

Interactive comment on “Observation of new particle formation and measurement of sulfuric acid, ammonia, amines and highly oxidized molecules using nitrate CI-API-TOF at a rural site in central Germany” by Andreas Kürten et al.

Anonymous Referee #2

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Summary: The motivation for this publication was to use concurrent ambient measurements of ultrafine particles and gaseous precursors to particle formation as evidence to investigate the hypothesis that different gaseous species are more important than others for forming particles at this measurement site. Another important feature of this publication included the investigation of nitrate CIMS as a novel method for measuring ammonia, amines and iodine-containing compounds. Analysis of the variability of mechanisms controlling new particle formation in different areas where the chemical composition of the lower atmosphere is influenced heavily by unique emission sources, such as feedlots, is a pursuit with high scientific merit. The authors attempt to analyze

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how different sources could be contributing to NPF well by exploiting the capabilities of the nitrate CIMS technique and considering contributions of HOMs to NPF potentially sourced from a local mixed forest. This manuscript is recommended for publication. Included are general comments, technical suggested corrections, and recommendations for improvements of analysis and the method of measurement for future studies.

Comments on analysis and suggestions for improvement:

One of the things that is pointed out in the introduction is that new measurement techniques for amines have appeared over the past few years and it is unclear how spatially variable amines are because it is uncertain how well these techniques actually, quantitatively, measure amines. I think future studies should include a more rigorous approach at an attempt to calibrate this technique to different amines. Attempts at a rigorous calibration of amines for this technique would help to understand, with greater confidence, the spatial variability in concentrations amines around the area of study in this publication, as well as, set a higher standard for measurement of these species by other users of this nitrate CIMS technique. A more rigorous approach to calibration would help advance the understanding of the abundance of atmospheric amines globally, in addition to advancing the understanding of how significant of a role atmospheric amines play in NPF.

Line 154 It would be helpful to add in chemical equations describing the ionization reactions thought to dominate ionization chemistry using the nitrate CIMS technique that are additions to the descriptions on line 154.

Line 170 “while assuming the same ionization efficiency as for sulfuric acid, which has been argued to be a valid assumption” . . . In the supplemental, or appendix?, of Ehn (2014) the authors present the results of quantum computations of binding energies and calculate theoretical collisional rate constants for ELVOCs that are within the measured error for sulfuric acid. Additionally, they compare these calculated rate constants to the measured rate constant based on the sensitivity of the nitrate CIMS

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measurement to a perfluoroacid. This analysis presented in Ehn (2014), in my opinion, is really good because authentic standards of HOMs are not available. Additionally, because the quantum calculations used structure-activity relationships to derive theoretical dipole moments for some theoretical HOM structures, the results suggesting that clustering of HOMs occurs at the collisional limit only applies to HOMs. It seems one of the primary motivations for the publication of the mass-dependent transmission efficiency study by Heinritzi (2016) was to characterize these effects for HOMs. I believe quantification of amines using nitrate CIMS through direct calibrations would greatly improve the confidence in the measurement technique, and may even help further support previous attempts at quantifying HOMs with this technique if many directly calibrated compounds appear to undergo ionization at the collisional limit. The importance of direct calibrations is further underscored through the authors suggestion that the nitrate CIMS technique may be particularly less sensitive to ammonia than other compounds they are able to measure.

Line 296 An argument is made here that a simpler model can be used to estimate sulfuric acid concentration because the results from this model consistently agree with the results from a more detailed model, which includes RH and CS as variables, within a factor of three. Mikkonen (2011) also points out the minor dependence of the approximated sulfuric acid concentrations on CS. The authors suggest a simplified equation in the conclusions which is only dependent on radiation, the rate constant, and SO₂ mixing ratio if particle data is not available. I would argue that if a modeled approximation, and not a measurement, is being used to represent data then it should be treated as rigorously as possible. Including the RH and CS as sinks for SO₂, even if they contribute in minor ways, I think is important when forming this approximation, if the data is available. To constrain the approximated data by a factor of three, I think, is a worthwhile action that the authors of the current manuscript took when using the detailed sulfuric acid approximation equation.

The discussion section provides some constructive suggestions for improving future

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measurements!

Technical suggestions: **Suggestions for technical corrections ARE IN ALL CAPS

Line 25 "WE DEMONSTRATE HERE that the nitrate CI-API-TOF is suitable for sensitive measurements. . ."

Line 114 "...the site is not too far away 114 from the University of Frankfurt, which allowed US to visit the station for instrument maintenance" . . . That sentence either needs to be modified or changed by the above suggestion because right now, grammatically, it doesn't make any sense.

Line 121 "As mentioned in the introduction, livestock ARE known to emit a variety of amines as well as ammonia. . ."

Line 303 . . . Please make an explicit statement of the reasons that it was useful to estimate the OH radical concentration as the introduction to this section. This would help to disambiguate the meaning of "further data evaluation", but also help guide, and preview to, the reader to the logic of what the authors saw as the ultimate purpose of doing analyses using estimated OH radical concentrations. This should be a quick and easy modification.

Line 309 . . . Please explicitly define the quantity [OH]day. Adding the "day" notation to this quantity makes the exact meaning confusing. I believe this quantity just refers to the steady-state approximated concentration of OH radicals at some time that it is calculated. A similar quantity, OHday, is used in the PAM/OFR literature to refer to an estimate of the day-averaged expected OH exposure.

Line 339 . . . "by tentatively adopting the same calibration constant for iodic acid AS sulfuric acid"

Line 367 . . . I believe the idea reported by the authors that "iodic acid (and, if present, probably also its clusters) can be detected with high sensitivity due to the high negative mass defect of the iodine atom" is inaccurate. Sensitivity is formally defined as

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the change in instrument response with respect to a change in some amount of analyte. The sensitivity of the CIMS measurement to any compound is a function of the ionization chemistry and ion transmission through the instrument. What the authors are describing here is the one of the reasons why iodide ionization is valued as an ionization method in CIMS measurements. The high negative mass defect of iodine produces a characteristic pattern of appearance in the mass spectrum which is useful when trying to unambiguously identify peaks when performing high resolution peak fitting, but this feature doesn't have any reflection on the sensitivity of this particular CIMS measurement to iodic acid. If the authors are measuring the concentrations of iodic acid that they estimate to be measuring then nitrate CIMS is probably particularly sensitive to some iodine compounds, but the logic reported on line 367, I believe, is misleading.

Line 375 . . . "the same calibration constant for iodic acid AS sulfuric acid"

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