



Supplement of

Improved chloride quantification in quadrupole aerosol chemical speciation monitors (Q-ACSMs)

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Figure S1. The change of the chloride concentration to apparent negative concentrations could not be related to changes in meteorological parameters (relative humidity, rainfall, wind speed, wind direction and temperature).



Figure S2. Highly time-resolved signal of (a) m/z 35 and (b) m/z 36 for NaCl under different vaporizer temperatures over a filter cycle (sample (dark grey)/filter (light grey)).



Figure S3. Temporal evolution of (a) *m/z* 35 and (b) *m/z* 36 of KCl under different vaporizer temperatures over a filter cycle (sample (dark grey)/filter (light grey)).

Between 8 January and 15 February 2018, positive chloride concentrations were reported by the instrument using the standard fragmentation table. During this period, we estimate an average error of 26 % when using the standard fragmentation table.



Figure S4. Time series of the chloride concentrations during 8 January and 15 February 2018, based on the original (red) and corrected (green) fragmentation table.

S1 RIE calculation

The RIE calculation is done on the raw signal of the species in amps (not in $\mu g m^{-3}$). There are two ways to calculate the RIEs in the ACSM. They result in the same RIEs, however, we recommend the approach that is first presented here, as it is much cleaner, being solely based on the measured signal and the molar weight of the salts that are used in the calibration.

Approach 1 (recommended)

The RIE_{NH4} is defined as

$$RIE_{NH_{4}} = slope \ of \left(Signal_{NH_{4}} \cdot RIE_{NO_{3}} \cdot MW_{NO_{3}}\right) vs \left(Signal_{NO_{3}} \cdot MW_{NH_{4}}\right)$$
(S1)

The RIE_{NO3} is introduced as the IE calibration is only based on m/z 30 and 46 and not on the total signal of NO₃. Before the calculation of the RIE_Chl' is calculated, the fragmentation table is adapted as described in Section 3.3, so that only frag_HCl is taken into account for the chloride signal. Similarly to RIE_{NH4} then the RIE_Chl' is calculated:

$$RIE_{Chl'} = slope\left(Signal_{Chl'} \cdot RIE_{NH_4} \cdot MW_{NH_4}\right) vs\left(Signal_{NH_4} \cdot MW_{Chl}\right)$$
(S2)

Approach 2

The other possibility is to calculate the RIEs based on a RF for each substance. As this includes CPC concentrations in each step, it is not as clean as the approach mentioned above. Nevertheless, it results in the same RIEs within uncertainties. From the RF calibration with NH_4NO_3 , the RIE_{NH4}, noted here as $RIE_{NH4, NO3}$, is determined:

$$RIE_{NH_4,NO_3} = \frac{RF_{NH_4}}{RF_{NO_3}} \tag{S3}$$

Similarly, the RIE_{NH4, Chl} can be calculated, based on the calibration with NH₄Cl. For this calibration, the updated fragmentation table was used, so that only the frag_HCl signals are taken into account for the determination of the RF_{Chl}.

$$RIE_{NH_4,Chl'} = \frac{RF_{NH_4}}{RF_{Chl'}} \tag{S4}$$

To determine the $RIE_{Chl'}$, which is the ratio of the electron impact ionization efficiency of chloride to the measured ionization efficiency of nitrate on a per unit mass basis, Eq. (S3) and Eq. (S4) are combined:

$$RIE_Chl' = \frac{RIE_{NH_4,NO_3}}{RIE_{NH_4,Chl}}$$
(S5)