

**Total sulphate vs.
sulphuric acid
monomer in
nucleation studies**

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Total sulphate vs. sulphuric acid monomer in nucleation studies: which represents the “true” concentration?

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Abstract

Sulphuric acid is known to be a key component for atmospheric nucleation. Precise determination of sulphuric acid concentration is crucial factor for prediction of nucleation rates and subsequent growth. In our study, we have noticed a substantial discrepancy between sulphuric acid monomer and total sulphate concentrations measured from the same source of sulphuric acid vapour. The discrepancy of about one to two orders of magnitude was found with similar formation rates. The reason for this difference is not yet clear and it can have great impact on predicting atmospheric nucleation rates as well as growth rates. To investigate this discrepancy and its effect on nucleation, a method of thermally controlled saturator filled with pure sulphuric acid (~97 %) for production of sulphuric acid vapour is introduced and tested. Sulphuric acid-water nucleation experiment was done using a laminar flow tube. Two independent methods of mass spectrometry and online ion chromatography were used for detecting sulphuric acid concentrations. The results are compared to our previous results, where a method of evaporating weak sulphuric acid-water solution droplets in a furnace was used to produce sulphuric acid vapour (Brus et al., 2010, 2011). Measured sulphuric acid concentrations are compared to theoretical prediction calculated using vapour pressure and simple mixing law. The calculated prediction of sulphuric acid concentrations agrees very well with the measured values when total sulphate is considered. Sulphuric acid monomer concentration was found to be about two orders of magnitude lower than the prediction, but with similar temperature dependency as the prediction and the results obtained with ion chromatograph method. Formation rates agree well when compared to our previous results with both sulphuric acid detection and sulphuric acid production methods separately.

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1 Introduction

Secondary particle formation by gas to liquid conversion is widely recognized as an important source of aerosol particles in the atmosphere worldwide (Weber et al., 1996; Kulmala et al., 2004; Spracklen et al., 2006). These particles affect the radiative balance of the Earth by scattering and absorbing the incoming radiation (Feingold and Siebert, 2009). Aerosols can seriously reduce visibility and have also potential health effects (Davidson et al., 2005). Model calculations and observations suggest that new particle formation events can contribute a significant amount to Cloud Condensation Nuclei (CCN) which can alter the lifetime and albedo of clouds (Lihavainen et al., 2003, 2009; Merikanto et al., 2009).

Significant effort has been done by field measurements and laboratory studies together with computer simulations to understand the particle formation mechanism itself and the atmospheric conditions involved in the gas to liquid conversion. Despite the effort and numerous results, the underlying mechanism is not yet solved.

It is widely accepted that sulphuric acid plays a key role in atmospheric nucleation (Kulmala et al., 2006; Sipilä et al., 2010; Brus et al., 2011; Kirkby et al., 2011). Binary nucleation of sulphuric acid and water (Vehkamäki et al., 2002; Yu, 2006; Kirkby et al., 2011), ternary nucleation involving also ammonia and/or amines (Ball et al., 1999; Korhonen et al., 1999; Napari et al., 2002; Benson et al., 2009; Berndt et al., 2010; Kirkby et al., 2011; Zollner et al., 2012) and ion-induced nucleation (Lee et al., 2003; Lovejoy et al., 2004; Yu et al., 2008, 2010; Nieminen et al., 2011) have been suggested as possible mechanisms for the nucleation to occur in the atmosphere. Ions have been shown to lower the thermodynamic potential of nucleation (Arnold 1980; Winkler et al., 2008; Kirkby et al., 2011) but the role of ions in boundary layer nucleation have been shown to be minor (Manninen et al., 2010; Paasonen, et al., 2010, Kerminen et al., 2010; Hirsikko et al., 2011). However, study made by Yu and Turco (2011) suggest that the role of ion-mediated nucleation is underestimated in the smallest particle sizes, indicating ion-mediated nucleation to dominate over the neutral cluster nucleation.

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Recently several laboratory studies have been conducted concerning the role of sulphuric acid in atmospheric nucleation (e.g. Benson et al., 2008, 2011; Young et al., 2008; Berndt et al., 2008, 2010; Brus et al., 2010, 2011; Sipilä et al., 2010; Kirkby et al., 2011; Zollner et al., 2012) with different methods of producing the gas phase sulphuric acid with their own advantages and drawbacks. For example, evaporation method of weak sulphuric acid solution used by Viisanen et al. (1997) and Brus et al. (2010 and 2011) introduces a thermal gradient into the beginning of the flow tube. Production of the sulphuric acid with $\text{SO}_2 + \text{OH}$ reaction, is used in most of the experiments since it is similar to that observed in atmosphere (e.g. Benson et al., 2008; Berndt et al., 2008, 2010; Sipilä et al., 2010; Kirkby et al., 2011). SO_2 oxidation method involves usage of UV light to produce OH radicals. The excess OH must be removed so that it would not disturb the nucleation process itself (Berndt et al., 2010). Other way is to have excess of SO_2 , so all OH will react rapidly with SO_2 but for the calculation of produced H_2SO_4 concentration, the exact concentration of OH produced must be known (Benson et al., 2008). Ball et al. (1999) and Zollner et al. (2012) produced sulphuric acid vapour by saturating N_2 flow in a glass saturator containing pure ($\sim 96\%$ and $\sim 98\%$, respectively) sulphuric acid. Ball et al. (1999) varied the temperature of the saturator as Zollner et al. (2012) kept the saturator at constant temperature (303 K) and varied the carrier gas flow rate to change the sulphuric acid concentration.

As stated by others in literature (e.g. Benson et al., 2011; Brus et al., 2011; Kirkby et al., 2011) contaminants are most probably present in all the laboratory nucleation studies. These contaminants arise from different sources like water used for humidifying the carrier gas or the carrier gas itself contains some trace levels of contaminants. It is almost impossible to get rid of these contaminants which most probably affect the nucleation process itself.

Here we present a way to produce sulphuric acid vapour from thermally controlled saturator in a wide range of sulphuric acid concentration. The method is described, formation rates, size of the particles and produced sulphuric acid vapour concentrations of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation experiment are presented and compared to the

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results measured with previous setup where furnace was used to produce sulphuric acid vapour (Brus et al., 2010, 2011). The new setup, where saturator is used, was tested with two independent analytical methods to measure sulphuric acid concentration based on different principles. Total losses of sulphuric acid within the flow tube were determined and both analytical methods of detecting sulphuric acid compared. The level of ammonia contaminant in the setup was also determined.

Introducing saturator as the source of sulphuric acid vapour reduces disadvantages associated with other methods, like a temperature gradient arising from usage of furnace, or calculations of OH concentration produced with UV light and removal of excess OH associated with the oxidation of SO₂. The major disadvantage using this method is the handling of pure sulphuric acid when filling the saturator. Luckily, the saturation vapour pressure of sulphuric acid is very low and therefore, the sulphuric acid is consumed very slowly. Due to the high hygroscopicity of sulphuric acid, the saturator should not be exposed to humid flow as the pure liquid sulphuric acid would draw water vapour from the flow contaminating the sulphuric acid. This would lead to a significant error in the predicted concentration due to a much higher vapour pressure of water compared to sulphuric acid.

2 Experimental

The measurement setup presented here is partially introduced in Brus et al. (2010) and only the main principle of the method and the most significant changes are described here. The setup for testing the output of the saturator with two independent sulphuric acid detection methods is described. The instrumentation for sulphuric acid and freshly formed particles detection is shortly presented.

2.1 Saturator

The saturator is a horizontally placed cylinder made of iron with Teflon insert inside the cylinder (I.D. 5 cm). It is thermally controlled with a liquid circulating bath (LAUDA RC 6) and the temperature is measured just above the liquid surface with a calibrated PT100 probe (± 0.05 K) inserted from the outlet side of the saturator (Fig. 1). The saturator is filled with 150–200 mL pure sulphuric acid (~ 97 % w.t., Baker analyzed). H_2SO_4 vapour is produced by flowing purified, dry, particle free air through the saturator in the range of 0.05 to 1 L m^{-1} (litres per minute) saturating the flow with vapour according to the temperature of the saturator. The saturator flow is thermally controlled to the same temperature as the saturator before entering it to ensure temperature stability inside the saturator.

The theoretical prediction of sulphuric acid vapour concentration was calculated using equation for vapour pressure from Kulmala and Laaksonen (1990) which is extended to the lower range of temperatures used in this study:

$$\ln p = \ln p_0 + \frac{\Delta H_v(T_0)}{R} \times \left[-\frac{1}{T} + \frac{1}{T_0} + \frac{0.38}{T_c - T_0} \times \left(1 + \ln \frac{T_0}{T} - \frac{T_0}{T} \right) \right] \quad (1)$$

Where p is the vapour pressure (atm), $p_0 = -(10156/T_0) + 16.259$ atm (Ayers et al., 1980), T_c is critical temperature, 905 K and T_0 is chosen to be 360 K so $\Delta H_v(T_0)/R = 10156$. See Kulmala and Laaksonen (1990) for more details. Here the predicted value depends only on saturator temperature and flow rate through the saturator and mixing flow.

2.2 Setup for testing saturator with mass spectrometers and online ion chromatograph

The saturator was tested in two different tests. First with mass spectrometers: Chemical Ionization Mass Spectrometer (CIMS) (Eisele and Tanner, 1993; Mauldin et al., 1998;

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Petäjä et al., 2009) and Atmospheric Pressure interface Time Of Flight mass spectrometer, (CI-API-TOF, Tofwerk AG, Thun, Switzerland and Aerodyne Research Inc., USA, Junninen et al., 2010) with similar Chemical Ionization inlet as the CIMS (Jokinen et al., 2012). Second test was done with the instrument for Measuring AeRosols and GAses (MARGA, Metrohm Applikon Analytical BV, Netherlands, ten Brink et al., 2007). Both measurements were performed with the same setup. The setup is presented in Fig. 1. The flow from the saturator (0.5 L m^{-1}) was mixed with dilution air (20 or 40 L m^{-1}) after the saturator to meet the inlet flows of the instruments. The relative humidity (RH) was set by 2 or 3 Nafion humidifiers (MD-series, Perma pure, USA) and monitored from the excess flow. The temperature of the saturator was increased in 5 degree steps from approximately 273 K to 303 K (MARGA) and 313 K (CIMS and CI-API-TOF) in order to increase the sulphuric acid concentration. The temperature was kept constant from 2 to 8 h in order to achieve a steady state. The measured sulphuric acid monomer and total sulphate concentrations were compared to theoretical values calculated from the vapour pressure of sulphuric acid using Eq. (1) (referred as K&L from now on).

2.3 Flow tube setup for nucleation measurements

The flow tube setup consists of four main parts: a saturator, a mixing unit, a flow nucleation chamber, sulphuric acid and particle detection (Fig. 2). The sulphuric acid vapour is produced in the saturator and turbulently mixed with clean, particle free air in the mixing unit. After the mixing unit, nucleation and subsequent growth take place in the 2×100 cm-long laminar flow chamber. The flow chamber is a stainless steel cylinder (I.D. 6 cm) positioned vertically and it is thermally controlled with a liquid circulating bath (LAUDA RC 6). One of the 100 cm long parts of the chamber has four holes on the sides every 20 cm from the beginning of the chamber with one hole in 5 cm Teflon connector between the 100 cm pieces. These holes are used to continuously measure temperature in the flow tube with PT100 probes to ensure constant desired nucleation temperature. The RH of the mixing flow is controlled by 2 or 3 Nafion humidifiers. RH and temperature are measured also at the end of the tube with Vaisala HMP37E

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and humidity data processor Vaisala HMI38. Both saturator and mixing flow of the tube are controlled by a mass flow rate controller (MKS type 250) with an accuracy of $\pm 3\%$. Flow rates through saturator for nucleation measurements were kept between 0.13 L m^{-1} and 0.27 L m^{-1} . The mixing flow was kept at approximately 11 L m^{-1} . The line from the saturator to the mixing unit was kept at the same temperature as the saturator to prevent condensation of sulphuric acid.

2.4 H_2SO_4 monomer, sulphate and particle detection

Gas phase sulphuric acid monomers were measured with CIMS or CI-API-TOF. The CI-inlet used in both instruments works as follows: The sulphuric acid molecules are ionized in ambient pressure via proton transfer between nitrate ions (NO_3^-) and sulphuric acid molecule (H_2SO_4). The nitrate ions are produced from nitric acid with radioactive ^{241}Am -source and mixed in a controlled manner in a drift tube utilizing concentric sheath and sample flows together with electrostatic lenses.

After the ionization in the inlet the instruments differ from each other. In the CIMS sample flow is dried using a nitrogen flow to dehydrate the molecules before entering the vacuum system. In the CI-API-TOF a flow rate of 0.8 L m^{-1} is guided through a critical orifice. The ions are guided through the differentially pumped API and finally to the TOF for detection according to the ions' m/z ratio.

The monomer concentration is determined by the ratio of the resulting ion signals (HSO_4^- and $\text{HSO}_4^- \bullet \text{HNO}_3$) and the reagent ion signals (NO_3^- and $\text{NO}_3^- \bullet \text{HNO}_3$). This ratio is then multiplied with the instrument dependent calibration factor in both instruments. Calibration factor used here was $5 \times 10^9 \text{ molecules cm}^{-3}$ for both instruments. For more information about the calibration of CIMS, see Berresheim et al. (2000), Petäjä et al. (2009) and Zheng et al. (2010). The nominal sample flow rate of these instruments is $\sim 10 \text{ L m}^{-1}$. We considered only the monomer concentration, although detection of dimers and even larger clusters of pure sulphuric acid is possible. This is due to following reasons: the dimer concentration was always in the magnitude of $\sim 1\%$ of monomer concentration and larger (trimer and tetramer) cluster concentrations

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were even lower (e.g. Jokinen et al., 2012). The charging efficiency might not be the same for these clusters as it is for monomer. This would cause the calibration factor to change and the calculated concentration to be erroneous. The uncertainty in the resulting monomer concentration is estimated to be a factor of ~ 2 .
 5 The nominal lower detection limits of CIMS and CI-API-TOF are estimated to be 5×10^4 and 3.6×10^4 molecules cm^{-3} , respectively, and the upper limit is approximately 10^9 molecules cm^{-3} for both instruments. At this high concentration the primary ion concentration start to deplete causing the calibration constant to change.

The total sulphate concentration was measured with an online ion chromatograph MARGA 2S ADI 2080. MARGA is able to detect 5 gases from the gas phase (HCl, HNO₃, HONO, NH₃, SO₂) and 8 major inorganic species from aerosol phase (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺). The sample flow is $\sim 16.7 \text{ L m}^{-1}$. From the sample flow all (more than 99.7 %) of water soluble gases are absorbed in to a wetted rotating denuder (WRD). Based on different diffusion velocities, aerosols will pass WRD and enter Steam-jet-aerosol-collector (SJAC) (Slanina et al., 2001). In the SJAC conditions are supersaturated with water vapour, which condenses on particles and the particles drop to the bottom of the SJAC. Sample solutions are drawn from the WRD and the SJAC into syringes (25 mL) and are analysed one after another once an hour. Samples are injected in cation and anion chromatographs with an internal standard (LiBr). Components are detected by conductivity measurements. The detection limits are $0.1 \mu\text{g m}^{-3}$ or better. For more information about the instrument, see Makkonen et al. (2012).
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In our previous study (Brus et al., 2010) the total sulphate concentration was measured using method of bubblers, where a known flow rate from the flow tube was bubbled through alkaline solution thus trapping sulphate. This solution was then analysed using offline ion chromatography. See Brus et al. (2010) for details. The method of bubbler is analogous to the MARGA and the main difference is that MARGA is an online as bubbler is an offline method.
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The total particle number concentration was measured with a Particle Size Magnifier (PSM, Airmodus Oy, Finland, Vanhanen et al., 2011) coupled with CPC TSI model 3772) and with Ultra-Fine CPC's (UCPC, TSI models 3776, 3025A) with cut-off diameters of ~ 1.5 nm and ~ 3 nm, respectively. Differential Mobility Particle Sizer (DMPS) was used to measure particle number size distribution from 3 to ~ 250 nm in closed loop arrangement (Jokinen and Mäkelä, 1997) using a blower to measure the wet size of the particles. The DMPS was run with a sheath flow of ~ 11 L m $^{-1}$ and sample flow of 1.5 L m $^{-1}$ in the short HAUKE-type Differential Mobility Analyzer (DMA). The DMA was coupled with UCPC (TSI model 3025A) and with a bipolar radioactive (63 Ni) neutralizer. The charging efficiencies were calculated following the parameterization of Wiedensohler (1991). The RH of the sheath flow was monitored to ensure that it is same as the RH in the chamber.

3 Results and discussion

To quantify the sulphuric acid input for flow tube nucleation measurements, the saturator output was tested in two experiments, first with CIMS and CI-API-TOF and latter with MARGA. After the tests, nucleation measurements of sulphuric acid-water system were done. This enabled direct comparison to the sulphuric acid production method used in our previous studies (Brus et al., 2010, 2011). Presented values with CIMS, CI-API-TOF and MARGA are residual, i.e. measured values at the end of the flow tube accounting for dilutions, if not mentioned to be different.

3.1 Test of the saturator

Results of the saturator test are presented in Fig. 3 as measured sulphuric acid concentrations and predicted values by K&L as a function of temperature of the saturator. The mixing flows were 40 (dry and RH 15 %) or 20 L m $^{-1}$ (for RH 29 %) for CIMS and API-TOF and 20 L m $^{-1}$ (only dry conditions) for MARGA measurements. Saturator flow

rate was 0.5 L m^{-1} . Mass spectrometers were tested at dry and humid conditions. Dry experiments were run with two inlet flow rates (6 and 10 L m^{-1}) and with extra 1 m (I.D. 4 mm) Teflon tubing between the saturator and the mixing unit to test the effect of wall losses. Humidified experiments were done with two inlet flow rates (6 L m^{-1} for RH 29% and 10 L m^{-1} for RH 15%). MARGA experiments were conducted at dry conditions.

The total sulphate concentration measured with MARGA (black squares) fit the prediction (solid line) very well with small overestimation at lower temperatures of the saturator and with better agreement at higher temperatures. MARGA has relatively high inlet flow rate ($\sim 16.7 \text{ L m}^{-1}$) so inlet losses are low, but with increased temperature of the saturator diffusional losses are visible.

Sulphuric acid monomer concentration measured with CIMS and CI-API-TOF fit each other very well but they show about two orders of magnitude lower concentrations than predicted by K&L and measured with MARGA. The trend is same as the prediction and as the points measured with MARGA.

Relative humidity does not have any significant effect on the measured values by CIMS and CI-API-TOF. RH can affect the wall losses by preventing the sulphuric acid to evaporate from the inlet walls as the vapour pressure of water is several orders of magnitude higher than sulphuric acid. The prediction by K&L does not consider relative humidity as the flow through the saturator is always dry. The relative humidity of the mixing flow will cause the sulphuric acid molecules to get hydrated as sulphuric acid is very hygroscopic but because the results from humid and dry measurements are in the same space, CIMS and CI-API-TOF can be considered measuring well in humid conditions also. The effect of RH is discussed in Eisele and Tanner (1995) and our results agree with the discussion there.

Change of the nominal inlet flow rate of CIMS and CI-API-TOF do not have large effect either. The inlet lines were short ($\sim 20 \text{ cm}$) in the saturator tests so the wall losses due to lower inlet flow rate does not play a big role. Using the instruments with lower flow rate may alter the calibration factor as it is acquired with inlet flow rate of 10 L m^{-1} .

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Tests with different saturator flow rates ($0.05\text{--}1\text{ L m}^{-1}$) were conducted to estimate the limits of the saturator flow (not shown in Fig. 3). With 0.05 L m^{-1} saturator flow rate diffusional losses to the walls dominated causing unexpected behaviour of the measured sulphuric acid concentrations. In the saturator flow rate range from 0.2 up to at least 1 L m^{-1} , sulphuric acid concentrations behaved as expected.

3.2 Losses of sulphate and sulphuric acid in the flow tube

Total losses were not directly measured but they were determined by comparing results from saturator tests to the results from nucleation measurements. The setup of the measurements was similar in both experiments except for the flow tube that was used in nucleation measurements. By accounting for the different mixing ratios of saturator flow rate and mixing flow rate, these measurements become comparable and the total losses in the flow tube can be determined. Total Loss Factor (TLF) includes wall losses and losses to the particle phase (nucleation and condensational losses).

Figure 4 presents the measured sulphuric acid monomer and total sulphate concentration from the saturator tests (squares) and nucleation measurements (stars) as a function of the saturator temperature. Saturator tests are done in dry conditions and nucleation measurements in RH 30%. Inlet pipe is used to connect a mass spectrometer to the flow tube. Brus et al. (2011) state that the Wall Loss Factor (WLF) in the inlet pipe of length $100 + 22\text{ cm}$ is $\text{WLF}_{\text{inlet}} = \sim 4$. This factor, together with the mixing ratios, was used to account for the data so that they would be directly comparable.

A linear fit was applied to the data and TLF were determined from the fits. The TLF were determined for a saturator temperature range of $286\text{--}300\text{ K}$ for CIMS and $284\text{--}297\text{ K}$ for MARGA depending on the measurement range of the data. The average TLF are 14.2 ± 4.2 for CIMS and 10.0 ± 1.2 for MARGA. The R^2 -values for the fits are 0.96, 0.87, 0.90 and 0.61 for CIMS saturator test, CIMS nucleation measurement, MARGA saturator test and MARGA nucleation measurement, respectively.

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From Fig. 4 it is evident that wall losses are not the only losses affecting the measured concentrations as the trends in the fits for nucleation measurements are less steep than the ones from saturator tests. The losses to the particle phase also affect the situation. The maximum losses of sulphuric acid to particle phase are calculated using the DMPS data. The total volume of the particles is calculated within the size distribution assuming that the particles are composed only of pure sulphuric acid with density of 1.84 g cm^{-3} . The losses of sulphuric acid to particles range from 0% (dry conditions, $T_{\text{sat}} = 273 \text{ K}$) up to maximum of 1.4% (RH = 30%, $T_{\text{sat}} = 292 \text{ K}$) of the total sulphate concentration. The losses of sulphuric acid to the particles compared to the gas phase sulphuric acid monomer range from 0% (dry conditions, $T_{\text{sat}} = 273 \text{ K}$) up to 42.6 times the gas phase sulphuric acid monomer concentration (RH = 30%, $T_{\text{sat}} = 310 \text{ K}$). Higher saturator temperature increases the number and the diameter of the particles and relative humidity increases the diameter of the particles. The losses to the particle phase are significant at highest values of saturator temperature but this estimate is the maximum limit as the particles are not composed only of pure sulphuric acid molecules. Contaminants from the flow will condense to the particle phase or get bound with sulphuric acid. Also, when using humid conditions sulphuric acid particles will uptake water as sulphuric acid is very hygroscopic. At the highest temperature of the saturator the size distribution unfortunately extends out of the DMPS range (3–250 nm) and particles larger than 250 nm are not accounted for the losses to the particle phase, thus on the other hand underestimating the losses. Losses to the clusters smaller than the cut-off size of the particle counters, are probably significant. More details of losses to the particle phase see supplementary material.

3.3 Nucleation measurements

Formation rates J of sulphuric acid-water were measured in the range from 0.1 to $\sim 300 \text{ cm}^{-3} \text{ s}^{-1}$ with sulphuric acid monomer concentration approximately from 5×10^5 to 10^7 molecules cm^{-3} or in total sulphate concentration approximately from 4×10^8 to 3×10^9 molecules cm^{-3} . Formation rates should be reported as $J_{1.5}$ or J_3 (cut-off sizes

of the particle counters are 1.5 nm for PSM and 3 nm for TSI models 3776 and 3025) as discussed in Kulmala et al. (2012). Particles measured at the end of the flow tube were almost always in the range of 8–20 nm or larger, formation rates are simple reported as J . The results will be discussed below.

5 Figure 5 presents DMPS and CIMS data for one cycle of saturator temperatures. The upper most panel presents the number size distribution as a function of time, 2nd panel from top the total particle number concentration, 3rd panel from top shows the hourly averaged sulphuric acid monomer concentration with standard deviation as the error bars and the lower most panel shows hourly averaged saturator temperature. One
10 can see from Fig. 5, 1st and 2nd panels from the top that when the temperature of the saturator changes, the number concentration and the number size distribution are not stable immediately. The sulphuric acid concentration overshoots a bit at the beginning as system is stabilizing to steady state. We excluded first hour from averages from each of the saturator temperatures to ensure only stable state data ($\text{std}(T) = \pm 0.05 \text{ K}$)
15 in the averages. When a new cycle started, the T_{sat} dropped from the maximum value ($\sim 315 \text{ K}$) to the minimum (273 K) causing a long period of unstable data even though this time period was set to last at least 6 h, first two hours were excluded from the beginning of the cycle. In the upper most panel in Fig. 5, nucleation is the main process below temperature of $\sim 290 \text{ K}$ and growth takes over at higher temperatures. This can
20 be seen as the bimodal distribution at highest saturator temperatures.

Figures 6 and 7 present the number concentration N_{exp} (upper left panel), geometric mean diameter D_p (upper right panel) and formation rate J (lower left panel) of freshly nucleated particles with sulphuric acid monomer concentration $[\text{H}_2\text{SO}_4 \text{ monomer}]$ or total sulphate $[\text{SO}_4^{2-}]$ (lower right panel) as a function of saturator temperature T_{sat} for
25 nucleation temperature of 298 K with several different saturator flow rates. Averages of all variables have been taken over the time period where the T_{sat} was constant ($\pm 0.05 \text{ K}$) and first hour was removed to ensure the stability of the averaged data.

From Fig. 6 one can see that in the flow tube measurements with CIMS and CI-APi-TOF all the variables behave as expected to the increasing saturator temperature.

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Increasing saturator temperature increases number concentration and diameter of freshly nucleated particles. The number concentration and formation rate seems to saturate at the highest temperatures but this apparent saturation is due to the limits of the PSM (coupled with CPC, TSI model 3772). The upper limit of particle concentration for CPC 3772 is 10^4 cm^{-3} , so higher concentrations were still measured as 10^4 cm^{-3} . This is also supported by DMPS data which shows higher total particle concentration than PSM. Coagulation has a minor effect on the particle number due to a short residence time ($\tau = 30\text{s}$) and relatively low particle concentration. The relative humidity affects mostly the diameter of the particles but also decreasing RH decreases the formation rate if similar sulphuric acid concentration is considered. Lower formation rate with decreased RH might be caused by the diminishing of the particle diameter below the detection limit of UCPC (TSI model 3776).

In Fig. 7, squares present measurements at dry conditions and stars with RH 30 %. The lower right panel shows also the detection limit of MARGA for total sulphate concentration. Detection limit was determined from 20 h of measurements with saturator flow rate set to zero and averaged over the time period. Detection limit was $1.35 \times 10^9 \text{ molecules cm}^{-3}$. All the total sulphate concentrations measured below this detection limit were considered as erroneous and rejected from further analysis, even though these values are presented in Fig. 7. MARGA can be used with concentration columns to measure lower concentrations of species but it was not available in this study.

From Fig. 7 one can see that all the variables responded in a similar manner as CIMS and CI-APi-TOF experiment (Fig. 6). As the temperature of the saturator approaches to the temperature of the mixing unit (laboratory temperature, $\sim 294 \text{ K}$) the number concentration of particles drops and starts to increase again when saturator temperature is higher than the mixing unit. This is an artefact of the setup.

Main difference between Figs. 6 and 7 can be found in the mean diameter of the particles. In the experiment with CIMS and CI-APi-TOF, the diameter ranges all the way up to $\sim 130 \text{ nm}$ (Fig. 6, right upper panel) as in the experiment with MARGA, maximum

diameter is only approximately ~ 23 nm (Fig. 7 right upper panel). The main reason is that in the CIMS and CI-API-TOF experiment the saturator temperature was increased 15 K higher than in the MARGA experiment. This will increase sulphuric acid vapour concentration approximately order of magnitude which will condense on the surface of the particles growing their diameter. At lower saturator temperatures (< 290 K) the mean diameters are closer to each other at similar saturator temperatures and relative humidities. The residence times in the flow tube are same in both experiments (~ 30 s).

3.4 Formation rates and comparison to our previous results

Figure 8 presents formation rates J of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system as a function of sulphuric acid monomer concentration $[\text{H}_2\text{SO}_4 \text{ monomer}]$ measured with CIMS at nucleation temperature of $T = 298$ K and relative humidity of $\text{RH} \sim 30\%$. Sulphuric acid was produced with method of furnace (red squares, Brus et al., 2011) and with saturator (the black squares, this study). Sulphuric acid concentration for data from Brus et al. (2011) is presented here as residual concentration (i.e. at the end of the flow tube) so that these two measurements would be comparable. Brus et al. (2011) present their data as the initial concentration. Both data sets have almost identical slopes (1.3 and 1.2) and the data sets have a difference of a factor of 2. For the set measured with production method of furnace, the residence time ($\tau = 15$ s) is defined as the time the particles spend in the flow tube after the nucleation zone. Nucleation zone was experimentally determined (Brus, et al., 2010) and confirmed with CFD model (Herrmann et al., 2010) to be at the middle of the flow tube. For the saturator measurements, the residence time ($\tau = 30$ s) was defined as the whole time the particles spend in the flow tube. The difference of the residence time is exactly factor of 2. Formation rate is defined as the number concentration divided by the residence time, so these two sets of data lie on top of each other if the same residence time would have been used for formation rate determination.

Figure 9 presents formation rates J of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ as a function of residual total sulphate concentration $[\text{SO}_4^{2-}]$ at relative humidity of $\text{RH} \sim 30\%$ and at nucleation

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temperature of $T = 298\text{ K}$. Stars present the data from measurements where sulphuric acid vapour was produced with furnace and total sulphate measured with bubbler method (Brus et al., 2010). The residence time used in there was $\tau = 15\text{ s}$. Squares present the data from this study with different flow rates through the saturator, total sulphate measured with MARGA and residence time was $\tau = 30\text{ s}$. All the points have standard deviation as error bars and each point is an average over the time period of constant saturator temperature ($\pm 0.05\text{ K}$). The detection limit of MARGA is also marked as a dashed vertical line. Formation rates are similar with both production methods. If the same residence time would have been used, the formation rates marked with blue stars would be a factor of 2 lower and the bubbler measured points would agree even better with those measured with MARGA.

Figures 8 and 9 show that formation rate data is reproducible with both sulphuric acid production methods. The data is more scattered in Fig. 9 due to the larger integration times used in MARGA and bubbler measurements. During several hours of integration time, a small change in flow rates can cause a significant difference in the resulting concentration. MARGA data is close to the detection limit of the instrument which also causes larger scattering.

Figure 10 shows comparison of formation rates J as a function of residual sulphuric acid monomer [H_2SO_4 monomer] or total sulphate concentration [SO_4^{2-}] from this study to our previous studies with standard deviation as error bars. In Fig. 10, residence time for data from Brus et al. (2011) has been changed to 30 s (compare to Fig. 8), so that the data sets would be directly comparable. Squares show values measured using mass spectrometers (PSM, red and black squares; TSI 3776, green squares). Stars present data measured using ion chromatograph (i.e. total sulphate) methods with two different UCPC's (TSI 3025A, black stars and TSI 3776, red stars). Figure 10 shows that the production method does not have significant effect as the results lie on same line when comparing results obtained with mass spectrometers or MARGA and bubbler method. The conditions for all the measurements were similar ($T = 298\text{ K}$, $\text{RH} \sim 30\%$, $\tau = 30\text{ s}$).

In this study, particle formation is assumed to take place in the beginning of the flow tube, where the temperature is reduced to 298 K. Estimating the sulphuric acid concentration (monomer or total sulphate) at the vicinity of the particle formation, TLF's mentioned earlier can be used directly.

The slope of the data measured using MARGA or bubblers is steeper (5.0 ± 0.6) than the slope of the results measured with mass spectrometers. There is a discrepancy of one to two orders of magnitude between sulphuric acid monomer and total sulphate concentration for similar formation rates. The CPC 3776 (green squares) was probably undercounting at the lowest sulphuric acid concentrations. This can be seen in Fig. 10 as the green squares are not on the line with the other squares. This is probably caused by the small size of the particles at so low sulphuric acid concentration ($1\text{--}2 \times 10^6$ molecules cm^{-3}) (Sipilä et al., 2010).

Comparison to similar laboratory studies is done in Brus et al. (2010) and Zollner et al. (2012) and is not shown here. The results obtained in this study are very similar to the results in Brus et al. (2010) as seen in Fig. 8, so the comparison is not necessary here.

3.5 Contaminants

In our previous study (Brus et al., 2011) we used ion chromatograph to measure the background levels of ammonia and we found out that it is below the detection limit (500 pptv). The concentration of background ammonia was measured with the MARGA system in this study. An average concentration of ammonia was 60 pptv for dry conditions and 126 pptv for RH 30 % supporting our previous results. The concentration did not change as a function of saturator temperature and thus, it is assumed to originate from the purified, particle free air used as carrier gas in all measurements and the ultrapure water (Milli-Q, Millipore) used for humidification. The concentration for dry conditions is in the same order of magnitude as the concentration of total sulphate at the lowest (273 K) temperature of the saturator. With increasing the saturator

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temperature, ammonia to total sulphate-ratio decreases from $\sim 1:1$ to $\sim 1:10$ or less for dry conditions and from $\sim 3:1$ to $\sim 1:5$ for humid conditions.

4 Conclusions

A method of saturator to produce sulphuric acid vapour from pure liquid sulphuric acid for laboratory studies is presented. It has been tested with two independent methods to measure sulphuric acid monomer or total sulphate concentration and shown to produce exact concentrations as theoretical prediction for the total sulphate case (Fig. 3). Concentration of sulphuric acid monomer measured by CIMS and CI-API-TOF is about two orders of magnitude lower than the total sulphate values measured with MARGA and the prediction by K&L. This discrepancy cannot be explained by the formation of larger clusters containing solely sulphuric acid (dimer, trimer, etc.), because the concentration of these clusters is in the order of 1 % or lower than the monomer. The prediction is done by using temperature dependent vapour pressure from Kulmala and Laaksonen (1990) and then accounting for mixing ratios.

The saturator has been used in combination with a flow tube described earlier (Brus et al., 2010) to measure characteristics of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation. The saturator is shown to produce stable, steady state conditions with the flow tube for nucleation measurements. It takes about 1 h to stabilize the sulphuric acid vapour concentration after changing the saturator temperature. The characteristics of the freshly nucleated particles together with the conditions used for the nucleation has been identified and presented (Figs. 4 to 7). Total losses of sulphuric acid to the whole flow tube setup have been determined for both methods to detect the concentration of sulphuric acid monomer or total sulphate.

The average Total Loss Factors determined are $\text{TLF} = 10.0 \pm 1.2$ ($T_{\text{sat}} = 284\text{K} - 297\text{K}$) for MARGA and $\text{TLF} = 14.2 \pm 4.2$ ($T_{\text{sat}} = 286\text{K} - 300\text{K}$) for CIMS, both having a slight increasing trend as a function of saturator temperature (Fig. 4). If the wall losses were the only losses, there would not be any trend. The trend is most probably arising

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from the second order losses to the particle phase, which increases with increasing saturator temperature. Maximum losses to the particle phase range from 0% up to 1.4% with an average below 1% for total sulphate. The losses to the particle phase compared to the gas phase monomer concentration range from 0% up to 42.6 times the monomer concentration, but even with combining the gas phase monomers with the lost to particle phase does not reach the total sulphate concentration for the same saturator temperature.

Formation rates of sulphuric acid-water system were compared to our previous studies (Figs. 8–10). Results obtained using mass spectrometers lie on the same line independent of the sulphuric acid vapour production method (furnace vs. saturator). At the lower end of the sulphuric acid monomer concentration ($1\text{--}2 \times 10^6$ molecules cm^{-3}) the UCPC used (TSI model 3776) was undercounting which is caused by the small size of the particles. The slopes of the fits to the formation rate data as a function of sulphuric acid monomer concentration are very similar (1.3 and 1.2 for using furnace and saturator, respectively) as obtained in Brus et al. (2011). The discussion of the meaning of the slopes can be found there in Sect. 3.1 and comparison to the atmospheric data in Sect. 3.5. Nucleation results obtained using bubbler or MARGA agree well when compared to each other. Conditions for these studies were similar ($T = 298\text{ K}$, $\text{RH} \sim 30\%$, $\tau = 30\text{ s}$) but at similar formation rates, the monomer concentration is one to two orders of magnitude lower than the total sulphate. Losses to the particle phase can explain only a minor part of this discrepancy as losses to particle phase reach only about 1.4% of total sulphate concentration.

Other possible reasons for this difference between sulphuric acid monomer and total sulphate is that sulphuric acid molecules are most probably bound to some molecule (e.g. amines, ammonia, organics) and not been detected by CIMS. As Kurten et al. (2011) state, base molecules can be only in minor importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base out in the CIMS charging process. Nevertheless, there is expected substantial pool of clusters formed of sulphuric acid-base molecules in our system, which are too small to be detected by current

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state-of-art particle counters such as PSM. On the other hand, these clusters have not been identified from the CI-API-TOF mass spectra yet (Kulmala et al., 2013).

Average ammonia concentration of 60 pptv was found in the system for dry conditions and 126 pptv for RH 30 % as a contaminant and it was independent of the saturator temperature. It is assumed to originate from the purified, dry, particle free air used as carrier gas and from the ultrapure water used for humidifying the mixing flow. Ammonia concentration is enough to affect the nucleation process itself significantly but the magnitude of this effect was not studied in this work. Ammonia can bind sulphuric acid by forming clusters which might reduce the monomer concentration measured with CIMS and CI-API-TOF slightly but as the contaminant level was constant as saturator temperature was increased, reducing the contaminant to total sulphate-ratio from $\sim 1:1$ to $\sim 1:10$ for dry conditions and from $\sim 3:1$ to $\sim 1:5$ for humid conditions, it does not explain the discrepancy between the two sulphuric acid detection methods.

The saturator is shown to be very useful tool for producing sulphuric acid vapour for laboratory measurements. It is stable and very easy to use device with a very simple calculation to predict the output of the saturator. It is shown that using saturator as the source for sulphuric acid vapour for H_2SO_4 - H_2O nucleation can produce quantitatively same results as when producing the vapour with furnace method.

The difference between total sulphate and the sulphuric acid monomer needs more and deeper investigation. Is it the monomer that ignites nucleation? To which cluster monomers are bound and how these clusters are distributed? Does mass spectrometers measure only surplus of monomers if there are monomers bound to other molecules and these cannot be charged at the CI-inlet? How does total sulphate affect nucleation? What is the contribution of total sulphate to the early growth of the particles? These are few most important questions that need to be answered before we can truly understand the substances involved and their effect in nucleation.

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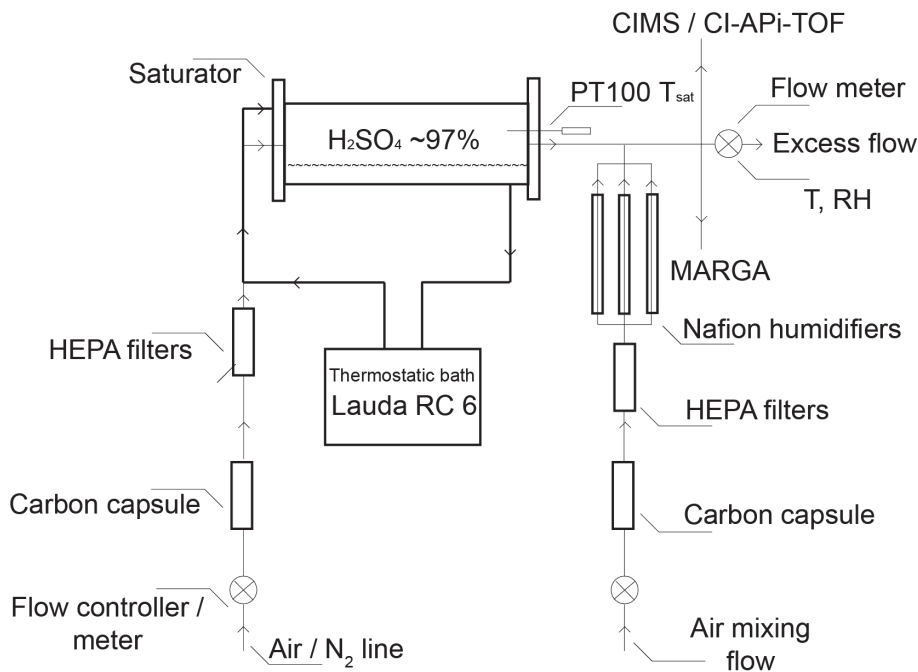


Fig. 1. Schematic figure of the setup for testing the saturator.

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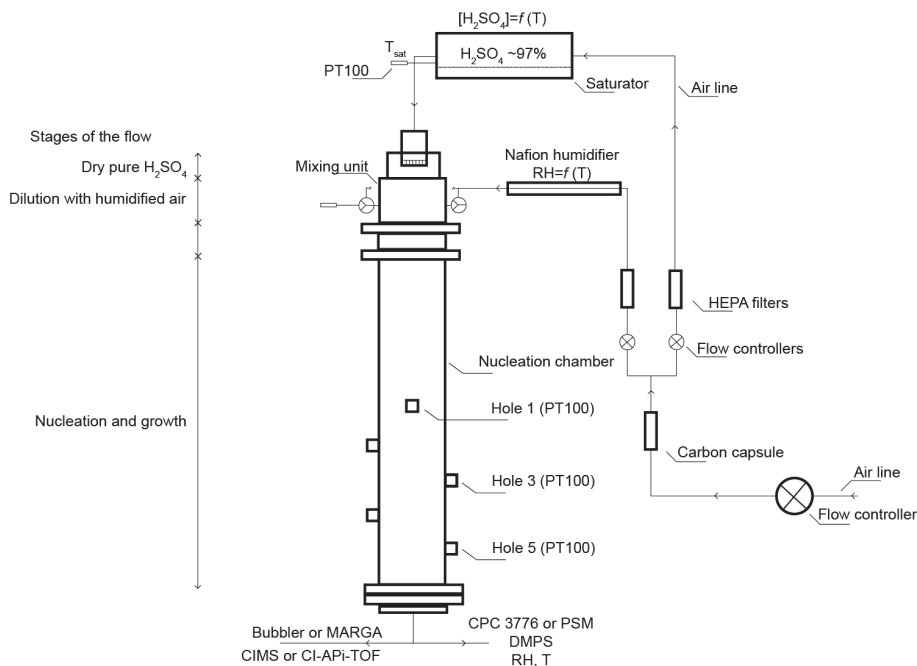


Fig. 2. Flow tube setup.

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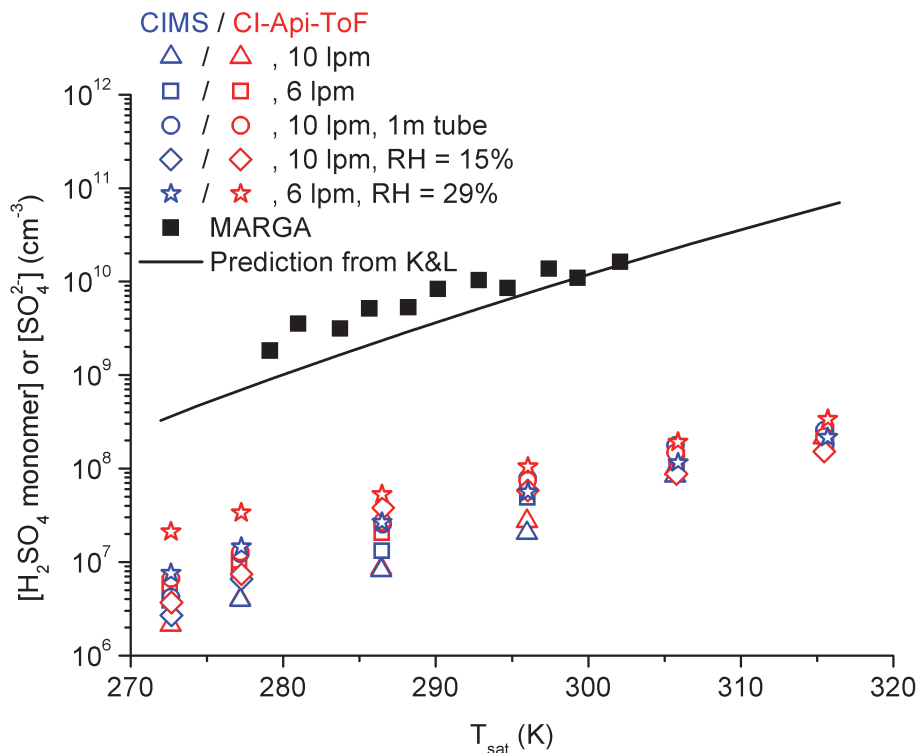


Fig. 3. Measured sulphuric acid monomer $[H_2SO_4 \text{ monomer}]$ and total sulphate $[SO_4^{2-}]$ (black squares) concentrations together with predicted values by K&L as a function of saturator temperature T_{sat} . Saturator flow rate is $Q_{\text{sat}} = 0.5 \text{ L m}^{-1}$ and mixing flow rates were 40 L m^{-1} (dry for CIMS and CI-API-TOF and RH 15%) and 20 L m^{-1} (MARGA and RH 29%). CIMS (blue markers) and CI-API-TOF (red markers) have been tested with 6 L m^{-1} and 10 L m^{-1} (nominal) inlet total flow rates and also with an extra 1 m Teflon tubing after saturator.

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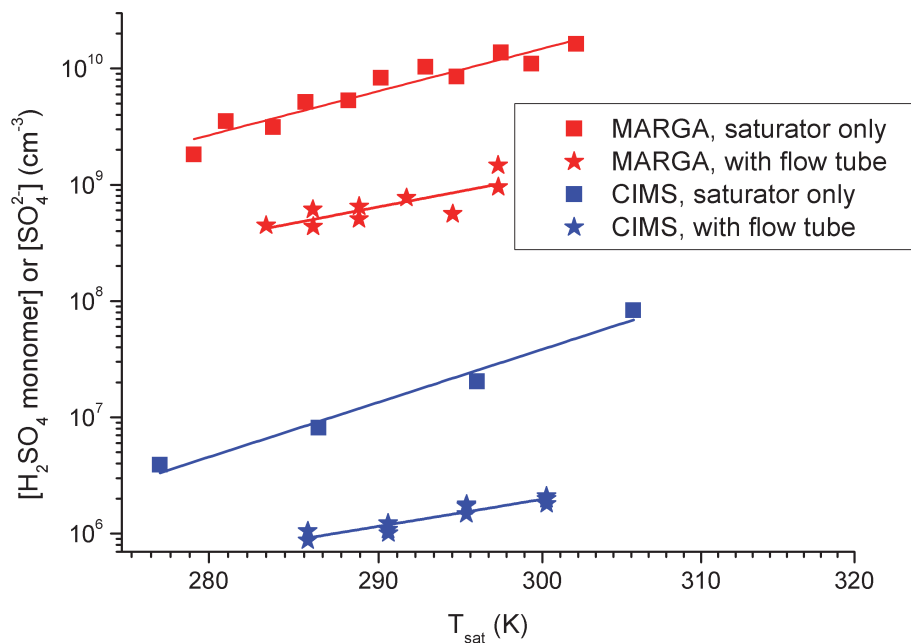


Fig. 4. Comparison of MARGA and CIMS data between test with only saturator (dry conditions, squares) and with saturator and flow tube (RH ~ 30 %, stars). Different flow rates through saturator have been accounted for. Average total loss factors are $\text{TLF}_{\text{MARGA}} = 10.0 \pm 1.2$ and $\text{TLF}_{\text{CIMS}} = 14.2 \pm 4.2$. See text for details.

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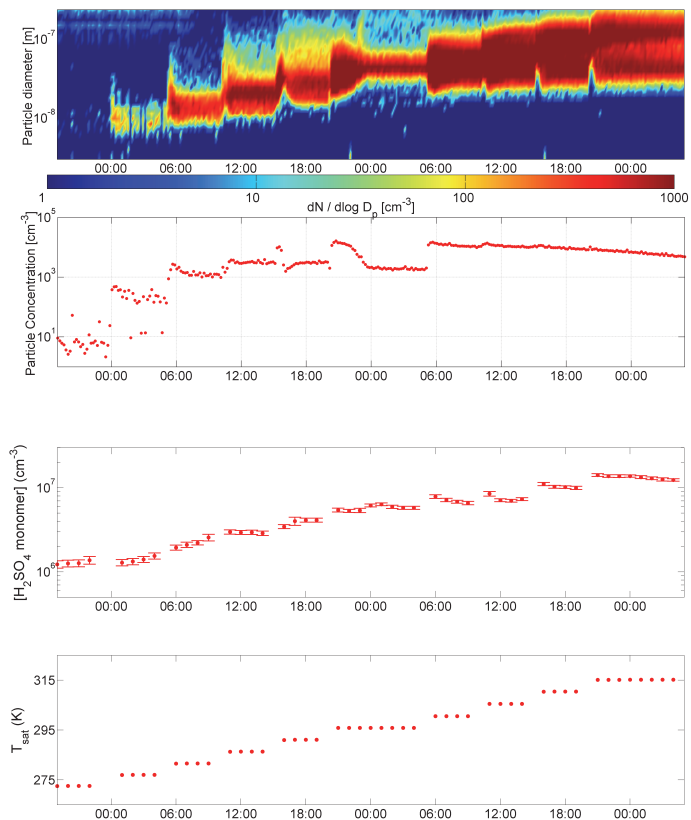



Fig. 5. DMPS and CIMS data from one T_{sat} cycle. Upper most panel shows the number size distribution, 2nd panel from top shows the total number concentration from DMPS, 3rd panel presents the CIMS measured sulphuric acid monomer concentration averaged over one hour with standard deviation as error bars and the last panel shows hourly averaged temperature of the saturator.

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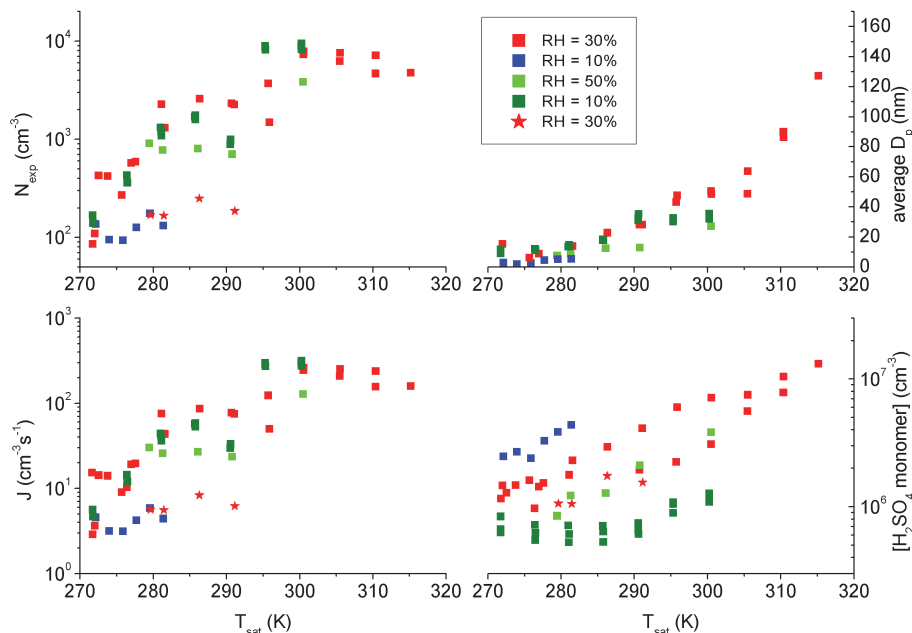


Fig. 6. Number concentration (left upper panel) measured with PSM and UCPC TSI 3776, geometric mean diameter (right upper panel), formation rate J (left lower panel) of the freshly nucleated particles and sulphuric acid monomer concentration measured with CIMS (squares) or CI-APi-TOF (stars) with several relative humidities as a function of saturator temperature. All data is averaged over time period of constant saturator temperature extracting first hour. Stars are measured with CI-APi-TOF and squares with CIMS. All data is averaged over time period of constant saturator temperature (± 0.05 K) extracting first hour.

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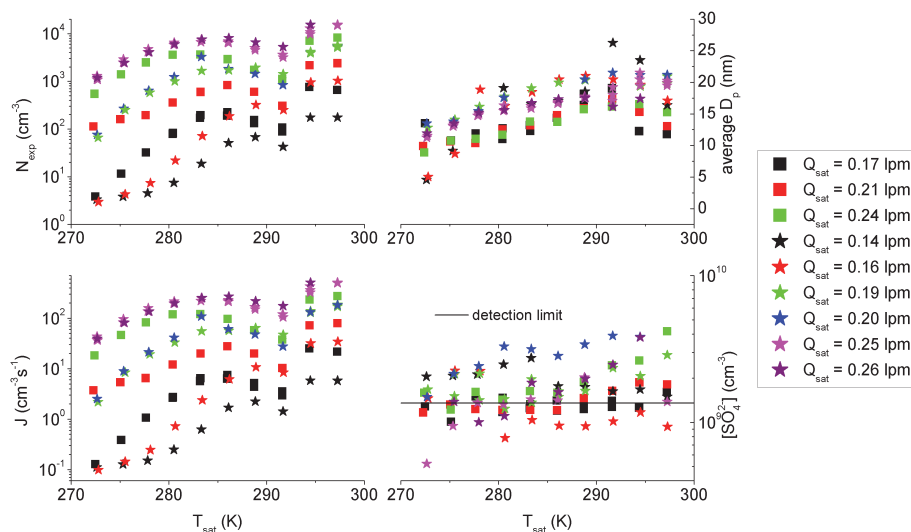


Fig. 7. Number concentration (left upper panel) measured with UCPC TSI 3776, geometric mean diameter (right upper panel), formation rate J (left lower panel) of the freshly nucleated particles and total sulphate concentration from MARGA (right lower panel) with detection limit of MARGA with several different saturator flow rates as a function of saturator temperature. Squares represents measurements at dry conditions, stars are measured with RH of $\sim 30\%$. All data is averaged over time period of constant saturator temperature (± 0.05 K) extracting first hour.

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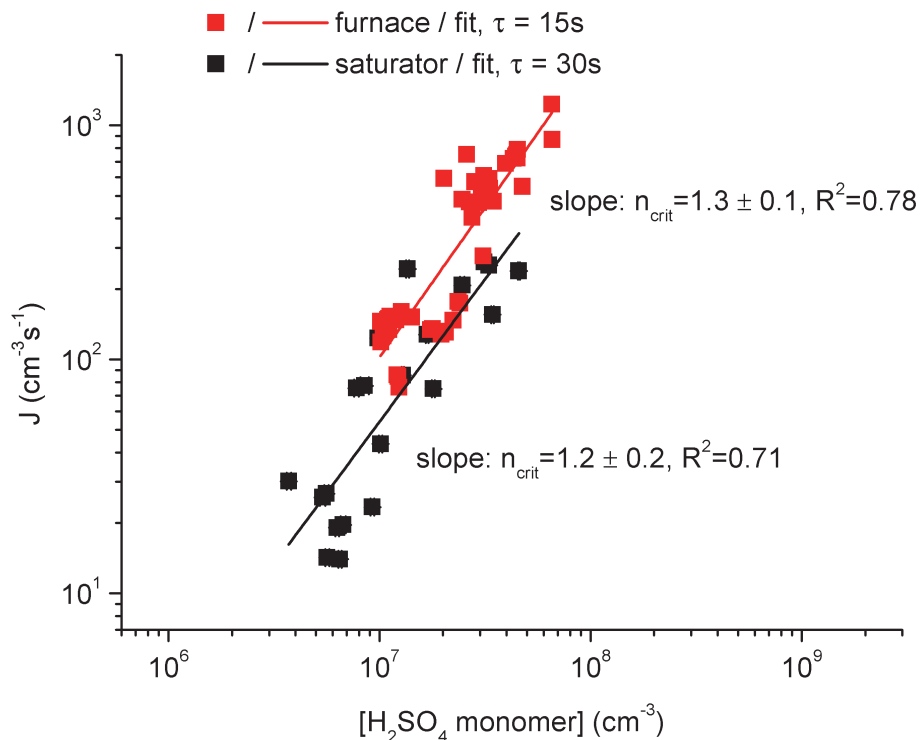


Fig. 8. Formation rates J as a function of residual sulphuric acid monomer concentration $[\text{H}_2\text{SO}_4 \text{ monomer}]$ at $T = 298\text{K}$ and $\text{RH} \sim 30\%$ measured using CIMS. In the first data set (red squares) sulphuric acid vapour was produced with furnace method and residence time was defined to be 15 s (Brus et al., 2010).

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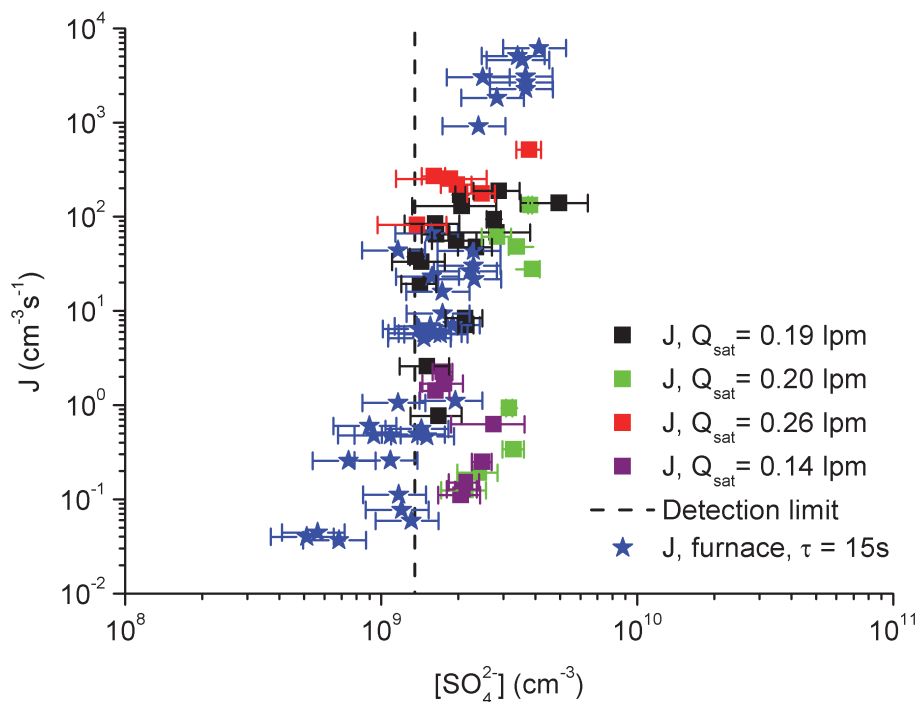


Fig. 9. Formation rates J as a function of residual total sulphate concentration $[\text{SO}_4^{2-}]$ measured with MARGA or bubbler with different saturator flow rates. Slope is 5.0 ± 0.6 with $R^2 = 0.45$ and it is calculated for bubbler and MARGA data together. MARGA's detection limit is marked with the dashed line. Relative humidity $\text{RH} \sim 30\%$ and nucleation temperature $T = 298\text{K}$. Sulphuric acid vapour was produced with furnace method (Brus et al., 2010) for bubbler measurements and with saturator method for MARGA.

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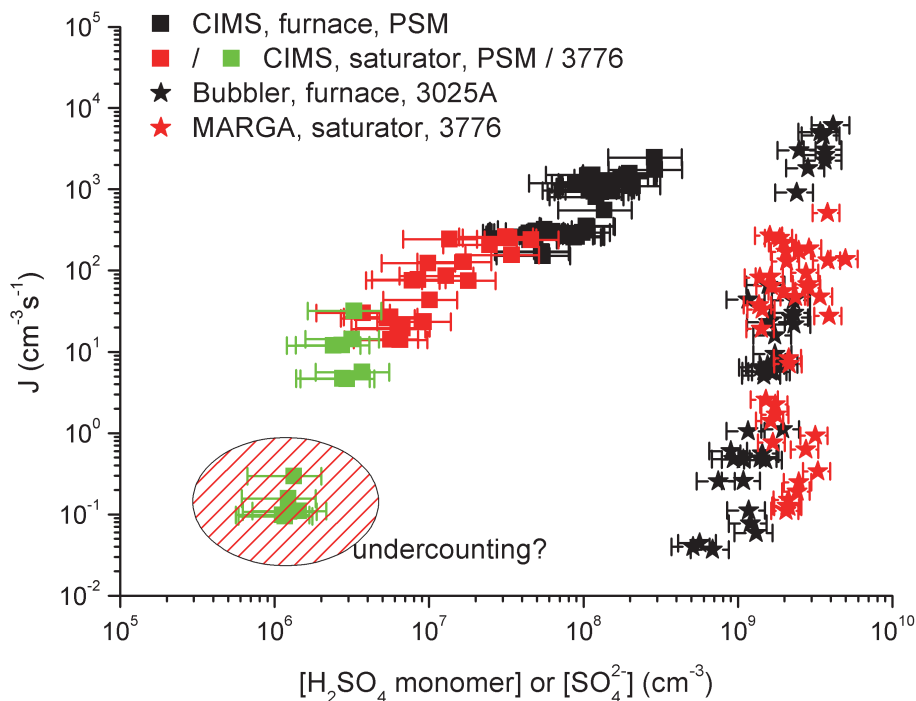


Fig. 10. Comparison of formation rates J as a function of residual sulphuric acid monomer concentration $[\text{H}_2\text{SO}_4]$ or total sulphate concentration $[\text{SO}_4^{2-}]$ to our previous results. Conditions are similar ($T = 298\text{K}$, $\text{RH} \sim 30\%$, $\tau = 30\text{s}$). Sulphuric acid vapour was previously produced with furnace method and total sulphate concentration measured with bubbler method (Brus et al., 2010).

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