Estimation of sulfuric acid concentrations using ambient ion composition and concentration data obtained by ion mass spectrometry measurements (APi-TOF)

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Abstract
Sulfuric acid (H₂SO₄, SA) is the key compound in atmospheric new particle formation. Therefore, it is crucial to observe its concentration with sensitive instrumentation, such as chemical ionisation inlets coupled to Atmospheric Pressure Interface Time-of-Flight mass spectrometers (CI-APi-TOF). However, there are environmental conditions and physical reasons when chemical ionisation cannot be used, for example in certain remote places or flight measurements with limitations regarding chemicals. In these cases, it is important to estimate the SA concentration based on ambient ion composition and concentration measurements that are achieved by APi-TOF alone. Here we derive a theoretical expression to estimate SA concentration and validate it with accurate CI-APi-TOF observations. The developed estimate works very well during daytime and with SA concentrations above 2⋅10⁶ cm⁻³.

1 Introduction
Sulfuric acid (H₂SO₄, SA) is the key compound in atmospheric new particle formation (e.g. Weber et al., 1995, 1996; Birmili et al., 2003; Kulmala et al., 2004; Kuang et al., 2008; Kerminen et al., 2010; Wang et al., 2011; Kulmala et al., 2014; Yao et al., 2018; Cai et al., 2021), therefore it is crucial to have accurate observations of its concentration. However, ambient concentrations of H₂SO₄ are low, commonly less than a part per trillion by volume (∼2⋅10¹² molecules cm⁻³), making it challenging to detect this concentration. During the recent years there has been clear steps towards the reliable detection of H₂SO₄ in the atmosphere, particularly via the development of a Chemical Ionisation Atmospheric Pressure Interface Time-of-Flight mass spectrometer (CI-APi-TOF, Jokinen et al., 2012), using nitric acid as a reagent ion.
During the past decade or so, Atmospheric Pressure interface Time-of-Flight mass spectrometers (APi-TOF, Junninen et al., 2010) have been deployed in several measurement campaigns where the use of a CI inlet was either not possible or desired. In these instances, the APi-TOF only observed the composition and concentration of ambient ions. The APi-TOF is capable of directly sampling and detecting naturally charged gas-phase ions, including molecular clusters, and is often being used to detect clustering processes as a first step of new particle formation on a molecular basis (e.g. Schobesberger et al., 2013; Jokinen et al., 2018; Beck et al., 2021). While a CI-APi-TOF at best has a limit of detection around ~10^4 molecules cm^-3 (~ ppq level), the APi-TOF can detect 1% of the ambient ion concentration. With an average ion concentration of ~1000 cm^-3 per polarity (Hirsikko et al., 2011), the APi-TOF is measuring 10 ion cm^-3 s^-1 with a limit of detection of ~0.01 counts per second, hence 0.1 ions cm^-3. This corresponds to approximately ppb level (1000 10^-20), showing that the limit of detection of APi-TOF in comparison to CI-APi-TOF is lower by five orders of magnitudes.

A detailed description of this instrument can be found in Junninen et al., (2010). Since concentrations of neutral clusters are below the detection limit of CI-APi-TOF in many atmospheric conditions and environments, using the APi-TOF is currently the only way to directly detect atmospheric clustering. Therefore, if we can estimate H_2SO_4 concentration particularly during initial steps of new particle formation, based on the same dataset, we can readily get better insight into the process itself.

Since there are only limited long term observations of H_2SO_4 concentrations, several proxies on this concentration have also been developed (e.g. Petäjä et al., 2009; Mikkonen et al., 2011; Lu et al., 2019; Dada et al., 2020). These proxies attempt to approximate the ambient H_2SO_4 concentrations using more readily measured quantities, in particular the sulfur dioxide concentration, (UV) radiation intensity and pre-existing particle number size distribution that can be used to calculate the condensation sink for gas-phase H_2SO_4. In case we are able to estimate the H_2SO_4 concentration from its influence on the ion mass spectra obtained by APi-TOF, that estimate may be more accurate than the use of H_2SO_4 proxies.

Motivated by the reasoning outlined above, we derive here an expression to estimate H_2SO_4 concentration based primarily on APi-TOF observations and validate it.

2 Theoretical estimation of sulfuric acid concentration with bisulphate ion and H_2SO_4 clusters

Ambient ion mass spectra commonly contain clear evidence of gas-phase H_2SO_4 predominantly in the form of bisulphate ion (HSO_4^-) and its adducts involving H_2SO_4, forming so-called dimers (H_2SO_4-HSO_4^-) as well as larger clusters (Ehn et al., 2010). These are due to the efficient scavenging of negative charge by ambient H_2SO_4 via proton donation, and due to the high stability of the sulfuric acid-bisulphate ion clusters, in particular for the dimer (Ortega et al., 2014). In order to estimate the sulfuric acid concentration (H_2SO_4) using the measured naturally charged ions (see Fig. 1), we theoretically explain that concentration by following the bisulphate ion HSO_4^- herein denoted SAmmonia, the dimer cluster H_2SO_4-HSO_4^- (SA_{dimer}) and trimer cluster (H_2SO_4)_2-HSO_4^- (SA_{trimer}). Any other H_2SO_4-containing ion clusters, in particular those larger than the SA_{trimer}, typically occur at much smaller concentrations and will be neglected.
The bisulphate ion HSO$_4^-$ and the H$_2$SO$_4$ clusters containing it were used for the estimation of H$_2$SO$_4$ concentration and are coloured in red.

If we assume that the concentration of SA monomer depends generally on its production rate ($P_1$) and that its loss is by condensation onto aerosol particles (condensation sink, CS) and its loss to the SAdimer, we get the following equation for this concentration:

$$\frac{d[S_{A\,\text{monomer}}]}{dt} = P_1 - CS \cdot [S_{A\,\text{monomer}}] - P_2,$$

(1)

where $P_2 = k_1 \times [S_{A\,\text{monomer}}] \times [H_2SO_4]$ is the dimer production rate due to $S_{A\,\text{monomer}}$-$H_2SO_4$ collisions, and the collision rate $k_1$ is assumed to be constant.

For the dimer concentration we consider the production $P_2$, the loss due to CS, and the clustering of the SAdimer with H$_2$SO$_4$ with a rate constant $k_2$:

$$\frac{d[S_{A\,\text{dimer}}]}{dt} = P_2 - CS \cdot [S_{A\,\text{dimer}}] - k_2 \cdot [S_{A\,\text{dimer}}] \cdot [H_2SO_4],$$

(2)

And with substituting $P_2$, eq. 2 for SAdimer changes to:
Finally, to produce $\text{SA}_{\text{monomer}}$ we consider the collision of the $\text{SA}_{\text{dimer}}$ with $\text{H}_2\text{SO}_4$ and the loss to the CS. For the sake of completeness, we would additionally have to consider the loss of $\text{SA}_{\text{trimers}}$ to form the tetramer ($\text{H}_2\text{SO}_4$)-$\text{HSO}_4^-$, however this additional term is rather small and will therefore be neglected in this derivation. Therefore, we get the simplified equation for $\text{SA}_{\text{monomer}}$:

$$\frac{d[\text{SA}_{\text{dimer}}]}{dt} = k_1 \cdot [\text{SA}_{\text{monomer}}] \cdot [\text{H}_2\text{SO}_4] - CS \cdot [\text{SA}_{\text{dimer}}] - k_2 \cdot [\text{SA}_{\text{dimer}}] \cdot [\text{H}_2\text{SO}_4].$$

(3)

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For simplification, we consider a pseudo-steady state condition for both dimers and trimers by setting the left-hand side of eqs. 3 and 4 to be zero, which is justified when the dimer and trimer concentrations change at rates smaller than their overall production and loss rates. Thereby, from eq. (3) we obtain:

$$k_1 \cdot [\text{SA}_{\text{monomer}}] \cdot [\text{H}_2\text{SO}_4] = CS \cdot [\text{SA}_{\text{dimer}}] + k_2 \cdot [\text{SA}_{\text{dimer}}] \cdot [\text{H}_2\text{SO}_4]$$

(5)

and from eq. (4) we obtain:

$$k_2 \cdot [\text{SA}_{\text{dimer}}] \cdot [\text{H}_2\text{SO}_4] = CS \cdot [\text{SA}_{\text{trimer}}].$$

(6)

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If we now deploy equation (6) in equation (5) and solve for $\text{H}_2\text{SO}_4$, the result is:

$$k_1 \cdot [\text{SA}_{\text{monomer}}] \cdot [\text{H}_2\text{SO}_4] = CS \cdot [\text{SA}_{\text{dimer}}] + CS \cdot [\text{SA}_{\text{trimer}}].$$

(7)

$$[\text{H}_2\text{SO}_4] = \frac{CS \cdot [\text{SA}_{\text{dimer}}] + [\text{SA}_{\text{trimer}}]}{k_1 \cdot [\text{SA}_{\text{monomer}}]}.$$
To estimate the H$_2$SO$_4$ concentration with the ion mode APi-TOF, we can therefore use this theoretical approach, in particular Eq. 8. For the collision rate of H$_2$SO$_4$ with HSO$_4^-$ we use $k_1 = 2 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ as in Lovejoy et al. (2004). The value of CS is calculated based on Kulmala et al. (2012). Even if the CS was unknown due, for example, to the lack of particle measurements, the daytime variability of the H$_2$SO$_4$ concentration could still be estimated only by using the relation of the H$_2$SO$_4$-containing cluster with HSO$_4^-$, as it is proportional to the H$_2$SO$_4$ concentration (see eq. 9).

![Graph 2](https://doi.org/10.5194/amt-2021-259)

**Figure 2** Time series of measured H$_2$SO$_4$ concentration from the CI-API-TOF (black) and estimated H$_2$SO$_4$ concentration from the API-TOF (blue) between 19 and 28 May 2017. The concentration is given in molecules cm$^{-3}$.

### 3 Validation

We tested the expression derived above using a dataset collected during inter-comparison measurements at the SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005). In Fig. 2 we show the time series of estimated and observed H$_2$SO$_4$ concentrations, based on API-TOF measurements together with Eq. 8 and CI-API-TOF measurements, respectively. The estimated H$_2$SO$_4$ concentration agrees well with the measured one during most of the daytime. During night-time, however, the estimated H$_2$SO$_4$ concentration seems to be considerably higher than the measured one. This could be because the SA$_{dimer}$ concentration is considerably lower than the SA$_{monomer}$ (see Fig. 3).

The scatter plot in Fig. 4 shows that the estimated H$_2$SO$_4$ concentrations agree well with the observed one when the H$_2$SO$_4$ concentrations are larger than $2 \times 10^6$ cm$^{-3}$, demonstrating that our method works particularly well during conditions that favour the formation of H$_2$SO$_4$-containing clusters.
Figure 3 Time series of the bisulphate ion (HSO$_4^-$, SA monomer), H$_2$SO$_4$ clustered with bisulphate (H$_2$SO$_4$⋅HSO$_4^-$, SA dimer) and two H$_2$SO$_4$ molecules clustered with the bisulphate ion ((H$_2$SO$_4$)$_2$⋅HSO$_4^-$, SA trimer) between 19 and 28 May 2017. The concentration is given in ions s$^{-1}$ as measured by the APi-TOF.

Figure 4 Measured H$_2$SO$_4$ concentration using a CI-APi-TOF (x-axis) versus estimated H$_2$SO$_4$ concentration based on APi-TOF results (y-axis). The colour is indicating the hour of the day and the black line is the 1:1 ratio. Between 08:00 and 16:00 local time, the concentrations are agreeing well. The shown data contains the time period from 19 to 28 May 2017. The overall correlation coefficient (Pearson) is 0.92.
4 Conclusions

Here we derived a theoretical expression to estimate $\text{H}_2\text{SO}_4$ concentrations based on APi-TOF measurements of ambient ions. The estimation agrees well with the measured concentration during daytime and with high enough $\text{H}_2\text{SO}_4$ concentrations, indicating that the estimation is able to give accurate enough $\text{H}_2\text{SO}_4$ concentrations during most of the time when active clustering of sulfuric acid is taking as the initial step(s) of atmospheric new particle formation.

The APi-TOF’s “ion mode”, i.e. direct ion sampling without chemical ionisation, remains a crucial tool in many field deployments and laboratory studies, since it is extremely sensitive and allows for observing atmospheric clustering molecule by molecule, which in most cases is impossible when relying on chemical ionization. Therefore, having available a reliable estimate of $\text{H}_2\text{SO}_4$ concentration allows us to utilise the APi-TOF ion mode even more effectively.

Data availability

The data can be accessed via Zenodo (not yet published, the correct link and doi will follow).

Author contribution

LJB, SS, VMK and MK designed the study. LJB performed the measurements. SS and LJB derived the equations. LJB processed and analysed the data and performed the data visualisation. MK and VMK supervised the process. All authors commented and edited the paper.

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References


