1 # Estimation of sulfuric acid concentrations using ambient ion

2 # composition and concentration data obtained by ion mass

3 # spectrometry measurements (APi-TOF)

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15

16 **Abstract**

17 Sulfuric acid (H_2SO_4, SA) is the key compound in atmospheric new particle formation. Therefore, it is crucial to

18 observe its concentration with sensitive instrumentation, such as chemical ionisation inlets coupled to

19 Atmospheric Pressure interface Time-of-Flight mass spectrometers (CI-APi-TOF). However, there are

20 environmental conditions and physical reasons when chemical ionisation cannot be used, for example in certain

21 remote places or flight measurements with limitations regarding chemicals. In these cases, it is important to

22 estimate the SA concentration based on ambient ion composition and concentration measurements that are

23 achieved by APi-TOF alone. Here we derive a theoretical expression to estimate SA concentration and validate it

24 with accurate CI-APi-TOF observations. The developed estimate works very well during daytime and with SA

25 concentrations above $2 \cdot 10^6$ cm^{-3}.

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27

28 **1 Introduction**

29 Sulfuric acid (H_2SO_4, SA) is the key compound in atmospheric new particle formation (e.g. Weber et al., 1995,

30 1996; Birmili et al., 2003; Kulmala et al., 2004; Kuang et al., 2008; Kerminen et al., 2010; Wang et al., 2011;

31 Kulmala et al., 2014; Yao et al., 2018; Cai et al., 2021), therefore it is crucial to have accurate observations of its

32 concentration. However, ambient concentrations of H_2SO_4 are low, commonly less than a part per trillion by

33 volume (~$2 \cdot 10^7$ molecules cm^{-3}), making it challenging to detect this concentration. During the recent years there

34 has been clear steps towards the reliable detection of H_2SO_4 in the atmosphere, particularly via the development

35 of a Chemical Ionisation Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-APi-TOF,

36 Jokinen et al., 2012), using nitric acid as a reagent ion.

37

38 During the past decade or so, Atmospheric Pressure interface Time-of-Flight mass spectrometers (APi-TOF,
39 Junninen et al., 2010) have been deployed in several measurement campaigns where the use of a CI inlet was
40 either not possible or desired. In these instances, the APi-TOF only observed the composition and concentration
41 of ambient ions. The APi-TOF is capable of directly sampling and detecting naturally charged gas-phase ions,
42 including molecular clusters, and is often being used to detect clustering processes as a first step of new particle
43 formation on a molecular basis (e.g. Schobesberger et al., 2013; Jokinen et al., 2018; Beck et al., 2021). While a
44 CI-APi-TOF at best has a limit of detection around $\sim10^4$ molecules cm^{-3} ($\sim$ ppq level), the APi-TOF can detect
45 1% of the ambient ion concentration. With an average ion concentration of $\sim$1000 cm^{-3} per polarity (Hirsikko et
46 al., 2011), the APi-TOF is measuring 10 ion cm^{-3}s^{-1} with a limit of detection of $\sim$0.01 counts per second, hence
47 0.1 ions cm^{-3}. This corresponds to approximately pps level ($100\cdot10^{-21}$), showing that the limit of detection of APi-
48 TOF in comparison to CI-APi-TOF is lower by five orders of magnitudes.

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

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

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

68 **2 Theoretical estimation of sulfuric acid concentration with bisulphate ion and H_2SO_4 clusters**
69 Ambient ion mass spectra commonly contain clear evidence of gas-phase H_2SO_4, predominantly in the form of
70 bisulphate ion (HSO$_4$-) and its adducts involving H_2SO_4, forming so-called dimers ($H_2SO_4\cdot$HSO$_4$-) as well as
71 larger clusters (Ehn et al., 2010). These are due to the efficient scavenging of negative charge by ambient H_2SO_4
72 via proton donation, and due to the high stability of the sulfuric acid-bisulphate ion clusters, in particular for the
73 dimer (Ortega et al., 2014). In order to estimate the sulfuric acid concentration (H_2SO_4) using the measured
74 naturally charged ions (see Fig. 1), we theoretically explain that concentration by following the bisulphate ion
75 HSO$_4$-, herein denoted SA$_{monomer}$, the dimer cluster $H_2SO_4\cdot$HSO$_4$- (SA$_{dimer}$) and trimer cluster (H_2SO_4)$_2\cdot$HSO$_4$-
76 (SA$_{trimer}$). Any other H_2SO_4-containing ion clusters, in particular those larger than the SA$_{trimer}$, typically occur at
77 much smaller concentrations and will be neglected.

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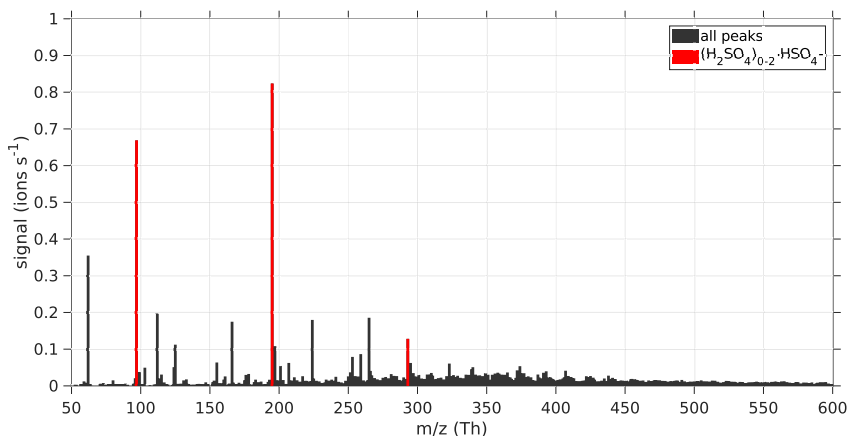
80
81 **Figure 1** Mass spectrum from 50 to 600 Th measured with the APi-TOF on 24 May 2017 during the time period 08:00 – 18:00
82 (local time). The bisulphate ion HSO_4^- and the H_2SO_4 clusters containing it were used for the estimation of H_2SO_4
83 concentration and are coloured in red.
84
85
86 If we assume that the concentration of $SA_{monomer}$ depends generally on its production rate (P_1) and that its loss is
87 by condensation onto aerosol particles (condensation sink, CS) and its loss to the SA_{dimer}, we get the following
88 equation for this concentration:
89

$$\frac{d[SA_{monomer}]}{dt} = P_1 - CS \cdot [SA_{monomer}] - P_2, \qquad (1)$$

90
91 where $P_2 = k_1 \times [SA_{monomer}] \times [H_2SO_4]$ is the dimer production rate due to $SA_{monomer}$-H_2SO_4 collisions, and the
92 collision rate k_1 is assumed to be constant.
93
94 For the dimer concentration we consider the production P_2, the loss due to CS, and the clustering of the SA_{dimer}
95 with H_2SO_4 with a rate constant k_2:
96

$$\frac{d[SA_{dimer}]}{dt} = P_2 - CS \cdot [SA_{dimer}] - k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4], \qquad (2)$$

97
98 And with substituting P_2, eq. 2 for SA_{dimer} changes to:
99

$$\frac{d[SA_{dimer}]}{dt} = k_1 \cdot [SA_{monomer}] \cdot [H_2SO_4] - CS \cdot [SA_{dimer}] - k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4]. \tag{3}$$

100

101 Finally, to produce SA_{trimer} we consider the collision of the SA_{dimer} with H_2SO_4 and the loss to the CS. For the sake

102 of completeness, we would additionally have to consider the loss of $SA_{trimers}$ to form the tetramer $(H_2SO_4)_3 \cdot HSO_4^-$

103 , however this additional term is rather small and will therefore be neglected in this derivation. Therefore, we get

104 the simplified equation for SA_{trimer}:

105

$$\frac{d[SA_{trimer}]}{dt} = k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] - CS \cdot [SA_{trimer}]. \tag{4}$$

106

107 For simplification, we consider a pseudo-steady state condition for both dimers and trimers by setting the left-

108 hand side of eqs. 3 and 4 to be zero, which is justified when the dimer and trimer concentrations change at rates

109 smaller than their overall production and loss rates. Thereby, from eq. (3) we obtain:

110

$$k_1 \cdot [SA_{monomer}] \cdot [H_2SO_4] = CS \cdot [SA_{dimer}] + k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] \tag{5}$$

111

112 and from eq. (4) we obtain:

113

$$k_2 \cdot [SA_{dimer}] \cdot [H_2SO_4] = CS \cdot [SA_{trimer}]. \tag{6}$$

114

115 If we now deploy equation (6) in equation (5) and solve for H_2SO_4, the result is:

116

$$k_1 \cdot [SA_{monomer}] \cdot [H_2SO_4] = CS \cdot [SA_{dimer}] + CS \cdot [SA_{trimer}], \tag{7}$$

$$[H_2SO_4] = \frac{CS \cdot ([SA_{dimer}] + [SA_{trimer}])}{k_1 \cdot [SA_{monomer}]}. \tag{8}$$

117

118 Besides the steady-state assumption, it should be noted that in deriving eq. 8 monomers, dimers and trimers were

119 assumed to have the same loss rate (CS) onto pre-existing aerosol particles. This causes an additional, yet minor,

120 uncertainty in estimated H_2SO_4 concentrations, as such loss rates are dependent on the size/mass of the clusters

121 (e.g. Lehtinen et al., 2007).

122

123 From equation 8 we also see that the concentration of H_2SO_4 is proportional to relative concentrations of sulfuric

124 acid monomers, dimers and trimers clustered with the bisulphate ion:

125

$$[H_2SO_4] \sim \frac{[SA_{dimer}] + [SA_{trimer}]}{[SA_{monomer}]} \tag{9}$$

126

127 To estimate the H_2SO_4 concentration with the ion mode APi-TOF, we can therefore use this theoretical approach,

128 in particular Eq. 8. For the collision rate of H_2SO_4 with HSO_4- we use $k_1 = 2 \cdot 10^{-9}$ cm^3 molecule^{-1} s^{-1} as in Lovejoy

129 et al., (2004). The value of CS is calculated based on Kulmala et al., (2012). Even if the CS was unknown due,

130 for example, to the lack of particle measurements, the daytime variability of the H_2SO_4 concentration could still

131 be estimated only by using the relation of the H_2SO_4-containing cluster with HSO_4-, as it is proportional to the

132 H_2SO_4 concentration (see eq. 9).

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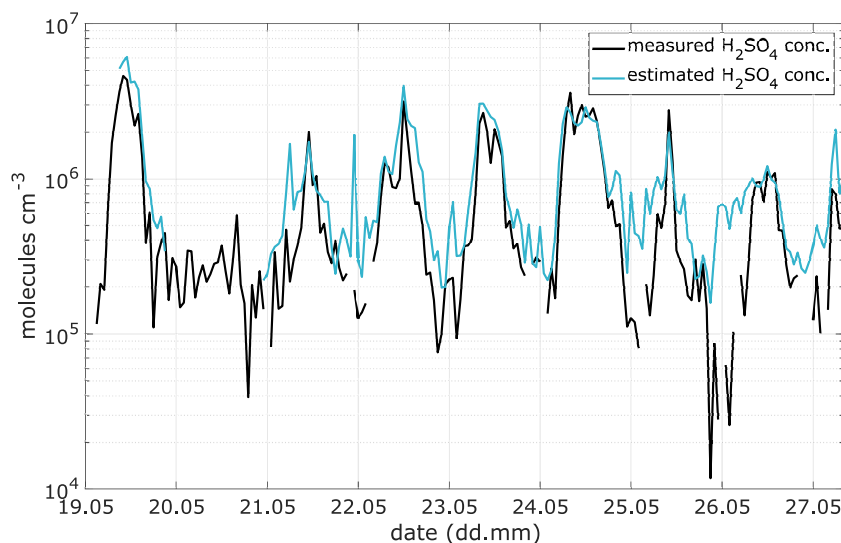

135 **Figure 2** Time series of measured H_2SO_4 concentration from the CI-APi-TOF (black) and estimated H_2SO_4 concentration from

136 the APi-TOF (blue) between 19 and 28 May 2017. The concentration is given in molecules cm^{-3}.

137

138

139 **3 Validation**

140 We tested the expression derived above using a dataset collected during inter-comparison measurements at the

141 SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005). In Fig. 2 we show the time series of estimated

142 and observed H_2SO_4 concentrations, based on APi-TOF measurements together with Eq. 8 and CI-APi-TOF

143 measurements, respectively. The estimated H_2SO_4 concentration agrees well with the measured one during most

144 of the daytime. During night-time, however, the estimated H_2SO_4 concentration seems to be considerably higher

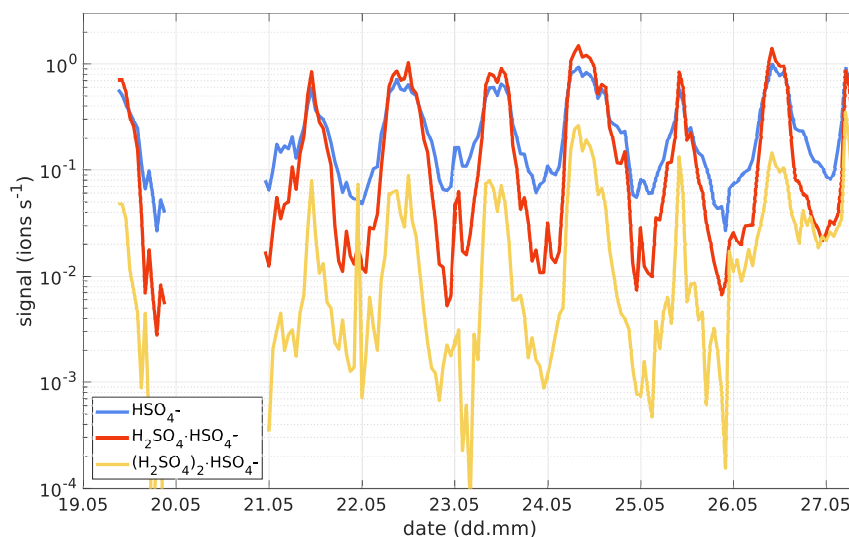
145 than the measured one. This could be because the SA_{dimer} concentration is considerably lower than the $SA_{monomer}$

146 (see Fig. 3).

147

148 The scatter plot in Fig. 4 shows that the estimated H_2SO_4 concentrations agree well with the observed one when

149 the H_2SO_4 concentrations are larger than 2×10^6 cm^{-3}, demonstrating that our method works particularly well

150 during conditions that favour the formation of H_2SO_4-containing clusters.

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152   **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

153   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

154   concentration is given in ions s^{-1} as measured by the APi-TOF.

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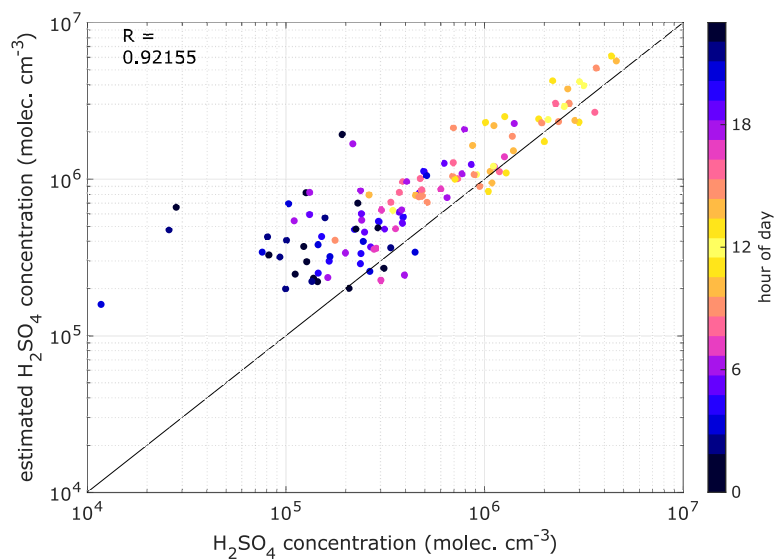
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157   **Figure 4** Measured H$_2$SO$_4$ concentration using a CI-APi-TOF (x-axis) versus estimated H$_2$SO$_4$ concentration based on APi-

158   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

159   local time, the concentrations are agreeing well. The shown data contains the time period from 19 to 28 May 2017. The overall

160   correlation coefficient (Pearson) is 0.92.

161

162

4 Conclusions

Here we derived a theoretical expression to estimate H_2SO_4 concentrations based on APi-TOF measurements of ambient ions. The estimation agrees well with the measured concentration during daytime and with high enough H_2SO_4 concentrations, indicating that the estimation is able to give accurate enough H_2SO_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 H_2SO_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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