

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

Anna K. Tobler¹, Alicja Skiba², Dongyu S. Wang¹, Philip Croteau³, Katarzyna Styszko⁴, Jarosław Nęcki², Urs Baltensperger¹, Jay G. Slowik¹ and André S. H. Prévôt¹

¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

²AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Department of Applied Nuclear Physics, 30-059 Krakow, Poland

³Aerodyne Research, Inc, Billerica, Massachusetts, USA

⁴AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Coal Chemistry and Environmental Sciences, 30-059 Krakow, Poland

Correspondence to: Jay G. Slowik (jay.slowik@psi.ch) and André S.H. Prévôt (andre.prevot@psi.ch)

Author's response to anonymous Referee #1

We thank anonymous Referee #1 for the careful revision and useful comments, which helped improve the quality of the manuscript. The referees' original comments (in *italic*) is followed by the author's answer (in regular typeset). Changes to the manuscript are indicated in **green font**.

The manuscript provides the pathway for chloride quantification in the ACSM measurements. It is very timely and needed paper as, currently, despite the caveats listed in the paper, the Cl quantification is normally taken for granted. The manuscript is very well structured and nicely written, real pleasure to read.

1.1) *However, I have a major concern with the lack of method validation. The corrected Cl data were not compared or validated to anything. Indeed, the signal does become positive after the corrections, however, there is no indication that that positive signal is quantitative. Since it is very important to show that the method works quantitatively, I would strongly suggest including a corrected Cl comparison with an independent measurement. Speciated Cl measurements would be ideal, but might not be readily available, so, at least, Cl an improvement of total volume/mass measured with ACSM and independent instrument/ instruments should be shown. Subject to this validation, I deem this manuscript suitable for the AMT.*

There are no online mass concentrations measured at AGH where the ACSM was installed. However, during a short period of time (15 March to 10 April 2019), an Xact 625i[®] Ambient Metals Monitor was measuring the elemental concentrations in ambient aerosols by X-ray fluorescence next to the ACSM in one hour resolution. The Xact was equipped with an automated alternating PM_{2.5} and PM₁₀ inlet. For the following, we present a comparison of the ACSM measurements and selected PM_{2.5} elemental concentrations.

As presented in Figure R1 a and b, the correlation of the chloride measurements by the ACSM and the Xact noticeably improves (R^2 increases from 0.35 to 0.94) when the proposed correction is applied. As a comparison, similar correlation is observed between the ACSM sulfate measurement and the Xact sulfur measurement. While the difference in absolute concentration likely represent a

general calibration issue from the ACSM or the Xact (i.e. absolute sensitivity), the improved correlation demonstrates that the correction is working very well. Discrepancies between the absolute concentrations between the ACSM and the Xact could be additionally caused by uncertainties in the collection efficiency ACSM (estimated CE = 0.5 according to Middlebrook et al. (2012)) or loss of semi-volatile chloride from Xact during the sampling collection.

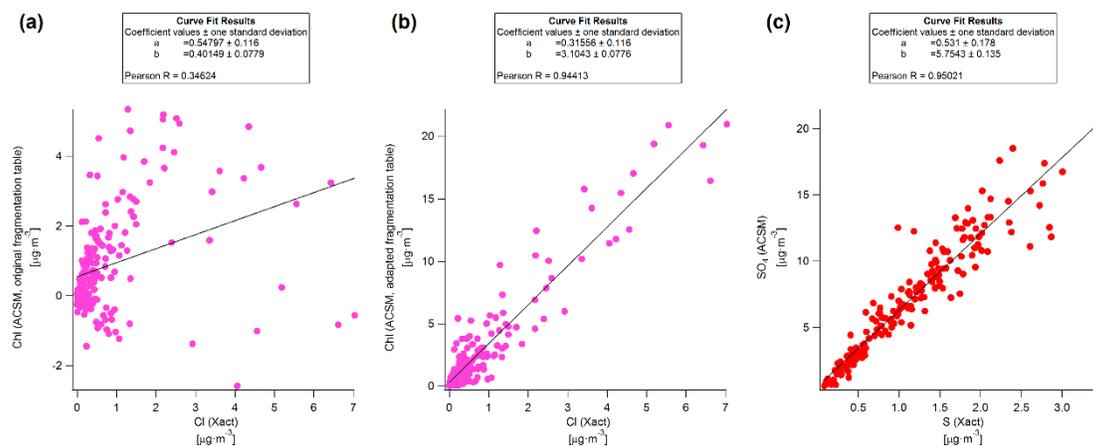


Figure R1. Comparison of the chloride (original fragmentation table (a) and after correction (b)) and sulfate (c) concentrations measured by the ACSM with chloride and sulfur measurements of the Xact, measured between 15 March and 10 April 2019.

1.2) *Another important aspect, but, maybe, not as crucial as the one above, is higher than standard vaporiser temperature for this instrument. Why was this implemented, how does this compare to the standard t-re measurements? There are some indications, that 720C might still be comparable to standard 600C for some m/z, but better discussion around this is required. With some information on why this temperature was selected provided in the methods section as well. Were ambient measurements performed at this temperature as well?*

During the initial setup, the vaporizer voltage was set to 7.7 V in order to reach a vaporizer temperature of 600 °C as read by the thermocouple. In retrospect, the higher than usual voltage required reaching the target temperature likely stem from issues with thermocouple placement or contact with the vaporizer. To ensure data consistency throughout the campaign, the voltage was kept at 7.7 V for the ambient measurements as well as all the calibrations and chloride salt experiments (except when noted otherwise for the temperature dependencies).

The standard vaporizer temperature of 600 °C is chosen as a compromise between efficient vaporization of $(\text{NH}_4)_2\text{SO}_4$ and high ionization efficiency of NH_4NO_3 and organics. This is illustrated in Figure R2, which shows the measured ionization efficiency of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and malonic acid as a function of vaporizer current and temperature. The boxed region denotes the temperature at which the above criteria are optimally balanced. Using a higher temperature for the vaporizer would likely lead to a decreased ionization efficiency for NH_4NO_3 , but this will not bias the measurements because calibrations and ambient measurement were performed under identical instrument conditions. Therefore, the measurements should be comparable to measurements done with a vaporizer temperature of 600 °C.

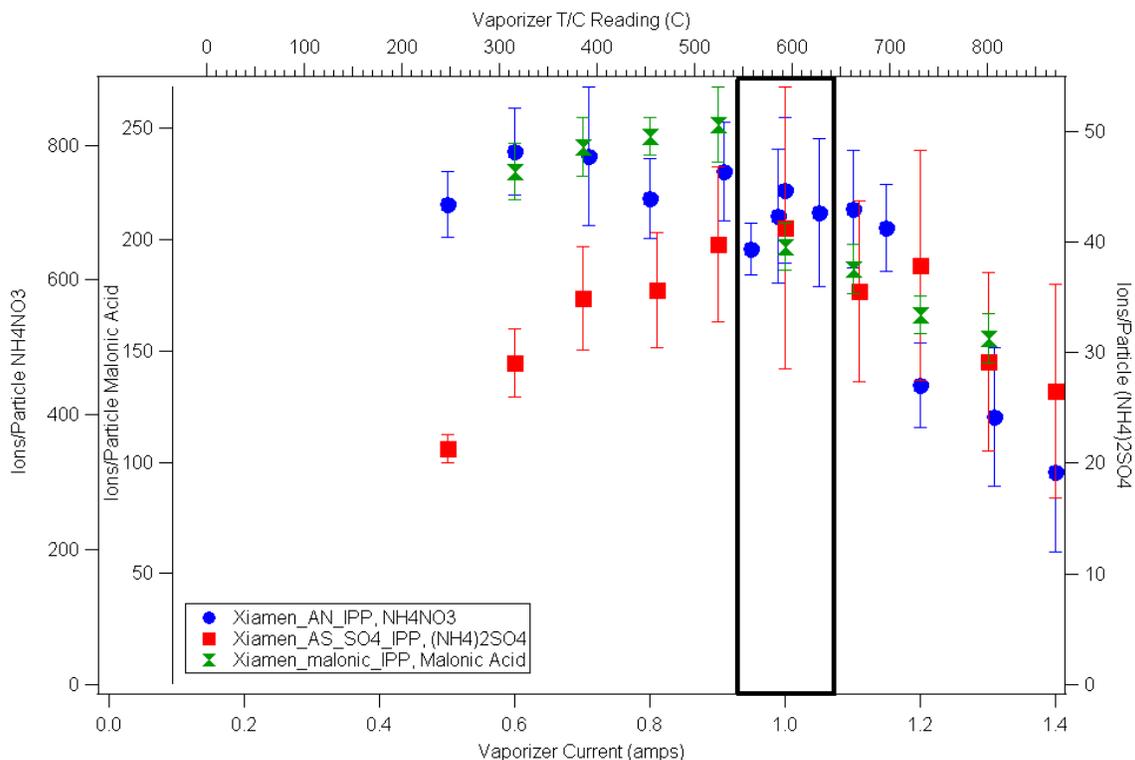


Figure R2. IPP measurements for NH₄NO₃, (NH₄)₂SO₄ and malonic acid to determine the ideal vaporizer temperature (from: 11th AMS Users Meeting, Hyytiälä, Finland, Sept. 4-6, 2010, <http://cires1.colorado.edu/jimenez-group/wiki/index.php/AMSurMtgs>).

For more clarification we added in the manuscript:

line 85: While using a higher temperature for the vaporizer could lead to a decreased response for NH₄NO₃, this will also be reflected in the calibrations as these were done under the same conditions. Therefore, the measurements should be comparable to measurements done with a vaporizer temperature of 600 °C.

1.3) Finally, the assumption that it was indeed NH₄Cl contributing to Cl signal is still not fully convincing. Better discussion on NH₄Cl origins and potential sources in this region is required, also discussing the potential lack of other salts (why other salts are not likely) in the region. Correlation with Na is still significant, why?

As described in the manuscript (line 40), NH₄Cl can form from HCl or particulate chloride. A major source for such emissions are refuse incineration and coal combustion. The most common chloride salts besides NH₄Cl are typically NaCl and KCl, which are characterized in the experiments described in the manuscript. Other chloride salts such as MgCl₂ and CaCl₂ can also be found in the particle phase but are undetectable by ACSM. Typical sources for NaCl can include sea salt. However, the distance to sea is > 480 km, so this source is unlikely to be significant. There is a salt mine southeast of Krakow, which could be a source for coarse-mode chloride. Biomass burning can be a source for KCl, depending on the type of biomass material; however, conversion of KCl to KNO₃ and K₂SO₄ in the atmosphere is also likely (Li et al., 2016).

We added to the manuscript:

line 219: Typical NaCl sources such as sea salt are unlikely (distance to sea > 480 km). The salt mine southeast of Krakow is a potential source of chloride, but only in the coarse mode. Biomass burning

can be a source for KCl, depending on the type of biomass material; however, conversion of KCl to KNO_3 and K_2SO_4 in the atmosphere is likely (Li et al., 2016).

In the manuscript, we present the correlation of m/z 36 with fragments from NaCl (m/z 23 and m/z 58) and KCl (m/z 39 and m/z 74). In addition, we here report the correlation of m/z 23 with the ACSM species. The correlation of chloride with NH_4 is significantly higher than its correlation with m/z 23. Although the correlation of m/z 23 could still be regarded as significant, the highest correlation of this ion is with NH_4 . The correlation with the other species are all rather similar. The observed vaporization time scale of ambient chloride, which is consistent with that of NH_4Cl , suggests that the contribution of ambient NaCl is likely minor.

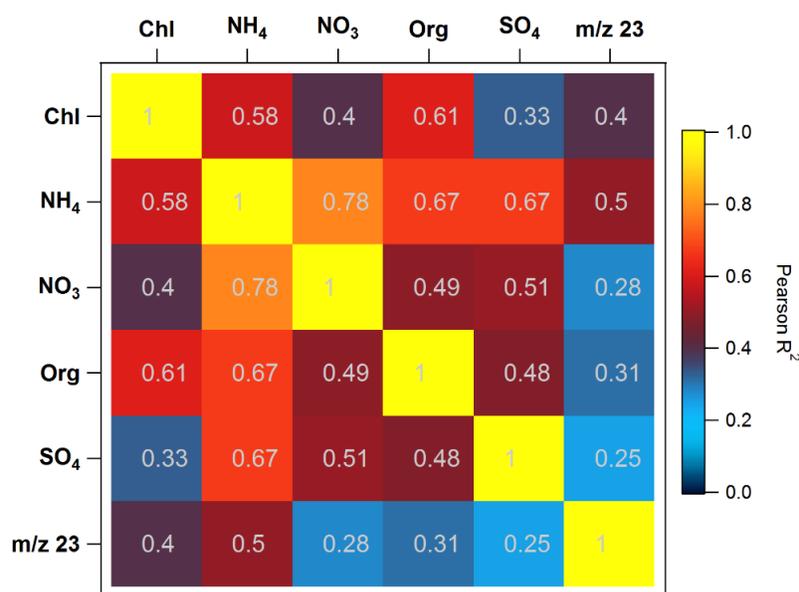


Figure R3. Correlation matrix of m/z 23 and the ACSM species.

1.5) Minor:

Line 79: provide details for salts (sources, purity)

The requested information was added to the manuscript:

line 79: Ammonium chloride (NH_4Cl , $\leq 100\%$, Merck), sodium chloride (NaCl , $\geq 99.5\%$, Fluka) and potassium chloride (KCl , $\geq 99.5\%$, Merck) were separately dissolved in ultrapure water.

line 89: Calibrations were performed with the same setup using aqueous solutions of ammonium nitrate (NH_4NO_3 , $\geq 99.5\%$, Fluka), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, $\geq 99.5\%$, Fluka) and ammonium chloride (NH_4Cl), [...]

Line 82: provide info for drying (type of dryer, humidity after drying, RH stability)

We clarified the information:

Mono-disperse particles with a diameter of 300 nm were generated using a Topas atomizer. Subsequently, the aerosol passed through a silica diffusion gel dryer, a krypton source as a bipolar charger and a custom-made differential mobility analyzer (DMA).

Line 148: 'likely to suppress the m/z 36 signal and enhance the m/z 35 signal' – do you mean background, not diff? specify.

We rephrased for clarity:

Line 148: Regardless of the reactions, any of these multi-step processes would be much more likely to suppress the m/z 36 signal and enhance the m/z 35 signal **in the background**. For example, it can be expected that tungsten oxide chlorides, produced by reaction with the vaporizer, will result in a Cl^+ signal rather than an HCl^+ signal.

Lines 197 *very high (40%) variability of RIE_{Cl} , was that temperature dependent? Discuss it. Also, discuss the exceptionally low RIE_{NH_4} . Was humidity stable during calibrations?*

Although the RIE_{NH_4} is typically between 3 and 6, this is strongly instrument-dependent as shown by Crenn et al. (2015) in the ACSM intercomparison study where they observed values between 3.17 and 14.72 (jump scan). In the second intercomparison campaign (Freney et al., 2019), values between 2.9 and 7.6 (full scan) were reported. Our value ($\text{RIE}_{\text{NH}_4} = 2.43$) are close to the lower end of this and are relatively consistent and stable throughout the campaign. During the calibration the RH was not monitored. However, from independent experiments with the dryer, it can be assumed that the aerosol was well dried.

The RIE_{Chl} is slightly less stable than RIE_{NH_4} and RIE_{SO_4} , however, this likely reflects the lower signal intensity during calibration, as only the HCl signal is taken into account. Since the signal to noise ratio is inherently lower, it makes sense that the RIE_{Chl} is a bit more uncertain. In addition, the value we report includes also a filament switch from filament 1 to filament 2.

Author's response to anonymous Referee #2

We thank anonymous Referee #2 for the careful revision and useful comments, which helped improve the quality of the manuscript. The referees' original comments (in *italic*) is followed by the author's answer (in regular typeset). Changes to the manuscript are indicated in **green font**.

General Comments:

The manuscript by Tobler et al. focused on particulate chloride detection and quantification issues observed for some quadrupole aerosol chemical speciation monitors, which presented an approach to correcting the chloride concentration. This is an important and necessary work, which can be applied for measurements in environment where chloride is dominated by NH_4Cl . Overall the paper is well written. I recommend acceptance for publication on AMT after minor revisions.

Specific comments:

2.1) *What is the reason for setting the voltage to 7.7 V (line 83, 84)? Please elaborate it.* A similar question was raised by Referee #1.

The original setting of 7.7 V was due to miscommunication at the beginning of the campaign and was retained after the issue was discovered to maintain data consistency. It is unlikely to significantly affect the results presented here, as discussed in response to comment 1.2.

2.2) Please consider placing the high resolution peak fit of m/z 23, 39, 58 and 74 (line 208-215) in the supplementary.

As described in the manuscript, interferences with organics are possible and highly likely for m/z 39, 58 and 74. However, all the measurements were done with a Q-ACSM and therefore only UMR data is available.

2.3) Before March 2018, the chloride shows the positive concentration (Fig.2), please compare this with the chloride after recalculation based on fragmentation table adjustments, and elaborate the error margin.

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.

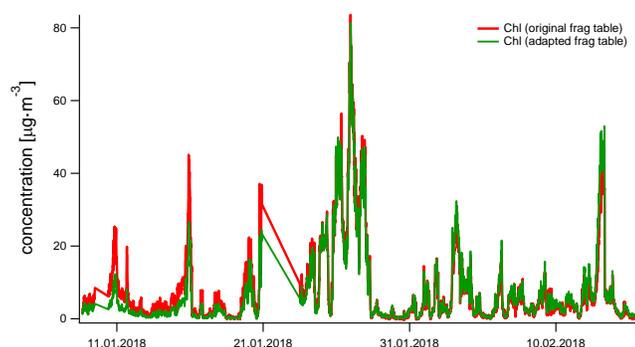


Figure R4. Time series of the chloride concentrations during 8 January and 15 February 2018, based on the original and corrected fragmentation table.

The comparison of the chloride concentrations based on the original and adapted fragmentation table has been added to the supplement, with the following text added to the manuscript:

line 223: An average error of 26 % is estimated using the standard fragmentation table instead of the here proposed correction and calibration for the time between 8 January and 15 February 2018, when positive chloride concentrations were reported with the standard fragmentation table and RIE_{Chl} (Fig. S3).

2.4) I suggest that the sample/filter cycle in Fig.3 and 4 be shaded as an indicator, just like Fig.2.

We agree and we have also updated the corresponding supplementary figures as suggested. The updated plots and legends in the main text are shown below.

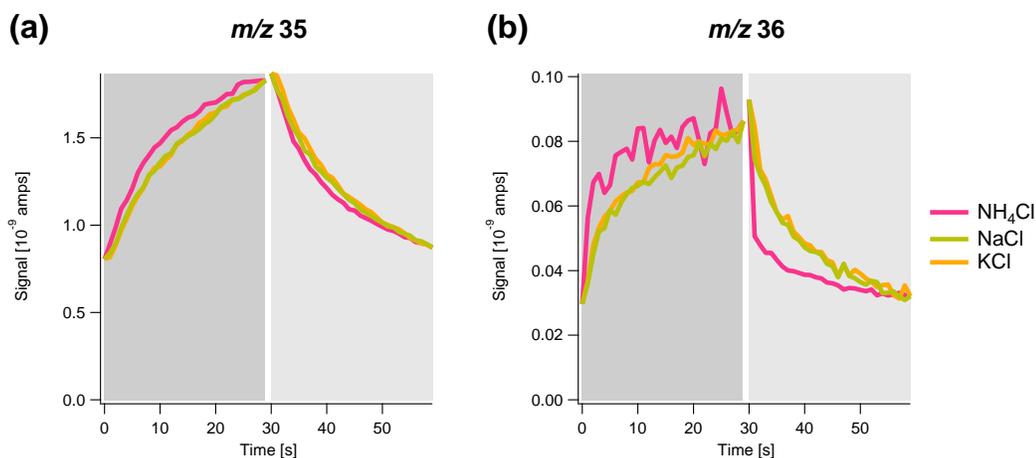


Figure 3. Time series of the signal of (a) m/z 35 and (b) m/z 36 with 1 s resolution over a simulated sample (dark grey)/filter (light grey) cycle for NH_4Cl (pink), NaCl (green) and KCl (orange). The maximum and minimum signals of NaCl and KCl are normalized to the maximum and minimum of NH_4Cl .

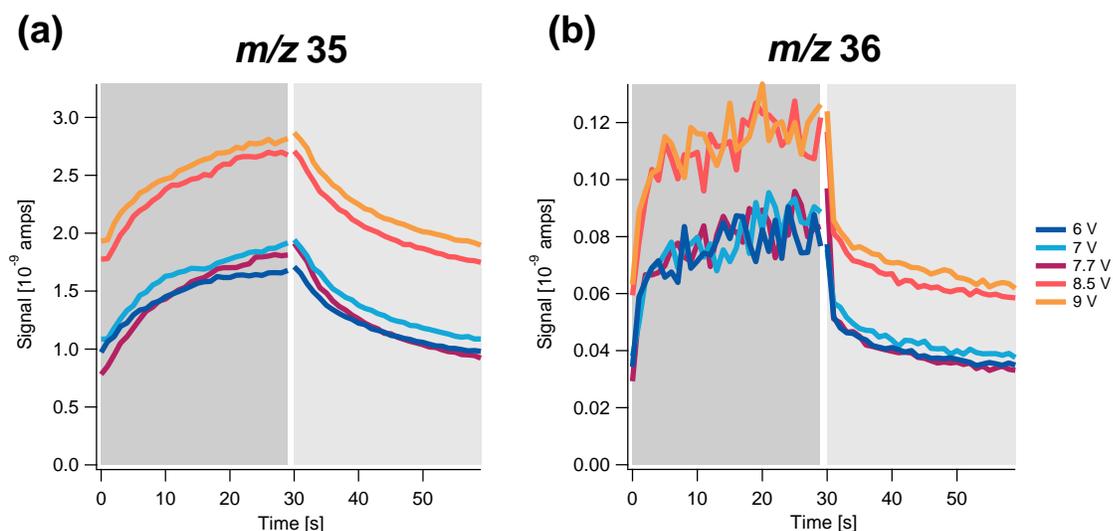


Figure 4. Highly time-resolved signal of (a) m/z 35 and (b) m/z 36 as a function of time at different vaporizer voltages (i.e. temperatures) over a simulated sample (dark grey)/filter (light grey) cycle for NH_4Cl .

Author's response to anonymous Referee #3

We thank anonymous Referee #3 for the careful revision and useful comments, which helped improve the quality of the manuscript. The referees' original comments (in *italic*) is followed by the author's answer (in regular typeset). Changes to the manuscript are indicated in **green font**.

This manuscript describes the presence of a negative chloride signal measured in the widely used aerosol chemical speciation monitor (ACSM) instrument. This is an issue that has been observed in several instruments and up to now has not been formally addressed. In this work, the authors present long term observations of this artefact and perform additional detailed tests on instrument performance. The authors illustrated that this negative signal is essentially an artefact (stating that no other information regarding

the source of Cl can be extracted), and propose a simple correction to the standard fragmentation table to account for it. Given the widespread use of the ACSM, this type of work is essential to providing homogenous measurements among all operating instruments. This manuscript is well written with clear and concise text and well-presented figures. Although I recommend the manuscript for publication, I have some questions and comments below.

3.1) *It is stated in the manuscript that there are a number of uncertainties related to how this artefact manifests itself in different instruments. The authors cite a personal communication whereby changing out the filament removes this artefact. Can the authors provide more information on this; does the artefact return after some time or is this artefact only present in instruments with an iridium filament?*

The Q-ACSM in Romania reported apparent negative chloride concentrations from September 2017 until December 2018, when the iridium filament was replaced with a tungsten filament. Afterwards, apparent negative chloride concentrations were not measured.

We have evidence to believe that this artefact can also be present with tungsten filaments. However, it is more likely with iridium filaments to report apparent negative concentrations while with the tungsten filament we are not aware of reported apparent negative concentrations. As discussed in the manuscript, the m/z 35 signal is impacted by the slow-vaporization behavior also with a tungsten filament and therefore not accurately represented.

3.2) *Was this instrument newly installed at the start of sampling. Could the inversion of Cl be a result of the build-up of material (the total PM concentrations observed during the field campaign are very high)? The appearance of the negative m/z -35 was very sudden, did it correspond to any changes in meteorological conditions?*

The instrument was newly installed at the measurement site in Krakow. However, the instrument has been used in other campaigns before, including the ACSM intercomparisons in 2013 and 2016 as well as in a campaign in Cabauw (NE).

As shown in Fig. 1d in the manuscript, the instrument response changes over time. The instrument history and the current state of the vaporizer clearly influence the magnitude of this outcome. The changed behavior is likely influenced by changes in the surface chemistry of the vaporizer due to Cl exposure (Drewnick et al., 2015). However, the exact mechanism of this not fully clear.

As described in the manuscript, the appearance of apparent negative chloride is due to the slow-vaporizing nature of m/z 35. We could not find indications that a change in meteorological conditions is related to the appearance of apparent negative chloride concentrations (Figure R5). We added the full meteorological data to the supplementary and added to the manuscript:

line 103: *The change to apparent negative concentrations cannot be related to a change in meteorological conditions (Fig. S1).*

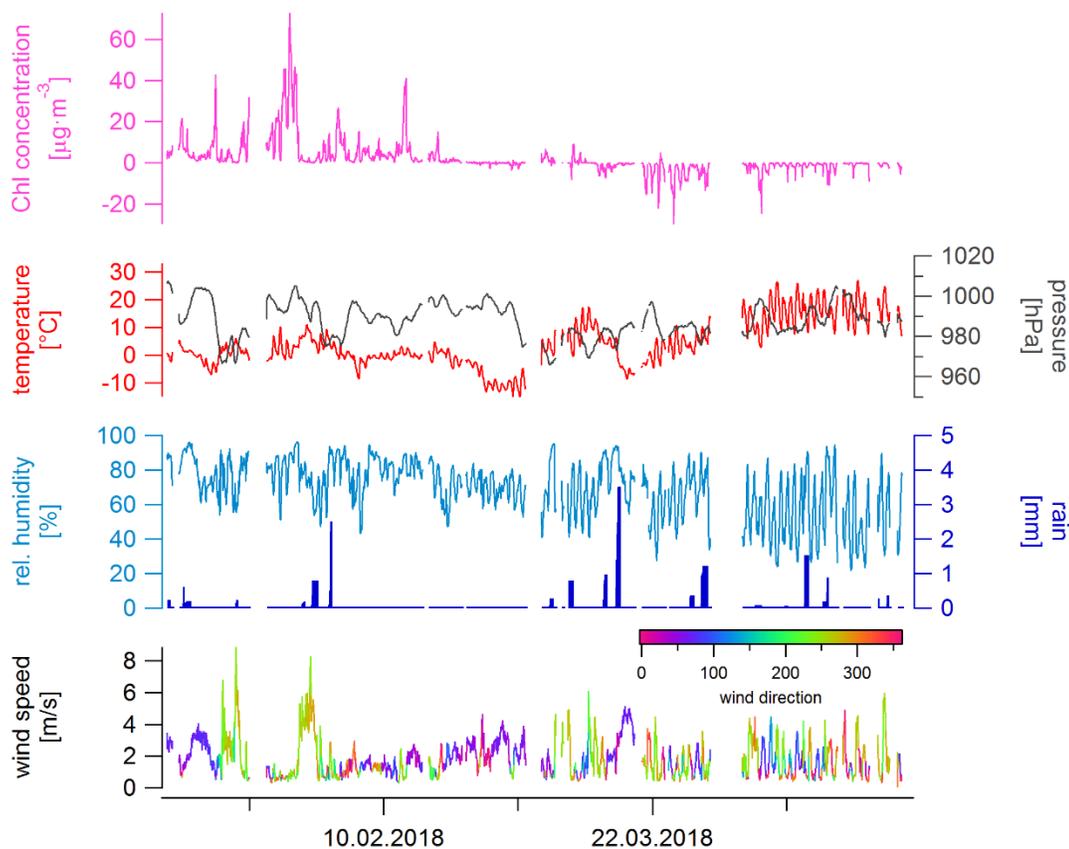


Figure R5. Meteorological data (relative humidity, rainfall, wind speed, wind direction and temperature) does not imply that the apparent negative chloride is related to a change in meteorological parameters.

3.3) *A slow decay and slow build-up (as well as an artefact that disappears when the filament was changed) would suggest that material is built up on the vaporizer and the surrounding area. Was the filament changed (in this instrument) after the experiment to investigate this? Do you have an approximate temperature range for your experiments (that correspond to the voltages used)? Were any improvements observed after heating the vaporizer to > 800 C over extended periods of time? Line 110 (Figure 2): Is it possible to change the instrument settings so the sampling periods correspond to the end of the filter and sample run. This would better represent species that slowly build up and slowly decay?*

The ACSM is typically equipped with two filaments of the same type. During the campaign, we switched from filament 1 to filament 2 on 3 January 2019 following the failure of filament 1 . A physical exchange of intact filaments did not take place during or after the campaign. Based on the vaporizer temperature calibration performed by the manufacturer (Aerodyne Research, Inc.) prior to the delivery of the instrument, the experiments presented in the manuscript span a temperature range from 600 °C to 770 °C. When heating the vaporizer to > 800 °C overnight, no significant improvements were observed.

The issue of slow-vaporizing species is not unique to chloride or particular ions; it potentially affects all ions of the measured mass range and is the reason why all instrument calibrations are now performed in full scan mode (i.e., using the same timing scheme as the standard measurement).

The ACSM does allow changing the scan settings to enable for example longer filter/sample periods would be longer, down instead of up scanning, or that a delay after switching between the two modes. However, changing the instrument settings enough to get rid of this issue, this would result in a considerably long waiting time so that the instrument time resolution and signal to noise ratio would be considerably compromised. Therefore, this is not a desirable approach for general use.

- 3.4) *Why is the Chloride (m/z 35) signal in the negative so much larger than in the positive? As is observed in the latter part of 2018 and early 2019. At the very end of the sample period, it appears that the total reported Cl returned positive again, is this the case?*

In general, the signal intensity at m/z 35 is higher compared to m/z 36 (Cl^+ formation is favored over HCl^+), so any negative/underestimation artifacts will also be larger. The reported chloride concentration based on the standard fragmentation table is slightly positive again towards the end of the campaign, as a result of a more dominant m/z 36 compared to m/z 35. However, the signal at m/z 35 never recovers to positive values after the reported negative values in February 2018 and leads to underestimation of total chloride mass when the original fragmentation table is applied.

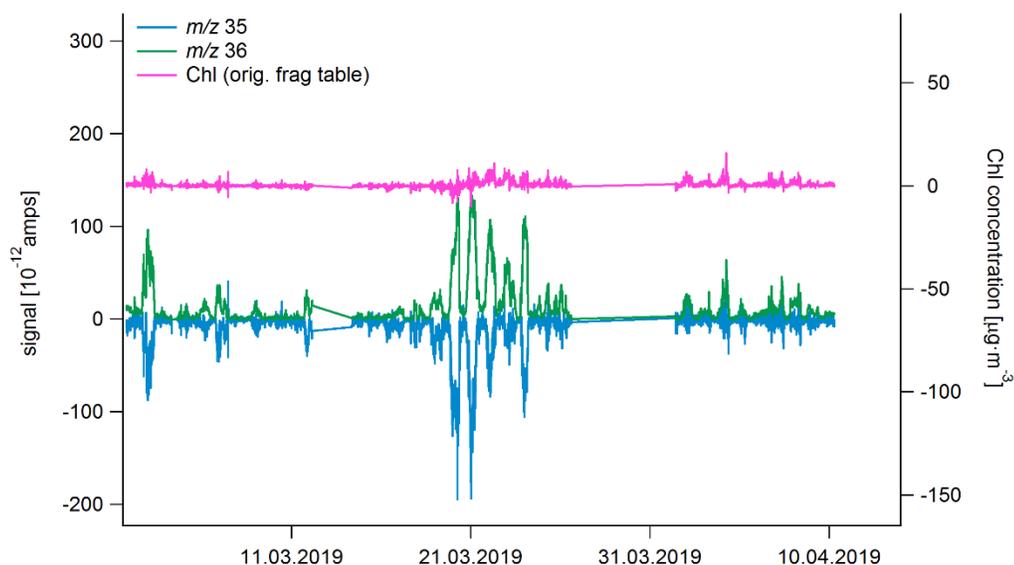


Figure R6. Signal of m/z 35 and m/z 36, together with the reported chloride concentrations (original fragmentation table) towards the end of the campaign. The signal at m/z 35 is still negative and can lead to significant underestimation of the total chloride mass when included in its calculation.

- 3.5) *During the 14 month sampling period what other instruments were sampling along- side the ACSM, e.g. number and size distribution, filter measurements etc. Were any complementary measurements of refractory species made during this time.*

There are only very limited external measurements available throughout the campaign. There are additional measurements of eBC measured by the aethalometer AE33. Although this instrument should automatically compensate for loading effects, there are some issues with it during high pollution episodes. Additionally, elemental concentrations measured by an Xact 625i[®] Ambient Metals Monitor are available for a limited time (15 March to 10 April 2019).

3.6) How did the measured ACSM total mass compare with the total mass measured by the SMPS (if present) during these sample periods (excluding the negative chloride peaks periods)? Are there indicators of the presence of refractory species during this time.

The ACSM measurements were accompanied by eBC measurements using an aethalometer AE33 and from 15 March to 10 April 2019, an Xact 6251[®] Ambient Metals Monitor was measuring the elemental concentrations in ambient aerosols by X-ray fluorescence next to the ACSM. A comparison of two ACSM species and Xact metals is shown in response to comment 1.1).

3.7) Line 213: were any correlations observed between m/z 35 and Na^+ (m/z 23) and or K^+ (39)?, could these peaks also have interference with species other than NaCl^+ and KCl^+ ? When the correction is applied, is all the NH_4 measured accounted for by that predicted from Cl^- , NO_3^- , and SO_4^{2-} (in the form of NH_4Cl , NH_4NO_3 , and $(\text{NH}_4)_2\text{SO}_4$ respectively).

Little correlation between m/z 35 and Na^+ (m/z 23) and or K^+ (m/z 39) can be observed ($R^2 = 0.04$ and 0.16 , respectively). Typical HR-AMS measurements show no interferences at m/z 23, whereas interferences by C_3H_3^+ at m/z 39 can be expected (line 209 in the manuscript), with the possible addition of C_2HN^+ , though these interferences cannot be characterized with UMR ACSM measurements.

Overall, the aerosol is mostly neutralized. The following plot shows the measured NH_4 versus the predicted NH_4 , assuming NH_4 is fully neutralized by Cl^- , NO_3^- and SO_4^{2-} . For the plot, hourly averaged data was used and color-coded by the signal of m/z 35.

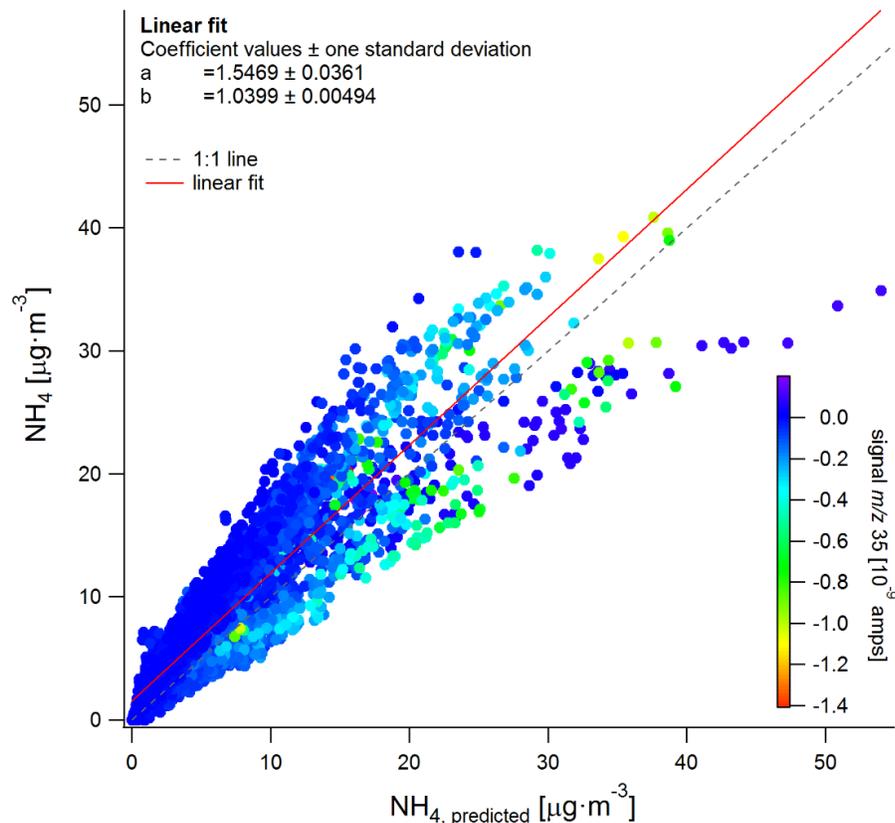


Figure R7. Ion balance for the ACSM measurements (1 hour resolution). The measured NH_4 concentrations are on the y-axis, the predicted NH_4 concentrations ($\text{NH}_{4, \text{pred}} = 18 \times (\text{NO}_3/62 + 2 \times (\text{SO}_4/96) + \text{Chl}/35.45)$) are on the x-axis. The grey line represents the 1:1 and corresponds to the neutralized aerosol. The points are color-coded based on the signal measured at m/z 35.

3.8) *What recommendations should be given to data that is already submitted to data sets (e.g EBAS)?*

As shown in the manuscript, this correction is clearly important for environment with high chloride concentrations that are dominated by NH_4Cl and improves the quantification significantly.

The proposed fragmentation table correction could be applied to any pre-existing dataset to assess qualitatively the trend of chloride. If chloride was included during calibrations, a quantitative estimation of RIE_{Cl} and quantification of chloride mass is possible, assuming stable conditions in the instrument. For a majority of environments, the chloride contribution are likely minor (though this could be in part due to the negative chloride artefact). We expect the proposed correction to have only minor effects on the bulk non-refractory aerosol mass and composition derived from pre-existing data in most datasets, but strongly encourage the inclusion of chloride in future ACSM/AMS calibrations, as well as re-evaluation of chloride signal in existing datasets on an individual basis.

3.9) *Given the described behaviour of the 35 signal is there a general recommendation to apply this correction to all versions of the AMS instrument (AMS, ACSM, ToF ACSM etc)?*

It can be assumed that a similar behavior can also be found for other types of AMS instruments (line 216 onwards). In general, it is recommended to use fast vaporizing species, consistent with Ovadnevaite et al. (2012), where the NaCl^+ ion was suggested as a surrogate for sea salt.

While this presented technique for the chloride quantification could be applied to other versions of the AMS, more characterization of those systems would be needed to for a general assessment. The effect is reduced in the AMS and ToF-ACSM systems because they do not rely on the very slow scanning we use in the Q-ACSM, so their m/z 35 and m/z 36 measurements represent averages over the entire open or closed, sample or filter time rather than a single point in time along the rise/decay curve.

In addition, there are circumstances under which the effect is small enough and instrument performance is good enough, so that the answers are equivalent and there can be a trade-off between using the fast vaporizing species and the signal to noise ratio in the instrument. For instrument that do a chloride calibration, it is possible that they are compensating the behavior of m/z 35 by use of a different RIE, assuming that the instrument conditions are stable throughout the calibration and campaign period.

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¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

²AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Department of Applied Nuclear Physics, 30-059 Krakow, Poland

³Aerodyne Research, Inc, Billerica, Massachusetts, USA

⁴AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Coal Chemistry and Environmental Sciences, 30-059 Krakow, Poland

Correspondence to: Jay G. Slowik (jay.slowik@psi.ch) and André S.H. Prévôt (andre.prevot@psi.ch)

Abstract. Particulate chloride is an important component of fine particulate matter in marine air masses. Recent field studies also report elevated concentrations of gas-phase reactive chlorine species and particulate chloride related to anthropogenic activities. This work focuses on particulate chloride detection and quantification issues observed for some quadrupole aerosol chemical speciation monitors (Q-ACSM), which are designed for long-term measurement of ambient aerosol composition. The ACSM reports particle concentrations based on the difference between measurements of ambient air (sample mode) and particle-free ambient air (filter mode). For our long-term campaign in Krakow, Poland, the Q-ACSM reports apparent negative total chloride concentration for most of the campaign when analyzed with the default fragmentation table. This is the result of the difference signal from m/z 35 ($^{35}\text{Cl}^+$) being negative which dominates over the positive difference signal from m/z 36 (H^{35}Cl^+). Highly time-resolved experiments with NH_4Cl , NaCl and KCl particles show that the signal response of m/z 35 is non-ideal, where the signal builds up and decreases slowly for all three salts, leading to a negative difference measurement. In contrast, the m/z 36 signal exhibits a near step-change response for NH_4Cl during sampling and filter period, resulting in a positive difference signal. The response of m/z 36 for NaCl and KCl is not as prompt as for NH_4Cl but still fast enough to have a positive difference signal. Furthermore, it is shown that this behavior is mostly temperature-independent. Based on these observations, this work presents an approach to correct the chloride concentration time series by adapting the standard fragmentation table coupled with a calibration of NH_4Cl to obtain a relative ionization efficiency (RIE) based on the signal at m/z 36 (H^{35}Cl^+). This correction can be applied for measurements in environments where chloride is dominated by NH_4Cl . Caution should be exercised when other chloride salts dominate the ambient aerosol.

1 Introduction

Aerosols are known to have a significant influence on regional to global climate and visibility (Fuzzi et al., 2015). Furthermore, severe adverse health effects have been linked to aerosol exposure (Pope and Dockery, 2006). Therefore, a better understanding of the aerosol composition is crucial. In recent years, different types of Aerodyne aerosol mass spectrometers (AMS (Jayne et al., 2000)) and aerosol chemical speciation monitors (ACSM (Ng et al., 2011)) have been widely used to quantify the chemical composition of non-refractory (NR) particulate matter (PM) with high time resolution. They allow simultaneous quantification of NR-PM chloride, ammonium, nitrate, organics and sulfate. For many environments, chloride does not significantly contribute to the total mass (Jimenez et al., 2009). Exceptions include coastal regions influenced by marine aerosol masses which are rich in inorganic sea salt (Ovadnevaite et al., 2012) and

polluted inland regions influenced by anthropogenic chloride emissions. Anthropogenic chloride emissions include HCl which then forms NH_4Cl with ammonia (NH_3). Particulate chloride can enable heterogeneous production of ClNO_2 via reactive uptake of N_2O_5 during nighttime, which photolyzes to produce highly reactive chlorine radicals in the daytime (Yang et al., 2018; Le Breton et al., 2018). The chlorine radical undergoes hydrogen-abstraction reactions with hydrocarbons to form HCl which then again forms NH_4Cl (Chang and Allen, 2006). This can lead to exceptionally high chloride concentrations as has been reported for New Delhi by Gani et al. (2019) and Tobler et al. (2020).

ACSMs equipped with a quadrupole mass spectrometer (Q-ACSM, (Ng et al., 2011)) have been used in numerous field campaigns in various environments. The first ambient intercomparison of 13 individual Q-ACSMs, carried out in the vicinity of Paris, revealed good correlation between the Q-ACSMs for all species except chloride. It was not clear if this was due to low concentrations near the detection limit or due to the non-ideal vaporization behavior of chloride, which depends on the specific conditions in the individual instruments (Crenn et al., 2015). During our long-term (> 1 year) measurement campaign in Krakow, Poland, we observed significant apparent negative chloride concentrations, especially during the winter season when aerosol concentrations are high in general. The fragmentation table (Allan et al., 2004) attributes each m/z to one or more of the bulk species, i.e. nitrate, ammonium, sulfate, organics and chloride. By default, the chloride concentration is calculated based on the measured $^{35}\text{Cl}^+$ (m/z 35) and H^{35}Cl^+ (m/z 36) ion signals and the estimated $^{37}\text{Cl}^+$ (m/z 37) and H^{37}Cl^+ (m/z 38) ion signals, calculated based on the natural isotope ratio of chlorine (see Table 1). Measurements with negative signal from either m/z 35 or 36 can therefore result in total negative chloride concentrations. The behavior of some chloride salts in the AMS has been studied. For example Ovadnevaite et al. (2012) demonstrated that sea salt can be quantified by an AMS despite the mostly refractory nature of NaCl. Drewnick et al. (2015) showed that chloride salts appear to be sticky on the vaporizer surface and are only slowly removed. Also, chloride can undergo chemical reactions with the tungsten vaporizer surface resulting in WO_2Cl_2 , among other compounds. Furthermore, they showed that chloride detection suffers from vaporizer memory effects, as demonstrated by the presence of several iron chloride signals when iron nitrate nonahydrate was injected after chloride experiments. For the Q-ACSM, detection and quantification issues for organic chloride have been reported for isoprene-derived secondary organic aerosol (Wang and Hildebrandt Ruiz, 2017). To our knowledge, there are no studies focused on the response of Q-ACSM to inorganic chlorides.

In this study, we are able to attribute the issue of reported negative chloride concentrations in Q-ACSMs to a negative difference signal at m/z 35. We present a highly time-resolved characterization of the Q-ACSM response to three different chloride salts at different vaporizer temperatures. Finally, we propose a calibration procedure coupled with a change in the fragmentation table to improve chloride detection and quantification using the Q-ACSM.

2 Method

The operating principle of the ACSM is described in detail by Ng et al. (2011) and is briefly summarized here. The ACSM alternatively samples directly from ambient air (“sample”) and through a particle filter (“filter”), switching every 30 s. After passing through a 100 μm critical orifice, the submicron particles are focused into a narrow beam by an aerodynamic lens. Non-refractory particles are flash-vaporized upon impact with the standard tungsten vaporizer at ~ 600 °C, where it is assumed that the solid particle is quickly turned into a vapor without undergoing any other processes besides thermal decomposition. For the ACSM used in this study (SN 140-145), an yttriated iridium filament was used to ionize the resulting vapors via electron impact (EI). The ions are detected by a quadrupole residual gas analyzer (RGA, Pfeiffer Vacuum Prisma Plus). The difference of the sample and the filter measurements represents the aerosol mass

spectrum. The obtained mass spectrum typically ranges between m/z 10 and 150 with unit mass resolution (UMR).

Investigations with different high-purity chloride salts were performed. Ammonium chloride (NH_4Cl , $\leq 100\%$, Merck), sodium chloride (NaCl , $\geq 99.5\%$, Fluka) and potassium chloride (KCl , $\geq 99.5\%$, Merck) were separately dissolved in ultrapure water. Mono-disperse particles with a diameter of 300 nm were generated using a Topas atomizer. Subsequently, the aerosol passed through a silica diffusion gel dryer, a krypton source as a bipolar charger and a custom-made differential mobility analyzer (DMA). Mono-disperse particles with a diameter of 300 nm were generated using a Topas atomizer, a krypton source as a bipolar charger and a custom-made differential mobility analyzer (DMA). The particles were simultaneously injected into the ACSM and a condensation particle counter (CPC, TSI model 3022A). The standard vaporizer voltage was set to 7.7 V, corresponding to a vaporizer temperature of 720 °C, throughout the full campaign and was not changed unless otherwise mentioned. While using a higher temperature for the vaporizer could lead to a decreased response for NH_4NO_3 , this will also be reflected in the calibrations as these were done under the same conditions. Therefore, the measurements should be comparable to measurements done with a vaporizer temperature of 600 °C. Calibrations were performed with the same setup using aqueous solutions of ammonium nitrate (NH_4NO_3 , $\geq 99.5\%$, Fluka), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, $\geq 99.5\%$, Fluka) and ammonium chloride (NH_4Cl), following the new recommended calibration procedure, which measures in full scan mode, meaning that the same scanning protocol as during ambient measurements is used during the calibration (Freney et al., 2019).

The presented ambient online measurements were conducted at the AGH University of Science and Technology in Krakow, Poland (50°04' N, 19°55' E) between 8 January 2018 and 10 April 2019. The inlet was installed 2 m above the rooftop of the building and was equipped with a 5 L min⁻¹ PM_{2.5} cyclone (BGI, Mesa Labs, Inc.). The aerosol was dried through a Nafion dryer in the temperature-controlled room before being sampled by the ACSM. The data was recorded with a resolution of 10 min unless specified otherwise. All data were analyzed using ACSM Local 1.6.1.3 (Aerodyne Research Inc.) in Igor 6.37 (Wavemetrics Inc.).

3 Results and discussion

3.1 Observations in ambient measurements

The Q-ACSM was installed at AGH University in Krakow for > 14 months. The time series of chloride and the other NR-PM species are shown in Fig. 1a and 1b. During the first month of the measurements, significant positive chloride concentrations were measured. However, shortly after, the contribution of chloride decreased and, from the end of February 2018 until the end of the campaign, apparent negative chloride concentrations were recorded. The change to apparent negative concentrations cannot be related to a change in meteorological conditions (Fig. S1).

The chloride concentration is calculated based on the m/z 35 ($^{35}\text{Cl}^+$), m/z 36 (H^{35}Cl^+), m/z 37 ($^{37}\text{Cl}^+$), and m/z 38 (H^{37}Cl^+) signals (Table 1). The $^{35}\text{Cl}^+$ and H^{35}Cl^+ are measured, whereas the $^{37}\text{Cl}^+$ and H^{37}Cl^+ signals are calculated based on the natural isotopic ratio of ^{35}Cl to ^{37}Cl and therefore will not be discussed further. While the signal of m/z 36 is positive throughout the full campaign (Fig. 1c), the signal of m/z 35 turns negative in February 2018 (Fig. 1d), which results in an apparent negative concentration of the total chloride signal (Fig. 1b). Similar observations of apparent negative chloride concentrations have been seen in Măgurele, Romania, during long-term field measurements (L. Marmureanu, personal communication).

Under typical operating conditions, the Q-ACSM scans the mass range from m/z 10–150 at a scan rate of 200 ms amu⁻¹, which produces a full mass spectrum roughly every 30 s. To better understand the transient

behavior of m/z 35 and m/z 36, only those two ions were scanned with high time resolution, leading to a signal with 1 s resolution. To simulate the typical ambient ACSM sample/filter switching, the filter was switched every 30 s. Results shown in Fig. 2 explain how the different response times of Cl^+ and HCl^+ result in the apparent negative chloride: While HCl^+ behaves nearly ideally and the signal instantaneously reacts after the filter change, Cl^+ slowly builds up or slowly decays in the 30 s following a filter change. During normal full-spectra scans, the ions are subsequently measured in the quadrupole, meaning that the Cl^+ and HCl^+ signals used to calculate the difference signal are measured approximately 5 s after the filter switch, as indicated by the markers in Fig. 2. Consequently, the difference signal (i.e. “sample” – “filter”) for m/z 36 is positive, whereas the difference signal for m/z 35 is negative under normal operating conditions.

3.2 Behavior of selected chloride salts in the Q-ACSM

The behaviors of the slowly vaporizing Cl^+ and the rapidly vaporizing HCl^+ of three of the most abundant chloride salts in the atmosphere were studied in more detail using NH_4Cl , NaCl and KCl . Similarly to the highly time-resolved targeted m/z measurements for the ambient sample, only m/z 35 and m/z 36 were monitored on a 1 s resolution basis with filter switching every 30 s.

In Fig. 3 the averaged temporal development of the signal in sample and filter mode for each of the three chloride salts is shown. The signals for NaCl and KCl are normalized to the signal of NH_4Cl . There are apparent differences between NH_4Cl and the other two salts, as well as between the m/z 's. The signal for NH_4Cl responds faster after the filter switching, particularly for m/z 36 where a prompt increase and decrease of the signal after the filter switch can be observed. In contrast, the signal of NaCl and KCl evolves much more slowly. This different response time between the salts is also observed for m/z 35, however to a much smaller extent. The observation of the m/z 36 (HCl^+) signal for NaCl and KCl , even though their direct thermal composition products do not include $\text{HCl}(\text{g})$, is probably the result of heat-induced chemical reactions between chloride and background water vapor (Drewnick et al., 2015).

In addition, the behavior of the different chloride salts at different vaporizer voltages (i.e. temperatures) was studied. The relative temporal evolution is mostly independent of the vaporizer temperature for all three salts investigated. The temporal behavior of the signal of NH_4Cl is shown in Fig. 4. Similar to the usual vaporizer temperature of this instrument (7.7 V), the signal at m/z 35 evolves much more slowly than the signal at m/z 36 at all temperatures. Near identical temporal trends are observed for the signal at m/z 36 for vaporizer voltages below 7.7 V. Above this voltage, a jump in the ion baseline intensity is observed. For the signal m/z 35 a similar trend is visible, however, the differences between the signals for vaporizer voltages ≤ 7.7 V are larger. For NaCl and KCl a similar trend is observed (Fig. S24 and S32), where the background signal for NaCl is already starting to build up at 7.7 V. The signal of the background is a combination of several processes that can be expected to be enhanced or suppressed by the higher temperature, including increased flash vaporization of chloride at vaporizer surface, suppressed condensation at/near the vaporizer surface, enhanced re-desorption at/near vaporizer surface, and condensation and re-desorption near the filament. To which extent each of these processes contribute to the jump in the instrument background cannot be decoupled based on the available measurements.

In the AMS (and therefore also in the ACSM), NH_4Cl is expected to undergo thermal decomposition via the reaction $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ (Hu et al., 2017) and references therein). This flash-vaporizing dissociation pathway results in signal at m/z 36 from HCl^+ . However, it is also possible that the particles can remain on the vaporizer or bounce off the vaporizer and land on a nearby, cooler surface, e.g., on the ionization chamber walls, and vaporize at a slower rate. During this process, further chemical reaction may occur, e.g. the vaporizer surface can act as catalyst for reactions with other aerosol components or material on the vaporizer or the vaporizer material itself. For instance, production of different tungsten oxide chlorides are reported for a porous tungsten vaporizer (standard vaporizer) (Drewnick et al., 2015).

Regardless of the reactions, any of these multi-step processes would be much more likely to suppress the m/z 36 signal and enhance the m/z 35 signal in the background. For example, it can be expected that tungsten oxide chlorides, produced by reaction with the vaporizer, will result in a Cl^+ signal rather than an HCl^+ signal.

The quantification of ACSM (and AMS) data relies on the imperfect assumption that all measured particles flash-vaporize on the initial impact with the vaporizer. However, the behavior of some compounds such as ammonium sulfate and certain organic molecules can deviate from that of an ideal non-refractory component (Huffman et al., 2005). The behavior of semi-refractory compounds can strongly depend on the instrument history, vaporizer temperature, instrument tuning, filament material, and the physical alignment of the filament and is therefore hard to predict. The temperature in the ionization chamber is influenced by the vaporizer temperature itself, the filament temperature, and the alignment of those to each other. Nowadays, ACSMs are equipped with tungsten filaments. However, older ACSMs were delivered with yttriated iridium filaments, which is also the case for the ACSM used here for all measurements. There are no direct measurements available to compare the temperature of the ion source between these two systems. However, based on the material properties, the iridium filament is expected to have a lower temperature compared to the tungsten filaments and therefore the iridium filament is expected to have more slow-vaporizing components compared to the tungsten filament. For example, apparent negative chloride concentrations were reported for the Romanian ACSM mentioned earlier when operated with an iridium filament. After changing to a tungsten filament, the total chloride concentration was positive (L. Marmureanu, personal communication). Based on the observations, it is also possible that the capture vaporizer (Hu et al., 2017; Xu et al., 2017) can increase the possibility of negative m/z 35, as there is more collision of $\text{HCl}(\text{g})$ with the hot vaporizer surface which could result in more m/z 35 signal.

Regardless of how consistent the effect is between different Q-ACSMs, the fact that a difference between m/z 35 and m/z 36 regarding the vaporization times can be observed, suggests that the m/z 35 signal should be utilized with caution even when negative difference signals are not detected. Analogous to Ovadnevaite et al. (2012), where the NaCl^+ ion was suggested as a surrogate for sea salt due to its more rapid evaporation, here we recommend to use the HCl^+ ion as the signature for NH_4Cl , as it is the direct product of thermal decomposition and less influenced by secondary, lower-temperature vaporization. It also leads to more consistent results over time as the time-response of Cl^+ at m/z 35 is hard to predict as described above.

3.3 Corrections

The chloride calculation is based on the frag_chloride entry in the fragmentation table (Allan et al., 2004), which is actually a combination of frag_Cl and frag_HCl (Table 1, in black). Our experimental results suggest that the Cl^+ signal originates from slow thermal decomposition of NH_4Cl and biases the calculation of the total chloride concentration. HCl , the thermal decomposition product of NH_4Cl , also fragments into Cl^+ , however, this is calculated based on the HCl^+ signal. Therefore, the Cl^+ signal from frag_Cl should not be used in the calculation and we suggest to adapt the fragmentation table by multiplying the frag_Cl by zero (Table 1, in red). Similar suggestions were made for the quantification of organochlorides (Wang and Hildebrandt Ruiz, 2017).

As described by (Ng et al., 2011), the mass concentration C_s of the species s is calculated from the ion signals I at its mass spectral fragments i , taking into account the molar weight MW_s and the ionization efficiency (IE) of the species, the volumetric sample flow Q_v , Avogadro's number N_A and a conversion factor of 10^{12} :

$$C_s = \frac{10^{12} \cdot MW_s}{IE_s \cdot Q \cdot N_A} \sum_{\text{all } i} I_{s,i} \quad (1)$$

The slower detection electronics of a Q-ACSM do not allow a direct measurement of the IE, but the response factor (RF) of the instrument is related to the IE through Avogadro's number N_A , the molar mass MW , the flow Q_{cat} and the electron multiplier gain G_{cat} :

$$IE_{NO_3} \cdot \frac{N_A}{MW_{NO_3}} = \frac{RF_{NO_3}}{Q_{cat} \cdot G_{cat}} \quad (2)$$

Instead of determining the IE_s for each species, it is more convenient to express the IE_s relative to the IE of NO_3 (IE_{NO_3}) as the so-called relative ionization efficiency (RIE_s) for each species.

$$\frac{IE_s}{MW_s} = RIE_s \cdot \frac{IE_{NO_3}}{MW_{NO_3}} \quad (3)$$

Routinely, the ACSM is calibrated with NH_4NO_3 and $(NH_4)_2SO_4$ to determine the RF_{NO_3} , RIE_{NH_4} and RIE_{SO_4} . Whereas the RF_{NO_3} is based on m/z 30 and 46, the RIE_{NH_4} and RIE_{SO_4} are based on all ion signals of the species. In order to quantify the chloride mass properly, the ACSM is also calibrated with NH_4Cl to determine the RIE_{Chl} '. While the standard RIE_{Chl} is based on all ion signals for chloride assigned in the standard fragmentation table, we firstly adapted the fragmentation table as described above for the calculation of the RIE_{Chl}' , meaning that the RIE_{Chl}' is only based on the ion signals of $frag_{HCl}$ and does not include $frag_{Cl}$. Details on the calculation of the RIEs can be found in the supplement section S1. Five calibrations over the course of 7 months (October 2018 – April 2019) resulted in an average $RIE_{Chl}' = 0.41 \pm 0.17$, $RIE_{NH_4} = 2.43 \pm 0.58$ and $RIE_{SO_4} = 0.38 \pm 0.11$ with $RF_{NO_3} = 4.68 \pm 1.66 \cdot 10^{-11}$ amps ($\mu g m^{-3}$)⁻¹. In general, the calibrated RIE values are lower than the default values commonly used in the ACSM. Notably, the RIE_{Chl}' is significantly lower than the default value of 1.3. The ACSM is recommended to be routinely calibrated not only with NH_4NO_3 but also with $(NH_4)_2SO_4$, because it has been shown that the RIE_{SO_4} value can be quite different from the default value of 1.2 (Budisulistiorini et al., 2014; Crenn et al., 2015; Freney et al., 2019), as it is also the case for this instrument.

The relation of m/z 36 to the total chloride mass depends strongly on the chloride salt present, as discussed in Section 3.2. NH_4Cl exhibits a prompt signal response at m/z 36, whereas the $NaCl$ and KCl signals build up more slowly. It still results in a slightly positive difference signal for those two chloride salts. However, the ratio of m/z 36 to the total chloride mass will be different. Therefore, in the absence of a single dominant cation, quantification should be treated with care due to the effect of the salt-dependent vaporization kinetics on the m/z 36 difference signal.

Comparison of the highly time-resolved chloride salt calibrations with ambient measurements, as well as the correlation of m/z 36 with NH_4^+ ($R^2 = 0.58$), m/z 23 (Na^+ , $R^2 = 0.37$) and m/z 39 (K^+ , $R^2 = 0.13$, though possibly influenced by $C_3H_3^+$ ions) suggest that NH_4Cl was likely the dominant fine chloride species in the ambient aerosol in Krakow, Poland. The correlation of m/z 36 and m/z 58 (potentially $NaCl^+$, $R^2 = 0.71$) and m/z 74 (potentially KCl^+ , $R^2 = 0.79$) is high, though this is likely the result of correlation of m/z 36 with total organics ($R^2 = 0.60$), which could produce ions at the same nominal m/z (e.g. $C_3H_6O^+$, $C_2H_2O_2^+$ and $C_4H_{10}^+$ at m/z 58, and $C_6H_2^+$, $C_3H_6O_2^+$ and $C_4H_{10}O^+$ at m/z 74), which cannot be separated from metal halide ions with UMR data. Typical NaCl sources such as sea salt are unlikely (distance to sea > 480 km). The salt mine southeast of Krakow is a potential source of chloride, but only in the coarse mode. Biomass burning can be a source for KCl, depending on the type of biomass material; however, conversion of KCl to KNO_3 and K_2SO_4 in the atmosphere is likely (Li et al., 2016). Therefore, application of the above described correction of the fragmentation table and calibration should yield accurate quantification of chloride. Fig. 5 shows the corrected chloride time series. An average error of 26 % is estimated using the standard fragmentation table instead of the here proposed correction and calibration for the time between 8 January and 15 February 2018, when positive chloride concentrations were reported with the standard fragmentation table and RIE_{Chl} (Fig. S4).

Time-of-flight instruments like the ToF-ACSM (Fröhlich et al., 2013) and ToF-AMS (Drewnick et al., 2005; DeCarlo et al., 2006) typically do not suffer from negative m/z 35 signal, even though similar vaporizer and ionizer configurations are used, due to the different measurement technique of the detector (no scanning over the full mass range). However, one would expect to measure roughly 0 at m/z 35 since the average value of the sample rise and the filter decay are about equal. Therefore, the calculation methodology presented here can provide more accurate/repeatable quantification regardless of the instrument.

4 Conclusions

Apparent negative chloride concentrations were measured during a long-term campaign in Krakow, Poland resulting from slow vaporization of NH_4Cl at m/z 35, when using the standard ACSM fragmentation table. Highly time-resolved measurements of different chloride salts confirm a different behavior of $^{35}\text{Cl}^+$ (m/z 35) and H^{35}Cl^+ (m/z 36). m/z 36 shows a prompt signal response, whereas m/z 35 responds more slowly which may lead to a negative difference signal for that ion. The extent to which this happens can strongly depend on instrument history, tuning and alignment in the ionizer cage and is hard to predict. Even when an instrument is not apparently affected by negative m/z 35 signal, one should consider using the revised fragmentation table presented here for chloride along with an instrument specific RIE_Ch1' so that the total chloride mass is calculated only based on the m/z 36 signal.

Q-ACSM users should consider modifying the fragmentation table and, when doing so, include NH_4Cl in routine calibrations throughout the campaign. The RIE_Ch1' value of 0.41 presented here should be considered as a guidance and is only valid for this particular instrument. We suggest that routine calibration with NH_4Cl be utilized to determine this value for a particular instrument when better quantification of chloride is desired. Future ACSM intercomparisons will provide an opportunity to study this issue in more detail.

Data availability. The data presented in the text and figures as well as in the supplement will be available upon publication of the final manuscript (<https://zenodo.org>). Additional related data can be made available upon request.

Competing interests. Philip Croteau was employed by Aerodyne Research Inc. when the experiments were conducted. The other authors declare that they have no conflict of interest.

Author contributions. AKT and AS carried out the data collection and the instrument calibration. AKT analyzed the data and wrote the manuscript. ASHP, JGS, JN, KS and UB were involved with the supervision. ASHP, DSW, JGS, PC and UB assisted in the interpretation of the results. All co-authors contributed to the paper discussion and revision.

Acknowledgement. This work was financially supported by the EU Horizon 2020 Framework Programme via the ERA-PLANET project SMURBS (grant agreement no. 689443) and the COST action CA16109

Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoLs COLOSSAL grant. JGS acknowledges support from the Swiss National Science Foundation (starting grant BSSGIO_155846).

We sincerely thank Leah R. Williams, Manjula R. Canagaratna and John T. Jayne for the discussion about technical details of the instrument and the agreement of the presented correction within other Aerodyne mass spectrometers.

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Table 1. The original fragmentation table (black) is a combination of the frag_Cl and frag_HCl. Because of the non-ideal behavior of m/z 35, it is recommended to adapt (red) the fragmentation table for chloride, so that it is only based on frag_HCl.

m/z	frag_chloride	frag_Cl	frag_HCl
35	frag_HCl[35], 0* frag_Cl[35]	35,-frag_HCl[35]	0.231*frag_HCl[36]
36	frag_HCl[36]		36,-frag_air[36]
37	frag_HCl[37], 0* frag_Cl[37]	0.323*frag_Cl[35]	0.323*frag_HCl[35]
38	frag_HCl[38]		0.323*frag_HCl[36]

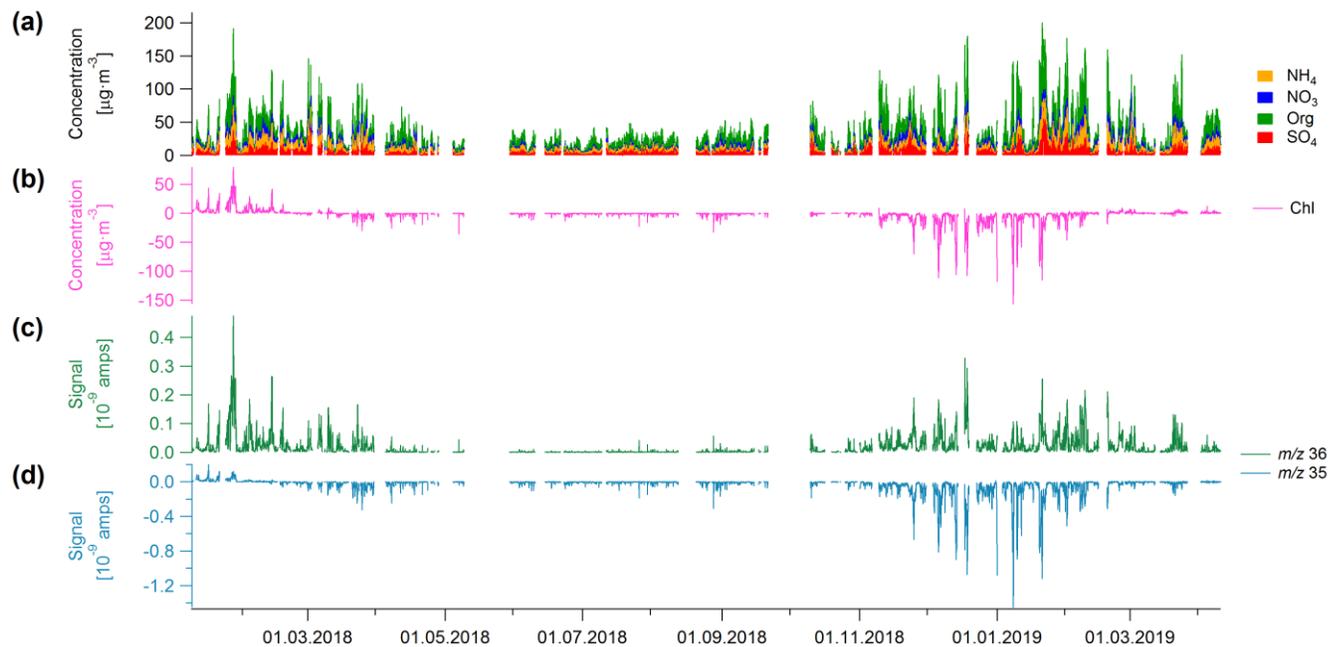


Figure 1. (a) Stacked time series of NH_4 , NO_3 , Org and SO_4 and (b) time series of chloride in $\mu\text{g}\cdot\text{m}^{-3}$. Panels (c) and (d) show the time series of m/z 35 and m/z 36 in amps, respectively. The negative chloride signal is driven by the negative m/z 35 signal.

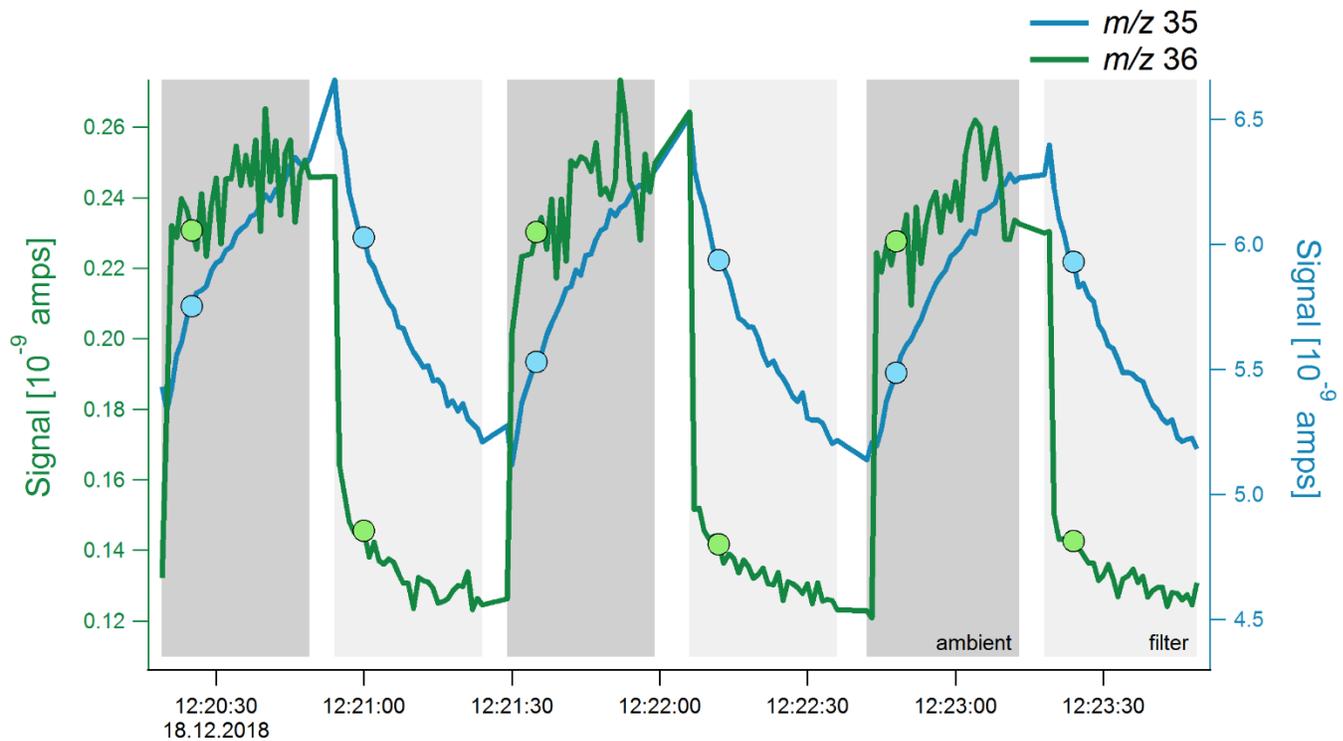


Figure 2. High-resolution time series (1 Hz) of the total ambient signal at m/z 35 (blue) and m/z 36 (green) signal. The filter was switched every 30 s to simulate normal measurements, the filter and ambient mode are indicated by the different shades of grey. The dots mark the time at which these m/z 's are scanned in the quadrupole during normal measurements, which is typically around 5 s after the filter switch.

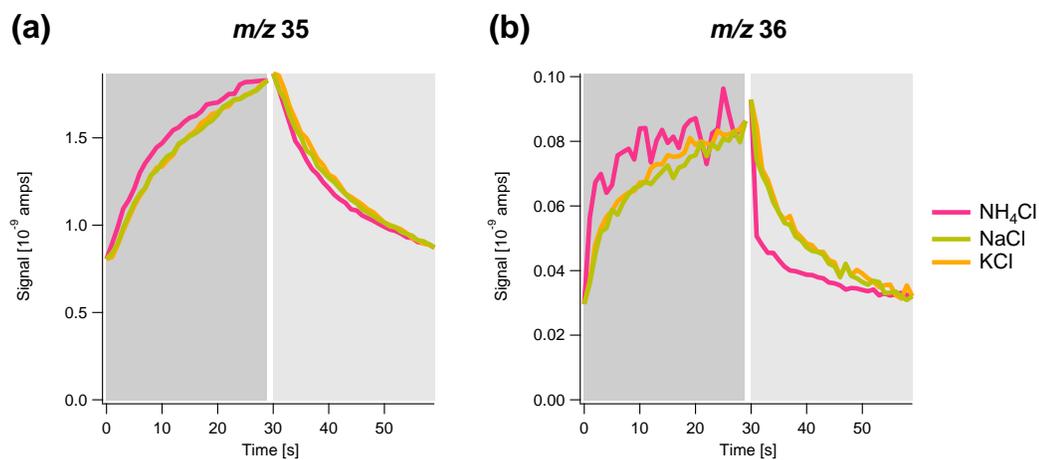


Figure 3. The signal of NaCl and KCl are normalized to the one of NH₄Cl. Time series of the signal of (a) m/z 35 and (b) m/z 36 with 1 s resolution over a simulated sample (dark grey)/filter (light grey) cycle for NH₄Cl (pink), NaCl (green) and KCl (orange). The maximum and minimum signals of NaCl and KCl are normalized to the maximum and minimum of NH₄Cl. Time series of the signal of (a) m/z 35 and (b) m/z 36 with 1 s resolution over a simulated sample/filter cycle for NH₄Cl (pink), NaCl (green) and KCl (orange).

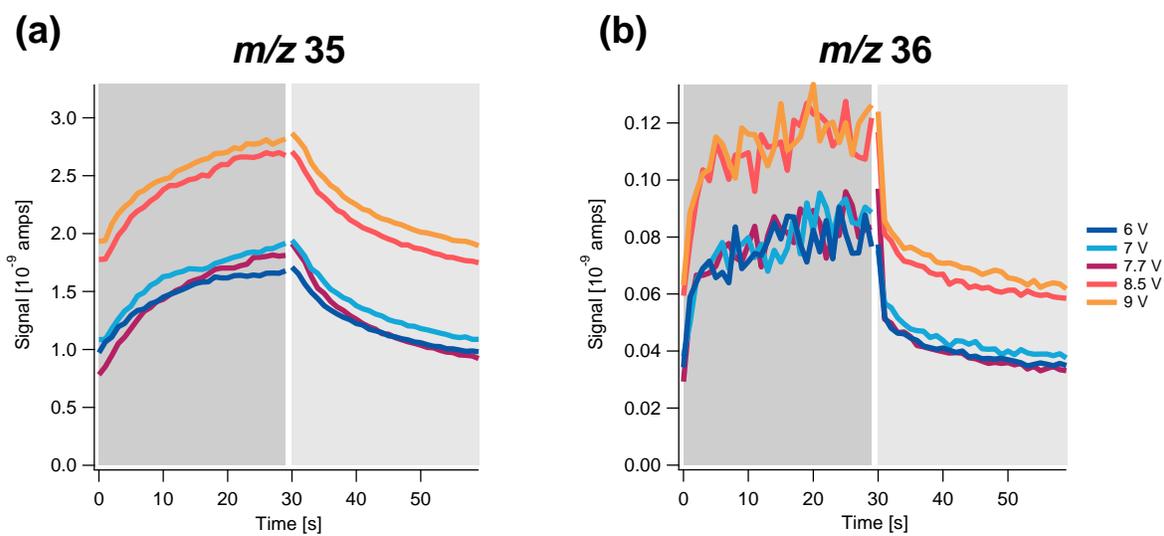


Figure 4. Highly time-resolved signal of (a) m/z 35 and (b) m/z 36 as a function of time at different vaporizer voltages (i.e. temperatures) over a simulated sample (dark grey)/filter (light grey) cycle for NH_4Cl .

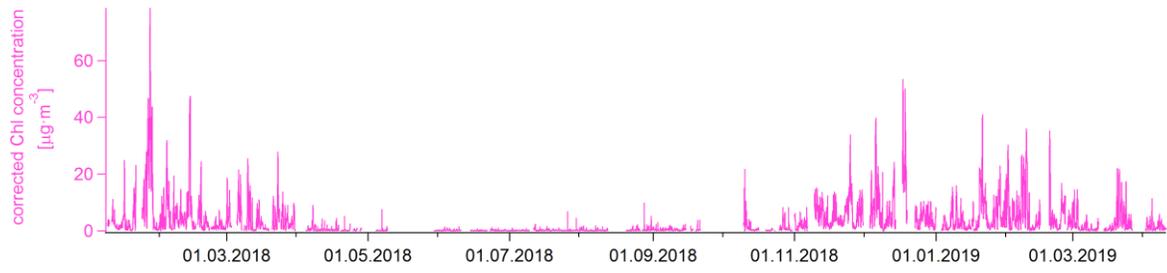


Figure 5. Time series of chloride after recalculation based on fragmentation table adjustments and RIE_Ch1' derived from NH₄Cl calibration.