Response to John Crounse review of:
"Calibration of Hydroxyacetonitrile ($HOCH_2CN$) and Methyl isocyanate (CH_3NCO) Isomers using I^- Chemical Ionization Mass Spectrometry (CIMS)", Finewax, Chattopadhyay, Neuman, Roberts, and Burkholder
Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2024-94, 2024

The authors thank the reviewer for their careful reading and constructive comments regarding our manuscript.

Reviewer Comment:
The authors should modify the strong, confrontational language used in abstract, introduction and conclusion where they apply results from this work to reports of previous measurements. Such statements may be hard to prove, and serve no good end. Statements including modifiers such as 'likely', 'may have', and 'it may be' should suffice to convey the authors' point.

Author Response:
The use of "contradict" in the abstract was a concern in the Farmer review as well and the text will be modified as outlined in that review response. It was not our intention to diminish the research reported in previous field studies, but to identify and clarify the error in MIC identification using I-CIMS detection. Our work is definitive regarding the identification of MIC. We are careful to say that the C2H3NO I-CIMS signal is most likely due to HAN, but we are not definitive on this point.

Action to be taken:
In addition to the revisions outlined in the Farmer review response, we will revise the conclusion text "Our work indicates that HAN is commonly present in the troposphere." As follows "Our work indicates that HAN is likely to be ~~commonly~~ present in the troposphere.".

Reviewer Comment:
Are there other stable isomers having formula C2H3NCO besides the two discussed in this paper? If so, authors should discuss the likelihood that these could contribute to ambient CIMS signals. Are there other 'nearby' isobars (ie, different atomic composition), considering the resolution of spectrometers in question, which could contribute to signal with nominal mass of C2H3NCO clusters?

Author Response:
We assume that the reviewer means the formula C2H3NO. There are other compounds with this chemical formula, e.g., N-methyleneformamide is a candidate. N-methyleneformamide, however, does not contain the necessary acidic or polar H that would likely be required for detection by I-CIMS. We are careful in the manuscript to say that HAN is the likely compound being detected, but we can't be definitive.

The HR-ToF I-CIMS mass resolution of 5000 allows for near unamibiguous detection of the C2H3NO chemical formula.

Action to be taken: None

Reviewer Comment:
The IR absorption bands and cross-sections used to quantify CH3NCO should be included. How stable was this compound in AL cylinders? How do Nr calibration of CH3NCO mixtures in AL bottles agree with FTIR determinations?

Author Response:
The infrared absorption spectrum of CH_3NCO (MIC) was reported in a previous study from this laboratory (Papanastasiou, Bernard, and Burkholder: Atmospheric fate of methyl isocyanate, CH_3NCO: OH and Cl reaction kinetics and identification of formyl isocyanate,

HC(O)NCO, Earth Space Chem., 4, 1626-1637, https://doi.org/10.1021/acsearthspacechem.0c00157, 2020.) as cited in the experimental section of our manuscript. The stability of the MIC sample prepared in aluminum cylinders was not tested. The I-CIMS response, however, was tested using both the diluted MIC samples in aluminum cylinders and using the ~3.5% mixture prepared in a 12 L Pyrex bulb and measured by FTIR. The text in the experimental section did not make this clear. N_r calibration of CH_3NCO samples was not part of the present study.

Action to be taken:
The text in section 2.1 "Methyl isocyanate standards were quantitatively added to the calibrated zero air flow sampled by the I-CIMS instruments." was revised as follows: "Methyl isocyanate bulb and aluminum cylinder standards were quantitatively added to the calibrated zero air flow sampled by the I-CIMS instruments.".

Reviewer Comment:
Are there other possible 'N' compounds produced in the syringe pump std method for HOCH2CN? How does the mixing ratio calculated from pumping rate and gas flow compare with Nr determination?

Author Response:
The most likely 'N' compound impurity in the $HOCH_2CN$ (HAN) sample was HCN. CIMS measurements using a diffusion source of the commercial HAN sample showed significant gas-phase HCN signals due to the much higher vapor pressure of HCN than HAN (explained in section 3.2). The infusion source, however, limited the gas-phase HCN concentration to below the CIMS detection level. In section 2.2, we state that the HAN concentration was not determined using pumping and flow rates. Instead the HAN concentration was determined using the N_r method.

Action to be taken: None

Reviewer Comment:
Figure 1: y-axis of Panel B is Nr signal or something else? If Nr, you should keep this label, and state in text explicitly the assumption that 100% (or whatever the assumption is) Nr signal is comprised of HAN.

Author Response:
Panel B y-axis label, [HAN] (ppb), was made by taking the N_r signal concentration to be equivalent to the HAN concentration. The figure caption can be revised to make this clear.

Action to be taken:
The figure caption text "Calibration of HAN concentration as a function of infusion source flow rate." Was revised as follows: "Calibration of HAN concentration, taking the N_r measured concentration, example in panel A, to be equal to the HAN concentration, as a function of infusion source flow rate.".

Reviewer Comment:
Figure 3: How do the authors interpret and deal with the ToF 30C and 35C and Quad 20C curves that seem to be out of family with the other curves, and the mechanism. Are these curves reproducible?

Author Response:
Figure 3 presents results obtained in multipoint calibration measurements performed over the course of this project, i.e., several weeks. The scatter in the data plotted represents the random and systematic errors in the measurement. The data obtained at 30C for the ToF I-CIMS instrument does not appear to cleanly follow the data trend. However, this does not discredit

the dataset. We have proposed a possible interpretation for the data trend in the text following Figure 3.

Action to be taken: None

Reviewer Comment:
LN272-281: This PP should be reformulated. Suggest that if the authors wish to put forward the idea that HAN is observed in the atmosphere it would be more appropriate, straightforward, and convincing, if they present their own data, rather than simply re-assigning previously published by other groups. [reviewer notes that the instrumentation calibrated within this work has been deployed I number of previous field campaigns from aircraft and ground-based platforms, with plenty of biomass burning influence]. In addition, the authors should discuss the more general importance of HOCH2CN to the nitrile budget. What fraction of nitriles does HOCH2CN comprise? Is there reason (and if so what are the reasons) to study its chemistry in more detail?

Author Response:
We understand the eagerness of the reviewer for an in-depth analysis of field measurements and we agree that it is a critically important component of an evaluation of MIC and HAN emissions. A thorough study of a field campaign dataset is, however, beyond the scope of the present work, but should be addressed in future studies. It is self-evident to readers of this journal that knowing the chemistry of an atmospheric trace gas plays a critical role in understanding its impact on the environment and human health, i.e., HAN is a toxic compound.

Action to be taken: None