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Atmospheric Measurement Techniques Discussions

A new smog chamber system for atmospheric multiphase chemistry study: design and characterization

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Atmospheric Measurement Techniques Discussions

Abstract. Multiphase chemistry is an important pathway for the formation of secondary organic aerosols in the atmosphere. In this study, an indoor 2 m^3 Teflon chamber system (Aerosol multIphase chemistry Research chamber, AIR) was developed and characterized to specifically simulate atmospheric multiphase chemistry processes. The temperature and humidity controls, diurnal variation simulation, and seed particle generation unit in this chamber system were designed to meet the needs of simulating multiphase atmospheric chemical reactions. The AIR chamber is able to accurately control temperature (2.5 ~ 31 ±0.15 ℃) and relative humidity (RH < 2 % ~ > 95% ±0.75%) over a relatively broad range. In addition, an RH regulation module inside the chamber was designed to simulate the diurnal variation of ambient atmospheric RH. The aerosol generation unit is able to generate pre-deliquescent seed particles with an organic coating across a wide range of phase states or morphologies. The organic coating thickness of the aerosols within the chamber can be precisely controlled through adjusting the condensation temperature, further helping to elucidate the roles of seed particles in multiphase chemical reactions. The inner walls of the AIR chamber are passivated to reduce the wall loss rates of reactive gases. Yield experiments of α-pinene ozonolysis with and without seed particles combined with a box model simulation demonstrate the high-quality performance of secondary aerosol formation simulation using the AIR chamber.

1 Introduction

Smog chamber is a mainstream tool in chemical laboratory studies to simulate the formation and evolution of air pollutants (Batchvarova et al., 2006; Chen and Lelevkin, 2006; Kolev and Grigorieva, 2006; Mocanu et al., 2006; Tolkacheva, 2006) and reveal the parameterization or mechanisms of atmospheric processes (Wenger, 2006; Olariu et al., 2006; Bejan et al., 2006; Mellouki, 2006; Barnes, 2006; Albu et al., 2006; Carter, 2006; Rudzinski, 2006; Zielinska et al., 2006). Chamber simulations have irreplaceable advantages over other laboratory methods such as oxidation flow reactors (Kang et al., 2007; Lambe et al., 2015; Corral Arroyo et al., 2018; Cosman and Bertram, 2008) and bulk solution experiments (Brunamonti et al., 2015; Turšič et al., 2003; Pratap et al., 2021; Fleming et al., 2020; Mekic et al., 2019) in tracking atmospheric transformation processes and understanding kinetic processes.

The development of chambers is closely related to advances in atmospheric chemistry research. Starting with studies of photochemical smog in Los Angeles in the 1940s (Haagensmit, 1952) and continuing to the 1970s, chambers were designed primarily to study the formation of ozone (Akimoto et al., 1979; Carter et al., 1982) as well as the chemistry of volatile organic compounds (VOCs) and NO_x (Morriss et al., 1957) in the atmospheric boundary layer. With the development of submicron particle measurement techniques, chambers were further used in secondary organic aerosol (SOA) formation studies from the 1980s leading to numerous important scientific discoveries (Hidy, 2019; Odum et al., 1996; Odum et al., 1997; Griffin et al., 1999; Paulsen et al., 2005; Rollins et al., 2009; Hu et al., 2014; Wang et al., 2014).

https://doi.org/10.5194/amt-2023-34
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Atmospheric Measurement Techniques Discussions

Since the beginning of the 21st century, many chambers have been built or upgraded to address integrated atmospheric scientific questions, including $PM_{2.5}$ pollution (Johnson et al., 2004; Hallquist et al., 2009; Hurley et al., 2001), reaction kinetic parameters, mechanisms of VOC oxidation intermediates (Brauers et al., 2003; Bohn et al., 2004; Ren et al., 2017), as well as multiphase processes (Warneke and C., 2004; Pöschl and Shiraiwa, 2015; Liu and Abbatt, 2021; Franco et al., 2021).

In recent years, multiphase chemistries have been invoked to explain the bursting growth of particles (Su et al., 2016; Wang et al., 2016; Su et al., 2020) and physicochemical processes of SOA formation under high ion strength conditions in the atmosphere (Cheng et al., 2015; Su et al., 2020; Liu et al., 2021). Atmospheric multiphase processes can undergo different reaction pathways that are influenced by different environmental conditions (e.g., light, temperature, and relative humidity (RH)) and aerosol physicochemical properties including aerosol liquid water content (ALWC), aerosol phase state, and morphology (George and Abbatt, 2010; Davidovits et al., 2011; Abbatt et al., 2012; Ziemann and Atkinson, 2012; Herrmann et al., 2015; Ravishankara, 97; George et al., 2015; Su et al., 2020). Thus, a precise control of such parameters in a chamber system is vital for simulating atmospheric multiphase chemistry. Different from outdoor chambers (Leone et al., 2010; Stern et al., 1987; Pandis et al., 1991; Johnson et al., 2004; Martin-Reviejo and Wirtz, 2005; Rollins et al., 2009; Cocker et al., 2001; Peng et al., 2017), indoor chambers are usually equipped with artificial light sources (Takekawa et al., 2003; Carter et al., 2005; Paulsen et al., 2005), that can provide controllable irradiation for the simulation of multiphase processes. Compared to large chambers (Brauers et al., 2003; Leone et al., 1985; Pandis et al., 1991), temperature and RH inside small chambers can achieve faster equilibria and provide a more precise simulation of parameters such as diurnal RH change and ALWC (Takekawa et al., 2003; Carter et al., 2005; Paulsen et al., 2005; Wang et al., 2014; Bin Babar et al., 2016), thus improving reproducibility and efficiency when conducting experiments. Adversely, the wall loss effects are more significant for small chambers (Carter et al., 1982; Carter and Lurmann, 1991; Dodge, 2000). As studies showed evidence that the morphology and phase state of aerosol particles play important roles in the atmospheric multiphase chemistry processes (Virtanen et al., 2010; Berkemeier et al., 2016; Wang et al., 2015a; Reid et al., 2018), focused chamber studies on multiphase chemistry require additional steps to control the morphology and phase state of seed particles in chamber design(Faust et al., 2017; Zhou et al., 2019; Zhang et al., 2018; Zhang et al., 2019).

In this study, we designed and built a new indoor 2 m^3 Teflon chamber system (Aerosol multIphase

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

process Research chamber, AIR) with a focus on accurately simulating atmospheric multiphase processes. The temperature and RH inside the AIR chamber were precisely controlled to within ± 0.15 ℃ and ± 0.75 %, respectively. A quantitative manipulation of the RH cycle was designed to simulate the diurnal variations in ambient RH. The seed generation subsystem, including an inorganic particle pre-deliquescence unit and an organic-coating unit, was designed to manipulate the aerosol phase state and organic-coated morphology. A series of experiments were conducted to characterize the spectral distribution and photolysis parameters of light sources, temperature, RH, wall loss behaviors of gas and particles, and particle morphology. Additionally, a series of experiments involving the oxidation of α-pinene with seed particles were conducted in the AIR chamber to demonstrate the effectiveness of the chamber in simulating atmospheric multiphase chemistry.

2 Facility

Figure 1 displays the schematic design of AIR chamber system, and the real picture of the reactor bag and enclosure system are shown in Fig. S1. The chamber system includes the 2 m^3 fluorinated ethylene propylene (FEP) Teflon film (75 μm, Du Pont, USA, light transmission ≥ 93%) reactor and the associated temperature and RH control, artificial light sources, zero air injection and humidification, gaseous/liquid precursor injection, seed aerosol generation, and the instrument-optional detection components. To achieve a precise control of thermodynamic parameters and aerosol morphology when simulating atmospheric multiphase chemistry processes, the temperature inside the reactor is precisely controlled to within ± 0.15 ℃. An RH regulation module is designed and built to simulate the ambient RH diurnal variation, which is capable of changing the RH in the reactor at a time scale of half an hour. In addition, a pre-deliquescing device and a coating device are custom-built to couple to the seed aerosol generation component, for manipulating the phase state (metastable aqueous or solid) and core-shell morphology (1 % ~ 12 % shell thickness) of seed aerosols. The detailed description of each system is shown in Section 2.1-2.4.

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

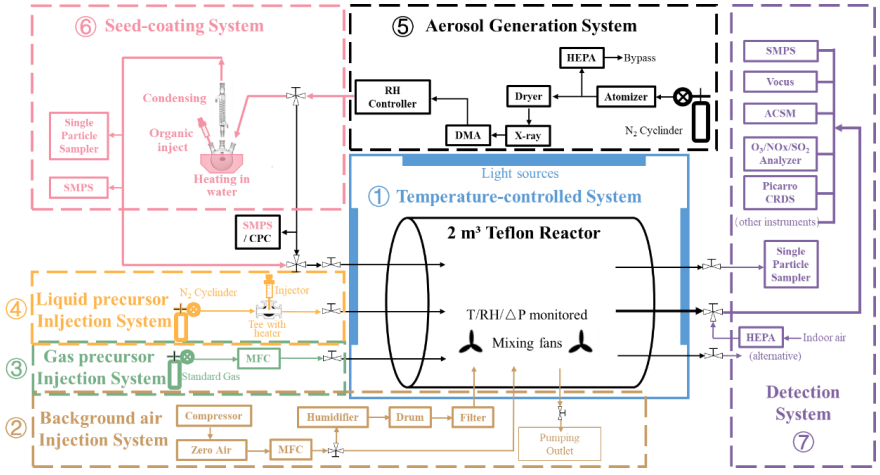

Figure 1. Schematic diagram of AIR chamber system.

2.1 The reactor and enclosure

The Teflon reactor is a 2 m^3 horizontal cylinder (1.2 m in diameter, 1.8 m in length). It is fixed on a stainless-steel frame with four ridges firmly adhered on the Teflon air bag (Fig. S1), so that the variable volume of the reactor during sampling is adequate (this chamber system is designed to operate in Batch Mode). As to each circle side of the cylinder, three stainless steel tubes are threaded through the Teflon film to act as the inlets (for injecting seeds and liquid phase precursors) or sampling outlets for the detection system, respectively. The interface between each tube and the film is sealed by a Teflon flange and a perfluorinated O-ring. At the bottom inside the reactor, two magnetic-levitation fans (patent number: 2019213329392, Beijing Convenient Environmental Tech Co. Ltd.) are equipped, with four speed levels (1000, 1350, 1700, 2000 rpm). A temperature and RH sensor (HMP110, Vaisala, Finland) and a differential pressure sensor (MSX-W10-PA-LCD, Dwyer, America) are also equipped at the bottom inside the reactor.

The rectangular enclosure (2.4 × 1.6 × 2.3 m, L, W, H) of the reactor is temperature-controlled by a circulation system. The indoor air is introduced from the top of the enclosure and exhausts through the bottom. The chiller power is constant, while the heating power is controlled through a proportional-integral-derivative (PID) feedback. Forty black lights (1.2 m, 40 W, Bulb-T12, GE, USA) are fixed on the inner wall of the enclosure as light sources for atmospheric process simulation. The number and position of these lights in work can be controlled by the system computer, so that the light intensity can be variable in experiments. Specular insulated material (SUS304, stainless steel, 8K, mirror plate) is used

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023


Atmospheric Measurement Techniques Discussions

as the enclosure inner wall so that the irradiation inside the reactor can be homogeneous. One side of the enclosure is a double door for entering and reactor maintenance.

2.2 Cleaning and humidifying system

The background gas in the reactor is from the indoor air. An air compressor (FOHUR, FH-50L) compresses the indoor air into a zero-air generator (Aadco, 737-14-A-CH4-240) for purification, removing airborne contaminants such as particulate matters, hydrocarbons, water vapor, NOx, O_3 and SO_2 to produce zero air (RH can be dried to < 2%, and the background concentrations of other contaminants are displayed in Table S2). Then, with the control of a mass flow controller (MFC, HORIBAMETRON, S4832/HMT), zero air is fed into the reactor through a 1/2" stainless steel tube (sealed at the bottom interface by a 304 stainless steel flange) at a flow rate of ≤ 50 L/min (to ensure the cleaning efficiency of the zero-air generator is sufficient), acting as the background gas and cleaning gas for the reactor. At the same time of feeding into the cleaning zero air, a pump beside the chamber system will exhaust the air from the reactor with a flow rate of 20 L/min to accelerate the gas exchange. The positive differential pressure inside the reactor is monitored. When the differential pressure reaches 30 Pa, the MFC will stop the zero-air feed, and when the value falls below 20 Pa, zero air feed will restart. This is designed to avoid damaging the Teflon film of the reactor during cleaning.

The zero air is also used as humidifying gas. When switching to the humidification mode, the zero air will go into a humidification tank filled with deionized water (Milli-Q, 18MΩ) switched by a three-way valve, generating humidified zero air. Then, the humidified air flows through a filter (Waterman, HEPA) to remove the water droplet, and injects into the reactor to humidify. During the humidifying, the exhaust pump mentioned above keeps working. The flow rate of the humidified zero air (20 ~ 25 L/min) is set to be slightly higher than the exhausting rate for fast reaching the target RH inside the reactor.

2.3 Precursor injection system

According to the phase state of precursor reagents, the precursor injection system of this chamber system contains two types. One is used for the injection of gaseous precursors. Standard gas cylinders containing reactive gas (such as SO_2, NO_2, NH_3, HCHO, etc.), inject relevant gaseous precursors into the reactor at a set flow rate and injecting duration under the control of a computer-connected MFC. The oxidant O_3 is produced through the decomposition of O_2 (from a standard O_2 cylinder) exposed to the 185 nm UV light.

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023


Atmospheric Measurement Techniques Discussions

After flowing through the MFC, the gaseous species enter the reactor via a stainless-steel tube at the bottom of the chamber.

The other type is used for the injection of liquid precursors. Note that, the liquid precursors here mean the species is in liquid phase before injected into the reactor, but should be gaseous after injecting into the chamber, such as α-pinene standard solvent. A tee (the inlet on the left side of the chamber, as shown in the 'Liquid precursor Injection System' in Fig. 1) is fitted in the pipeline before the liquid precursors entering the reactor, with a 1 mm thick silicone membrane clamped to the right-angled end. The specific amount of the liquid precursors is taken with a microsyringe, penetrating the silicone membrane and slowly injected into the tee. At the same time, pure N_2 is used as the carrier gas to vaporize the liquid precursor and carry it into the reactor under a specific gas cylinder pressure (0.25 MPa). After injection, N_2 is continuously purged for 60 seconds to ensure that no liquid precursors remain in the pipeline.

2.4 Seed generation system

The seed aerosol generating system is a complex subsystem of AIR chamber system designed in this study. In addition to the common aerosol generation device, this study couples an RH-controlling device and a coating device to control the phase state and morphology of the seeds for supporting the simulation of atmospheric multiphase processes.

Commonly, the species used to generate the seed particles (typically dissolved inorganic salts such as ammonium sulfate and sodium chloride) are first dissolved in deionized water (Milli-Q, 18 MΩ) and then generate a solution. Then, it is atomized as humid aerosol flow by an atomizer (TSI 3076) with N_2 blowing. Passing through a Nafion tube (PERMA PURE, MD-700-24F-3), the humid flow is dried and forms dry polydisperse seed aerosols. The drying is realized by pumping the air at the outer layer of the Nafion tube to a negative pressure (~20 kPa). It is tested that, within the range of the aerosol generation flow rate (≤ 3 L/min), the RH of the aerosol flow can be dried to below 30 %. An X-ray neutralizer and DMA (DMA, Model 3082, TSI, Inc., USA) are optional, for selecting monodisperse aerosols from the polydisperse aerosol flow (flow rate ratio of sheath flow to aerosol flow is controlled between 5:1 and 10:1), to support monodisperse experiments.

Besides, an RH controlling device is designed in this study to pre-deliquesce the generated dry seeds that forming metastable seed aerosols. As shown in Fig. S9, N_2 is used as the initial gas, which is then divided into two paths, one is the dry N_2, and the other goes through the deionized water (Milli-Q, 18MΩ, heated

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

to 45 ℃) to act as the wet gas. The flow rate of each path is controlled by an MFC (GAS TOOL INSTRUMENT, GT 130MAX). Then the two flows mix into one as the humidifying gas and enter the outer layer of a Nafion semi-permeable tube (PERMA PURE, MD-700-24F-3). The flow with seed aerosols goes through the inner layer of the Nafion tube and then is humidified. The RH of the humidified flow is detected by an RH sensor (HYGROCLIP2, HC2A-S). The two MFCs of each flow path and the RH sensor are connected to a computer and controlled by a Labview program with PID feedback. Through the two MFCs adjusting the ratio of the flow rates of the dry and wet flow path, the RH of seed aerosol flow is controlled. This device has been tested to enable rapid changes in RH between 5 % and 90% within 5 mins, and the RH variability can be within ± 0.2 %.

In order to investigate the effect of aerosol coating on atmospheric multiphase process, a device is designed in this study to generate a thickness-controlled and species-known coating on the generated dry monodisperse seed aerosols. The constitution of the coating device is shown in Fig. S10. This device consists of a water bath (Changfeng, HW.SY11-KP1), a three-necked flask (250 mL, 19#-24#-19#), a condensing glass tube (30 cm, 24#), and a thermostatic bath (BiLon, SC-05B). The organic species (~ 400 μL) with low volatility (saturated vapor pressure in the order of 10^{-4} ~ 10^{-5} mmHg at room temperature) used to form coating is set at the bottom of the three-necked flask, which is heated in the water bath to evaporate the organic vapor. The dried seed aerosol flow enters through the side port of the three-necked flask, and then carries the hot organic vapor into the condensing tube (condensing temperature is controlled at 20 ℃ by the thermostatic bath in this study). Due to the reduced temperature, the saturated vapor pressure of the organic drops, and the organic vapor will preferentially condense on the surface of seed aerosols that forming a coating.

2.5 Detection system

As shown in Figure 1, three stainless steel tubes are fixed on the right side of the reactor to act as sampling outlets. The middle steel tube of them is 3/8 " in size and acts as the main sampling tube, connected to a 3/8 " stainless steel three-way plug valve. One outlet of the plug is attached to a HEPA filter, and the other outlet is attached to the line to sampling instruments. This design allows a quick sampling switch between indoor air and the reactor. The other two stainless steel tubes are both 1/4 " and are used as auxiliary sampling outlets (e.g. temporarily collect single particle samples for a few minutes).

An SMPS system (a DMA, Model 3082, and a CPC, Model 3772, TSI, Inc., USA), and a CPC (Model

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023


Atmospheric Measurement Techniques Discussions

3750, TSI, Inc., USA) downstream of the seed generation system, are the standing instruments for the chamber system, used to measure the particle number size spectrum distribution and particle total number concentration in the reactor, respectively. Other instruments are optional according to the specific research aim, and typically the total sampling flow rate should be lower than 6 L/min.

The other detection instruments involved in this study, include the instruments for gaseous species detection (Thermo Scientific gas analyzer (Model 43i-TLE for SO2, Model 42i-TL for NOx, Model 49i for O3, Model 48i-TLE for CO), Picarro cavity ring-down spectroscopy (Picarro CRDS, G2401) for CO_2 and CH_4, Summa Canister (SILONITE, 1869) and GC-MS (Agilent, 7890A/5975C) for non-methane hydrocarbon (NMHC)), instruments for particulate species detection (Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM, Aerodyne)), and instruments for volatile organic compounds (Vocus Proton-Transfer Reaction Time-Of-Flight Mass Spectrometry (Vocus-PTR-TOF-MS, Vocus S, Tofwerk), shorted as Vocus).

The sampling flow rate of each instrument is calibrated before each experiment. For Thermo Scientific instruments and Vocus, a single standard concentration is tested at each experiment, to act as a basis for instruments status verification and data quantification. For the data collected by ACSM, the calibration is performed based on the mass concentration calculated from SMPS data.

3 Characterization of the AIR chamber

A series of experiments were carried out to evaluate the performance of this chamber system, including leakproofness, sample-volume support, background concentrations, mixing performance, light characteristics, temperature and RH control, gas and particle wall loss, as well as characterizations of aerosol particles with the core-shell morphology. All the instruments for measurement are included in Section 2.5.

3.1 Fundamental parameters

Leakproofness of the reactor was characterized by the positive pressure difference between the air inside the reactor and the ambient air and the change in the total number concentration of background particles inside the reactor. When the reactor was filled with zero air, the positive pressure difference inside the reactor was maintained at > 3 Pa for more than 25 hours (Fig. S2a), then slowly decreased to ~ 0.5 Pa after several days. When the air inside the reactor was sampled at a flow rate of 5 L/min, the positive

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023


Atmospheric Measurement Techniques Discussions

pressure difference decreased to zero after 2 hours, and then total particle number concentration slowly increased from ~ 0 cm^{-3} to a final < 10 cm^{-3} in ~3.5 hours (Fig. S2b). This concentration is negligible for a particle number concentration of 10^3 ~ 10^4 cm^{-3} that are usually used in experiments. Moreover, this chamber system is designed to operate in batch mode, and the reactor can provide a sampling volume of 1000 ~ 1200 L (Fig. S3) and a sampling time of more than 3 hours at a total sampling flow rate of 5~6 L/min. The results above indicate that the system leakproofness is reliable for further experiments.

The reactor background was also characterized after repeated cleaning with zero air. As shown in Fig. S4, the background particle total number concentration was < 1 cm^{-3}, and increased only to 4 cm^{-3} with the mixing fans turned on. Irradiation slightly increased the background particle concentration but still only to < 10 cm^{-3}, which is negligible when compared with normal reaction conditions. Table S1 shows the background concentrations of chemical species in AIR chamber reactor under dry and high RH conditions. Compared with data reported for other chambers (White et al., 2018; Bin Babar et al., 2016; Wang et al., 2014; Platt et al., 2013; Carter et al., 2005; Chen et al., 2019b), the background concentrations of gaseous pollutants including SO_2, NOx, O_3 and CO in the reactor were comparable or lower for the AIR chamber. The background concentration of total non-methane hydrocarbon (NMHC) was higher than literature values due to the presence of chemically inert $CHClF_2$ (half of the total NMHC concentration), which originates from the indoor refrigeration system and is hard to eliminate within the zero-air generation system. Nevertheless, this species does not interfere with the reactions under most experimental conditions. The reactor can be cleaned to background levels with a volume of zero air >5 times that of the reactor (Table S2) after each experiment. The cleaning process can be completed in less than 9 hours, as shown in Section 2.2.

The mixing performance of the injection into the reactor was examined using NO_2 concentration and total particle number concentration as tracers (Fig. S5). The mixing time to uniformity was 5 minutes without running fans and less than 1 minute with the fans on. Furthermore, the mixing time was independent of the fan speed.

3.2 Light source characterization

The reflective inner wall (SUS304, stainless steel, 8K, mirror plate) of the AIR chamber is equipped with 40 UV lamps (1.2 m, 40 W, Bulb-T12, GE, USA) to provide irradiation during the experiments. There are 10 lamps on the left, right, back, and top of the wall, respectively, and each lamp can be turned on or

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023


Atmospheric Measurement Techniques Discussions

off separately by the control system, so that the light intensity in experiments varies from 2.5% to 100% intensity. These light sources can also be replaced by lamps with different emission spectra to provide a variety of irradiation conditions.

For current light sources, a portable UV spectrometer (StellarNet Inc., Tampa FL, USA) was used to characterize the irradiance spectrum in the reactor (Fig. S6). The irradiance is mainly distributed in the range of 360 ~ 390 nm, peaking at 370 nm, which is within the range of peak irradiance of UV lights used in other indoor chambers (340 ~ 371 nm) (Wang et al., 2014; Ma et al., 2022; Bin Babar et al., 2016; Chen et al., 2019b; Lane and Tang, 1994; Thuner et al., 2004). Another small peak appears at 405 nm, which is convenient for directly checking the status of the lamps.

The photolytic rate constant for NO_2 can be used to characterize the irradiation intensity. Previous literature (Wang et al., 2014; Bin Babar et al., 2016; Ma et al., 2022) often characterize irradiation intensity through the photolytic rate constant of NO_2 (J_NO_2), calculated through the steady-state concentrations of NOx and O_3 (Atkinson et al., 2004). This study mainly used a spectrometer, namely the Jvalue instrument (AVANTES, AvaSpec-ULS-TEC-EVO), to measure the irradiance and directly calculate the photolytic rate constants of a few important species in atmospheric photochemistry. Notably, the Jvalue instrument was also calibrated using the J_NO_2 values derived from the steady NOx-O_3 concentration under several light schemes to correct for the geometry defect of the Jvalue instrument when placed inside the AIR chamber. The calibration factor of the traditional J_NO_2 method is 1.49 ± 0.06. As shown in Table S3, the current light source is more suitable for the photolysis of HONO and NO_2 (photolytic rate constants on the order of $10^{-4} \sim 10^{-3}$ s^{-1}). However, the photolysis of HCHO, H_2O_2, and O_3 is slow (photolytic rate constants on the order of 10^{-8}~10^{-7} s^{-1}). The J_NO_2 maxima of other chambers are usually in the range of $2 \sim 9 \times 10^{-3}$ s^{-1} (Chen et al., 2019a; Li et al., 2017; Wang et al., 2014; Bin Babar et al., 2016; Ma et al., 2022). In comparison, J_NO_2 due to the light source in the AIR chamber is 4.10×10^{-3} s^{-1}, close to the median value of the other chambers. Moreover, the photolytic rate constant of HONO due to the light source in this chamber (J_HONO at the level of 10^{-4} s^{-1}) is comparable to or slightly higher than the value of HONO photolysis in the ambient atmosphere in China (J_HONO at the level of $10^{-5} \sim 10^{-4}$ s^{-1}) (Zheng et al., 2020).

When only lamps on two sides of the AIR chamber were turned on (four schemes with 20 lights on, noted as ‘only back/top’, ‘left and right’, ‘odd’ and ‘even’ in Table S3), the photolytic rate constants in the reactor under different configurations were almost the same (J_HONO = 5.10 ± 0.12 × 10^{-4} s^{-1}, J_NO_2 =

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

$2.16 \pm 0.05 \times 10^{-3}$ s^{-1}), and nearly equal to half of that with all 40 lights on. In addition, the photolytic rate constant of the scheme 'left and right' (40 lights) was the sum of that of 'only left' (20 lights) and 'only right' (20 lights). These results indicate that the irradiation in the reactor is uniformly distributed. Notably, because the measurement interface of Jvalue was a little biased to the left during detection, the value for 'only left' was higher than that for 'only right'.

3.3 Performance of temperature and RH control

The temperature and RH in the reactor are measured by a high-accuracy sensor (HMP110, Vaisala, Finland). Detailed descriptions of temperature and RH control are given in Section 2.1 and 2.2. The accuracy for RH of this sensor is shown by its measurement error of < 1% from that measured by a hygrometer (chilled mirror hygrometer, Edgetech Instrument, USA), with an $R^2 > 0.99$. The temperature in the reactor can be stably controlled in the range of 2.5 ℃ ~ 31 ℃, and the control range of RH is < 2% ~ > 95%. The fluctuations in the temperature inside the reactor are within ± 0.15 ℃ of any set temperature, and the corresponding RH fluctuations for RH > 80 % are within ± 0.75 %. The stability achieved with the temperature and RH controls across a wide range of temperatures is shown in Table S4. The illumination of lamps raises the lowest achievable temperature by 3 ℃ for every 10 lights on. However, the illumination of the reactor does not affect the stability of temperature and RH inside the reactor. When the set temperature is close to room temperature (20 ℃ in Table S4), the fluctuation is < 0.1 ℃, demonstrating a more accurate temperature and RH control performance compared with other chambers (Table S5) (Wang et al., 2014; Wu et al., 2007; Bin Babar et al., 2016; Ma et al., 2022; Wang et al., 2015b). Sampling operation (lasting more than 3 hours with flow rate at 5 L/min, Fig. 2) does not significantly affect the stability of temperature and RH control either, which also indicates the permeation and wall loss of water molecules do not affect a lot.

In order to simulate the diurnal variations in ambient air temperature and RH, a proportional-integral-derivative (PID) feedback controlling function was designed. The RH in the reactor can reach the target RH by controlling the temperature. After receiving the target RH input, the control program calculates the stepwise theoretical RH value at each time increment and the corresponding temperature control steps based on current temperature and RH in the reactor. This calculation is also adjusted in real-time to optimize the gradual change of RH. Figure S7 demonstrates two examples to show alternate linear change and constant control of RH. The RH can reach the set value within a few hours with fluctuations < 0.75%.

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

This function performs even better at low temperatures, suggesting the potential of using this chamber system to simulate diurnal variations of RH in the ambient atmosphere in wintertime.

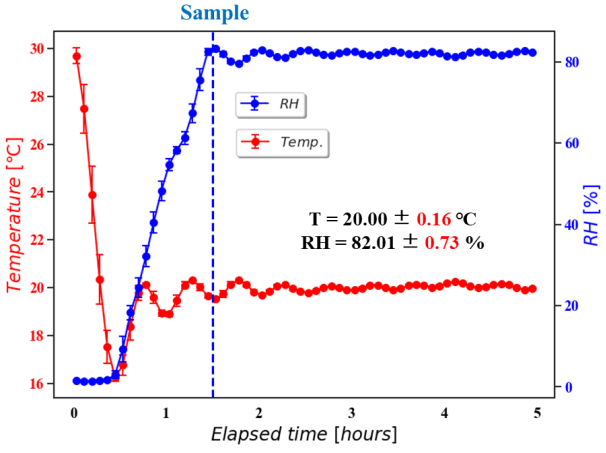

Figure 2. Stability of temperature and RH control in the reactor during sampling.

3.4 Wall loss of gas and particles

The wall loss process is considered as a first-order kinetic process, in that the decay rate of a concentration is proportional to the concentration:

$$\frac{dC(t)}{dt} = -k * C(t) \quad (1)$$

where C(t) is the species concentration at time t, and k is the wall loss rate constant (in units: s^{-1} or min^{-1}). The wall loss rates of gaseous species such as NO_x and O_3 in this study are shown in Table S6, the values of which are lower than other small Teflon chambers (2 ~ 5 m^3) (Wu et al., 2007; Wang et al., 2015b; Li et al., 2017; Bernard et al., 2016), as a result of passivation of the inner surface of the reactor with 2 ppm O_3 for 3 days.

The wall loss rate constant k of particles is dependent on particle size (diameter, noted as D_p). Smaller or larger particles often have higher k values (Crump and Seinfeld, 1981) due to higher diffusion or sedimentation rates, respectively. The dependence of k values for particles with D_p < 50 nm is rarely reported in previous chamber studies. This study demonstrates that the constant k decreases as a function of decreasing D_p when particles are smaller than 50 nm, which is also shown in Fig. S7 of Ma et al (Ma et al., 2022). The $\log_{10}(k)$ value for particles can be approximated with a segmented linear function of $\log_{10}(D_p)$ [93, 94]. In addition to the slopes to be determined, the inflection point D_p, where the loss trend

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

inverses, changes with different chambers. In this study, two inflection points are identified at 50 nm and 150 nm (Fig. S8). Furthermore, the k-Dp dependence has been reported to deviate in different experiments even in the same reactor. This study found that such deviations can be corrected through an up-and-down shift of the $\log_{10}(k)$-$\log_{10}(Dp)$ function curve. Even for deliquescent particles (RH = 90 % in Fig. S8, the Dp of the x-axis represents the liquid particle diameters), this method still accurately described the relationship between k and Dp (R^2~0.95) when considering the hygroscopic growth of the particle size.

Another commonly used parameter to characterize the particle wall loss behavior in chambers is the total volume wall loss rate constant (k_v). For small Teflon chambers of 2 ~ 3 m^3 in size (Takekawa et al., 2003; Li et al., 2017; Liu et al., 2019), k_v values typically range from 2.84 ~ 4.72 * 10^{-3} min^{-1}. The particle wall loss is slightly higher in the chamber in this study, with the k_v found to be 5 × 10^{-3} min^{-1} (Table S7).

3.5 Morphology of seed particle generation

Seed particles are typically used to simulate aerosol formation by the multiphase chemistry pathway. The AIR chamber is designed to couple to a subsystem for generating seed particles with different phase states through pre-deliquescing, adopted from a previous study (Faust et al., 2017). A volatilizing-condensing method is used to generate known-composition organic-coated inorganic particles in the AIR chamber, with a detailed description in Section 2.4.

As shown in Figure 3, squalane is coated onto dry 200-nm monodisperse NaCl seed particles to produce a core-shell morphology for the particles. The coating thickness is controlled by adjusting the water bath heating temperature while maintaining a fixed condensation temperature of 20 ℃. Using the Clausius-Clapeyron equation that describes the relationship between saturation vapor pressure and temperature, as well as the Maxwell equation that describes the condensation growth rate of particle size under a certain supersaturated vapor pressure, the coating thickness can be predicted in relation to the heating temperature (Fig. 3a), to assess the feasibility of the selected coating species. The coating thickness is calculated as half of the difference in peak Dp of the monodisperse particle size distribution before and after the seeds are coated (Fig. 3b). For squalane, the device allows for a relatively accurate control of coating thickness in the range of 5 to 25 nm (1 % ~ 12 % shell thickness). For organic species with similar volatilities (saturated vapor pressure in the order of 10^{-4} ~ 10^{-5} mmHg at room temperature), the device could provide similar control performance.

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

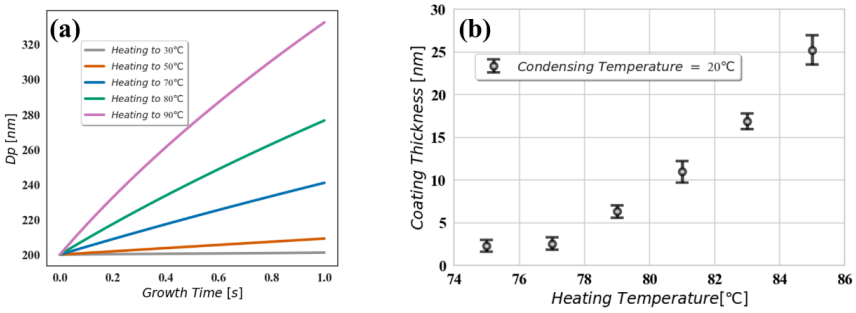

Figure 3. Relationship between coating thickness on dry 200 nm NaCl seed and heating temperature in the coating device, with squalane as the coating species and 20 ℃ condensing temperature. (a) Theoretical estimation in different growth times. (b) Measured results by SMPS.

4 Applications in SOA generation——α-pinene ozonolysis researches

4.1 SOA yield of seed-absent experiments

SOA are generated from α-pinene ozonolysis in the AIR chamber to evaluate its performance, with experiment conditions given in Table S8 (NO.1 ~ 5). The key parameter Y, representing the yield of SOA, is defined as:

$$Y = \frac{\Delta mo}{\Delta ROG} \quad (2)$$

where Δmo represents the total mass concentration of generated SOA, and ΔROG represents the total mass concentration of reactive organic gas that was consumed in the reaction (specifically referring to α-pinene in this study), with both units in μg/m^3. SOA mass concentration was measured by a ToF-ACSM (Section 2.5). The organic mass measurement was also corrected based on the particle size distribution data from SMPS, where the α-pinene-derived SOA density was assumed as 1.3 g/cm^3. This density value is also used in many previous researches (Bahreini et al., 2005; Alfarra et al., 2006; Ma et al., 2022), but higher than the unit density assumption used in some other chamber studies (Wang et al., 2011; Wang et al., 2014; Bin Babar et al., 2016; Cocker Iii et al., 2001; Li et al., 2021; Zhang et al., 2015).

Odum et al (Odum et al., 1996) found that the two-product model reproduces well the non-linear relationship between the SOA yield Y and the particulate organic mass concentration (mo):

$$Y = mo * \sum \frac{\alpha_i * K_{om,i}}{1 + mo * K_{om,i}} \quad (3)$$

where α_i and $K_{om,i}$ are the mass-based stoichiometric and partition coefficient for species i, respectively, and mo is the total mass concentration of organic aerosol. Figure 4 shows the results of the two-product

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

model that fits the seed-absent SOA yield results in this study. The Odum model fits results from other chamber studies are also shown in Figure 4 for comparison. Detailed model fitting parameters are shown in Table S9. In contrast, Y in this study is a little higher than those in other small or medium-sized chambers, which may be owing to the lower gas wall loss in our Teflon reactor (Section 3.4). The four fitting parameters in this study, α1, α2, K1, K2, are 0.62479, 0.0326791, 0.0121589, 0.0121596, respectively. K1 and K2 are close and are moderate values; however, α1 is significantly higher than those in other chambers. Such higher value for α1 can be an indication of a lower volatilizing loss of the gas phase intermediates within the AIR reactor compared with the other chambers. The good fitting from our experiment indicates that the chamber system in this study is stable. These results imply a reliable performance of our chamber system for experimental simulation studies of atmospheric secondary transformation process.

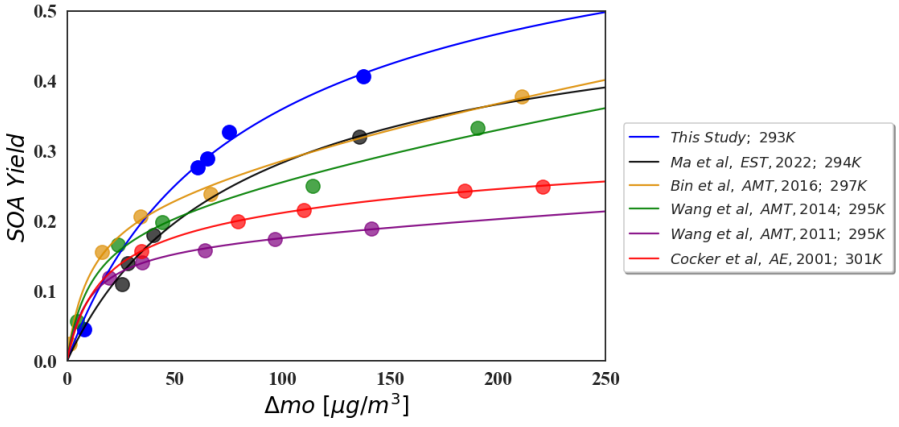

Figure 4. Two-product model fitting curve of seed-absent α-pinene-derived SOA yield in this study and the comparison with other literature results. The data of the blue line is from this study, and other data is obtained from these references (Cocker Iii et al., 2001; Wang et al., 2011; Wang et al., 2014; Bin Babar et al., 2016; Ma et al., 2022).

4.2 Effects of seed phase state on SOA yield

The effects of different seed phase state on the yield of α-pinene-derived SOA were further investigated using ammonium sulfate as the seed particles (Table S8, NO.6 ~ 8). Figure S11 shows the relevant measured parameters during one reaction (e.g., experiment NO.8). The yields of all the experiments are summarized in Fig. 5. In general, the yield in the presence of dry seeds is not significantly different from that in the absence of seeds, consistent with the outcome of Odum et al (Odum et al., 1996). However,

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

Atmospheric Measurement Techniques Discussions

in the presence of aerosol liquid water and ammonium sulfate seeds, the α-pinene-derived SOA yield is reduced. This suppressing phenomenon is also reported by Cocker et al (Cocker Iii et al., 2001), which may be related to the finding of Lutz et al (Lutz et al., 2019) that an inhibition of organic species partitioning in the particulate phase exists at high sulfates level. However, to our knowledge, the suppressing phenomenon above may not be common, that has only been reported in the α-pinene ozonolysis system with ammonium sulfate seeds.

The subplot in Fig. 5 demonstrates the SOA yield at each elapsed time point in these experiments. Liquid water can significantly promote the initial SOA yield and generation rate (Zhang et al., 2018), and our results have reproduced this phenomenon (subplot in Fig. 5). However, the oxidation reaction proceeds, it is observed that the SOA yield with liquid seeds decreases, and larger seed aerosol liquid water contents produce greater decreases in the yield. These indicate the AIR chamber system facilitates the researches of aerosol properties on atmospheric multiphase processes.

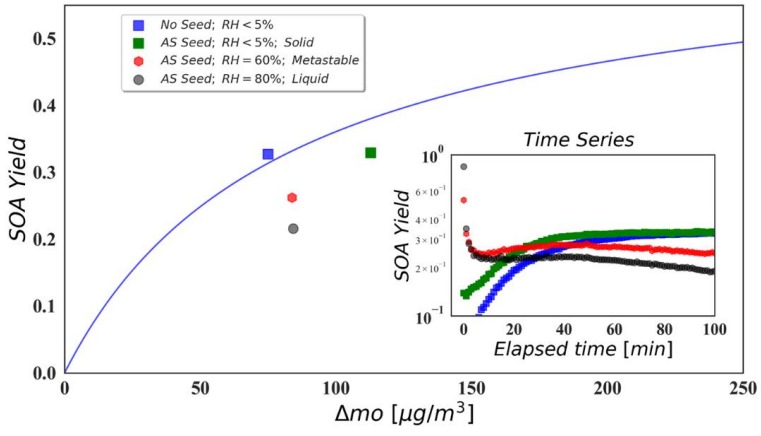

Figure 5. Effects of phase state and liquid water content of ammonium sulfate seed particles on the SOA yield of α-pinene ozonolysis (α-pinene = 60 ±13 ppb, O3 = 296 ±30 ppb). In the main plot, the blue line is the fitting two-product curve from no-seed experiments data in this study, which is a replicate of the curve in Fig. 4. The subplot shows the current yield since the initial time point of each experiment, where the blue points represent the data of no-seed experiment, green points represent the data of solid seed experiment, red points represent the data of metastable seed experiment, and grey points represent the data of liquid seed experiment.

5 Conclusions

The reported special phenomena relying on specific particle properties are well reproduced in AIR

https://doi.org/10.5194/amt-2023-34
Preprint. Discussion started: 18 April 2023

chamber benefitting from the seed phase state control, and the accurate temperature and RH control facilitates the quantization of the effects of aerosol liquid water. Besides, compared to other chambers, the manipulation of composition and thickness of organic coating could provide a more clarity surface property. Broad temperature range, adjustable irradiation intensity, and the fast-responding RH cycle, make this chamber system suitable for simulating diurnal ambient atmosphere in different seasons. These performances of handling key parameters suggest the potential of this AIR chamber system for the laboratory simulation of atmospheric multiphase processes.

Data availability

The data in this study are available from the authors upon request (zhijunwu@pku.edu.cn).

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Author contributions

TZ and ZW conceived the study. TZ, ZW, JW, WF conducted the laboratory measurements. TZ carried out the data analysis. TZ, KB, YY, XY, ZB, XM, YZ participated in the instrument managements. SG, YC, CL, YZ, S-ML and MH supported this research. TZ wrote the paper with inputs from all co-authors.

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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