Technical Note

A Sampler for Collecting Fine Particles into Liquid Suspensions

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ABSTRACT

In this study, we developed a particle sampler for aerosol suspensions (PSAS) that collects ambient PM_{2.5} directly as liquid suspensions. The PSAS, which operates at a sampling rate of 50 L min⁻¹, first pre-selects fine particles with a custom-designed PM_{2.5} inlet and then enlarges them into 2–5 µm droplets via condensational growth with a saturation-condensation unit. Subsequently, the enlarged droplets are sequentially collected in our novel collection impactor as liquid suspensions. Laboratory evaluations indicate good collection efficiencies for the PSAS with both polydisperse and monodisperse fine particles, with 85% of the particles being effectively preserved in the collected suspensions. Field evaluations suggest good agreement between the PSAS suspensions and parallel filter samples for the analyzed chemical components (water-soluble Fe(II) and Cr(VI)) in the ambient PM_{2.5}. Thus, the PSAS is suitable for long-term particle collection and can be used to facilitate the online chemical and toxicological analysis of ambient PM_{2.5}.

Keywords: Aerosol sampler; PM_{2.5}; Suspension samples; Condensational growth; Droplet impactor.

INTRODUCTION

Adverse health outcomes caused by exposure to particulate matter (PM), especially PM_{2.5} (particles with aerodynamic diameter equal or less than 2.5 µm), have been well documented (Lelieveld *et al.*, 2015; Zhao *et al.*, 2018). The PM-induced health effects are strongly depending on the chemical and toxicological properties of particles (Charrier and Anastasio, 2012; Saffari *et al.*, 2015). Conventional PM analysis usually involves filtration or inertial impaction processes in which particles are collected on substrates such as filters or foils, and PM chemical and toxicological analysis are performed offline. Although these methods have been widely adopted, they are associated with drawbacks, including long time intervals for sampling and intensive labor for sample preparation and analysis, underestimations of insoluble PM components due to incomplete extractions (Wang *et al.*, 2013b; Gao *et al.*, 2017), as well as potential sampling artifacts for volatile species during long-term sampling (Eatough *et al.*, 2003). Efforts have been made to eliminate particle collection procedure, and to accomplish real-time direct

measurements/analysis of particle chemical composition by introducing advanced mass spectrometers (Jayne *et al.*, 2000; Smith *et al.*, 2004; Ng *et al.*, 2011). These techniques have significantly contributed to the further understanding of PM chemical characteristics, as well as their potential sources and formation mechanism (Canagaratna *et al.*, 2007; Smith *et al.*, 2010; Sun *et al.*, 2012).

Another alternative is to capture particles into liquid as suspension samples which can be directly analyzed. Such techniques include applying wet collection surfaces into filtration or impaction devices (Cofer *et al.*, 1985; Buhr *et al.*, 1995; Phan and McFarland, 2004; Takeuchi *et al.*, 2005; Orsini *et al.*, 2008; Puthussery *et al.*, 2018), as well as devices involving condensational growth method (Okuyama *et al.*, 2007; Dong *et al.*, 2012). In later techniques, the sampled particles are firstly mixed with vapors of working fluids (i.e., water, butanol etc.) (Hering and Stolzenburg, 2005). The mixture of particles and vapors is then cooled down to promote vapors condensing on particle surfaces, and enlarge particles into larger droplets that are easier to be detected (i.e., with a condensation particle counter (CPC)) (Stolzenburg and McMurry, 1991; Hering and Stolzenburg, 2005; Hering *et al.*, 2014), or collected directly as suspension samples. For example, a steam jet aerosol collector (SJAC) was developed by Khlystov *et al.* (1995) and was further enhanced by Slanina *et al.* (2001), in which particles are mixed with water steam for condensational growth and the grown droplets are

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then collected by cyclones. Another widely used technique is the Particle-into-Liquid Sampler (PILS) (Weber *et al.*, 2001; Orsini *et al.*, 2003). In PILS, the grown droplets are collected by a single-nozzle impactor, and the liquid sample collected on the impactor surface is removed by a small, constant flow of purified water that also contains an internal standard. Both SJAC and PILS have been adopted for online measurements of ionic components of PM in combination of ion chromatograph (IC) (Perrino *et al.*, 2015; Stieger *et al.*, 2019). A similar aerosol sampler was introduced by Wubulihairan *et al.* (2015a, b), in which a condensed water splitter is included to prevent sample dilution. Kidwell and Ondov (2001) also reported a high-flow-rate sampler with flow rate up to 170 L min⁻¹. These advanced techniques have effectively overcome some drawbacks in conventional particle collection methods.

There have been concerns on the change of chemical properties of sampled particles due to the usage of high-temperature water steam, as well as the decrease of pollutants' concentrations in liquid suspensions due to the usage of transport flow on collection surface (Perrino *et al.*, 2015). As a different approach, the Versatile Aerosol Concentration Enrichment System (VACES) in tandem with a liquid impinger (BioSampler; SKC-West Inc., Fullerton, CA, USA) was developed to collect PM directly as aqueous suspension samples (Kim *et al.*, 2001a, b). In VACES-BioSampler tandem, a water tank is used as saturator where water is gently warmed up to generate vapors, instead of using high-temperature steam generation devices. Based on the condensational growth components of VACES, Wang *et al.* (2013b, 2016) introduced a high-flow-rate (200 L min⁻¹) aerosol-into-liquid collector in which grown droplets are directly collected and accumulated as liquid suspensions without introducing transport flow onto collection surface, and further deployed this PM collector as online PM metal monitors. Recently a new water-based condensational growth technology was reported, in which a tandem of "conditioner-initiator-moderator" is included in order to improve condensational growth performance (Hering *et al.*, 2014). It has been applied into a liquid spot sampler to collect particles as suspensions (Fernandez *et al.*, 2014). These devices have provided new insights on the developments of advanced particle collection techniques for online analysis of chemical and toxicological properties of PM.

In order to achieve relatively high pollutant concentrations in collected liquid suspensions and good preservation of their chemical properties, a relatively high sampling flow rate, a gentle generation of water vapor, as well as exemption of the transport flow on collection surface are favorable for advanced PM collection techniques. Here we present a particle sampler for aerosol suspensions (PSAS) for collecting fine particles directly as liquid suspension samples with a flow rate of 50 L min⁻¹. The PSAS contains a custom-designed PM_{2.5} inlet, a saturator tank and a condenser for condensational growth, as well as a novel single-nozzle collection impactor for collecting the grown droplets as suspension samples. The collection impactor utilizes several unique configurations compared to conventional inertial impactors, including a Teflon gasket for restraining impacted droplets from bouncing

back to air stream, and a mesh surrounding the impaction surface to wick the collected droplets into sample outlet. Both laboratory and field evaluations indicate that the PSAS is capable for ambient PM collections and can be further modified for online monitoring of PM chemical and toxicological characteristics.

METHODS

Description of the System Configuration and its Components

The schematic of the PSAS system configuration is presented in Fig. 1. The PSAS has a design flow rate of 50 L min⁻¹ and contains four major components: the PM_{2.5} inlet, the saturator, the condenser and the collection impactor. The PM_{2.5} inlet is a custom-designed impactor containing two slit nozzles (each nozzle is 1 mm in width and 57.6 mm in length) which is designed to have a 50% cutpoint of 2.5 µm under a flow rate of 50 L min⁻¹. While for the collection impactor of PSAS, it is a single-round-nozzle impactor (nozzle diameter: 4 mm) designed to have a 50% cutpoint of 1.5 µm under a flow rate of 50 L min⁻¹. For inertial impactors, the 50% cutpoint size is determined by Stokes number as below (Hinds, 1999):

$$Stk = \frac{\rho_p d_p^2 U C_c}{9\eta D_j} \quad (1)$$

where *Stk* is the Stokes number, and in current designs 0.59 and 0.24 were used for rectangular slit nozzle and round nozzle, respectively (Hinds, 1999). ρ_p is the particle density (1000 kg m⁻³). d_p represents the diameter of a particle having a 50% probability of impaction. *U* is the jet velocity at the nozzle, which is calculated based on designed flow rate and nozzle dimension. *C_c* is the Cunningham slip correction factor, and η is the dynamic viscosity of the air (1.8 × 10⁻⁵ kg ms⁻¹). *D_j* is the geometry dimension of nozzle(s) in the impactor, which is the width for rectangular nozzle and the diameter for round nozzle.

In the PSAS system, the sampled air firstly passes through a PM_{2.5} inlet for preliminary size selection. PM_{2.5} then enters the saturator (stainless steel, 400 mm × 150 mm × 120 mm in dimension) filled with deionized water for saturation, in which a heater is deployed to gently heat up the water. The temperature of aerosol-water vapor mixture (measured by a type K thermal couple) is maintained at around 38°C by adjusting the voltage applied to the heater. The saturated mixture then passes the condenser (500 mm in length and 20 mm for inner diameter) which is connected to a circulating chiller. The coolant in the chiller is maintained at 4–5°C to cool down the mixture to 21–22°C, promoting particle condensational growth and finally enlarging particles into droplets with larger sizes. The condenser is slightly angled from horizontal in order to assist the drainage of condensed water accumulating on the tube inner surface. The grown droplets are finally collected via inertial impaction in the collection impactor. The new designed collection impactor utilizes several unique configurations. Different from

Fig. 1. System schematic of particle sampler for aerosol suspensions (PSAS). The inserted figure shows the structure of the collection impactor.

conventional impactors, a Teflon gasket is placed above the quartz impaction surface in order to create a groove surrounding the impaction surface. Such a groove serves as the droplets' accumulation/transportation area in combination of a stainless steel mesh around the impaction surface's outside edge as a wicking material (Orsini *et al.*, 2003). When droplets are impacted on the quartz surface, the spreading airflow blows the impacted droplets into the groove, but the air streams turn around at the inner surface of the Teflon gasket. Therefore, impacted droplets are restrained from bouncing back into airflow, resulting in better collection efficiencies. A multi-channel peristaltic pump continuously transfers condensed water from the condenser and the collection impactor, as well as the collected droplets. Although PSAS has a medium sampling flow rate (i.e., 50 L min^{-1}) compared to some previously reported samplers with very high sampling flow rates (Kidwell and Ondov, 2001; Kim *et al.*, 2001a, b; Wang *et al.*, 2013a), it is more flexible to move and to be deployed into field collections due to its smaller size and lighter weight. All components and accessories of PSAS are mounted on a custom-built wheeled aluminum frame, with a dimension of $1000 \text{ mm} \times 700 \text{ mm} \times 800 \text{ mm}$ and a total weight of 40 kg.

Laboratory Evaluations of PSAS Collection Efficiency

The first part of laboratory evaluations of PSAS is to characterize the collection efficiencies of the $\text{PM}_{2.5}$ inlet and the collection impactor. Polydisperse NaCl particles, with a peak diameter around $3\text{--}3.5 \mu\text{m}$, were generated by a supermicron particle generation system (Chen *et al.*, 2016). Briefly, NaCl

solution was injected via a syringe pump into an ultrasonic nozzle (60 KHz, Model 8700-60; Sono-Tek Corp., Milton, NY, USA) motored by an ultrasonic generator (Model 06-05018; Sono-Tek Corp., Milton, NY, USA) to generate micron-sized NaCl droplets. A mixing chamber was placed beneath the ultrasonic nozzle where filtered air was supplied and mixed with generated droplets for dilution and stabilization. The tested units (i.e., the $\text{PM}_{2.5}$ inlet and the collection impactor) were placed inside the chamber and particle size distributions before and after the tested units were measured by an Aerodynamic Particle Sizer (APS Model 3321; TSI Inc., Shoreview, MN, USA). The collection efficiencies of tested units were determined by comparing the upstream and downstream APS measurements.

In the second step of laboratory evaluations, the performance of condensational growth within PSAS under certain operation parameters was examined. Polydisperse ammonium fluorescein particles were generated by an atomizer and mixed with HEPA-filtered make-up air. Before entering PSAS, the size distributions of intake ammonium fluorescein particles were detected by a Scanning Mobility Particle Sizer spectrometer (SMPS), which contains an electrostatic classifier (Model 3081; TSI Inc., Shoreview, MN, USA), a soft X-ray neutralizer (Model 3088; TSI Inc., Shoreview, MN, USA), a Differential Mobility Analyzer (DMA Model 3081A; TSI Inc., Shoreview, MN, USA) and a condensation particle counter (Model 3772; TSI Inc., Shoreview, MN, USA). During the evaluation tests, the saturator and condenser of PSAS were maintained at 38 and 5°C , respectively. These temperature parameters were selected among different

temperature combinations who has the highest overall collection efficiencies of PSAS, and were consistently used in all evaluation tests throughout this manuscript. The size distribution of grown droplets after condensational growth was measured by APS at the exit of condenser. The measured size distributions for intake particles and grown droplets are normalized by their corresponding peak concentrations, since different types of instrument were used for intake particles and grown droplet measurements (i.e., SMPS for intake particles and APS for grown droplets).

Lastly, the overall collection efficiencies of PSAS were determined using polydisperse/monodisperse ammonium fluorescein particles generated by atomizer. It should be noted that ammonium fluorescein particles are highly hydrophilic, therefore they may not fully represent hydrophobic particles generated from certain sources (i.e., combustions). The experiment system schematic is shown in Fig. 2. For polydisperse tests, the generated particles were mixed with HEPA-filtered air and collected by PSAS. For monodisperse tests, the generated particles were classified by the neutralizer-DMA tandem mentioned previously, and a certain size of particles were selected and directed into PSAS after dilution. A portion of sampled particles were directed into a 5 L min⁻¹ sampling line where a 47 mm quartz filter was placed to collect upstream sample. Another 47 mm quartz filter was placed at the exhaust flow of collection impactor to capture particles escaped from PSAS. After each collection, the upstream and downstream filters were extracted by 20 mL of 10% ammonia solution as upstream and downstream sample extracts. Besides, the condensed water from condenser was also preserved to evaluate particle depositions/losses within the condenser. The residuals on the nozzle and impaction surface of collection impactor were also extracted by 20 mL of 10% ammonia solution to evaluate the particle losses on nozzle and impaction surface. Extracts of upstream and downstream filters, condensed water in condenser, extractions of nozzle and impaction wall, as well as the actual suspension sample collected by

PSAS were measured for their fluorescent signals. The fluorescent measurements were performed using a module fluorescent monitor, which contains a LED light source with wavelength of 470 nm (LLS-470; Ocean Optics, Inc., Dunedin, FL), a fluorescent flow cell (FIA-SMA-FL-ULT; Ocean Optics, Inc., Dunedin, FL), and a portable spectrometer (USB4000-UV-VIS; Ocean Optics, Inc., Dunedin, FL). Based on fluorescent signals from upstream filter extracts, percentage of particle depositions in condenser, collection impactor nozzle and impaction surface, as well as actual particle collection in suspension sample and particles escaped into exhaust were calculated based on corresponding fluorescent signals and flow rates (the unapportioned percentage is defined as “others”).

Field Evaluations of PSAS Performance and Comparison with Parallel Filters

After laboratory evaluations, the PSAS system was deployed in the field for collections of ambient PM_{2.5}. The field sampling campaign were carried out at the 6th floor of Sino-Italian Tsinghua Ecological and Energy Efficient Building in Tsinghua University during September and October in 2019. The building is located 100–200 m from a local street with some traffic densities during most of the day, as well as restaurants nearby (Ren *et al.*, 2019). Ambient PM_{2.5} were collected as suspension samples via the PSAS system and each sample was collected for 3 hours. In parallel, PM_{2.5} were also collected by conventional filter sampling method, in which a PM_{2.5} cyclone (URG-2000-30EH; URG Corp., Chapel Hill, NC, USA) with flow rate of 16.7 L min⁻¹ was used as sampling inlet followed by a 47 mm quartz filter for particle collection. In total 12 sets of samples (i.e., suspension and parallel filter) were collected. It should be noted that the main purpose of current field sampling campaign is to demonstrate the agreements for analyzed chemical components between suspensions collected by PSAS and conventional filter sampling, therefore the sampling hours were not specifically set and were randomly chosen during daytime.

Fig. 2. Experimental setup for testing the collection efficiency.

Concentrations of water-soluble Fe(II) and Cr(VI) in collected samples were determined by spectrophotometry, similar to the method reported in previous studies (Sowlat *et al.*, 2016; Wang *et al.*, 2016). Fe(II) and Cr(VI) were measured since they are important metal species participating/promoting the reactive oxygen species in human body (Valko *et al.*, 2005; See *et al.*, 2007). Briefly, the quartz filter samples were extracted in 20 mL of deionized water with assistance of sonication for 45 minutes. Both filter extracts and suspensions were filtered by 0.20 μm polypropylene syringe filters to separate the insoluble components. For Fe(II) measurements, ferrozine reagent was added into measured samples (5% v/v) and standard curves was determined by measuring Fe(II) standard solutions (0–100 ppb) prepared by serial dilution. For Cr(VI) measurements, diphenylcarbazide reagent was added into measured samples (5% v/v) and standard curves was determined by 0–20 ppb standards. Spectrophotometry measurements were performed using a deuterium and tungsten halogen light source (DT-MINI-2-GS; Ocean Optics, Inc., Dunedin, FL), a 100 cm Liquid Waveguide Capillary Flow Cell (LWCC 3100; WPI Inc., Sarasota, FL, USA) and a portable spectrometer (USB4000-UV-VIS; Ocean Optics, Inc., Dunedin, FL). Maximum absorptivities were observed and recorded at 562 and 540 nm for Fe(II) and Cr(VI) measurements, respectively. Finally, the measured concentrations were converted to corresponding ambient concentration based on sampling flow rate and time.

RESULT AND DISCUSSIONS

Characterization of $\text{PM}_{2.5}$ Inlet and Collection Impactor

Laboratory evaluations indicate good particle separation/collection performance for the $\text{PM}_{2.5}$ inlet and the collection impactor. The experimentally measured collection efficiency curves for the $\text{PM}_{2.5}$ inlet and the collection impactor of PSAS are presented in Fig. 3(a)–(b). It can be seen that the 50% cutpoint size is approximately 2.2 and 1.2 μm for $\text{PM}_{2.5}$ inlet and collection impactor, respectively. These experimentally

determined 50% cutpoint sizes agree well with the theoretically designed values (2.5 and 1.5 μm for $\text{PM}_{2.5}$ inlet and collection impactor, respectively). In addition, collection efficiency curve of the $\text{PM}_{2.5}$ inlet is also compared to International Standard for $\text{PM}_{2.5}$ separation efficiency curve (ISO 7708) (ISO, 1995). As shown in Fig. 3(a), the collection efficiency curve of the designed $\text{PM}_{2.5}$ inlet has similar 50% cutpoint size as ISO 7708 standard curve, but a steeper slope over the size separation range compared to ISO 7708, indicating the good separation performance in the current designed $\text{PM}_{2.5}$ inlet.

Evaluations on Condensational Growth

In PSAS, we show that submicron particles can be effectively grown to larger droplets for sequential collection. The size distributions of intake particles and grown droplets after condensational growth are measured, which is presented in Fig. 4. As shown in Fig. 4, the sizes of intake particles are mostly located in submicron ranges, with a peak diameter around 120 nm. After condensational growth, the intake particles are enlarged into micron droplets, with a peak diameter between 2–5 μm . These grown droplets can be effectively collected by the following collection impactor, since majority of these particles are larger than the 50% cutpoint size of collection impactor as indicated in previous section. Moreover, the size distributions of grown droplets also validate the choice of temperature parameters (i.e., saturation and condensation temperatures of 38 and 5°C, respectively), under which the intake particles are grown to certain sizes above the cutpoint of collection impactor, but not oversized to cause significant losses at the impactor nozzle (shown in the following sections).

Evaluations of Overall System Collection Efficiency

Good overall system collection efficiencies were obtained for polydisperse (with particle size distribution similar to intake particles in Fig. 4) and DMA-selected monodisperse ammonium fluorescein particles. The collection efficiencies

Fig. 3. Collection efficiency curves as a function of aerodynamic diameter for: (a) the $\text{PM}_{2.5}$ inlet; (b) collection impactor. Error bars represent the standard deviations of multiple measurements.

Fig. 4. Normalized size distributions for intake particles and grown droplets. The measured size distributions are normalized by their corresponding peak concentrations. Error bars represent normalized standard deviations from multiple measurements.

for polydisperse and monodisperse aerosols as well as their losses across different parts of PSAS are presented in Fig. 5. The collection efficiency for polydisperse fluorescent particles are about 85%, with about 7% of particles escaped into exhaust and 5% of particles deposited on the tapered nozzle and impaction surface. Despite these losses, the overall collection performance of the PSAS is still acceptable for $PM_{2.5}$ collections. Regarding monodisperse aerosols, for 30 nm particles, the collection efficiency is about 76%, with 16% escaped into exhaust, possibly due to insufficient activation of small particles during condensational growth. In order to activate very small particles during condensational growth, a higher super-saturation ratio (i.e., by increasing temperature differences between saturator and condenser) is

usually required. However, as discussed in previous sections, the current temperature parameters are used to restrain particle losses on tapered nozzle of the collection impactor, considering that majority of the tested aerosols are above 30 nm. For particles between 50 and 200 nm, the collection efficiencies are generally above 90%, with few particles deposited on the nozzle of collection impactor. Both polydisperse and monodisperse results indicate that in general the PSAS can effectively activate submicron particles for condensational growth, and eventually preserve the grown droplets into collected suspensions.

Field Campaign and Comparison with Parallel Filters

Good agreements between suspensions collected by PSAS and parallel filters for certain water-soluble metals were obtained. Fig. 6(a)–6(b) illustrates the comparisons for water-soluble Fe(II) and Cr(VI) between PSAS suspension samples and parallel filters. In general, agreements for both Fe(II) and Cr(VI) are observed between suspensions and parallel filters ($R^2 > 0.8$). The observed water-soluble Fe(II) and Cr(VI) concentration levels are generally in the same order compared to concentrations of water-soluble Fe and Cr of $PM_{2.5}$ reported in previous studies (Wang *et al.*, 2015). The slopes of linear regressions for Fe(II) and Cr(VI) are 0.92 and 0.95, respectively. These slopes are consistent with the PSAS collection efficiency discussed in previous sections. In summary, agreements for certain chemical components between PSAS suspensions and parallel filters indicate that PSAS can effectively preserve chemical properties of collected particles, making it a promising technique for further deployment for online chemical and toxicological analysis of ambient $PM_{2.5}$.

It should be noted that denuders are usually recommended for PM collections involving condensational growth processes in order to get rid of soluble gaseous species (Buhr *et al.*, 1995; Weber *et al.*, 2001; Dong *et al.*, 2012). In current PSAS system, denuders are not included which may result

Fig. 5. Overall collection efficiencies for polydisperse and monodisperse particles.

Fig. 6. Comparison between suspensions and parallel filters for: (a) water-soluble Fe(II); (b) water-soluble Cr(VI). Dash lines represent 1:1 line.

in positive artifacts in certain species such as volatile/semi-volatile organic compounds (VOCs/SVOCs). A previous study by Wang *et al.* (2013a) showed that the positive artifacts for gas-phase organics can be up to $1.5\text{--}2\ \mu\text{g m}^{-3}$. Therefore, when PSAS is deployed for certain cases in which the concentration of soluble gaseous species are substantial, appropriate denuders should be added, or potential sampling artifacts of these species should be carefully evaluated. Despite these limitations, the PSAS is still adaptable for PM field sampling campaign and continuous measurements of PM chemical and toxicological analysis and monitoring.

CONCLUSIONS

We designed and evaluated a particle sampler for aerosol suspensions (PSAS) that directly collects aerosols as liquid suspensions. A saturation-condensation component enlarges fine particles into micron-sized droplets via condensational growth; these droplets are then sequentially collected through inertial impaction as liquid suspensions. Laboratory

evaluations indicate that the PSAS possesses a collection efficiency above 85% for submicron particles, and field evaluations suggest good agreement (with linear regression slopes near 1 and R^2 values above 0.8) between the liquid suspensions and parallel filter samples for the analyzed chemical components. Therefore, the PSAS can be employed for online chemical and toxicological analyses of the ambient PM.

ACKNOWLEDGEMENTS

We acknowledge financial support from the National Natural Science Foundation of China (21707076) and the China Postdoctoral Science Foundation (2017M610928) on this study. The authors declare no competing financial interest.

REFERENCES

Buhr, S.M., Burr, M.P., Fehsenfeld, F.C., Holloway, J.S.,

- Karst, U., Norton, R.B., Parrish, D.D. and Sievers, R.t.E. (1995). Development of a semi-continuous method for the measurement of nitric acid vapor and particulate nitrate and sulfate. *Atmos. Environ.* 29: 2609–2624.
- Canagaratna, M.R., Jayne, J.T., Jimenez, J.L., Allan, J.D., Alfarra, M.R., Zhang, Q., Onasch, T.B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L.R., Trimborn, A.M., Northway, M.J., DeCarlo, P.F., Kolb, C.E., Davidovits, P. and Worsnop, D.R. (2007). Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrom. Rev.* 26: 185–222.
- Charrier, J.G. and Anastasio, C. (2012). On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: Evidence for the importance of soluble transition metals. *Atmos. Chem. Phys.* 12: 9321–9333.
- Chen, X., Jiang, J., Deng, J., Duan, L. and Hao, J. (2016). Development and performance evaluation of a supermicron particle generation system for aerosol instrument calibration *Environ. Sci.* 37: 789–794. (in Chinese)
- Cofer, W.R., Collins, V.G. and Talbot, R.W. (1985). Improved aqueous scrubber for collection of soluble atmospheric trace gases. *Environ Sci Technol* 19: 557–560.
- Dong, H., Zeng, L., Hu, M., Wu, Y., Zhang, Y., Slanina, J., Zheng, M., Wang, Z. and Jansen, R. (2012). Technical note: The application of an improved gas and aerosol collector for ambient air pollutants in China. *Atmos. Chem. Phys.* 12: 10519–10533.
- Eatough, D.J., Long, R.W., Modey, W.K. and Eatough, N.L. (2003). Semi-volatile secondary organic aerosol in urban atmospheres: Meeting a measurement challenge. *Atmos. Environ.* 37: 1277–1292.
- Fernandez, A.E., Lewis, G.S. and Hering, S.V. (2014). Design and laboratory evaluation of a sequential spot sampler for time-resolved measurement of airborne particle composition. *Aerosol Sci. Technol.* 48: 655–663.
- Gao, D., Fang, T., Verma, V., Zeng, L.G. and Weber, R.J. (2017). A method for measuring total aerosol oxidative potential (OP) with the dithiothreitol (DTT) assay and comparisons between an urban and roadside site of water-soluble and total OP. *Atmos. Meas. Tech.* 10: 2821–2835.
- Hering, S.V. and Stolzenburg, M.R. (2005). A method for particle size amplification by water condensation in a laminar, thermally diffusive flow. *Aerosol Sci. Technol.* 39: 428–436.
- Hering, S.V., Spielman, S.R. and Lewis, G.S. (2014). Moderated, water-based, condensational particle growth in a laminar flow. *Aerosol Sci. Technol.* 48: 401–408.
- Hinds, W.C. (1999). *Aerosol technology: Properties, behavior, and measurement of airborne particles*, 2nd ed. Wiley-Interscience.
- ISO (1995). ISO 7708: Air quality - particle size fraction definitions for health-related sampling.
- Jayne, J.T., Leard, D.C., Zhang, X.F., Davidovits, P., Smith, K.A., Kolb, C.E. and Worsnop, D.R. (2000). Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Sci. Technol.* 33: 49–70.
- Khlystov, A., Wyers, G.P. and Slanina, J. (1995). The steam-jet aerosol collector. *Atmos. Environ.* 29: 2229–2234.
- Kidwell, C.B. and Ondov, J.M. (2001). Development and evaluation of a prototype system for collecting sub-hourly ambient aerosol for chemical analysis. *Aerosol Sci. Technol.* 35: 596–601.
- Kim, S., Jaques, P.A., Chang, M.C., Barone, T., Xiong, C., Friedlander, S.K. and Sioutas, C. (2001a). Versatile aerosol concentration enrichment system (VACES) for simultaneous in vivo and in vitro evaluation of toxic effects of ultrafine, fine and coarse ambient particles Part II: Field evaluation. *J. Aerosol Sci.* 32: 1299–1314.
- Kim, S., Jaques, P.A., Chang, M.C., Froines, J.R. and Sioutas, C. (2001b). Versatile aerosol concentration enrichment system (VACES) for simultaneous in vivo and in vitro evaluation of toxic effects of ultrafine, fine and coarse ambient particles Part I: Development and laboratory characterization. *J. Aerosol Sci.* 32: 1281–1297.
- Lelieveld, J., Evans, J.S., Fnais, M., Giannadaki, D. and Pozzer, A. (2015). The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* 525: 367–371.
- Ng, N.L., Herndon, S.C., Trimborn, A., Canagaratna, M.R., Croteau, P.L., Onasch, T.B., Sueper, D., Worsnop, D.R., Zhang, Q., Sun, Y.L. and Jayne, J.T. (2011). An aerosol chemical speciation monitor (ACSM) for routine monitoring of the composition and mass concentration of ambient aerosol. *Aerosol Sci. Technol.* 45: 780–794.
- Okuyama, K., Kousaka, Y. and Motouchi, T. (2007). Condensational growth of ultrafine aerosol particles in a new particle size magnifier. *Aerosol Sci. Technol.* 3: 353–366.
- Orsini, D.A., Ma, Y., Sullivan, A., Sierau, B., Baumann, K. and Weber, R.J. (2003). Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition. *Atmos. Environ.* 37: 1243–1259.
- Orsini, D.A., Rhoads, K., McElhoney, K., Schick, E., Koehler, D. and Hogrefe, O. (2008). A water cyclone to preserve insoluble aerosols in liquid flow - An interface to flow cytometry to detect airborne nucleic acid. *Aerosol Sci. Technol.* 42: 343–356.
- Perrino, C., Catrambone, M., Farao, C., Salzano, R., Esposito, G., Giusto, M., Montagnoli, M., Marini, A., Brinoni, M., Simonetti, G. and Canepari, S. (2015). Improved time-resolved measurements of inorganic ions in particulate matter by PILS-IC integrated with a sample pre-concentration system. *Aerosol Sci. Technol.* 49: 521–530.
- Phan, H.N. and McFarland, A.R. (2004). Aerosol-to-hydrosol transfer stages for use in bioaerosol sampling. *Aerosol Sci. Technol.* 38: 300–310.
- Puthussery, J.V., Zhang, C. and Verma, V. (2018). Development and field testing of an online instrument for measuring the real-time oxidative potential of ambient particulate matter based on dithiothreitol assay. *Atmos. Meas. Tech.* 11: 5767–5780.
- Ren, H., Xue, M., An, Z., Zhou, W. and Jiang, J. (2019).

- Quartz filter-based thermal desorption gas chromatography mass spectrometry for in-situ molecular level measurement of ambient organic aerosols. *J. Chromatogr. A* 1589: 141–148.
- Saffari, A., Hasheminassab, S., Wang, D., Shafer, M.M., Schauer, J.J. and Sioutas, C. (2015). Impact of primary and secondary organic sources on the oxidative potential of quasi-ultrafine particles (PM_{0.25}) at three contrasting locations in the Los Angeles Basin. *Atmos. Environ.* 120: 286–296.
- See, S.W., Wang, Y.H. and Balasubramanian, R. (2007). Contrasting reactive oxygen species and transition metal concentrations in combustion aerosols. *Environ. Res.* 103: 317–324.
- Slanina, J., ten Brink, H.M., Otjes, R.P., Even, A., Jongejan, P., Khlystov, A., Waijers-Ijpelaar, A. and Hu, M. (2001). The continuous analysis of nitrate and ammonium in aerosols by the steam jet aerosol collector (SJAC): Extension and validation of the methodology. *Atmos. Environ.* 35: 2319–2330.
- Smith, J.N., Moore, K.F., McMurry, P.H. and Eisele, F.L. (2004). Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry. *Aerosol Sci. Technol.* 38: 100–110.
- Smith, J.N., Barsanti, K.C., Friedli, H.R., Ehn, M., Kulmala, M., Collins, D.R., Scheckman, J.H., Williams, B.J. and McMurry, P.H. (2010). Observations of ammonium salts in atmospheric nanoparticles and possible climatic implications. *PNAS* 107: 6634–6639.
- Sowlat, M., Wang, D., Simonetti, G., Shafer, M.M., Schauer, J.J. and Sioutas, C. (2016). Development and field evaluation of an online monitor for near-continuous measurement of iron, manganese, and chromium in coarse airborne particulate matter (PM). *Aerosol Sci. Technol.* 50: 1306–1319.
- Stieger, B., Spindler, G., van Pinxteren, D., Gruner, A., Wallasch, M. and Herrmann, H. (2019). Development of an online-coupled marga upgrade for the 2 h interval quantification of low-molecular-weight organic acids in the gas and particle phases. *Atmos. Meas. Tech.* 12: 281–298.
- Stolzenburg, M.R. and McMurry, P.H. (1991). An ultrafine aerosol condensation nucleus counter. *Aerosol Sci. Technol.* 14: 48–65.
- Sun, Y., Wang, Z., Dong, H., Yang, T., Li, J., Pan, X., Chen, P. and Jayne, J.T. (2012). Characterization of summer organic and inorganic aerosols in Beijing, China with an aerosol chemical speciation monitor. *Atmos. Environ.* 51: 250–259.
- Takeuchi, M., Ullah, S.M.R., Dasgupta, P.K., Collins, D.R. and Williams, A. (2005). Continuous collection of soluble atmospheric particles with a wetted hydrophilic filter. *Anal. Chem.* 77: 8031–8040.
- Valko, M., Morris, H. and Cronin, M.T. (2005). Metals, toxicity and oxidative stress. *Curr. Med. Chem.* 12: 1161–1208.
- Wang, D., Pakbin, P., Saffari, A., Shafer, M.M., Schauer, J.J. and Sioutas, C. (2013a). Development and evaluation of a high-volume aerosol-into-liquid collector for fine and ultrafine particulate matter. *Aerosol Sci. Technol.* 47: 1226–1238.
- Wang, D., Pakbin, P., Shafer, M.M., Antkiewicz, D., Schauer, J.J. and Sioutas, C. (2013b). Macrophage reactive oxygen species activity of water-soluble and water-insoluble fractions of ambient coarse, PM_{2.5} and ultrafine particulate matter (PM) in Los Angeles. *Atmos. Environ.* 77: 301–310.
- Wang, D., Sowlat, M.H., Shafer, M.M., Schauer, J.J. and Sioutas, C. (2016). Development and evaluation of a novel monitor for online measurement of iron, manganese, and chromium in ambient particulate matter (PM). *Sci. Total Environ.* 565: 123–131.
- Wang, Q., Ma, Y., Tan, J., Zheng, N., Duan, J., Sun, Y., He, K. and Zhang, Y. (2015). Characteristics of size-fractionated atmospheric metals and water-soluble metals in two typical episodes in Beijing. *Atmos. Environ.* 119: 294–303.
- Weber, R.J., Orsini, D., Daun, Y., Lee, Y.N., Klotz, P.J. and Brechtel, F. (2001). A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. *Aerosol Sci. Technol.* 35: 718–727.
- Wubulihairen, M., Jiang, S.Y. and Ning, Z. (2015a). Prototype development and laboratory evaluation of an aerosol to hydrosol sampler. *Aerosol Air Qual. Res.* 15: 776–785.
- Wubulihairen, M., Lu, X., Lee, P.K.H. and Ning, Z. (2015b). Development and laboratory evaluation of a compact swirling aerosol sampler (SAS) for collection of atmospheric bioaerosols. *Atmos. Pollut. Res.* 6: 556–561.
- Zhao, B., Zheng, H., Wang, S., Smith, K.R., Lu, X., Aunan, K., Gu, Y., Wang, Y., Ding, D., Xing, J., Fu, X., Yang, X., Liou, K.N. and Hao, J. (2018). Change in household fuels dominates the decrease in PM_{2.5} exposure and premature mortality in China in 2005–2015. *PNAS* 115: 12401–12406.

Received for review, December 4, 2019

Revised, February 6, 2020

Accepted, February 7, 2020