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sulphuric acid and
neutral cluster
measurements**

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Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF

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Received: 20 October 2011 – Accepted: 22 November 2011 – Published: 6 December 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The first ambient measurements using nitrate ion based Chemical Ionization with the Atmospheric Pressure interface Time-Of-Flight mass spectrometer (CI-API-TOF) for sulphuric acid and neutral cluster detection are presented. We have found CI-API-TOF a highly stable and sensitive tool for molecular sulphuric acid detection. The lowest limit of detection for sulphuric acid was determined to be 3×10^4 molecules cm^{-3} for two hour averaging. Signals from sulphuric acid clusters up to tetramer accompanied by ammonia were also obtained but these were found to result from naturally charged clusters formed by ion induced clustering in the atmosphere during nucleation. Opposite to earlier studies with cluster mass spectrometers, we had no indication of neutral clusters. The reason is either less efficient charging of clusters in comparison to molecular sulphuric acid, or in low concentration of neutral clusters at our measurement site during these particular nucleation events. We show that utilizing high resolution mass spectrometry is crucial in separating the weak sulfuric acid cluster signal from the other compounds.

1 Introduction

Nucleation of new particles is one of the main sources of cloud condensation nuclei in the Earth's atmosphere contributing even up to $\sim 50\%$ to the global CCN budget (Merikanto et al., 2010). With the exception of certain coastal areas (O'Dowd et al., 2002), the initial steps of nucleation require the presence of sulphuric acid (Paasonen et al., 2010; Sipilä et al., 2010; Zhao et al., 2010). Sulphuric acid (H_2SO_4), however, does not nucleate itself at typical atmospheric conditions, but additional vapours are required. Based on recent laboratory experiments (Kirkby et al., 2011), in ambient H_2SO_4 concentrations water could serve as a binary compound in the upper tropospheric conditions. At the boundary layer temperatures the evaporation of clusters containing only sulphuric acid and water is too fast to allow freshly nucleated particles to grow and thus

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additional species are required. Kirkby et al. (2011) found ammonia and dimethylamine from the charged clusters formed by ion induced nucleation and concluded that they are plausible candidates for stabilizing also neutral clusters at lower atmospheric conditions. The enhancing effect of amines on new particle formation was observed also in laboratory studies by Berndt et al. (2010) and Benson et al. (2011). Ammonia has been observed to exist also in atmospheric ion clusters together with sulphuric acid (Ehn et al., 2010). Concentrations of amines in the atmosphere are orders of magnitudes lower than that of ammonia. Despite that, amines can bind the cluster much more strongly (Kurtén et al., 2008) and thus even ppt levels of amines can be enough to accounting for atmospheric nucleation rates (Petäjä et al., 2011).

Nucleation is a frequent phenomenon occurring approximately 30 % of the days in Hyytiälä (e.g., Kulmala et al., 2010) and similar to most continental sites it is connected to the presence of sulphuric acid (e.g., Paasonen et al., 2010). Suggested mechanisms of nucleation include both neutral and ion assisted pathways. Kulmala et al. (2007) suggested nucleation process to be initiated by activation of neutral clusters while modelling studies by Yu and Turco (2008, 2011) suggest that ions play a crucial role in boreal forest nucleation. Recent studies by Manninen et al. (2009) and Kulmala et al. (2010) find neutral nucleation dominant in the atmosphere and laboratory experiments by Sipilä et al. (2010) support the conclusion that neutral nucleation involving sulphuric acid can proceed fast enough to account for atmospheric observations. On the other hand, the experiments by Kirkby et al. (2011) confirmed the existence of the physical nucleation mechanism involving ions. That experiment was, however, performed in conditions not representative to boreal forest boundary layer. Recent progress in mass spectrometry has made direct measurement of ion induced nucleation possible (Ehn et al., 2010; Junninen et al., 2010; Kirkby et al., 2011). With our new instrument, CI-APi-TOF, we aim to investigate the initial steps of neutral nucleation and enlighten the role of sulphuric acid, ions and stabilizing compounds in atmospheric aerosol nucleation.

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The problem in understanding the molecular steps of neutral nucleation is that, though the detection of neutral clusters is made possible by the recent development of the condensation particle counting technology (Kulmala et al., 2007; Sipilä et al., 2008; Iida et al., 2009; Vanhanen et al., 2011), the measurement of their chemical composition is extremely tricky. For a mass spectrometer, the neutral cluster needs to be charged and that charging process initiates several problems. First, typical ion sources generate a vast amount of ions and ion clusters from atmospheric trace gases (Asmi et al., 2009). These artificial ions obscure the signal from originally neutral clusters charged upon collisions with the charger ions therefore hindering their identification. This problem can be partly solved by utilizing highly selective chemical ionization (Eisele and Hanson, 2000; Hanson and Eisele, 2002; Hanson and Lovejoy, 2006; Zhao et al., 2010; Jiang et al., 2011; Petäjä et al., 2011) which is also the approach used in the present study. A problem associated with selective ionization is that the proton affinity of a neutral cluster, composed of sulphuric acid and stabilizing compounds, can be very different from that of the pure sulphuric acid molecule. Therefore those clusters do not necessarily get charged upon collision with charger ions (Kurten et al., 2011). Nevertheless, if a cluster becomes charged, its stability may change and it can lose, depending on its size, partly or completely its binary or ternary constituents. In the experiments by Junninen et al. (2010) and Kirkby et al. (2011) it was found that negatively charged clusters that contained less than 3 molecules of sulphuric acid on top of the bisulphate ion (HSO_4^-) did not accommodate any other species while clusters containing more than 4 sulphuric acid molecules always contained base molecules at lower tropospheric temperatures. Therefore, direct measurement of the true molecular composition of neutral clusters is not possible by means of a chemical ionization mass spectrometer as some information will be lost upon charging. Nevertheless, such measurements can still yield significant new information on mechanics of nucleation in the atmosphere.

Imbued with the first successful field measurements by Zhao et al. (2010) and Jiang et al. (2011) who were able to detect sulphuric acid clusters up to the tetramer during

nucleation events, we constructed a Chemical Ionization (CI) source and combined it with an Atmospheric Pressure interface Time-Of-Flight mass spectrometer (APi-TOF, Tofwerk AG, Thun, Switzerland and Aerodyne Research Inc., USA). The aim of this study was to apply this instrument, CI-APi-TOF, to measure molecular sulphuric acid as well as sulphuric acid containing clusters in ambient air at the Hyytiälä boreal forest field site, in Southern Finland.

2 Methods

2.1 Instrumentation

The CI-APi-TOF instrument consists of three main components. These components are

1. a specially designed inlet for chemical ionization at the ambient pressure (CI),
2. an atmospheric pressure interface (APi) and
3. a time-of-flight mass spectrometer (TOF).

Design of the CI-inlet is similar to one described by Eisele and Tanner (1993), and by Kurtén et al. (2011). APi-TOF is also well described elsewhere (Junninen et al., 2010).

Ionization in the CI-system occurs in ambient pressure via proton transfer between nitrate ions and sulphuric acid:



The chemically ionized sample is guided to the instrument through the critical orifice with a flow rate of ~ 0.8 lpm. The ions are then guided through differentially pumped APi and further to the TOF for separation according to their m/Q . The final pressure inside the TOF is typically 10^{-6} mbar.

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Clusters in React. (R1) partly decompose in the vacuum of the APi-TOF. The sulphuric acid concentration (in molec cm⁻³) measured with the CI-APi-TOF is calculated from the measured ion signals according to:

$$[\text{H}_2\text{SO}_4] = \frac{\text{HSO}_4^- + \text{H}_2\text{SO}_4 \bullet \text{NO}_3^-}{\text{NO}_3^- + \text{HNO}_3 \bullet \text{NO}_3^- + \text{HNO}_3 \bullet \text{HNO}_3 \bullet \text{NO}_3^-} \times C, \quad (1)$$

where C is the calibration coefficient. We had no opportunity to directly calibrate our setup, but the calibration coefficient of 5×10^9 determined for a CI-source similar to the present one (Mauldin III et al., 1999) was applied at the first stage of the data conversion. We also performed an indirect calibration by running our instrument next to a calibrated CIMS in Hyytiälä for ca. 2 weeks (Fig. 1). From this inter-comparison an additional factor of 3.78 was obtained yielding a final calibration coefficient of $C = 1.89 \times 10^{10}$. As the inter-comparison was performed with CI-APi-TOF having a 60 cm long $3/4''$ sample tube in front of it, the diffusion losses in the sample tube are absorbed in the final calibration coefficient.

The sensitivity of the instrument was also studied. The CI-APi-TOF provides low signal-to-noise ratio and can also achieve very low detection limits. The limit of detection (LOD) for sulphuric acid monomer is defined as three times the standard deviation added to the mean value of the background signal. The LOD of sulphuric acid monomer is 3.2×10^4 molec cm⁻³ for two hour integration, which is equal to earlier CIMS instruments. As this value comprises also the diffusion losses in the sample tube, the loss corrected LOD is close to 2×10^4 molec cm⁻³. The LOD is probably due to the utilization of the TOF mass spectrometer, in which all mass channels are integrated simultaneously thus improving the statistics.

2.2 Field site

The measurements presented here were carried out at Hyytiälä Forestry Field Station (SMEAR II) located in Juupajoki, Southern Finland during HydeSpring2011 field

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campaign. Both neutral cluster and naturally charged sulphuric acid measurements were conducted simultaneously between 14 March and 11 April 2011.

2.3 Experimental setup and ambient measurements

Two APi-TOF instruments were deployed to measure gas phase sulphuric acid at the same location. The CI-APi-TOF was set to measure neutral sulphuric acid molecules and clusters. The second APi-TOF at the site was set up to measure naturally charged ambient molecules and clusters without using any accessory ionizing method. As also the naturally charged ions and ion clusters are sampled with the CI-APi-TOF running the normal APi-TOF in parallel provided information on how much these naturally charged ions contribute to the signals measured with the CI-APi-TOF. In addition, to quantify the effect of naturally charged ions CI-APi-TOF was operated without the ^{241}Am source installed for a few days and the spectra between the two instruments were compared.

Aerosol size distributions are measured with a Differential Mobility Particle Sizer (DMPS). The system (Aalto et al., 2001) measures particles from 3 nm to about 950 nm in diameter. The aerosol size distribution was used to classify the days in terms of new particle formation.

2.4 Data analysis

Data analysis is done using Matlab (version 7.10.0.499, R2010a) based program tofTools (Junninen et al., 2010). Before mass calibration the signal is averaged over 60 min. For mass calibration we used three known masses that are always present in the spectrum, nitrate ion (or its isotope) and its dimer and trimer (NO_3^- , $\text{HNO}_3 \bullet \text{NO}_3^-$, $(\text{HNO}_3)_2 \bullet \text{NO}_3^-$). Resolving power is approximately 3600 Th/Th for over 45 Th and in lower mass-to-charge ratios it is slightly lower for ideal peak fitting.

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3 Results and discussion

3.1 Peak identification

The CI-API-TOF signals are identified by defining the exact mass of the compounds under interest and their possible isotopic patterns. The advantage of the CI-API-TOF is that even at extremely low concentrations of sulphuric acid clusters, the high resolution makes it possible to separate the cluster signal from other closely located peaks. This means the cluster signal can be reliably separated from possible residual peaks overlapping the original cluster signal. This gives us more accurate information of existence and concentrations of clusters in the atmosphere.

The high resolution spectrum for deprotonated sulphuric acid monomer HSO_4^- , dimer $\text{H}_2\text{SO}_4 \bullet \text{HSO}_4^-$, trimer $(\text{H}_2\text{SO}_4)_2 \bullet \text{HSO}_4^-$, and tetramer $(\text{H}_2\text{SO}_4)_3 \bullet \text{HSO}_4^-$ measured with the CI-API-TOF on 30 March 2011 at 10:00 a.m. is presented in Fig. 2. The most abundant signal is sulphuric acid monomer at 97 Th, followed by the dimer (195 Th), trimer (293 Th) and tetramer (391 Th) in a decreasing order. At 97 Th only peak is detected with no interfering compounds. The sulphuric acid dimer is the dominant ion present at 195 Th, but almost half of this consists of other compounds partly extending over the dimer signal. In case of the trimer and tetramer these other compounds are already predominant, but the sulphuric acid signals can still be dependably separated.

Identifying the compounds overlapping the cluster signals of interest is challenging but we are able to narrow down a group of possible candidates with certain elemental compositions. Fluorinated compounds are one possibility that may originate from the PTFE-tubing used to carry sheath flow to the inlet. An example of this is the contaminant peak at 195 Th. This peak has no diurnal cycle (Fig. 3) and it has the same exact mass than a fluorinated compound $\text{C}_4\text{HF}_6\text{O}_2^-$, (possibly hexafluorobutanoate). When moving up to higher m/Q 's the number of possible combinations of elemental compositions increases rapidly. At 293 Th potential elemental compositions for the largest peak are for example $\text{C}_6\text{H}_8\text{F}_7\text{O}_5^-$, $\text{C}_9\text{H}_7\text{O}_4\text{F}_6^-$ or $\text{C}_8\text{H}_9\text{O}_{10}\text{N}_2^-$. This peak has a strong diurnal

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cycle (Fig. 3) and therefore the signal is likely to origin from atmosphere ($C_8H_9O_{10}N_2^-$) rather than the instrument's surfaces. For the peaks at 391 Th there are already dozens of possibilities within ± 0.001 Th from simple carbohydrates to complicated fluorinated or nitrogen containing compounds.

3.2 Neutral cluster concentration

As an example of neutral sulphuric acid and sulphuric acid cluster concentrations we chose two strong new particle formation event days observed on 29 and 30 March 2011. Since sulphuric acid is mainly produced photochemically, a distinct diurnal pattern is apparent with maximum measured values reaching up to 7×10^6 molec cm^{-3} . We measured naturally charged sulphuric acid using a second APi-TOF without any accessory ionizing method for comparison with the CI-API-TOF neutral cluster measurements. The DMPS instrument was used to measure particle size distribution to detect new particle formation.

Both two APi-TOF instruments were first run without chargers to be able to normalise results to get them respond to one another. After returning the CI-source, the CI-API-TOF results were then compared with naturally charged ion spectra measured on 29 and 30 March. Figure 3 presents results when only integer mass resolution data considered (green), total signal intensity of identified sulphuric acid clusters (blue) and the contribution of naturally charged ions to the total signal (red). Also signal from the main interfering compound at the integer mass is presented (black). When only one single peak is present, like in the case of sulphuric acid monomer, integer mass could be used for determination of concentrations. But like seen in Fig. 2, having non-sulphuric compounds overlapping nearly all cluster signals, the impact on the result is major. Indeed, reliable separation of ammonia containing sulphuric acid tetramer (408 Th) was rarely possible. However, though the signals from 408 Th should be taken with a grain they are presented because clear ion signal was observed with APi-TOF. Using integer mass only (Fig. 3), one could say that neutral sulphuric acid clusters are present at all times since the CI-API-TOF cluster signal exceeds the signal estimated

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to result from naturally charged ions. The presence of neutral clusters becomes highly unclear when peak fitting is done using the exact mass and the cluster signal has been separated from overlapping peaks.

Figure 4 demonstrates this effect even further by presenting sulphuric acid cluster signals in the beginning of the event on 30 March at 10:00 a.m. when all cluster signals were clearly visible. The figure shows that the only neutral compound that becomes charged using NO_3^- as the reagent ion and produces clearly larger signal than the corresponding natural ion signal is sulphuric acid monomer. Neutral sulphuric acid clusters do not produce strong enough signals to be separable from the signals from naturally charged clusters. In all cases the expected ion contribution to the signal is, within measurement accuracy, equal to the signal from the CI-API-TOF.

Our data are contradictory to the results presented by Zhao et al. (2010) and Jiang et al. (2011) who reported observations of neutral sulphuric acid clusters during nucleation up to the tetramer with concentrations ranging around 10^4 cm^{-3} . The reason for the disagreement can be that in our case, during nucleation events, the signal from naturally charged ions, if converted to concentration assuming the same calibration coefficient as for monomer, would be around $5 \times 10^4 \text{ cm}^{-3}$ for the dimer and trimer. For the tetramer and its cluster with ammonia, the concentration would be in the sub- 10^4 cm^{-3} range. If the concentrations of neutral clusters are lower, reliable separation of them from the data is not possible. To get rid of the ion background in future experiments, implementation of an ion filter in front of the CI-inlet is necessary.

Our results can not be explained by the findings of Petäjä et al. (2011) who, as a result of a laboratory experiment, reported close to collision limit formation of sulphuric acid dimers. To explain that observation they suggested that a stabilizing compound X with binding properties similar to dimethyl amine and concentration on the order of 10^7 – $10^8 \text{ molecules cm}^{-3}$ needs to be present in the system. Our signal from the neutral sulphuric acid dimer was never clearly separable from the signal caused by the naturally charged dimer. Thus, the neutral dimer concentration in Hyytiälä during nucleation events seems to be lower than a few 10^4 cm^{-3} . During the two days presented in Fig. 3,

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the sulphuric acid monomer concentration reaches 7×10^6 molecules cm^{-3} during both days. The coagulation sink (CoagS) for sulphuric acid dimers (calculated from DMPS data with RH-correction and assuming 1.2 nm mobility diameter, Ku and Fernandez de la Mora, 2009) during the times of maximum sulphuric acid concentrations on 29 and 30 March is $1.5 \times 10^{-3} \text{ s}^{-1}$ and $0.9 \times 10^{-3} \text{ s}^{-1}$, respectively. Let us assume that the evaporation rate of dimers is negligible (Petäjä et al., 2011) and that, besides coagulation, the second sink for dimers is the collision limited growth to trimers. In a steady state the production of dimers equals the loss:

$$k_{11} \times [\text{monomer}]^2 = \text{CoagS} \times [\text{dimer}] + k_{21} \times [\text{dimer}] \times [\text{monomer}] \quad (2)$$

Using collision rates of $k_{11} = 3.34 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $k_{21} = 3.69 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for dimer and trimer formation would result in dimer concentration on the order of $4\text{--}5 \times 10^6 \text{ cm}^{-3}$ which is significantly higher than one could estimate from the data. This indicates that though a laboratory system can be saturated with respect to stabilizing compounds leading to near zero evaporation rate of dimers, Hyytiälä air is necessarily not and thus the variation in observed nucleation rates can partly result also from changing concentrations of ternary species. Other possibility is that in the ambient atmosphere the oxidized organics rapidly condense on dimers forming compounds that can not be detected using nitrate ion based chemical ionization.

4 Conclusions

We have constructed a nitrate ion based Chemical Ionization Atmospheric Pressure interface Time-Of-Flight mass spectrometer (CI-APi-TOF) and presented ambient measurements of neutral sulphuric acid and its clusters from the atmosphere. We found the CI-APi-TOF a reliable and highly sensitive tool for measurements of low concentrations of atmospheric molecular sulphuric acid. We also measured signal from clusters containing sulphuric acid up to the tetramer with a fraction of tetramers containing one molecule of ammonia. All of the observed cluster peaks were associated with one or

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more peaks at the same integer mass, and therefore the high mass resolution of the APi-TOF was crucial in separating the cluster signal from unknown constituents. Furthermore, most of the observed masses followed a similar diurnal cycle as sulphuric acid, possibly indicating photochemical production pathways and therefore the diurnal behaviour could not have been straightforwardly used for concluding the composition.

The detected signals from sulphuric acid clusters were found to result, within the measurement accuracy, mostly or purely from naturally charged sulphuric acid clusters formed by ion induced nucleation in the atmosphere. In the case of sulphuric acid monomer, the artefact caused by naturally charged HSO_4^- was found to be 1–2% in the total sulphuric acid concentration. Due to ion interference no reliable data for neutral clusters were obtained. There are several possible reasons for that. First, neutral clusters may not become charged in collisions with nitrate ions, and will thus not be detected. Second, the concentrations of the neutral clusters are possibly not sufficient. If nucleation process in Hyytiälä was purely or mostly ion-induced or ion-mediated as suggested by Yu and Turco (2011) the absence of neutral clusters at the smallest sizes would be natural as only clusters formed upon recombination would contribute to the concentration of neutral clusters. We have estimated that the detection limit, if the charging probability of cluster is roughly equal to that of the monomer, is of the order of 10^4 molecules cm^{-3} assuming no contribution from naturally charged clusters and no overlapping peaks in the spectra. Therefore the existence of neutral clusters – chargeable with NO_3^- – below concentration of $\sim 10^4$ molecules cm^{-3} per species cannot be excluded and conclusions about the nucleation mechanism drawn. However, due to clear absence of neutral dimers, kinetically limited neutral sulphuric acid nucleation seems implausible. In presence of naturally charged ions and compounds at the same integer mass the detection limit for neutrals is obviously somewhat larger and for the future studies the sensitivity of the system will be increased by incorporating an ion filter in front of the instrument to remove the influence of ion clusters.

In terms of sensitivity the performance of our system is comparable to that of Zhao et al. (2010) and Jiang et al. (2011), as well as the system of Petäjä et al. (2011) but the

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results are contradictory. The reason for this is not clear, but certainly the measurement site and environmental parameters as well as the mass spectrometer differed between the experiments. As no reliable signal from neutral sulphuric acid dimers was obtained, it is plausible that, unlike many laboratory systems, atmospheric air is not saturated with respect of stabilizing compounds. This observation will hopefully boost future work on hunting for these stabilizing compounds.

Acknowledgements. Jenni Kontkanen is acknowledged for calculating the coagulation sink and Pauli Paasonen for useful discussions. Mikhail Paramonov, Jonathan Duplissy, Siegfried Schobesberger, Alessandro Franchin, Katrianne Lehtipalo, Hanna Manninen, Pasi Aalto, Silja Häkkinen, Stéphanie Gagné, Mikko Äijälä, Juha Kangasluoma, Emma Järvinen, Erik Herrmann and the personnel of the Hyytiälä forestry field station are acknowledged for help during field measurements. This work was partially funded by Academy of Finland (1251427, 1139656, Finnish centre of excellence 1141135) and European Research Council (ATMNUCLE).

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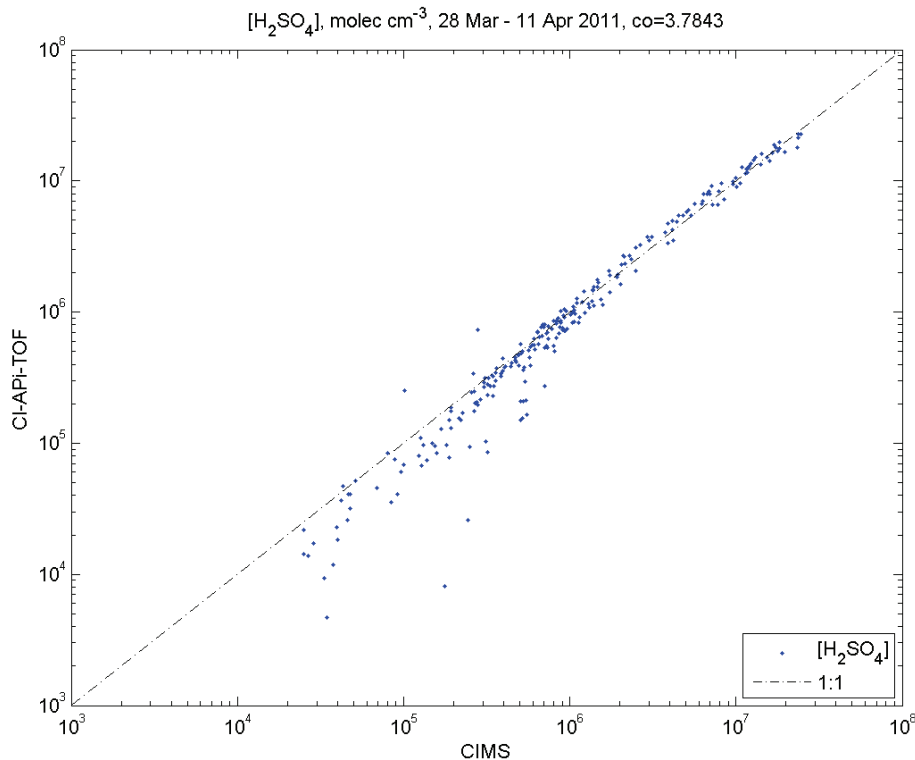


Fig. 1. Correlation between sulphuric acid concentrations measured with the CI-API-TOF (using a standard calibration coefficient $C = 5 \times 10^9$, Mauldin III et al., 1999) and calibrated CIMS from 28 March to 11 April 2011. Data sets are 60 min averages. The average ratio between the two data sets is 3.78. This factor includes diffusion losses in the CI-API-TOF sample line, and is used when converting the CI-API-TOF signals to concentrations.

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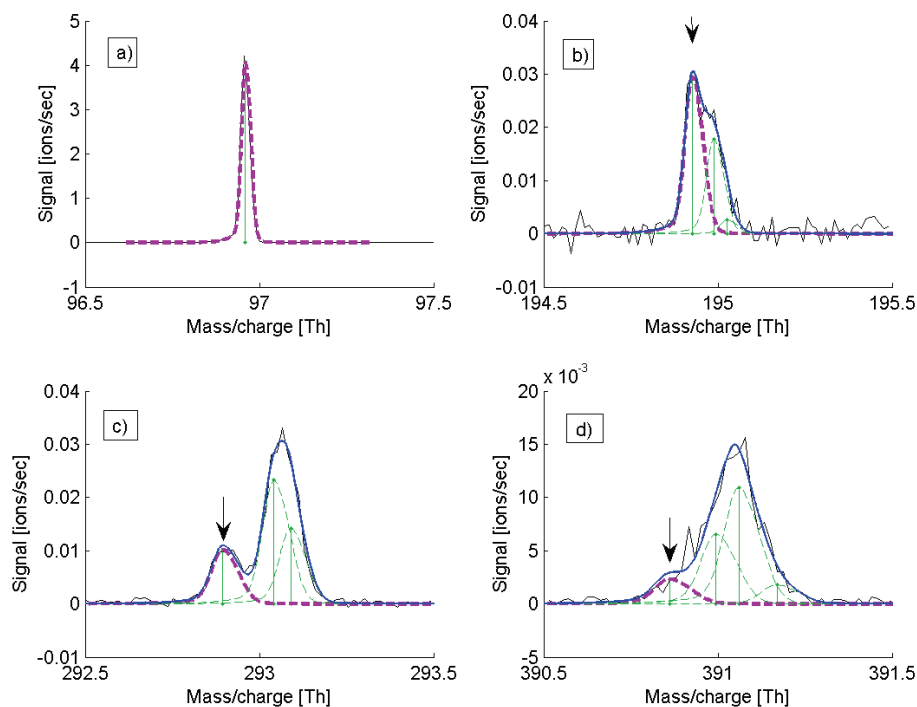


Fig. 2. Peak fitting for sulphuric acid monomer (a), dimer (b), trimer (c) and tetramer (d) clusters at 97 Th, 195 Th, 293 Th and 391 Th on 30 March 2011 at 10:00 a.m. The dashed purple lines correspond to the sulphuric acid signals. Isotopic patterns are not provided in the figure but were used to confirm accurate peak identification in addition to the exact masses. Signals are averaged over 120 min.

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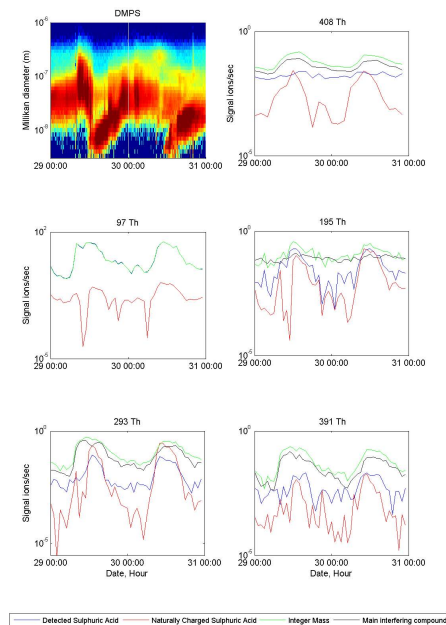


Fig. 3. Particle and ion concentrations (molec cm^{-3}) measured at Hyytiälä site on 29 and 30 March 2011. Particle size distribution measured with DMPS is shown in the upper left. Other pictures correspond to sulphuric acid monomer (97 Th), dimer (195 Th), trimer (293 Th), tetramer (391 Th) and ammonia-tetramer (408 Th). In case of ammonia-tetramer, the overlapping peaks were such numerous that the reliability of the determination of the signal is most of the time questionable. The blue lines represent neutral sulphuric acid measurements using the CI-API-TOF. The red lines represent naturally charged sulphuric acid measurements using the API-TOF without accessory ionizing method. The green lines represent the integer mass measured with the CI-API-TOF that includes the sulphuric acid and the contaminant signals. The black lines represent the signal originating from the strongest contaminant signal at the same integer mass. Most of the CI-API-TOF signal can clearly be explained by the sampled naturally charged ions.

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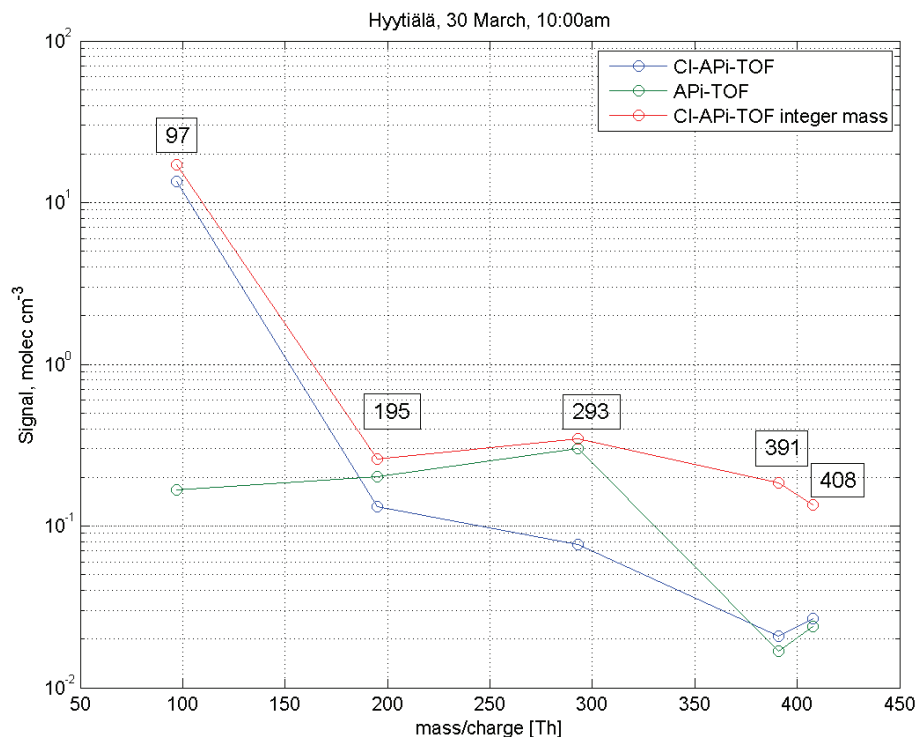


Fig. 4. Total sulphuric acid and cluster signals (blue), the contribution of naturally charged ions to the total signal (green) and integer mass (red) signals are present in this figure. Mass-to-charge ratios in the picture correspond to sulphuric acid monomer (97 Th), dimer (195 Th), trimer (293 Th), tetramer (391 Th) and sulphuric acid tetramer-ammonia cluster (408 Th). Neutral sulphuric acid monomer is the only compound to clearly being charged in the CI-API-TOF.

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