

# Implications of inorganic salt interferences on Aerodyne AMS and ACSM organic aerosol composition studies.

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The Aerodyne aerosol mass spectrometer (De Carlo et al., 2006) and aerosol chemical speciation monitor (Ng et al., 2011) have significantly advanced real-time measurements of the non-refractory aerosol particle composition, including organic aerosol (OA), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ). The mass spectral fingerprints are widely used to determine OA elemental composition and oxidation state, and to quantify OA sources. The  $\text{CO}_2^+$  fragment is among the most important measurement for such analyses. Here we assess the effect of inorganic matrices on measured OA mass spectra. We focus on the  $\text{CO}_2^+$  fragment signal, and the impact that inorganic salts can have on the determination of OA mass and degree of oxidation.

We examined six HR-ToF-AMS, one compact-ToF-AMS and one Q-ACSM, all equipped with inverted cone-shaped porous tungsten vaporizers, and find, that the mass spectra of pure  $\text{NH}_4\text{NO}_3$  particles contain in addition to the peaks expected from  $\text{NH}_4\text{NO}_3$  also  $\text{CO}_2^+$  at nominal *mass-to-charge* ( $m/z$ ) 44 (Fig. 1). We relate this to reaction of  $\text{HNO}_3$  and  $\text{NO}_2$  with pre-deposited carbonaceous material on the instrument's vaporizer. The  $\text{CO}_2^+$  signal scales proportionally with the nitrate signal. We derive a median  $\text{CO}_2^+$  interference signal of +3.4% relative to nitrate ( $P_{10-90} = +0.4$  to +10.2%) from 29 experiments on 8 instruments. Other nitrate salts, such as  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  show 2-10 times enhanced interference compared to that of  $\text{NH}_4\text{NO}_3$ , while the  $(\text{NH}_4)_2\text{SO}_4$  induced interference is 3-10 times lower. The interference, expressed as the linear relationship,  $k$ , between  $\text{CO}_2^+$  and the nitrate signal is independent of the salt concentration, particle diameter and mixing with OA, but varies on a given instrument with time due to vaporizer memory effects. The  $\text{CO}_2^+$  interference is affecting the calculated OA mass, mass spectra, molecular oxygen-to-carbon (O:C) ratio and  $f_{44}$ .

A potential bias depends on the status of the vaporizer (memory effects), and the fraction of inorganic salt relative to the total OA mass. The bias will be small for most ambient data sets, as  $\text{NH}_4\text{NO}_3$  fractions are typically low compared to OA, and  $(\text{NH}_4)_2\text{SO}_4$  (globally equal to OA) is less efficient in  $\text{CO}_2$  formation. However, it can become significant in particular environments (chamber experiments with inorganic seed

aerosols or combustion emissions aging), for periods of high inorganic mass fractions, and for specific ambient research questions (e.g. investigating temporal or spatial different aerosol compositions).

For sampling conditions with large biases, data should be corrected by subtracting the interference signal. As it is not constant across different instruments and will also vary over time for a given instrument depending on the level of exposure to aerosol and its composition, careful and frequent determination of the interference are crucial. Previous interpretations of OA oxygen content and related chemical and physical aerosol properties that were made based on simple comparison of  $f_{44}$  and  $f_{43}$  ratios, AMS/ACSM data derived O:C and H:C ratios, as well the interpretation of the AMS/ACSM  $m/z$  44 signal as organic acid-derived, need to be discussed with precaution by taking into account the possible impact of this interference.

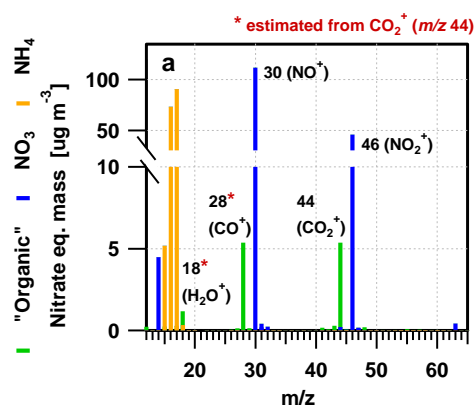


Figure 1. Mass spectrum from pure  $\text{NH}_4\text{NO}_3$  particles.  $m/z$  44 is  $\text{CO}_2^+$  generated from pre-deposited carbonaceous material.  $m/z$  28 and  $m/z$  18 are estimated from  $m/z$  44 using standard data processing assumptions.

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Ng N. L., et al. (2011) *An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol*. Aerosol Sci. Technol. 45, (7), 770-784.