 testing, based on superior results of the sample recovery and stability tests, and because it is inert and does not interact with the types of compounds investigated here (i.e. nitrate and sulfate). PEEK has a low water absorption percentage (0.1–0.5 %) which is important as the deposited aerosols are extracted in aqueous solutions. Also, PEEK has been previously used in other aerosol measurement instruments due to some of its characteristics noted above (e.g., Orsini et al., 2003; Morales-Riffo and Richter, 2004). Initial tests on the system were conducted through a manual setup where the operator would pipette the extracted deposit to vials, and the vials transferred to an auto-sampler for IC analysis.

The amount of time required for complete extraction of sulfate and nitrate from the dry deposits was evaluated using the combined seven anion standard from Dionex (the anions in the Dionex standards were prepared from sodium salts). Multiple samples were prepared by pipetting 10 μL of an aqueous standard of known concentration into each of the multiple wells on the well plate. Following sample transfer into the wells, a hot plate was used to warm the well plate to 32° for approximately 30 min to dry the deposit. The temperature of the hot plate is similar to that of the active well on the S3. The well plate was removed from heat and left to reach room temperature. Then 100 μL of a 0.01 mM LiBr solution was added to extract the deposited material in each well. The samples were allowed to soak, without agitation or ultrasonication. After a selected period of time (varied between 15 to 120 min to test the extraction efficiency) an 80 μL aliquot was pipetted from the well and analyzed by ion chromatography. Five independent measurements were made at each of 8 different soaking times.

PEEK well plates were investigated for possible background analyte interference from plate material and environmental contaminants that may have been introduced

from storing the plate in the S3, the autosampler, exposure to laboratory air during analysis, and in the freezer. Ultrapure water ($> 18.2\,\text{M}\Omega$) was deposited in the 24 wells of several well plates. On one well plate, some wells were immediately analyzed and some were analyzed after one week. Other well plates, with the ultrapure water deposit in the wells, were kept in the S3 while the system was running and while idle, others were held in the auto-sampler for different durations, some were kept in a freezer in sealed petri dishes, and some treated as if they contained sample deposits and extracted and analyzed following the same procedures.

In order to check the integrity of samples over time, $10\,\mu\text{L}$ of a combined seven anion standard from Dionex was deposited in each well of a 24 well plate. The concentration of the deposit was $960\,\mu\text{g}\,\text{L}^{-1}$ for sulfate and $640\,\mu\text{g}\,\text{L}^{-1}$ for nitrate. The first well was extracted and analyzed immediately, the second in a month, the third in two months and so on. When the plate was not being extracted, it was kept in a sealed petri dish in the freezer. The results from this experiment were repeated on 5 other well plates.

2.3 Field evaluation

During 13 June–5 July 2012, two S3 systems, a PILS-IC and URG annular denuder/filter-packs were used to measure ambient PM$_{2.5}$ sulfate and nitrate. The instruments were deployed inside and around a Colorado State University (CSU) mobile laboratory at a mountain site in Southern California, near the San Gorgonio Wilderness Area (34.10° N, 116.83° W) at an elevation of 8700 feet. This site, also used by the Interagency Monitoring of PROtected Visual Environments (IMPROVE) monitoring network, was chosen because of the typically wide range of concentrations of aerosol nitrate and sulfate experienced due to the influence of the nearby Los Angeles basin and diurnal mountain-valley wind circulation as shown by Lee et al. (2008). The large diurnal variability in ambient aerosol concentration provided an excellent range of concentrations for validating the performance of the S3.

The two S3 systems were set up side by side inside the mobile laboratory, sharing a common inlet of copper tubing (1/4″ ID) combined with conductive black tubing (TSI,

Shoreview, MN). This system has been briefly described in the previous sections of this paper and a complete description is provided by Eiguren-Fernandez et al. (2014) and Hering et al. (2014). A $PM_{2.5}$ cyclone (URG, $3 \, L \, min^{-1}$) was used for the common inlet of both S3 systems, coated denuders (URG) were used for removal of gases that might

5　interfere with the aerosol sample concentrations, although the wet walls of the growth tube are expected to efficiently remove soluble gases. Each S3 sampler was equipped with a critical orifice to regulate the flow of air through the system ($\sim 1.5 \, L \, min^{-1}$); this is in addition to the pump and valve furnished as a standard feature of the S3. The airflow was periodically checked with a DryCal flow meter (Butler, NJ). Samples were

10　collected in each well for an hour. Aerosols were deposited into the S3 well plates on site, the plates were removed daily and placed in sealed petri dishes and kept in a freezer and later transported to the laboratory at CSU for extraction and analysis using an autosampler (Dionex AS) connected to an IC (Dionex DX-500). Field blanks were collected for each S3 by connecting a high efficiency particulate arresting (HEPA)

15　filter to the common inlet of the S3s for 3 h (3 wells, one hour per well) at the beginning, mid-point and end of the study. The limit of detection (LOD) for this system was calculated using three times the standard deviation of the blanks collected throughout this study. The LOD was $0.5 \, \mu g \, m^{-3}$ for sulfate and $0.2 \, \mu g \, m^{-3}$ for nitrate for a one hour sample period. The system requires a flow and leak check after the installation of each

20　new plate. This process takes about 10 min and was accomplished using a DryCal for the flow check and a condensation particle counter (CPC) for the leak check. Outside of the normal setup and plate change requirements, operator intervention was required only once during this 23 day measurement period.

　　When analysis was planned, plates were removed from the freezer and left inside

25　the sealed petri dishes until they were at room temperature (~ 1 h). These plates were removed from the petri dishes and placed on a customized tray on a needle-based customized autosampler. For this field study a Dionex AS autosampler was modified and used to automate the deposit extraction and injection of the extracted sample from the well plates. Eiguren-Fernandez et al. (2014) used a similar system and describe

the setup in detail. The autosampler deposited a specific amount of extraction solution, usually 80–100 µL (typically IC eluent, 0.01 mM LiBr solution or ultrapure water) into one of the wells. After soaking for an hour the autosampler injected a portion of the extract into the IC for analysis. The IC analysis proceeded while the next well was prepared for analysis.

A PILS-IC was deployed alongside the pair of S3 samplers, and used for the semi-continuous measurement of ambient $PM_{2.5}$ chemical composition. Orsini et al. (2003) provide a comprehensive depiction of the PILS-IC system; a short description is provided here. Ambient air is mixed with supersaturated steam in order to grow fine particles into droplets which are inertially deposited on an impactor plate. The deposited particles are washed off the plate by a continuous flow of 0.01 mM LiBr and injected into an IC system for analysis. The PILS-IC system was located inside the CSU mobile laboratory, with an inlet collecting air from the outside. The air-flow for the PILS was set at $16 \, \text{L min}^{-1}$ using a critical orifice and verified using a DryCal flow meter. The PILS was equipped with a $PM_{2.5}$ cyclone (URG, $16 \, \text{L min}^{-1}$) to provide a defined size cut and coated denuders (URG) for the removal of gases that might interfere with the aerosol sample (e.g., nitric acid for nitrate and sulfur dioxide (after oxidation) for sulfate). Samples were injected into the IC and analyzed for bromide, nitrate, and sulfate every 15 min. Bromide is used as an internal standard to account for dilution of the liquid stream by condensed steam. A HEPA filter was connected to the inlet of the PILS, every week for 30 min, for the collection of field blanks from this system. The PILS-IC system was calibrated at the beginning and the end of the study. Each calibration included 5 points, using dilutions of the Dionex 7 anion standard, plus two blanks (ultrapure water).

Two URG denuder/filter-pack systems were deployed outside of the mobile laboratory in a field near the IMPROVE site. The two systems were not operated simultaneously but rather programmed for continuous collection of samples. These systems included a $PM_{2.5}$ cyclone (URG, $10 \, \text{L m}^{-1}$) and coated denuders for capturing ambient gaseous species such as nitric acid, ammonia, and sulfur dioxide. A 37 mm PALL nylon

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filter was in line after the denuders for the collection of $PM_{2.5}$ aerosols in the airstream; the nylon filter retains any nitrate volatilized as nitric acid (Yu et al., 2006). Filters were collected every 12 or 24 h, at 8.00 a.m.–8.00 p.m. or 8.00 a.m.–8.00 a.m. LT. The filters were sealed inside pre-cleaned petri dishes and stored in clean freezer bags after sampling, held in a freezer and later transferred to the laboratory for extraction and analysis using a Dionex IC system. Lee et al. (2008) provide a more detailed overview of the URG setup and the extraction and analysis of the filters. Eight field blank filters that were collected during the study had an average concentration of $0.2 \pm 0.05\,\mu g\,m^{-3}$ for nitrate and $0.08 \pm 0.05\,\mu g\,m^{-3}$ for sulfate.

3   Results and discussion

3.1   Laboratory results

As part of the sample extraction step, liquid (either IC eluent or ultrapure water) was injected in a well and left for a specified amount of time. The required extraction time for complete recovery of the deposited nitrate and sulfate in each well was investigated. A known concentration of the Dionex standard was deposited in each well, dried and then extracted manually. Different extraction times, ranging from 20–120 min, were tested in the laboratory. This experiment was repeated for 5 different concentrations of sulfate (65–$1600\,\mu g\,L^{-1}$) and nitrate (95–$2400\,\mu g\,L^{-1}$). Figure 2 shows the results of these experiments. For the standards used in this test, 60 min was an optimal extraction time, providing at least 95 % recovery of the deposited nitrate and sulfate. The recovery remained unchanged with increased extraction time.

After samples are collected on the multi-well plates, it may be desirable to store plates in the freezer before analysis for extended periods of time. Therefore, it is important to quantify the duration of time during which the deposited (or sampled) constituents are not lost or contaminated. Deposits in multi-well plates were stored and tested for 23 months. Figure 3 shows the data from this test. These results demon-

strate that the mass of the deposit for each analyte stays consistent during this time. The percentage of deposit recovered fell between 94–98 % for all 24 wells. This shows that the methods of storage and re-extraction of samples are suitable for periods up to at least 23 months.

Background concentrations for sulfate and nitrate for several well plates were checked using deposits of ultrapure water. It was found that the PEEK material of the plate and the process of injecting and extracting the sample did not add any artifact to the background concentrations of nitrate and sulfate. The laboratory tests demonstrate the suitability of the PEEK material for the construction of the well plates, the lack of environmental contaminants or artifacts in the procedures used to store and extract the plates, and the possibility of storing sampled well plates for future analysis without any loss of sample or contamination, all with respect to the analysis of nitrate and sulfate. Background concentrations were mostly below the LOD of the IC used for this analysis. The performance of the PEEK well plates was also examined by using sulfate salts associated with cations other than sodium, with similar results.

3.2 Field results

Concentrations of $PM_{2.5}$ nitrate and sulfate for each instrument for the duration of the field deployment are presented in Fig. 4. The concentrations of nitrate measured during this study ranged from 0.143 to $28.7\,\mu g\,m^{-3}$ and for sulfate between 0.564 to $10.1\,\mu g\,m^{-3}$. The wide range of concentrations observed for both nitrate and sulfate during the study presented a great opportunity for testing the S3 as a newly developed system. Figure 4 presents all the data collected from all of the instruments deployed during the measurement period. It shows the clear value of instruments with higher time resolutions (PILS-IC and S3) in being able to capture episodes of high nitrate and sulfate concentrations relative to the more typical, lower time resolution of the URG denuder/filter-pack.

The results from the side-by-side comparison of the two co-located S3 instruments for both nitrate and sulfate are presented in Fig. 5. For a least squares linear regression

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with the line forced through the origin, the r^2 (squared correlation coefficient) value is 0.99 and the slope is 1 for sulfate and the r^2 value is 0.99 and the slope is 0.98 for nitrate. Pooled relative standard deviations for the paired measurements of each species are 2.4 % for sulfate and 8.7 % for nitrate, demonstrating good precision for this method. The measured precision includes not only instrument sampling uncertainty, but also the precision in sample extraction and analysis by IC.

The data from two S3s were averaged for comparison of concentrations between the S3s and other measurements. All the data collected were averaged over the longer data collection period for comparison (i.e. PILS-IC averaged to S3 time, and S3 averaged to URG time). The comparison results are presented in Fig. 6. The r^2 for linear fits (least squares regression with intercept forced through the origin) of the comparison of sulfate concentrations from the S3 with each system are 0.90 with slopes of 1.0 and 1.1 for the PILS-IC and URG, respectively. The r^2 value for nitrate from the S3 compared to the PILS-IC is 0.90 with a slope of 0.99 and for the S3 compared to the URG filter-pack measurements the r^2 is 0.84 with a slope of 0.89.

4 Conclusions

PEEK was shown to be suitable for the construction of well plates for the S3 for the collection and analysis of aerosol sulfate and nitrate. Furthermore, the PEEK well plates can be sampled and stably stored in a freezer for future analysis (at least 23 months after the collection of the samples).

Field evaluation of the S3 systems demonstrated good precision with RSDs of 2.4 and 8.7 % (for sulfate and nitrate, respectively) from co-located samplers. When comparing the S3 instrument with other well-established methods, the S3 results performed well with r^2 values ranging between 0.84–0.90 and slopes between 0.89–1.1. The S3 was capable of successfully measuring PM$_{2.5}$ nitrate and sulfate at an hourly time resolution over a wide concentration range from less than $1\,\mu g\,m^{-3}$ to more than $10\,\mu g\,m^{-3}$.

The S3 is a compact system that can be deployed for field measurements to characterize the chemical composition of ambient aerosols. It requires low maintenance in the field as demonstrated during its deployment in the 23 day field measurement campaign discussed in this paper. Operator intervention was required for changing the plates, adding DI water to the S3 water reservoir and discarding wastewater, and in case of instrument malfunction. The S3 has a small footprint ($\sim 12'' \times 12'' \times 24''$), requires low amounts of electrical power and can be quickly deployed and setup in many different locations. The extraction and analysis procedures in the lab for the S3 well plates are automated and require minimal operator time and handling. This reduces the cost of analysis and the chance of contamination or error due to the extra steps needed when a human operator handles the samples. The consistent performance of the S3 during this study shows that it is suitable to use for long-term air quality measurements, especially for multi-site deployment where limited operator intervention and high and/or adjustable time resolution are valued.

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Evaluation of
a Sequential Spot
Sampler (S3)

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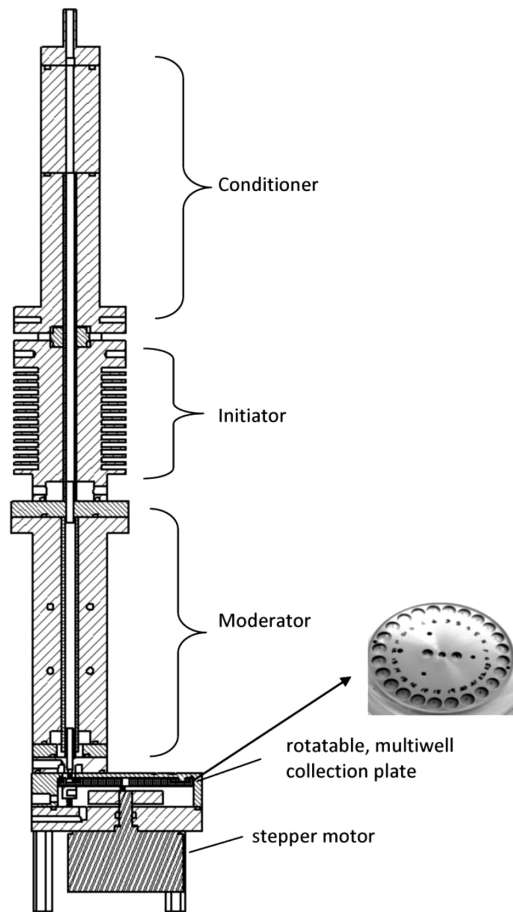
Figure 1. Diagram of S3 with sample collection steps (step 1: conditioner, step 2: initiator, step 3: moderator) and a multiwell plate where samples are deposited. (First published in Aerosol Science and Technology, 48, p. 656, 2014.)
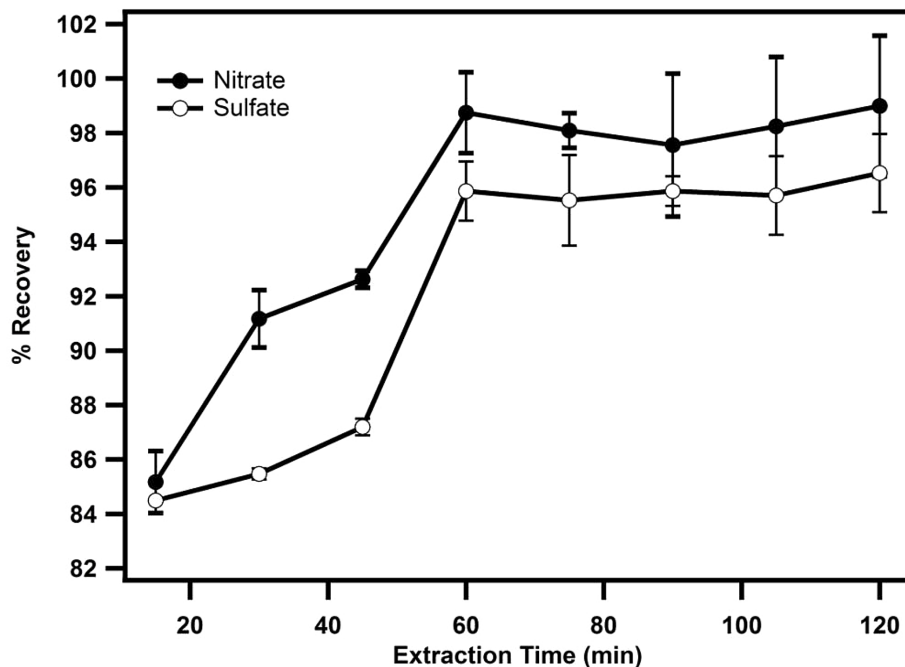
Figure 2. Percent recovery of nitrate and sulfate deposits for different sample extraction times. The error bars shown represent the standard deviations of recovery percentage from all 5 experiments at each extraction time.
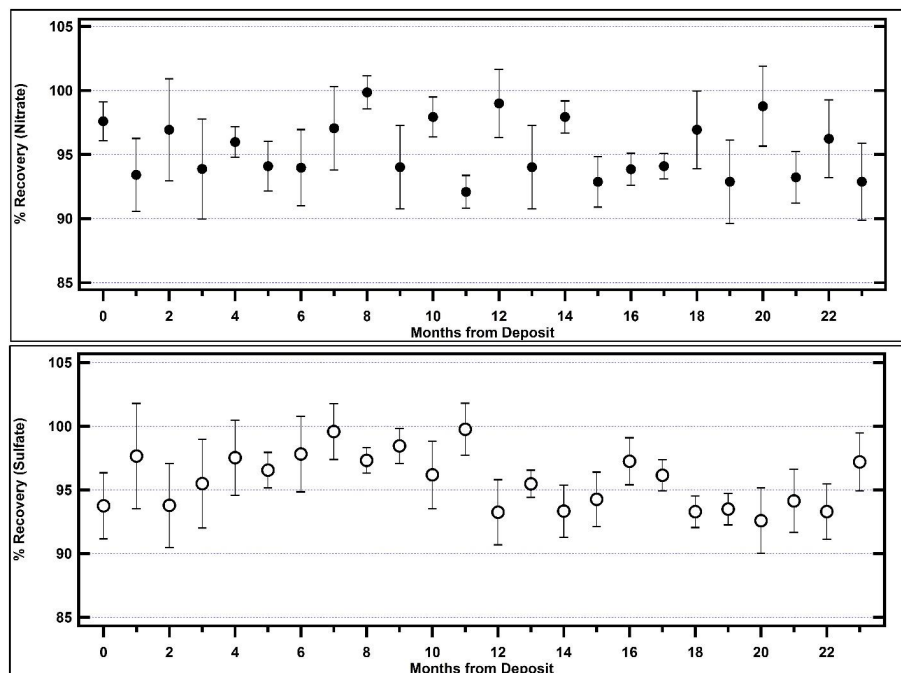
Figure 3. Percent recovery of deposited standard in wells after different plate storage periods (up to 23 months). The error bars represent the standard deviation of data from 5 well plates.
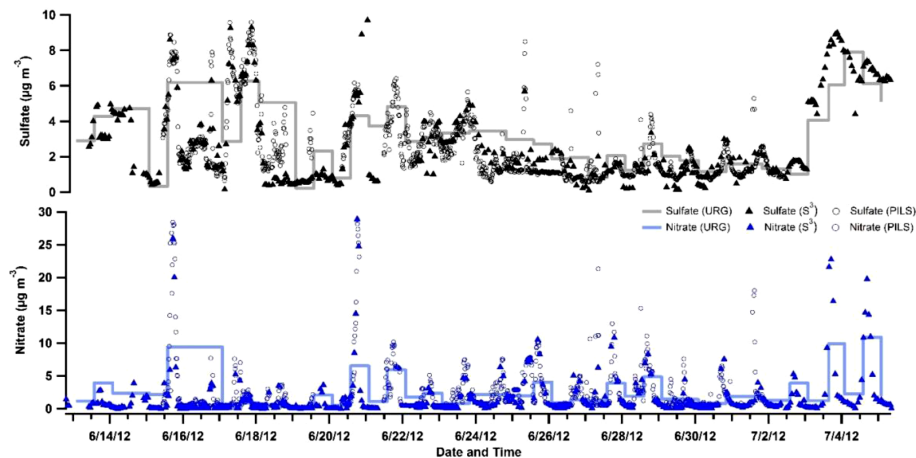
Figure 4. Time series of PM$_{2.5}$ nitrate and sulfate collected from June–July 2012 in San Gorgonio Wilderness area, CA, using one S3 sampler, PILS-IC and URG denuder/filter-packs.
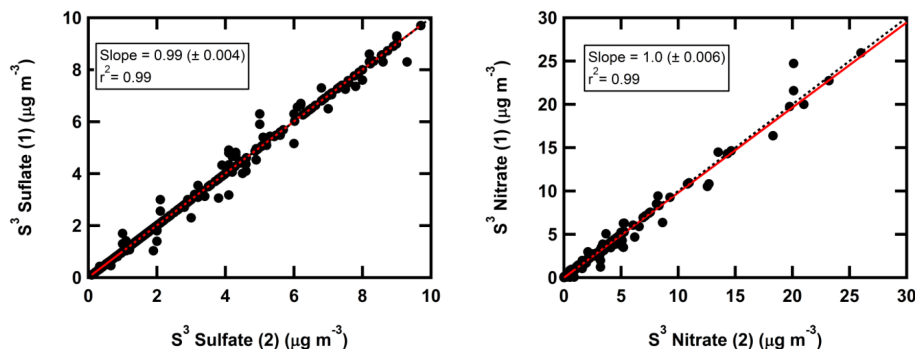
Figure 5. Intercomparison of PM$_{2.5}$ nitrate and sulfate collected using two S3 systems during the San Gorgonio, CA study. The dotted lines show a 1 : 1 relationship and the solid lines show the results of a least squares linear regression fit with the intercept forced through the origin.

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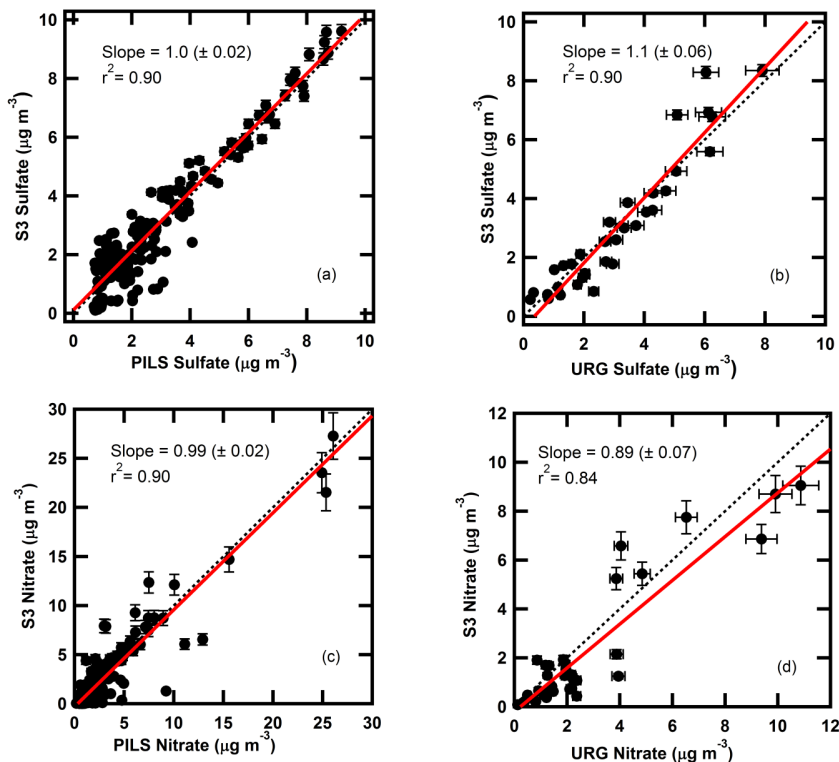Full Screen / Esc

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Figure 6. Comparison of aerosol nitrate and sulfate during the San Gorgonio, CA study between the S3, PILS-IC and URG systems. The Top panel (**a** and **b**) is a comparison of Sulfate between the averaged data from the two S3 samplers and PILS and URG respectively, and the bottom panel (**c** and **d**) presents the same comparison for Nitrate. The dashed lines are the 1 : 1 line; the solid red lines are the correlation between the data presented. The error bars show the pooled % RSDs for the two S3 systems used in this study and the error bars for the URG systems were taken from collocated observations reported by Yu et al. (2006).

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