**Atmospheric
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Discussions**

Technical Note: The application of an improved gas and aerosol collector for ambient air pollutants in China

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Abstract

An improved Gas and Aerosol Collector (GAC) equipped with a newly designed aerosol collector and a set of dull-polished wet annular denuder (WAD) was developed based on a Steam Jet Aerosol Collector (SJAC) sampler. Combined with Ion Chromatography (IC) the new sampler performed well in laboratory tests with high collection efficiencies for SO_2 (above 98 %) and particulate sulfate (as high as 99.5 %). When applied in two major field campaigns (rural and coastal sites) in China, the GAC-IC system provided high-quality data in ambient conditions even under high loadings of pollutants. Its measurements were highly correlated with data by other commercial instruments such as the SO_2 analyzer (43c, Thermo-Fisher, USA; R^2 as 0.96), the HONO analyzer (LOPAP, Germany; R^2 as 0.91 for nighttime samples), a filter sampler (Tianhong, China; R^2 as 0.86 for SO_4^{2-}), and Aerosol Mass Spectrometer (AMS, Aerodyne, USA; R^2 above 0.77 for major species) over a wide range of concentrations. Through the application of the GAC-IC system, it was identified that 70 % of chloride and nitrate by the filter method could be lost during daytime sampling due to high temperature in the rural site of Kaiping. In Changdao field campaign (coastal site) the comparison with the measurements by the GAC-IC suggested that the collection efficiency of AMS might be greatly influenced by high relative humidity (RH) especially in coastal or marine environment. Through laboratory and field studies, this instrument is proved highly reliable, which is particularly useful in future intensive campaigns or long-term monitoring stations to study various environmental issues such as secondary aerosol and haze formation, as well as climate change.

1 Introduction

Along with the fast economic development of China, significant amount of pollutants has been emitted into the atmosphere, which becomes a major problem that China is facing right now (Shao et al., 2006), and these air pollutants have caused many

environmental problems such as regional haze and photochemical smog. For example, Beijing, the capital city of China, has recently been listed as one of the top ten most polluted cities in the world (Chan et al., 2008). The effluents from some mega-cities in China are now seen as important sources of global atmospheric pollutants (Crounse et al., 2009).

To study the sources, formation processes, and fate of pollutants in the atmosphere, it is very important to develop fast and advanced instruments to accurately and quantitatively characterize concentration and composition of both aerosol and trace gases, which exhibit distinct spatial and temporal variations. Gases species such as SO_2, NO_2 and NH_3 are important precursors of secondary inorganic components in aerosol including sulfate, nitrate, and ammonium. These water-soluble components contribute about one-third of particulate matter mass in typical urban areas (Andreae et al., 2008). Besides their abundance in particulate matter, the environmental impacts are of particular concerns especially their role in aerosol acidification and the earth's radiation balance by directly scattering incoming solar radiation and indirectly by altering cloud properties as particles can serve as cloud condensation nuclei (Hillamo et al., 1998; Andrews et al., 2000; Chow et al., 2006; Seinfeld et al., 2006). Therefore, their formation mechanisms and sources have been widely and actively studied through measuring these components and their precursor gases in the ambient air along with meteorological measurements (Hu et al., 2002; Yao et al., 2002; Khoder, 2002). As products of particle formation, growth and processing in the atmosphere, water-soluble ions usually can be used as good indicators of chemical reactions occurring on the surface of particles (Wang et al., 2006).

Trebs et al. (2004) have summarized the most common on-line and off-line methods for measuring inorganic gaseous and particulate species in ambient air. Filter sampling is a traditional method for measuring particulate species, and is still being actively used in quite a lot of field campaigns nowadays. However, there are well-known disadvantages associated with this method such as underestimation of volatile components (semi-volatile organics and ammonium nitrate), various positive and negative artifacts,

labor intensive and so on (Chow, 1995; Keuken et al., 1989; Niessner et al., 1980; Slanina et al., 2001). An efficient way to reduce the artifacts due to filter sampling and storage and to meet the need for acquiring high time-resolution aerosol composition information is to develop continuous or semi-continuous air-monitoring techniques and instruments. At the end of 1980s, the development of wet denuder technique and particle growth in a saturated steam made it possible to semi-continuously measure the species in gas- and aerosol-phase simultaneously (Buh et al., 1995; Khlystov et al., 1995; Simon et al., 1995). Two representative instruments with such functions are the Steam Jet Aerosol Collector (SJAC) system developed by Khlystov of Netherlands Energy Research Foundation (ECN) (Khlystov et al., 1995) and the Particle-Into-Liquid Sampler (PILS) system developed by R. Weber of Georgia Institute of Technology (Weber et al., 2003).

The essential difference between PILS and SJAC is that particles are first grown with steam, then impacted and collected in PILS system (Weber et al., 2001) whereas SJAC applies a cyclone. Additionally, only aerosol components are measured in PILS system. Lots of inter-comparisons for semi-continuous instruments have been studied; however, these studies were mainly executed under clean environment with low sulfate and nitrate concentration (Drewnick et al., 2003; Homolya et al., 2005; Makkonen et al., 2012). The AIM (a commercial instrument based on the SJAC system, Model 9000, Dionex, USA), first developed and used in Europe, is very needed to be carefully evaluated and modified for its application in heavily polluted environment like urban cities in China. Under high loadings of ions, the water vapor supplied by the SJAC system seems insufficient to dissolve all water-soluble ions (Wu et al., 2007).

In the early 2000s, a SJAC sampler was introduced into Peking University from ECN and applied in air quality study in China. Connected with ion chromatography (IC) from Dionex Company (ICS-90), this system has been used in many field campaigns in Beijing and Guangzhou over these years (Hu et al., 2002; Su et al., 2008a,b). A few problems have been found in these applications, which are required for improvement to meet the need for high quality data in high pollution loading circumstance.

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In this study, we aim to modify and improve the SJAC sampler to extend its application in special environment especially heavily polluted areas such as mega-cities in China. The Gas and Aerosol Collector (GAC) is developed for such a purpose. The detailed improvements of GAC are presented in this study and its performance and efficiency are carefully evaluated by comparing with other techniques and measurements. The combination of GAC with Ion Chromatography (IC) can provide online measurements of concentration of water soluble gaseous and aerosol species. In this study, the application of an improved GAC-IC system in a few field campaigns is presented.

2 Methodology

2.1 The gas and aerosol collector (GAC)

The most important improvement of GAC is the newly designed aerosol collector, where particles can grow under supersaturated conditions. As shown in Fig. 1, it has three glass components including an aerosol mixing chamber (100 ml), a cyclone aerosol trapper and an impactor aerosol trapper. Steam is generated by ultra pure water (18.2 MΩ) at a flow rate of 1.0–1.2 ml min^{-1} under constant temperature of 120 °C. Particles grow to droplets in the aerosol mixing chamber and are finally collected by aerosol trappers composed of a glass cyclone and a glass impactor with constantly flowing cooling water (around 10 °C). The introduction of cycling cooling water and the impactor aerosol trapper were the essential difference between GAC and SJAC for the aerosol collector part which ensures aerosol fully collected under high loadings.

The wet annular denuder (WAD) used in the GAC is the same as that in the SJAC, but the inner-surface is dull polished. This change improved the hydrophilic performance of the denuder and enhanced the scavenging capacity of gaseous species for water film formed on the inner-surface of the denuder is quite uniform. The WAD is continuously rotated and the absorption solution can wet the inner surface. The absorption solution (usually ultra pure water or diluted alkaline solution) is pumped into the denuder by

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a micro pump (BIO-CHEM Fluidics, USA) at a flow rate of 1.0–1.2 ml min^{-1} and pumped out at the other side.

The GAC system developed in this study is schematically shown in Fig. 2. A cyclone with a cut-off size of 2.5 µm (URG, USA) will be installed before air pumped into the GAC at a flow rate of 16.7 l min^{-1} under a flow controller which is periodically checked by a bubble flow meter (Sensidyne, USA). The stream goes through the WAD by a direction reverse with absorption solution flowing in the WAD. Gaseous species diffuse to the inner surface and are scavenged by the absorption solution. Particulate matter below 2.5 micrometer (PM$_{2.5}$) passes through the denuder and enters into the aerosol collector. Both gaseous and aerosol samples are injected into two 30 ml glass bottles being weighted by weighting transducers separately. Gaseous samples are collected into one bottle in the first 15 min, and then aerosol samples are collected in the other bottle in the following 15 min. Therefore, the time resolution for the GAC is 30 min. The recorded weights of gaseous- and aerosol samples are used in the calculation of concentration of each species.

Two IC systems (ICS-90, Dionex, USA) are combined with the GAC sampler to quantify different gaseous and particulate species. One IC is equipped with a 4 × 25 mm guard column (type IonPac AG 14) followed by a 4 × 250 mm analytical column (type IonPac AS 14) with a mixture of 3.5 mM CO$_3^{2-}$ and 1.0 mM HCO$_3^-$ as eluent solution. The other IC is installed with a 4 × 25 mm guard column (type IonPac CG 12) followed by a 4 × 250 mm analytical column (type IonPac CS 12) with 20 mM methanesulfonic acid as eluent solution. Both ICs were electronically suppressed to reduce the background signal. Samples were injected through 20 µl loops of two ICs at a flow rate of 1.0 ml min^{-1}. During the period of sampling gaseous pollutants, the aerosol samples are automatically injected into two ICs, and then the concentrations of HCl, HONO, HNO$_3$, SO$_2$, NH$_3$ in gaseous phase and Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} in aerosol phase can be calculated.

Additionally, Micro pumps (BIO-CHEM Fluidics, USA) are firstly introduced into such kind of samplers instead of injection pumps or peristaltic pumps (used in PILS and

SJAC). They work in impulse mode with a constant flow rate about 20 µl per pulse and only 1/16 inch Teflon tube connected with no accessory easily worn out. The weighing transducers applied in the GAC allows recording the weight of each sample in order to accurately calculate concentrations of gaseous and aerosol species which is a much

5　cheaper but convenient way. This improvement is particularly helpful to immediately identify errors in sampling or invalid samples based on the recorded data of weight.

Through careful integration and efficient improvement, the GAC sampler becomes much smaller than the SJAC. It is more suitable for transportation to be applied into field campaigns.

10　## 2.2　The performance of GAC

2.2.1　Collection efficiency of SO_2

Both negative and positive artifacts occur when the WAD does not collect gases efficiently which can lead to underestimate of gaseous concentration. A less efficient denuder can result in overestimation of the signal of aerosol sample because soluble

15　gases not captured by the WAD will dissolve in the steam environment of the aerosol collector. Among those common gaseous species in air quality study such as HONO, HCl, HNO_3, the diffusion coefficient of SO_2 is relatively lower. Therefore, only the collection efficiency of SO_2 was tested in this study (Simon et al., 1993).

Zero air produced by a zero air source (Model 1001, Sabio, USA) was mixed with

20　certificated standard SO_2 gas from cylinder in a Dynamic Gas Calibrator (Model 146i, Thermo-Fisher, USA) which can provide stable SO_2 gas flow with different concentrations by adjusting the mass flow controller in the instrument. A gas flow rate of 20 l min^{-1} was produced where GAC sampled 16.7 l into WAD per minute. The majority of the gas diffuses to surface of the denuder and is collected by the absorption solution and

25　a small portion of SO_2 may pass through the denuder and is then trapped by steam. If G and A stand for sulfur concentration of the solution collected by the denuder and steam, respectively, the ratio of $G/(G + A)$ represents the collection efficiency of SO_2.

Alkaline solution is normally used as the absorption solution in previous research due to its better absorption efficiency for SO_2. However, HONO, an important gas that is also collected and measured by the GAC, is likely produced under the presence of both SO_2 and NO_2, especially in alkaline solution (Spindler et al., 2003; Vecera et al.,

5   1991). In this study, three absorption solutions including ultra pure water, 25 µM and 100 µM Na_2CO_3 solutions were tested for SO_2 collection efficiency.

As seen from Fig. 3, collection efficiency higher than 98 % was found when Na_2CO_3 solutions (25 µM and 100 µM) were used and such efficiency almost did not change when SO_2 concentration increased up to 90 ppb. However, the efficiency decreased

10   slightly when water was used as absorption solution (from 97.5 % to 94 % when SO_2 concentration increased from 20 to 120 ppb). In fact, ambient SO_2 concentrations in China are typically in the range of 20–100 ppb with significant seasonal variations from summer to winter. When field campaigns are carried on, different absorption solution can be chosen according to actual SO_2 concentration in environment.

15   **2.2.2   Aerosol collection efficiency**

Particle loss due to non-isokinetic sampling also results in negative and positive artifacts. In the denuder, some ions that should not be present due to their low vapor pressure are sometimes observed, indicating that particle loss actually occurs when air passes through the denuder and thus leads to negative artifact.

20   Particles were generated to investigate (1) particle loss in the wet denuder and (2) the collection efficiency of the aerosol collector. Ammonium sulfate solution in different concentrations (from 0.5 to 25 mM) was prepared to generate particles with different physical properties. The size and number of the generated particles change when the concentration of the solution used for particle generation changes (see TSI Atomizer

25   manual, Model 3097, TSI, USA). A constant low particle flow rate of $\sim 1\,l\,min^{-1}$ (2 psi) was mixed with a flow rate of $20\,l\,min^{-1}$ of zero air generated by a zero air source (Model 1001, Sabio, USA) and controlled by a mass flow controller in the Dynamic Gas Calibrator (Model 146i, Thermo-Fisher, USA). The zero air and generated particles were

mixed in a 4.5 l polypropylene mixing tank from where the GAC sampled continuously at a flow rate of 16.7 l min^{-1}. A Teflon filter (Whatman, UK) was connected following the aerosol collector in the GAC before air passing through the pump. The filter samples were extracted in the same way as introduced in Sect. 3.1.1.

A Scanning Mobility Particle Sizer (SMPS, Model 3080, TSI, USA) and a Condensation Particle Counter (CPC, Model 3775, TSI, USA) were connected to the mixing tank to measure the number size concentration of generated particles. The flow rate of SMPS and CPC were 3 and 0.3 l min^{-1} respectively and the particle size distribution was measured between 20 and 700 nm every 5 min. The particle volume size distributions were shown in Fig. 5.

Three types of sulfate concentration were obtained from this system including G (sulfate left in the denuder), A (sulfate trapped by the aerosol collector) and F (sulfate extracted from the filter). The ratio of $(A + F)/(G + A + F)$ and $A/(A + F)$ represent the percentage of aerosol penetrating the denuder and aerosol collection efficiency, respectively.

Figure 4 shows that the particle loss in the denuder is lower at higher concentrations of $(NH_4)_2SO_4$. When $(NH_4)_2SO_4$ concentration is greater than 5 mM, particle penetrating rate exceeds 90 %. The sulfate concentration detected in the WAD accounts for almost 15 % of total sulfate when $(NH_4)_2SO_4$ concentration is 2.5 mM. We estimate from Fig. 5 that particles larger than 120–150 nm can pass through the denuder and get into the aerosol collector. Because of the small inertia, smaller particles, which dominate at lower concentrations of $(NH_4)_2SO_4$, are easily diffused and captured by the WAD, leading to lower penetration ratio. Although ultra fine particles (<100 nm) dominate the total particle number concentrations in urban areas, their contributions to total PM$_{2.5}$ mass are negligible (Seinfeld et al., 2006). In ambient atmosphere, most of the aerosol mass is due to the particles with a diameter larger than 500 nm and particle number concentrations rarely reach as high as 10^6 cm^{-3} in ambient atmosphere. So the performance of the GAC sampler is adequate for being applied in the ambient atmosphere to monitor gaseous and particulate air pollutants.

Figure 6 shows excellent collection efficiency (> 99.5 %) of the aerosol collector and it is independent of the concentration of $(NH_4)_2SO_4$ used. However there is still a trend of higher collection efficiency with the increase of $(NH_4)_2SO_4$ concentration. This result clearly demonstrates that the aerosol collector used in the GAC sampler has excellent collection efficiency and performance.

2.2.3 Limit of detection (LOD)

Limit of detection for each species (Table 1) was determined in the laboratory by sampling zero air generated from zero air source (Model 1001, Sabio, USA) continuously. The detection limit is defined as the background value adding three times the standard deviation of the background.

3 Results and discussion

3.1 Field measurements

3.1.1 Field campaign in Pearl River Delta (PRD)

An intensive campaign supported by the Ministry of Science and Technology, China, was organized by Peking University in PRD from October to November, 2008 (Huang et al., 2011). As part of this campaign, the GAC-IC system was applied in a rural site (Kaiping) for measuring gaseous and aerosol species and compared with other commercial instruments. The absorption solution was Na_2CO_3 (25 µM) in the GAC-IC system with a $PM_{2.5}$ cyclone inlet installed on the roof of the site and a 3-m Teflon tube (protected by black material from sunlight) connecting the cyclone to the GAC sampler. Only anions were measured in the GAC and calibration was done by ionic standard mixture of 0.02, 0.05, 0.2, 0.5 and 1 ppb once a week. The flow rate of the GAC sampler (16.7 l min^{-1}) was checked once a week. The GAC-IC system continuously measured HCl, HONO, HNO_3, SO_2, SO_4^{2-}, NO_3^- and Cl$^-$ with time resolution of 30 min.

SO$_2$ concentration was also measured by online SO$_2$ analyzer (43c, Thermo-Fisher, USA), which was calibrated by zero air and SO$_2$ standard gas everyday. The measurement by the 43c is based on the absorption of ultraviolet (UV) light by SO$_2$ molecules with a time resolution of 10 s and Teflon tube as sampling inlet. A TEOM (1400, RP, USA) was used for PM$_{2.5}$ mass concentration measurement.

A Long Path Absorption Photometer (LOPAP) which continuously measured HONO concentration with a time resolution of 4 min was introduced from the Institute for Chemistry and Dynamics of the Geosphere (ICG-2), Forschungszentrum Jülich, Germany. A detailed introduction of this instrument is available in earlier publication by Heland et al. (2001). No sampling inlet tube was applied for the system during measurement in Kaiping.

Teflon filters with a diameter of 47 mm (Whatman, UK) were installed in the filter sampler (Tianhong instruments, China) to collect PM$_{2.5}$ samples twice a day in two periods (07:00 to 18:00 and 18:30 to 06:30). The exposed filters in Petri-dishes (Whatman, UK) were stored in a refrigerator at 4 °C. The filters were extracted in 20.0 ml of ultra pure water (18.2 MΩ, Millipore, USA) in an ultrasonic bath for off-line analysis of water-soluble ions under the same chromatographic conditions as the GAC-IC system.

3.1.2 Field comparison of aerosol species in Changdao

Another intensive campaign was conducted in Changdao, a small island town located in the Bohai Sea, where a GAC-IC system and an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) were placed side by side for comparison purpose from 20 March to 26 April 2011. Pure water was used as absorption solution in this campaign for the low background of SO$_2$ concentration in Changdao with a cut size of PM$_{2.5}$ cyclone and a 3-m Teflon tube (protected by black material from sunlight) connected on the roof. Because of the application of a cation chromatography in this campaign, NH$_3$ and NH$_4^+$ were also measured besides the anion species with the same routine calibration conducted in Kaiping site.

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The description of HR-ToF-AMS is available in previous publications (DeCarlo et al., 2006; Timonen et al., 2010; Huang et al., 2011). A PM_1 cyclone was used as the AMS inlet to remove coarse particles and introduced sampled air into the instrument through a copper tube with a flow rate of $10\,l\,min^{-1}$ and the AMS sampled isokinetically from the center of the copper tube at a flow rate of $80\,ml\,min^{-1}$. The time resolution of AMS was 4 min. The operation conditions, detection mode and data processing of the AMS were same as those introduced by Huang et al. (2011). The parameter of collection efficiency (CE) of 0.5 was applied since the sampled air was dried through a Nafion (MD-110, Perma Pure, USA) (Takegawa et al., 2009).

3.2 Overview of the GAC-IC performance in Kaiping site

During the period from 20 October to 14 November 2008, the time series and diurnal variations of major species measured by the GAC-IC and $PM_{2.5}$ mass by the TEOM are shown in Fig. 7. Statistical information of all results from the GAC-IC is summarized in Table 2.

The most abundant aerosol species at the site were SO_4^{2-} and NO_3^- with average concentration as $12.4\,\mu g\,m^{-3}$ and $4.6\,\mu g\,m^{-3}$ and accounting for 20.4 % and 6.2 % of $PM_{2.5}$ mass concentration, respectively. Though Cl^- was not enriched in fine particles, it showed similar variations with NO_3^- and sometimes could account for up to 9 % of $PM_{2.5}$ mass concentration (Fig. 7a and Table 2). Good correlation (R^2 as 0.85) was found between the sum of SO_4^{2-}, NO_3^-, Cl^- and NH_4^+-pre (predicted by the Eq. 1) and $PM_{2.5}$ mass measured by TEOM (Fig. 7c,g). About 43 % of total aerosol mass in $PM_{2.5}$ was water-soluble ions, which agreed with previous findings in this area (Hagler et al., 2006; Lai et al., 2007). From the time series in Fig. 7, it could be seen that there were two major episodes (one from 25 to 27 October the other from 5 to 6 November) for

both aerosol and gaseous species.

$$\text{Mass}(NH_4^+ - pre) = \left[\frac{\text{Mass}(SO_4^{2-}) \times 2}{96} + \frac{\text{Mass}(NO_3^-)}{62} + \frac{\text{Mass}(Cl^-)}{35.5} \right] \times 18 \tag{1}$$

Most of acidic gases exhibited same daily variation during the study period. A wide range of SO_2 concentration from 0.26 to 43 ppb was observed with a mean concentration of about 11.47 ppb, whereas the maximum concentration of other gases was all below 5.5 ppb including HONO. Whose concentration was much lower than other studies in China as well (Su et al., 2008a,b; Qin et al., 2009).

Distinct diurnal variations for NO_3^- and Cl^- with the highest concentration in the morning (about 06:00) and the lowest (about 15:00) in the afternoon were observed. However, gaseous HNO_3 and HCl exhibited reversed diurnal pattern, indicating that they were mainly produced by the evaporation of nitrate and chloride. SO_2 and SO_4^{2-} showed the same diurnal variation and peaked around 10:00, which were probably transported from urban area.

Generally, as a semi-continuous method, the GAC-IC system showed good condition during the campaign and the reasonable variations of abundant species indicated that the instrument could be applied in field campaigns for long-term observation. The newly designed aerosol collector could measure water soluble ions as high as 70 µg m^{-3}, which is particularly useful for highly polluted areas such as some major cities in China.

3.3 Inter-comparisons of the GAC-IC with other relevant commercial instruments in field measurements

3.3.1 Comparison of SO_2 measurement between GAC-IC and TE 43c

The data from the TE 43c was averaged to 30 min in order to compare with the data from the GAC-IC (30-min time resolution). Figure 8 presents the comparison of SO_2 measurements between two methods based on a large dataset ($N = 1010$) over 24 days from 20 October to 13 November 2008 in the PRD campaign.

The results from two instruments agreed well with a satisfying correlation coefficient (R^2 as 0.96) and a small intercept of 0.43 ppb though the measurement by the GAC-IC system was about 11 % lower than that of the SO_2 analyzer. Those results were consistent with those obtained by MARGA (a commercial version of SJAC instrument, Metrohm, Switzerland) in Finland (Makkonen et al., 2012). The high correlation indicated that the WAD used in the GAC sampler performed stable collection ability for SO_2 from a range of 11.5 to 43 ppb, which prohibited the GAC-IC giving the higher sulfate value at high SO_2 concentration (> 30 ppb) (Wu et al., 2007). In addition, because of the low diffusion coefficient of SO_2, the other acid gases (HNO_3, HONO and HCl) should be collected more efficiently and measured precisely with Na_2CO_3 solutions (25 µM) as absorptions in the GAC-IC system.

3.3.2 Comparison of HONO measurement between GAC-IC and LOPAP

The data from the LOPAP was averaged to 30 min for comparison with the GAC-IC. Figure 9 presents the comparison of HONO measurements between the GAC-IC and the LOPAP based on a dataset (N = 450) over 17 days. Night samples (from 18:00 to 06:00) and day samples (from 07:00 to 17:00) were compared separately.

The agreement of night samples (R^2 as 0.91) was much better than that of day samples (R^2 as 0.70) with the total agreement of 0.81. The GAC-IC system measurement was about 10 % higher than the LOPAP in the night which was primarily attributed to the 3-m long inlet tube connected in the GAC-IC system (no inlet tube used in the LOPAP) (Zhou et al., 2002; Su et al., 2008a). However, 36 % of HONO was lost in the daytime measurement for the GAC-IC. At the sampling site, HONO concentration less than 1 ppb was found during most of the sampling time. Higher concentration (> 1 ppb) also occurred, but it was almost at night. Larger uncertainty associated with the standard curve (used for calibration in the IC) at lower concentration might contribute to the lower measurement by the GAC-IC at daytime. In addition, oxidation of HONO by high concentration of O_3 during daytime might occur in the inlet tube, which could result

in the lower measurement by the GAC-IC. Future study should include research to improve the performance of the GAC-IC system at low HONO concentration.

3.3.3 Comparison between GAC-IC and filter sampler

The comparisons of SO_4^{2-}, NO_3^- and Cl^- between GAC-IC and filter sampler were made based on data ($N = 55$) of 28 days as shown in Fig. 10. The data from the GAC-IC system was averaged to the corresponding time period of the filter samples for comparison purpose.

A better comparison of SO_4^{2-} was seen with R^2 as 0.86, a slope of 0.94 and a small intercept (Fig. 10c). However, worse comparisons were seen for NO_3^- (R^2 as 0.66) and Cl^- (R^2 as 0.50) than the SO_4^{2-}. The lower concentrations of NO_3^- and Cl^- by the filter method could be attributed to high air temperature which enhanced negative artifacts from the evaporation loss of chloride and nitrate during sampling. The ambient air temperature of Guangzhou ranged from 19 to 32 °C during our sampling period. As shown in Fig. 10a,b, the evaporation loss becomes significant at temperature higher than 27 °C. To further investigate this problem, we grouped samples into day samples (sampled during the time from 07:00 to 18:00) and night samples (sampled from 18:30 to 06:30). Better correlations of NO_3^- and Cl^- could be seen for night samples with R^2 as 0.90 and 0.87, respectively. Poor correlations were found for day samples (R^2 as 0.30 for NO_3^- and 0.18 for Cl^-). On average, our data suggested about 67 % of NO_3^- and 71 % of Cl^- might be lost due to sampling during daytime at higher temperature.

Because cations were not measured by the GAC-IC system, the molar number of NH_4^+ measured by the filter sampler (only night samples, $N = 27$) was compared with total molar number of anions measured by the GAC-IC (Fig. 10d). High correlation (R^2 as 0.88) provided supportive evidence that aerosol species measured by the GAC-IC were reliable and a slope of 1.01 indicated that aerosol observed at the site was mainly neutral.

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Excellent agreement of SO_4^{2-} between GAC-IC and filter measurements indicated that the newly designed aerosol collector had stable collection efficiency for SO_4^{2-} over a wide range of concentration in this campaign (from 0.47 to 36.6 $\mu g\,m^{-3}$). About one fifth of the SO_4^{2-} data were higher than 20 $\mu g\,m^{-3}$ where the GAC-IC results were still consistent with filter method. The problem of measurement going down at high concentration of SO_4^{2-} as reported by Wu and Wang (2007) was not found in this study which indicated that the GAC-IC system could perform well in aerosol study under high loadings of SO_4^{2-} and SO_2. When day samples of filter measurement were excluded, much better agreements of NO_3^- and Cl^- were obtained even at the highest NO_3^- concentration (27.8 $\mu g\,m^{-3}$). The good correlation between GAC-IC and filter method in this work was comparable with previous studies of other countries where the observed concentrations were much smaller (below 25 and 14 $\mu g\,m^{-3}$ for SO_4^{2-} and NO_3^-) than observed in China (Drewnick et al., 2003; Wittig et al., 2004; Homolya et al., 2005; Makkonen et al., 2012). Most (semi-)continuous measurements were found much lower than filter-based method and the better comparison results done in Beijing and Shanghai were just part of data used as shown in Table 3. However, in our study, measurements of the GAC-IC system agreed much better with measurements of filter-based method as can be seen by a slope of 0.94, 0.98 and 1.08 for SO_4^{2-}, NO_3^- and Cl^- respectively over a larger range. In summary, the GAC-IC system could provide highly time-resolved and comparable SO_4^{2-} and NO_3^- data and it was particularly applicable in highly polluted areas.

3.3.4 Comparison between GAC-IC and AMS

The data from AMS was averaged to 30 min in order to compare with the data from the GAC-IC (30-min time resolution). Sea salt particles which can be easily captured and measured by the GAC-IC cannot be measured by the AMS (Takegawa et al., 2009). We estimated non-sea salt (nss) Cl^- based on the GAC-IC data assuming that all of the measured Na^+ was originated from sodium chloride (NaCl) in sea salt. Figure 11

presents the comparison of SO_4^{2-}, nss-Cl^-, NO_3^- and NH_4^+ measurements between two methods based on a large dataset ($N = 1450$) over 36 days from 20 March to 24 April 2010, in Changdao campaign.

Both the AMS and the GAC-IC system could track the temporal variations of air pollutants and agreed well. For example, measurements of four ions in aerosol from two instruments exhibited good and positive correlations (R^2 as 0.77, 0.84, 0.85 and 0.90 for SO_4^{2-}, nss-Cl^-, NO_3^- and NH_4^+, it is clear that the assumption of collection efficiency (CE) of 0.5 in AMS yields biases of 8 % or better for nitrate, sulfate and ammonium between AMS and GAC-IC. The nss-Cl^- concentration estimated above is lower than that AMS measured with a slope of 0.88. It was because Cl^- from sea salt could be partially or fully depleted by reaction between NaCl and acid such as nitric acid (HNO_3). Though the different cut size of particle measured in this campaign, the results were much better than the correlations between PILS-IC and AMS with R^2 ranged from 0.59 to 0.86 for different species and both of which were deployed PM_1 cyclones (Takegawa et al., 2009). For the major ions (NO_3^- and NH_4^+), about 90 % of the data points fell within areas between two regression lines (1.5 : 1 and 1 : 1.5, 50 % range), and the linear regression slopes for NO_3^- and NH_4^+ were 1.05 to 1.02, respectively. It indicated that agreement between the AMS and GAC-IC during this period was 50 % with respect to individual 30-min data points. For sulfate, about 70 % of the data points fell within this 50 % range.

Though in general the data between the GAC-IC and the AMS was correlated well in Fig. 12, significant difference could be seen during some specific periods when the AMS (PM_1) measured even higher concentration than the GAC-IC ($PM_{2.5}$). A negative correlation was found between the relative difference of GAC-IC and AMS and relative humidity (RH) (Fig. 12b) in deep analyzing the data. It can be seen that AMS tends to give higher values under higher RH environment (above 80 %, Fig. 12a). The sampled particles of the AMS were dried using a Nafion tube at the inlet and a typical CE of 0.5 was applied which was widely used but rather empirical than having a physical basis (Takegawa et al., 2009). However, because of the geographic location of the

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site, which is close to the Bohai Sea, the average RH was 55.5 % during the sampling period with one tenth of time above 85 % and maximum RH reaching 98 %. It is likely that high humid condition increases the uncertainty of CE of AMS which leads to poorer agreement for SO_4^{2-} as seen in Fig. 12b. The comparison reveals that RH may be an important factor for introducing higher uncertainty to the CE value and a typical CE value as 0.5 should be applied more carefully in future studies especially in coastal or marine environment with high RH.

4   Conclusions

Modifications and improvements have to be made in order to optimize the performance of some imported instruments in highly polluted urban areas such as some mega-cities in China. For this purpose, a Gas and Aerosol Collector (GAC) was developed basing on the original SJAC sampler in this study. With effective changes and improvements, the GAC sampler is not only simplified, but also more applicable than the SJAC in areas with high concentrations of air pollutants. The combination of the GAC with IC systems provides a powerful tool to carry out online field measurements and to simultaneously study chemical species in both gas and aerosol.

The GAC-IC system has been validated extensively both in the laboratory and the field. A dull-polished WAD was applied in the GAC sampler and a collection efficiency of > 98 % was observed when using Na_2CO_3 (25 µM) as the absorption solution and this efficiency remained stable from 20 to 90 ppb for SO_2. It is suggested that a higher concentration of Na_2CO_3 solution should be applied if ambient SO_2 concentration is higher than 90 ppb. The performance tests also showed that the penetrating ratio through the WAD was reasonable and a capture ratio higher than 99.5 % for particulate sulfate was obtained by the newly designed aerosol collector.

Inter-comparison experiments were also performed in an intensive campaign in Guangzhou. A high correlation coefficients of 0.96 found for SO_2 measurements between the GAC-IC system and TE 43c (SO_2 analyzer), indicating a high performance

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of the GAC sampler. Because of the long inlet tube, the GAC-IC measured 10 % higher HONO than the LOPAP at night with the agreement of nighttime samples (R^2 as 0.91) better than daytime samples (R^2 as 0.70). Further improvements for the GAC-IC system should be done to enhance the ability of low HONO concentration measurement. The comparison between the GAC-IC system and filter samples clearly revealed the evaporation loss of chloride and nitrate by the traditional filter method especially for samples collected during the daytime, when about 70 % of chloride and nitrate could be lost. For night samples, the agreements were rather good.

The developed GAC-IC system was also compared to AMS, a becoming widely used online instrument for aerosol, in a field campaign in Changdao close to Bohai Sea. The results between these two instruments agreed well with R^2 ranging from 0.77 to 0.90 for SO_4^{2-}, nss-Cl^-, NO_3^- and NH_4^+, respectively, but a higher measurement was often seen by the GAC-IC system. Based on our data, it was found that AMS measurements could be influenced by high RH in areas such as coastal and marine environments.

In summary, the high correlations with SO_2 and SO_4^{2-} in a wide range as well as good slopes of near one with filter-based method proved that the GAC-IC system performed stable collection efficiencies for both gas and aerosol under high loadings. The new system showed well condition in the inter-comparisons with the TE 43c, LOPAP, filter-based method and AMS, and it had been improved in a way that the developed instrument can be easily operated and data are processed quickly. It will be a powerful tool in future intensive campaigns or long-term monitoring stations to study various environmental issues.

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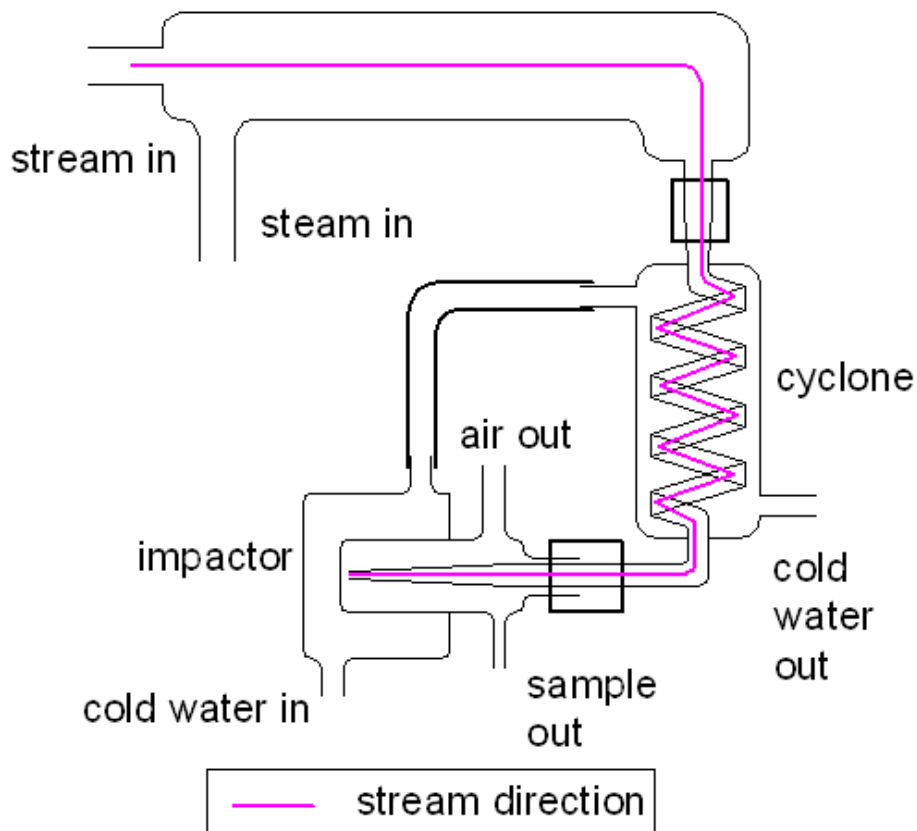Printer-friendly Version

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Table 1. LOD of each species GAC-IC measured.

Gaseous phase	HF	HCl	HONO	HNO_3	SO_2	NH_3
LOD (ppbv)	0.008	0.059	0.034	0.065	0.060	0.030
Aerosol phase	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	NH_4^+
LOD ($\mu g\,m^{-3}$)	0.008	0.043	0.023	0.034	0.159	0.030

Table 2. The statistics of major species measured by the GAC-IC system and $PM_{2.5}$ by the TEOM (hourly average).

	HCl	HONO	HNO_3	SO_2	Cl^-	NO_3^-	SO_4^{2-}	$PM_{2.5}$	$Cl^-/PM_{2.5}$	$NO_3^-/PM_{2.5}$	$SO_4^{2-}/PM_{2.5}$
			(ppb)				(μg m^{-3})			(%)	
Mean	0.55	0.48	1.07	11.47	0.76	4.57	12.37	62.22	1.22	6.16	20.38
Max.	2.95	2.61	5.33	43.00	4.95	27.82	36.62	207.44	9.02	20.05	38.12
Min.	0.05	0.02	0.04	0.26	0.03	0.03	0.47	11.17	0.08	0.19	2.91

Table 3. Summary of inter-comparison results of semi-continuous instrument with filter-based method.

Site	Instrument	Size		Range	R^2	Slope[*]	Intercept	Reference
New York	PILS	PM$_{2.5}$	SO_4^{2-}	0–25	0.91	0.71	0.13	Drewnick
	R&P 8400		SO_4^{2-}	0–25	0.95	0.73	0.34	et al.
	HSHP		SO_4^{2-}	0–25	0.92	0.68	0.63	(2003)
Pittsburg	R&P 8400	PM$_{2.5}$	SO_4^{2-}	0–25	0.83	0.71	0.42	Wittig et al.
			NO_3^-	0–8	0.89	0.78	0.20	(2004)
Seattle	R&P 8400	PM$_{2.5}$	SO_4^{2-}	0.5–5	0.89	1.22	0.28	Homolya
			NO_3^-	0.2–5	0.89	0.78	0.20	et al.
Phoenix			SO_4^{2-}	–	–	–	–	(2005)
			NO_3^-	0.2–15	0.86	0.59	0.99	
Deer Park			SO_4^{2-}	1–6	0.87	0.74	1.65	
			NO_3^-	0.2–2	0.21	1.23	0.53	
Chicago			SO_4^{2-}	0.5–21	0.84	0.47	0.99	
			NO_3^-	0.2–14	0.82	0.46	0.51	
Indianapolis			SO_4^{2-}	0.5–21	0.83	0.59	0.99	
			NO_3^-	0.2–12	0.85	0.56	0.25	
Beijing[**]	AIM (commer-cialized SJAC)	PM$_{2.5}$	SO_4^{2-}	< 20	0.94	0.97	0.60	Wu et al.
			NO_3^-	< 15	0.90	0.69	−0.20	(2007)
Shanghai[***]	AIM (commer-cialized SJAC)	PM$_{2.5}$	SO_4^{2-}	< 20	0.89	0.95	1.41	Wu et al.
			NO_3^-	< 15	0.86	0.89	0.03	(2007)
Finland	MARGA (commer-cialized SJAC)	PM$_{10}$	SO_4^{2-}	< 6	0.98	0.84	0.24	Makkonen
			NO_3^-	< 6	0.91	0.89	0.51	et al. (2012)
Kaiping	GAC	PM$_{2.5}$	SO_4^{2-}	0–37	0.86	0.94	−1.00	This study
			NO_3^-	0–28	0.90	0.98	0.17	
			Cl^-	< 5	0.87	1.08	0.08	

[*] Semi-continuous or continuous method = slope × filter method + intercept.

[**] SO_4^{2-} data bigger than $20\,\mu g\,m^{-3}$ and NO_3^- data bigger than $15\,\mu g\,m^{-3}$ were omitted.

[***] SO_4^{2-} data when daily top five SO_2 concentrations more than 30 ppb and NO_3^- data bigger than $15\,\mu g\,m^{-3}$ were omitted.

Fig. 1. The newly designed aerosol collector used in the GAC to enhance the aerosol collection efficiency.
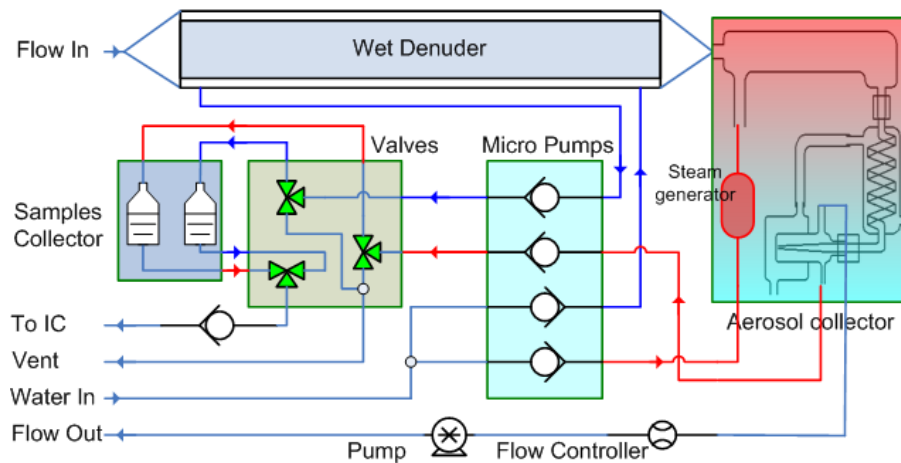
Fig. 2. Overview of the improved GAC sampler equipped with a newly designed aerosol collector.

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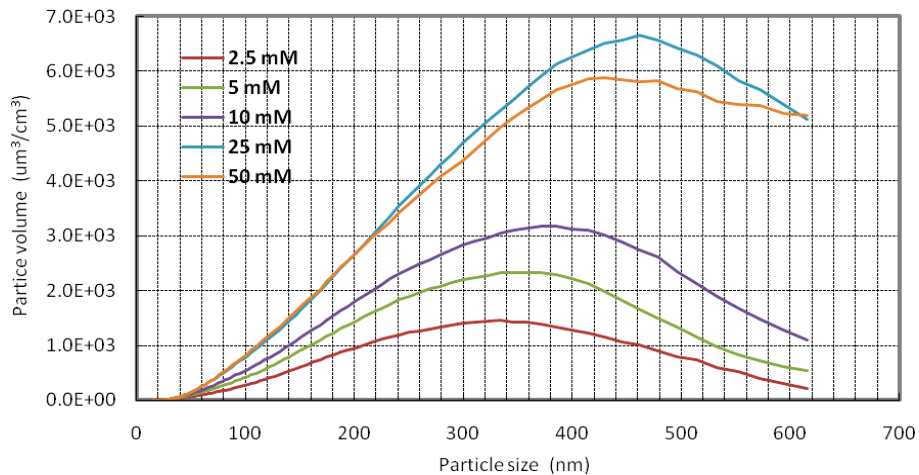Interactive Discussion

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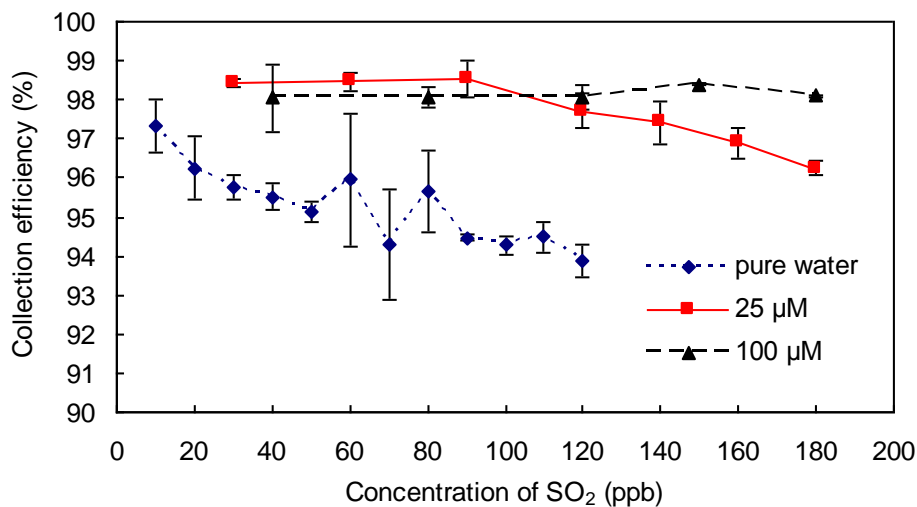
Fig. 3. Collection efficiencies of SO_2 by the WAD used in the GAC for three solutions with standard deviation labeled.

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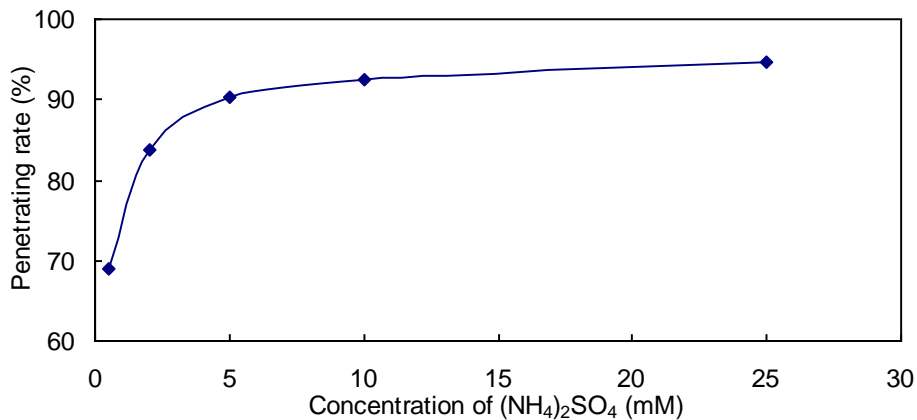
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Fig. 4. Aerosol penetrating rate through the WAD versus $(NH_4)_2SO_4$ concentrations used for particles generation.

Fig. 5. Particle volume size distributions for different $(NH_4)_2SO_4$ concentration used for particles generation.

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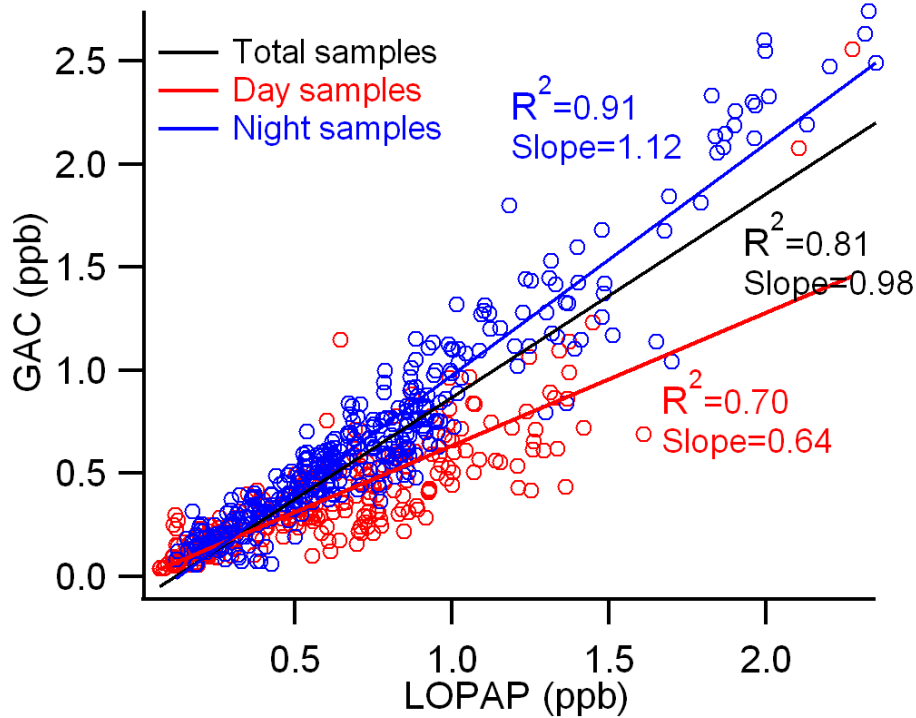Full Screen / Esc

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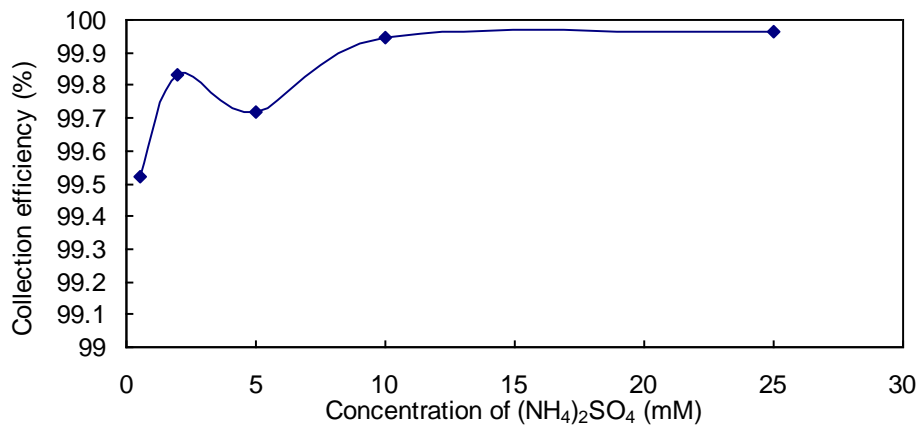
Fig. 6. Aerosol collection efficiency versus $(NH_4)_2SO_4$ concentrations used for particles generation.
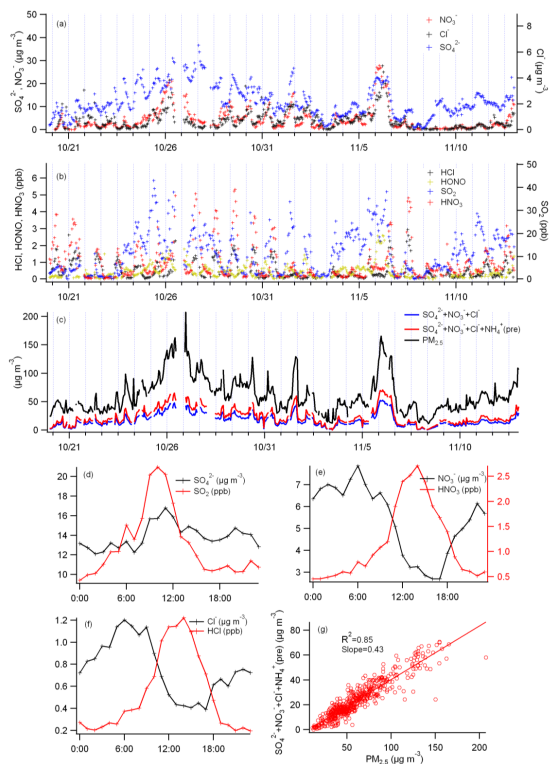
Fig. 7. The time series of **(a)** SO_4^{2-}, NO_3^- and Cl^-; **(b)** gaseous HCl, HONO, HNO_3 and SO_2; **(c)** SO_4^{2-} + NO_3^- + Cl^-, SO_4^{2-} + NO_3^- + Cl^- + NH_4^+ (pre) and $PM_{2.5}$; The diurnal variation of **(d)** SO_4^{2-} and SO_2; **(e)** NO_3^- and gaseous HNO_3; **(f)** Cl^- and gaseous HCl; The agreement between **(g)** SO_4^{2-} + NO_3^- + Cl^- + NH_4^+ (pre) and $PM_{2.5}$.
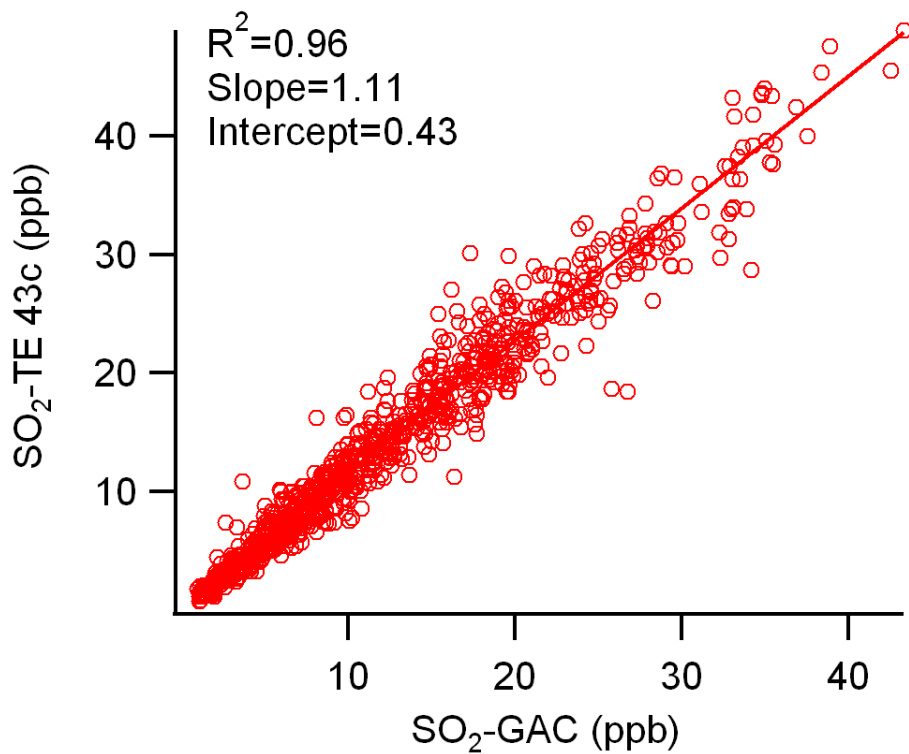
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Fig. 8. Correlation of SO$_2$ measurement by the GAC-IC system and the TE 43c analyzer.

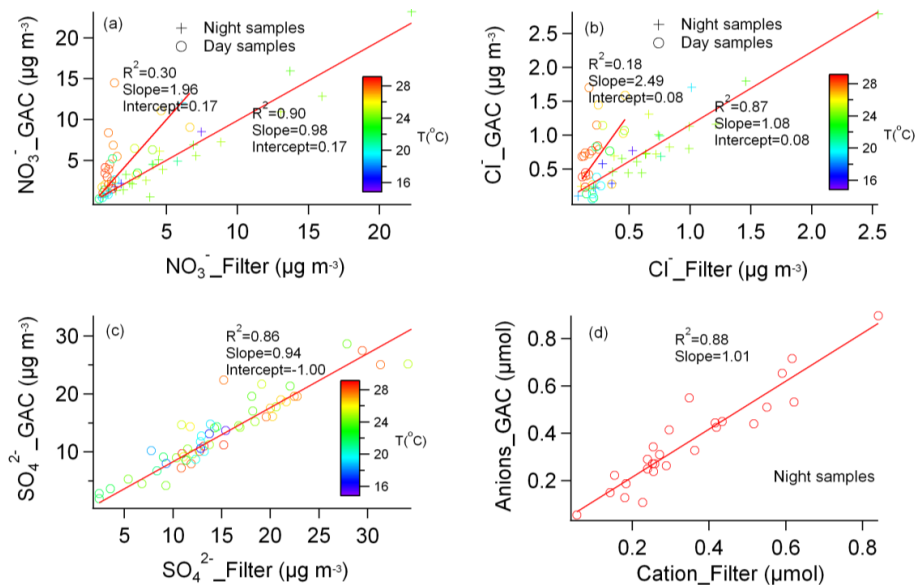**Fig. 9.** Comparison between the GAC-IC system and the LOPAP for the HONO measurement.

Fig. 10. Correlations of **(a)** NO_3^-; **(b)** Cl^- and **(c)** SO_4^{2-} between the GAC-IC and filter measurement and **(d)** correlation between $2SO_4^{2-} + NO_3^- + Cl^-$ measured by the GAC-IC system and NH_4^+ of night samples measured by the filter.
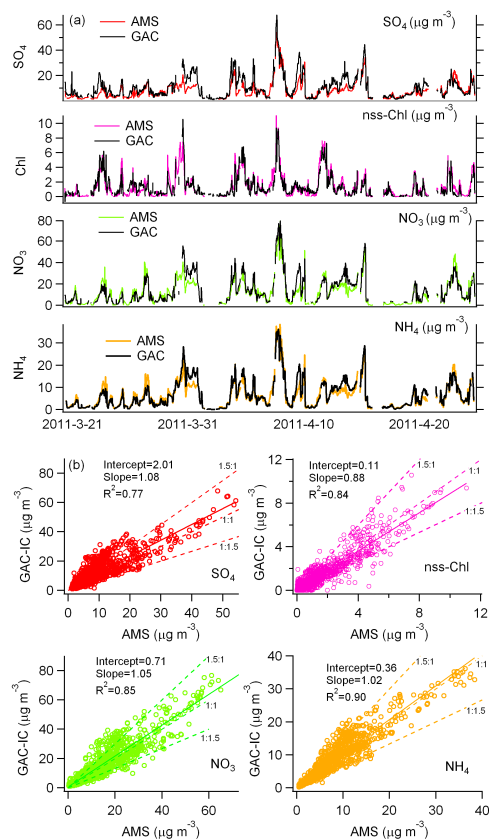
Fig. 11. Inter-comparison between the GAC-IC system and the AMS. We use 30-min average data for the inter-comparisons. The solid lines represent the regression lines. The dashed lines indicate 1.5 : 1, 1 : 1 and 1 : 1.5 correspondence lines.

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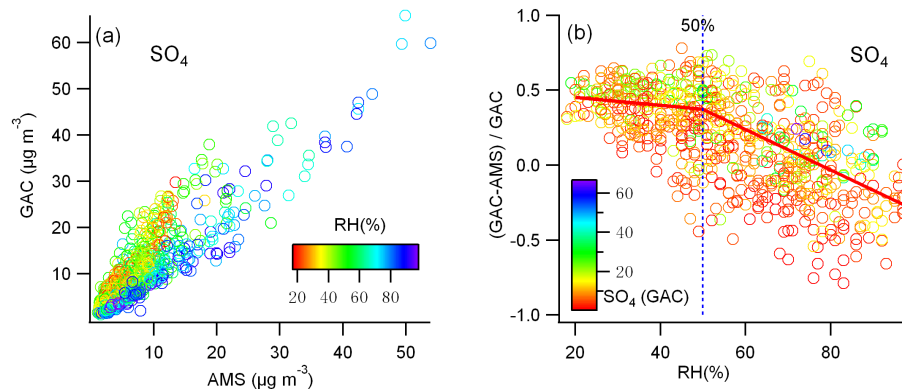Printer-friendly Version

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Fig. 12. Scatter plots of **(a)** the GAC-IC and the AMS for SO_4^{2-} measurement with color-coded according to the RH; **(b)** the relative difference of SO_4^{2-} measurement between the GAC-IC and the AMS vs. the RH.