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Bisulphate-cluster based atmospheric pressure chemical ionization mass spectrometer for ultra-high sensitivity (10 ppq) detection of atmospheric amines: proof-of-concept and first ambient data from boreal forest

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Atmospheric amines may play a crucial role in formation of new aerosol particles via nucleation with sulphuric acid. Recent studies have revealed that concentrations below 1 ppt can significantly promote nucleation of sulphuric acid particles. While sulphuric acid detection is relatively straightforward, no amine measurements to date have been able to reach the critical sub-ppt concentration range and atmospheric amine concentrations are in general poorly characterized. In this work we present a proof-of-concept of an instrument capable of detecting dimethyl amine (DMA) with concentrations even down to 8 ppq (parts per quadrillion, 0.008 ppt) for a 15 min integration time. Detection of ammonia and amines other than dimethyl amine is discussed. We also report results from the first ambient measurements performed in spring 2013 at a boreal forest site. While minute signals from some amines were observed, DMA concentration never exceeded the detection threshold of ambient measurements (20 ppq), suggesting that it is unlikely that nucleation at this location involves DMA.

1 Introduction

Formation of secondary aerosol particles and cloud condensation nuclei in the atmosphere is initiated by nucleation. The role of sulphuric acid in nucleation is well established (e.g. Weber et al., 1995; Riipinen et al., 2007; Sipilä et al., 2010). However, sulphuric acid alone, or with water, does not nucleate efficiently enough to explain atmospheric nucleation rates (Kirkby et al., 2011); rather additional vapours are required to stabilize nucleating clusters. Ammonia (Ball et al., 1999; Vehkamäki et al., 2004; Kirkby et al., 2011) and amines (Kurten et al., 2008; Berndt et al., 2010; Erupe et al., 2011; Kirkby et al., 2011; Berndt et al., 2014) are proposed to act as stabilizing agents of sulphuric acid clusters in atmospheric new particle nucleation. Recently, Almeida et al. (2013) showed that dimethyl amine concentrations well below 1 ppt can dramatically enhance formation rates of new sulphuric acid particles (by several orders of

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magnitude); further, concentrations as low as just few ppt can saturate the nucleation rate at atmospheric sulphuric acid concentrations. Enhancement of the particle formation rate is due to dimethyl amine's ability to stabilize molecular sulphuric acid clusters, minimizing evaporation and enabling further growth (Almeida et al., 2013). Amines Paper other than dimethyl amine can have a similar effect on nucleation (Berndt et al., 2013), but no experiments to date have probed the atmospherically important concentration

Atmospheric measurements of amines are rare (Ge et al., 2011; Hanson et al., 2011; Yu et al., 2012; Freshour et al., 2014). Gas phase concentrations of these bases are usually low, and reliable measurements of atmospheric amine concentrations is far from sufficient to evaluate their role in atmospheric chemistry and physics. For example, from the SMEAR II field station (Hyytiälä, Southern Finland; Hari and Kulmala, 2005), where the nucleation process has been seriously investigated for two decades, there is no reliable data for amine concentrations. First attempts to quantify concentrations of dimethyl or ethyl amine (DMA/EA) and trimethyl or propyl amine (TMA/PA) were performed by Sellegri et al. (2005), who applied an ambient pressure protonated water cluster based chemical ionization mass spectrometer. Sellegri et al. (2005) reported observations of TMA with the concentration exceeding 10 ppt. However, that signal is most likely explained by an isotope of protonated acetone, occurring at the same integer mass as protonated TMA, making the observation guestionable. No other amines were detected, suggesting that DMA concentrations were below few ppt. Note that DMA and EA (and also TMA and PA) have identical elemental composition and can thus not be separated from each other via MS.

range from ppg to a few ppt levels.

More recently, amine concentrations at SMEAR II were published by Kieloaho et al. (2013). Amines collected on phosphoric acid-impregnated fiberglass filters (through a polytetrafluoroethylene (PTFE) filter) were subsequently analysed via liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS). They reported remarkably high gas phase amine concentrations, with DMA/EA and TMA/PA concentrations exceeding 100 ppt in autumn. Concentrations in spring time, relevant for **AMTD**

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comparison to our present work, were also reasonably high, up to a few tens of ppt for both DMA/EA and TMA/PA. This observation is in conflict with Schobesberger et al. (2014) who measured natural ion cluster distributions at SMEAR II during nucleation and found much more ammonia than amine composition in bisulphate-sulphuric 5 acid-base clusters. Based on that observation and targeted laboratory experiments, Schobesberger et al. (2014) concluded that DMA concentration at the site should be less than 1 ppt. Obviously, this discrepancy should be resolved.

Despite some drawbacks, atmospheric pressure chemical ionization mass spectrometry (APCI-MS) as applied by Sellegri et al., 2005 is a promising approach for ultra high sensitivity online gas phase amine detection. Nitric acid has been measured by using bisulphate ion as primary ion (Mauldin et al., 1998). For acids, such as sulphuric acid, detection limits down to 1 ppg have been achieved with the APCI-MS technique when the nitrate ion has been used as the primary ion (e.g. Eisele and Tanner, 1993; Jokinen et al., 2012). With the APCI-MS technique, interference from compounds in particle phase is minimized whereas, in techniques utilizing sample collection and subsequent analysis (e.g. LC-MS), the separation between particle and gas phases is difficult.

APCI-MS approaches in use today rely on chemical ionization by either protonated water clusters (Hanson et al., 2011) or protonated ethanol or acetone (Yu et al., 2012). Product ions which are guided through a differentially pumped section comprising collision dissociation chamber and an octopole ion guide are subsequently detected by a quadrupole mass spectrometer (Hanson et al., 2011; Yu et al., 2012). Using the above technique with protonated ethanol, Yu et al. (2013) reported a limit of detection (LOD) of 7 ppt for dimethyl amine and from 8 to 41 ppt for a series of other small alkylamines. Hanson et al. (2011) reported amine detection at "sub-ppt" levels by means of protonated water cluster ionization. This sub-ppt measurement range is still above the ppq range reachable in case of NO₃-ionization detection of strong acids. These approaches may also suffer from flaws interfering with reliable amine detection and quantification: (i) outgassing of amines from gas lines and surfaces of chemical ionization system, (ii) non-collision limit charging efficiency, and (iii) uncertainty in identi-

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fication of the elemental composition of detected ion due to insufficient mass resolution of the quadrupole mass spectrometer. Further problems in high sensitivity amine measurements can be caused by amine contamination in the zero gas required for determination of instrument background.

Here we describe a chemical ionization system that utilizes ion induced clustering of sulphuric acid and amines or ammonia, with ions detected with an atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF, Junninen et al., 2010). This approach addresses the above issues that can complicate amine detection. Instrument response to ammonia and dimethyl amine was studied by calibrations performed in the CLOUD facility at CERN (e.g. Kirkby et al., 2011; Almeida et al., 2013). The instrument was used for quantification of ammonia and dimethyl amine as well as for qualitative detection of other amines in CLOUD at CERN and at the SMEAR II boreal forest field station in Hyytiälä, southern Finland, during the PEGASOS campaign in spring 2013.

Instrument

The instrument uses the nitrate ion atmospheric pressure chemical ionization (CI) system combined with an APi-TOF (Junninen et al., 2010) as described in Jokinen et al. (2012). Two modifications were made to the original instrument (Jokinen et al., 2012). First, due to multiple problems associated with use and transportation of radioactive materials, the radioactive 10 MBq Am-241 ion source was replaced by a Hamamatsu (model L9490) soft (< 9.5 keV) X-ray tube. Second, a system for introducing gaseous sulphuric acid (H₂SO₄) in the sample flow was developed. A schematic representation of the instrument is shown in Fig. 1.

Operation of the chemical ionization-ion induced nucleation inlet is based on chemical ionization of sulphuric acid, H_2SO_4 ($\equiv SA$) by nitrate ions, NO_3^- , to form bisulphate ions, HSO₄ (≡SA⁻), and subsequent formation of bisulphate ion-sulphuric acid clus-

$$SA^- + SA \rightarrow SA \cdot SA^-$$
 ("dimer") (R2)

$$SA \cdot SA^- + SA \rightarrow (SA)_2 \cdot SA^-$$
 ("trimer") (R3)

In presence of dimethyl amine (DMA):

$$(SA)_2 \cdot SA^- + DMA \rightarrow DMA \cdot (SA)_2 \cdot SA^-$$
 (R4)

Further clustering of sulphuric acid takes place:

$$(SA)_2 \cdot SA^- + SA \leftrightarrow (SA)_3 \cdot SA^-$$
 ("tetramer") (R5)

After which, besides DMA, ammonia (NH₃) can also stick to the clusters

$$(SA)_3 \cdot SA^- + DMA \rightarrow DMA \cdot (SA)_3 \cdot SA^-$$
(R6)

$$(SA)_3 \cdot SA^- + NH_3 \leftrightarrow NH_3 \cdot (SA)_3 \cdot SA^- \tag{R7}$$

If sufficient sulphuric acid is present in the ambient sample it is possible that DMA (at very low concentrations) is bound to sulphuric acid. In that case the following reaction can also occur:

$$^{15} SA \cdot SA^{-} + SA \cdot DMA \rightarrow DMA \cdot (SA)_{2} \cdot SA^{-}$$
 (R8)

Clusters formed in Reactions (R2)–(R8) can also decompose (evaporate), specifically in the reduced pressure in the APi interface to the mass spectrometer. Evaporation rates for Reactions (R1)-(R8) at +25°C have been calculated to be: Reaction (R2): 2.70×10^{-15} , Reaction (R3): 5.60×10^{-3} , Reactions (R4) and (R8): 5.28×10^{-2} , Reaction (R5): 24.1, Reaction (R6): 1.89 and Reaction (R7): 27.4 s⁻¹ (Ortega et al., 2014). In Reactions (R2)-(R4) and (R8), only the forward reaction needs to be considered. Due to their highly negative formation free energy, clusters formed in these reactions should be virtually non-evaporating in the 0.1s residence time the CI-system.

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DMA · (SA₃)SA formed in Reaction (R6) should also be stable in our timescale with a lifetime of the cluster of the order of 0.5 s at +25 °C. However, the most probable fate of DMA (SA₃)SA is not loss of SA but dissociation to neutral DMA (SA₂) and SA·SA⁻. Therefore, addition of another SA to the highly stable DMA·(SA₂)SA⁻ may result in a loss of the DMA altogether from the ion, especially when the instrument is operated at temperatures above +25°C.

This assumption of stability does not apply to Reactions (R5) and (R7), which complicate the detection of ammonia or amines which do not form stable adducts with (SA)₂SA⁻ similar to Reaction (R4). The backward (evaporation) rates for Reactions (R5) and (R7) will also be temperature sensitive. Thus, stable detection of compounds clustering only with (SA)₃·SA⁻ requires precise temperature control of the instrument.

Presence of (SA)₄·SA⁻ is unlikely at the ~ +20 °C operating temperature of our system (Ortega et al., 2014) but the clusters formed in reactions R4, R6 and R7 can still add another SA molecule, forming a reasonably stable cluster. E.g., for NH₃·(SA)₄·SA⁻, the evaporation rate is 2.29 s⁻¹ (+25 °C, Ortega et al., 2014). Evaporation rates for DMA·(SA)₄·SA⁻ are not reported. Attachment of a fifth sulphuric acid can give ion signals from the bases clustered with the SA trimer to pentamer (DMA) or with the tetramer or pentamer (NH₃). Further reactions where an additional DMA or NH₃ molecule attaches to cluster can occur but should not significantly affect the cluster distribution at expected low amine concentrations. These clusters containing multiple bases are readily detected with TOF-MS (see later).

An overview of sticking preferences of various amines is shown in Fig. 2, depicting signals observed from laboratory indoor air mixed with a high concentration (several 10¹⁰ molecules cm⁻³) of sulphuric acid vapour. While signals from DMA/EA, and diethyl/butyl amine (DEA/BA) are roughly as abundant with both the "trimer" and "tetramer", the signals from NH₃, MMA and TMA/PA are larger with the tetramer. This observation, albeit qualitative, indicates that DMA/EA and DEA/BA can be detected with higher sensitivity than ammonia and other small amines, because the "trimer"

concentration in the system is significantly higher than that of the "tetramer" and larger sulphuric acid clusters.

Figure 3 shows the operation of the NO₃⁻ CI-system in more detail (Eisele and Tanner, 1993; Jokinen et al., 2012), including COMSOL computational fluid dynamical modeling. The system is comprised of a 3/4 inch inlet tube through which the sample is drawn with a flow rate of 10 lpm. A cylinder (coaxial to the inlet tube) is held at -130 V potential, separating the ion production region from the sample tube at ground potential. Still coaxial to that is an outer cylinder also kept at -130 V potential. An X-ray source irradiates the space between these two cylinders through an aluminium window at outer cylinder surface.

Sheath gas (ideally cryogenic N_2) flows at 20 lpm in the air space between the cylinders and carries the ions produced in the ion production region downstream toward the ion-molecule reaction (IMR) tube. HNO $_3$ vapor added into the sheath flow promptly converts ions (formed from the X-rays) to NO_3^- (HNO $_3$) $_{n,n=0-2}$ ions or ion clusters. After entering the IMR region, an electric field ($-110\,V$) between the IMR tube and the ground potential of the sample tube pushes the ions toward the sample (centerline) flow. Flows (sheath and sample) and electric field strength are balanced so that ions do not hit the sample tube wall, rather following an axial trajectory after entering the sample flow. Ions then interact with the sample flow for up to 340 ms before the electric field guides the ions into the 0.7 lpm flow through the pinhole into the atmospheric pressure interface of the TOF mass spectrometer.

The upper panel of Fig. 3 shows the flow velocity profile and nitrate ion trajectory in absence of any electric potential in the drift tube or in the ion source. Ions travel close to the wall of the drift tube and exit the system with excess flow without interacting with the sample flow. In this case ions do not enter the mass spectrometer. The lower panel of Fig. 3 depicts the electric potential and the nitrate ion trajectory with the electric field on. The electric field and gas flows guide the ions from the ion production region to the centerline of the drift tube and eventually through the pinhole into the APi-TOF. This nitrate ion based CI-APi-TOF has been used in many recent laboratory and ambient

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air studies probing atmospheric chemistry and particle formation (e.g. Mauldin et al., 2012; Almeida et al., 2013; Ehn et al., 2014; Kürten et al., 2014). It has shown to be highly sensitive toward sulphuric acid, sulphuric acid-amine clusters, and highly oxidized low volatility organics.

However, NO₃ chemistry is inapplicable for direct amine measurements; bisulphatesulphuric acid clusters need to be generated. Therefore, preceding the nitrate CIsystem, a flow (1-2 lpm) saturated in sulphuric acid vapour is mixed with the sample air. The saturator is a temperature controlled (+20°C) rotating coaxial design (Fig. 4). The coaxial design allows a significantly more compact construction than a cylindrical design, while rotation continuously wets the walls with liquid sulphuric acid. This minimized unwanted wall effects; e.g. clean glass surfaces act as a sink to sulphuric acid vapour in contrast to liquid acid coatings. The glass tube connecting the rotating saturator to the sample inlet is as short as possible (5 cm). Mixing of sulphuric acid vapor and the sample gas then takes place in the 20 cm distance before the sample air enters the drift tube/ion interaction region. The detailed mixing process is not well known; it most likely involves both small scale turbulence and diffusion. Sulphuric acid concentration in the resulting mixture is in the range of $2-6 \times 10^{10}$ molecules cm⁻³. After entering the IMR tube, Reactions (R1)–(R8) result in prompt formation of bisulphate-sulphuric acidbase clusters for mass spectrometric analysis. Neutral sulphuric acid-base nucleation can occur both in the sample tube as well as in the IMR tube; in the latter, ionization of neutral clusters by NO₃ or SA⁻ can also occur. However, since ion induced clustering is significantly faster (due ion enhanced collision rate) than neutral cluster formation, neutral processes likely play a minor role.

Problems that have previously limited amine measurements (see Introduction) are, to a large extent, solved with the present approach. Firstly: (i) outgassing of amines from flow system walls is effectively prevented by acid coating of all gas lines and CI-source surfaces. Stainless steel surfaces in the sheath gas line are also extensively coated with HNO₃ added to sheath gas flow. Such acid coating activates tube walls

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with respect to base deposition and prevent desorption. Only the wall of 3/4 inch dia. 40 cm long inlet tube extending to ambient atmosphere is not actively acidified.

Second problem, (ii) non-collision limit charging efficiency, is solved for DMA by the choice of the ionization method. DMA sticks to sulphuric acid trimer and tetramer without significant evaporation. This, however, is not the case with ammonia. Other amines also need to be thoroughly investigated.

Third problem, (iii) identification of the atomic composition of detected ion is solved by application of high mass resolution TOF mass spectrometer. Mass resolution of APi-TOF is $\sim 4000\,\text{Th}\,\text{Th}^{-1}$ and mass accuracy is $< 20\,\text{ppm}$. This is facilitated in data post-processing utilizing high-resolution peak identification and isotopic patters (tofTools, Junninen et al., 2010). Combined with high selectivity of the ionization method, many unwanted compounds are not ionized, or resolved in a very clean mass spectrum.

3 Sensitivity studies

Sensitivity was studied in the CLOUD experiment at CERN. For a detailed description of the facility see Kirkby et al. (2011) and Almeida et al. (2013). Briefly, the CLOUD facility is designed for studying nucleation and growth of secondary aerosol, cloud droplet activation and freezing and the effect of galactic cosmic radiation on those processes, under precisely defined laboratory conditions. The CLOUD-chamber itself is a 26 m³ electropolished stainless steel tank equipped with a UV-light system and precise temperature control. Lifetime of condensable gases against wall loss is in the range of few minutes. Air inside the chamber is prepared from cryogenic nitrogen and oxygen. Input gases are precisely controlled and the gas composition is continuously monitored by an extensive suite of analyzing instruments.

DMA and/or NH_3 were mixed with the flows of cryogenic oxygen and nitrogen, prior entering the chamber. Concentrations of bases were calculated from the mixing ratio of the flows and confirmed by measurement with ion chromatography (> 1.0 pptv for DMA and > 3.7 ppt for NH_3 ; Praplan et al., 2012, Bianchi et al., 2012).

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The CIMS system described in this work was calibrated against the concentration in the CLOUD chamber with [DMA] ranging from 0.25 to 4 ppt. These experiments included simultaneous generation of sulphuric acid (from SO_2 oxidation) at atmospheric levels to investigate of sulphuric acid–DMA nucleation. Sulphuric acid present in the chamber could affect DMA detection via clustering with the DMA which could slightly affect the measurement to a pure DMA system. However, since sulphuric acid concentrations were representative of the atmosphere, the presence of sulphuric acid makes the calibration system more atmospherically relevant. In Fig. 5, example mass spectra around mass/charge 436 Th, the mass of the DMA-tetramer cluster, show signals with [DMA] = 0.25 ppt and with no added DMA (i.e. chemical background of the system with CLOUD tank cleaned and filled with cryogenic N_2/O_2 mixture). The main isotope at 437.92 Th is clearly visible demonstrating the sensitivity and the resolution of the method. The isotopic distribution and the exact mass of the main peak allow unambiguous identification of the atomic composition of the cluster ion.

Response of the instrument as a function of [DMA] is shown in Fig. 6. DMA is observed in the clusters with $(SA)_{2-4} \cdot SA^-$, with DMA· $(SA)_3 \cdot SA^-$ being the most abundant cluster. Summing up the detected clusters yields the total signal of DMA. Signal is normalized by $(SA)_2 \cdot SA^-$, the dominant reagent ion at the end of the IMR tube. $(SA)_2 \cdot SA^-$ should be the ion to which most of the DMA attach according to Reaction (R4) (before the further attachment of sulphuric acid), since DMA cannot attach to $(SA)_{0-1} \cdot SA^-$ and larger clusters $(SA)_{>2} \cdot SA^-$ are far more sparse. It is possible that significant fraction of neutral DMA molecules enter the IMR region bound to sulphuric acid. In that case, Reaction (R8) can play a role as well, and normalization to sum of bisulphate dimer and trimer might be appropriate. However, the results in Fig. 6 are independent on the choice of normalization method.

All detected ions correlate extremely well with the DMA concentration calculated from the flows injected in the chamber. The correlation between the normalized sum

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of detected clusters and DMA concentration is excellent, $R^2 = 0.9995$. Such linearity demonstrates the performance of our instrument and, also, the superior control and performance of the CLOUD chamber facility. DMA \cdot (SA)₂₋₄ · SA⁻ clusters are also very stable and, therefore, temperature variations in IMR tube do not alter cluster distributions or detection efficiency. The limit of detection (defined as three times the background signal) was found to be 8 ppq (or 0.008 ppt) for 15 min integration, representing roughly a hundred fold improvement in comparison to other existing techniques (Hanson et al., 2011; Yu et al., 2012). It should also be noted that with time-of-flight mass spectrometer all signals are integrated simultaneously while, in contrast, quadrupole MS only one mass is detected at a time. Thus, if several amines are to be measured, the LOD is unaffected. A calibration coefficient is obtained from the slope of the linear fit, C = 55.6 ppt. The calibration coefficient is used to convert signal to concentration according to.

$$[DMA] = C \times \frac{\sum_{n=2-4} SA^{-}SA_{n}DMA}{SA^{-}SA_{2}}$$
(1)

3.2 Sensititvity for ammonia

Sensitivity for ammonia was studied exactly as for DMA. Ammonia easily evaporates from the "trimer" SA cluster, unlike DMA; and since the "tetramer" cluster is relatively unstable at near room temperature in the IMR tube, much lower sensitivity is expected. Calibration results were far more scattered possibly due to either fluctuating (or poorly defined NH3 concentration, at low [NH3]) in the CLOUD chamber or temperature variations in the IMR tube affecting cluster stability. Instrument temperature was not controlled, e.g. drifted with ambient temperature in the facility; therefore, temperature sensitive evaporation rates would be reflected in ammonia detection sensitivity. If temperature fluctuations were the cause of variable signals, a LOD of few tens of ppt could be achieved with proper temperature control. Using only the highest ammonia concentration (50 ppt) used in calibration experiment, an approximate calibration coefficient

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$$_{5} [NH_{3}] = C \times \frac{\sum_{n=3-4} SA^{-}SA_{n}NH_{3}}{SA^{-}SA_{3}}$$
 (2)

is used for converting signal to concentration.

4 Application to field measurements at SMEAR II

Field measurements were conducted at the Smear II boreal forest field station (Hari and Kulmala, 2005) at Hyytiälä in southern Finland during the PEGASOS campaign, 1 April–15 June 2013. Initially ambient air filtered with amine specific gas mask filter (pumped using a standard membrane pump) was used to provide the 20 lpm sheath air flow for the ion source. Background signals from amines and ammonia, were unacceptably high, even though the acidified walls of the sheath gas lines likely scavenged a significant fraction of those bases. Therefore, the sheath air was promptly substituted with a flow of cryogenic nitrogen. Figure 7 shows how the change in sheath gas affected the signals, also indicating the sensitivity to any artificial source of amines, a problem associated with amine measurements in general.

The time series of ammonia and DMA is shown in Fig. 8, with concentrations calculated with the calibration coefficients obtained from the CERN calibration. Backgrounds, measured daily by substituting cryogenic nitrogen in the sample flow, are not subtracted; rather they are shown in the shaded blue regions. In the case of ammonia, N2 flushing yielded a factor of 5–10 decrease in detected signal, corresponding to background "concentration" of few tens of ppt (using the nominal calibration coefficient determined above). Average ammonia concentration during the stable operation period

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with N₂ sheath gas (from 7 May to 2 June 2013) was approximately 340 ppt, subject to significant uncertainty in the calibration coefficient. Thus, ammonia measurements reported here should only be taken as a proof-of-concept to monitor ammonia together with DMA and possibly other amines.

In the case of DMA, signals (always) increased during background N₂ flushing, reaching levels corresponding to 30 ppg (0.03 ppt) in concentration (Fig. 8, see also Fig. 9a). The source of DMA is likely somewhere in the stainless steel line, mass slow controller or pressure regulator between the N₂ Dewar and the sample inlet; or, less likely, from contamination (during flow switching) in the 40 cm long non-acidified part of the sample tube. Nevertheless, since no meaningful background level could be determined, the observed ambient signals, corresponding to 5 to 20 ppg amine concentration may be all due to chemical background in the instrument and, thus, not a single data point can be reliably attributed to DMA concentrations in the ambient atmosphere. An upper limit for DMA concentration can be obtained if we assume that the only artificial source of DMA was the zero air fed to instrument during the background measurement. In that case the upper limit of [DMA] ranges from few up to approximately 20 ppq during the whole measurement period when instrument worked stably (7 May to 2 June 2013).

During this time period, several nucleation events were observed. Our observation of very low DMA levels indicates that the nucleation process unlikely involved DMA to any significant extent (Almeida et al., 2013) and other amines or non-nitrous organics are needed to explain the new particle formation rates.

Though the DMA concentration was found to be extremely low, even negligible, other amines, TMA and possibly PA, exceeded the detection (background) threshold. Since no calibration exists for amines other than DMA, those signals cannot be reliably converted to concentrations. However, since bisulphate-sulphuric acid-DMA clusters are very stable, it is likely that other amines are detected with similar or lower sensitivity as DMA. Thus, we can report the lower limit concentrations for other detected amines by applying the calibration coefficient obtained for DMA. Example mass spectra from

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(a) DMA/EA, (b) ammonia, (c) TMA/PA and (d) a C_4 -amine (e.g. DEA) are presented together with corresponding zero measurements in Fig. 9. Signals from DMA/EA and C_4 amine increase during zero gas flushing, while ammonia and TMA/PA show clear and moderate reduction upon zero measurement, respectively, the latter suggesting the presence of TMA/PA with concentrations larger than few ppq. However, for these extremely small signals, exact mass determination is not definitive; nor could the isotopes cannot be resolved from the background spectrum. Therefore, the identification of the compound as TMA/PA is not certain.

Though the role of DMA in particle nucleation can almost entirely be excluded, the possible detection of TMA/PA leaves open the possibility that other amines might contribute to nucleation. Our result regarding [DMA] agrees with Schobesberger (2013), suggesting sub-ppt [DMA] concentrations. However, our values are in a serious conflict with the concentrations of DMA/EA reported by Kieloaho et al. (2013). The reason could be that the entire signal in Kieloaho et al. (2013) was due to EA while we were completely insensitive to EA. e.g., that we could only detect DMA. However, it would be surprising that, while we obviously detect several amines, including DMA, MMA, TMA and DEA (Fig. 2), the sensitivity for EA would be so poor. Another possibility could be in particle phase amine evaporation from the PTFE filter used to remove particulate matter from the sample in Kieloaho et al. (2013). Also, we performed our measurements at the open area of the measurement container field of SMEAR II, some 10-20 m from the uniform forested area, while Kieloaho et al. (2013) sampled inside the forest below the canopy. Amine lifetimes against oxidation and adsorption to particle phase should be at least few minutes (even with unity uptake coefficient), and therefore the small difference in measurement location should not cause such a major discrepancy.

5 Conclusions

A bisulphate-cluster based atmospheric pressure chemical ionization system was developed and integrated into a time-of-flight mass spectrometer. Calibrations demon-

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strated that, under ideal conditions, a limit of detection for dimethyl amine (DMA) of 8 ppq. Sensitivity of the system for DMA is approximately hundred-fold higher than reported for other existing methods. Superior performance results from minimization of amine outgassing from system surfaces, collision limited ionization detection and high ₅ mass resolution of the applied mass spectrometer. Extreme cleanliness of added gas flows is also critical.

Besides DMA, other small alkyl amines and ammonia are detected. Detection of ammonia with the present system, however, suffers from imperfect temperature control resulting in varying stability of bisulphate-sulphuric acid-ammonia clusters which is likely reflected in variable instrument response. Further efforts are required to understand the clustering dynamics of amines other than DMA and to calibrate instrument against well quantified concentration of these amines. In field measurements at a boreal forest site. DMA concentration was below ~ 20 ppg throughout the whole measurement period in May-June 2013, suggesting that it is unlikely that DMA played a major role in atmospheric nucleation of new aerosol particles observed simultaneously at the site. However, tentative observation on the existence of other amines (trimethyl and/or propyl amine) leaves open the possibility of amine contribution to new particle formation.

Acknowledgements. We thank CERN for supporting CLOUD with technical and financial resources. Support of Academy of Finland (251427, 139656, 264375, Finnish Center of Excellence 141135) is acknowledged. This research was partially funded by the European Commission 7th Frame work Programme via PEGASOS (FP7-ENV-2010-265148), ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network), Marie Curie Initial Training Network "CLOUD-ITN" and "CLOUDTRAIN-ITN" and Finnish Funding Agency for Innovation (TEKES) through APCI-project. Tinja Olenius, Oona Kupiainen-Määttä, Kenty Ortega, Hanna Vehkamäki, Antti-Jussi Kieloaho and Markku Kulmala are acknowledged for useful discussions. We thank the tofTools team for providing tools for mass spectrometry analysis. Finnish Antarctic Research Program is acknowledged for providing superior facilities for preparing the manuscript.

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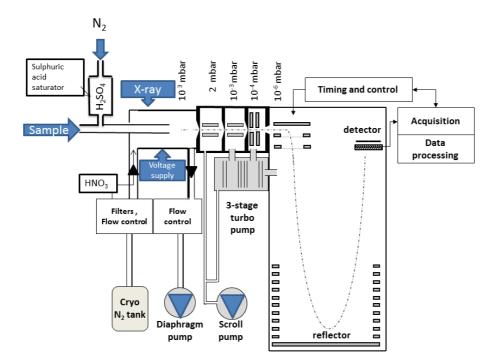


Figure 1. Schematic of the bisulphate-cluster chemical ionization atmospheric pressure interface time-of-flight mass spectrometer.

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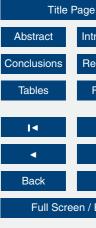
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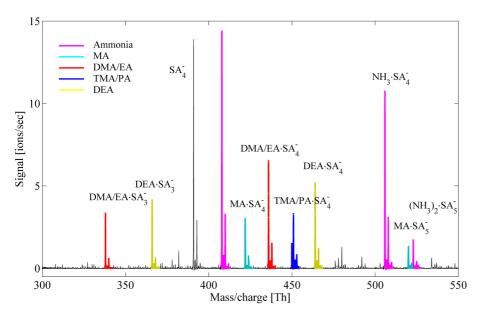


Figure 2. Dimethyl (DMA) and/or ethyl amine (EA) and diethyl amine (DEA) form stable clusters already with bisulphate "trimer", whereas ammonia, methyl amine (MA) and trimethyl/propyl amine (TMA/PA) are detected with "tetramer" or larger clusters.

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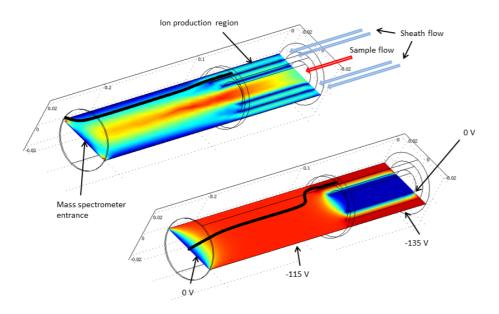


Figure 3. Operation principle of NO₂ CI-system used to produce bisulphate-sulphuric acid base clusters from ambient amines and added sulphuric acid present in the sample flow. Upper plot represents the flow profile inside the system. Lower plot depicts the electric potential inside the system. In upper panel, black thick line shows the ion trajectory in the case where all electric potentials are set to zero and ions "go with the flow". In lower panel, the black thick line shows electric fields guiding ions toward the centerline of the ion source, allowing ions to mix and interact with the sample and eventually be transported to the pinhole of the mass spectrometer. Original concept as presented by Eisele and Tanner (1993) was adopted by Jokinen et al. (2012) and coupled to the APi-TOF mass spectrometer.

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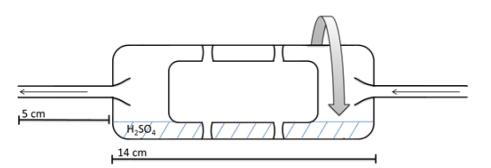


Figure 4. Schematic of the rotating sulphuric acid saturator. The saturator is connected to the sample tube as in Fig. 1.

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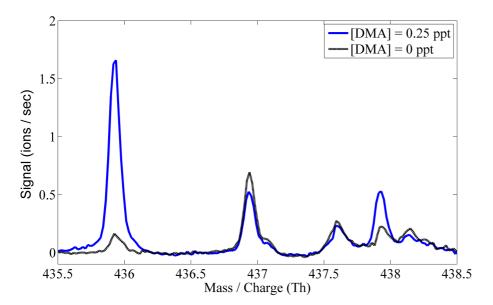


Figure 5. Mass spectra with [DMA] = 0.25 ppt, the lowest studied [DMA]; and the background signal (in absence of added DMA). Integration time is 15 min. Principal peak is located at 435.92 Th, first of the isotopes 436.92 Th is partly overlapping with signal from an unidentified compound. Second isotope at 437.92 Th is, however, clearly visible. Signal at 437.6 Th emerges from chlorine containing substance, whose source is unknown. Lowest detection limit was defined as three times the background signal at main peak (435.92 Th) and was found to be 8 ppg (0.008 ppt). Practically, ultimate sensitivity is limited by contamination in blank air or inlet surfaces.

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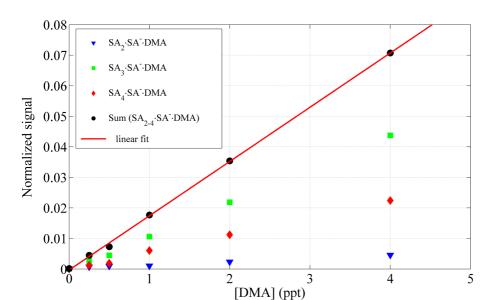


Figure 6. Response of bisulphate cluster signal to [DMA] = 0–4 ppt. DMA concentration in the CLOUD tank was adjusted by adjusting the DMA containing flow to the chamber.

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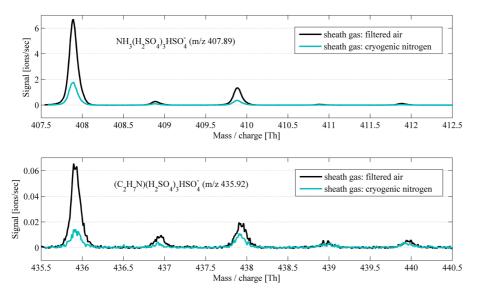


Figure 7. Purity of sheath gas is important for high sensitivity detection. Cryogenic N_2 resulted in 3–5 times lower background than ambient air filtered with particle filter and amine specific gas mask filter. Still both ammonia and dimethyl amine are visible in the spectra, with signals corresponding to several tens of ppt for ammonia and \sim 10 ppq for dimethyl amine. Data are taken with zero air (N_2) fed in the sample inlet.

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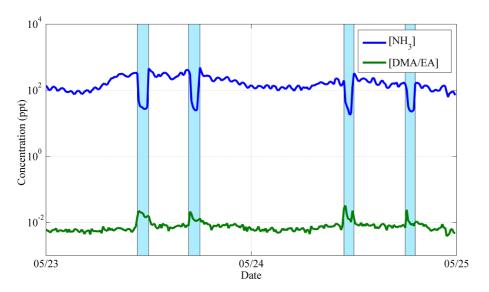


Figure 8. Portion of time series measured at SMEAR II boreal forest field station. While ammonia concentration exceeds the detection threshold determined by the zero measurement, DMA signal increases when zero air is fed in the instrument, indicating that DMA concentrations in ambient atmosphere were at maximum 20 ppq during the measurement period. Evaluation of ambient concentration is limited by apparent contamination in "zero air" from N_2 flushing of inlet lines. I.e. [DMA/EA] depicted here, represents the upper limit of ambient concentration. Blue shaded areas indicate zero air measurements.

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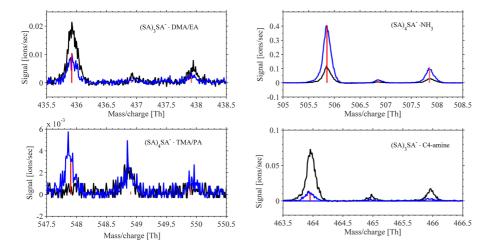


Figure 9. Examples of signals representing ambient measurement (blue) and zero (black) measurement. Zero gas (cryo N_2) contains more gas phase DMA/EA and a C_4 -amine (e.g. DEA) than ambient air. Only ammonia and potentially trimethyl/propyl amine (TMA/PA) signals exceed the signals from zero gas measurement. Red bars show exact masses of isotopes and expected isotopic distribution normalized to height of the main peak.

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