

Interactive comment on “The airborne mass spectrometer AIMS – Part 2: Measurements of trace gases with stratospheric or tropospheric origin in the UTLS” by T. Jurkat et al.

Anonymous Referee #3

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The manuscript “The airborne mass spectrometer AIMS – Part2: Measurements of trace gases with stratospheric or tropospheric origin in the UTLS” by Jurkat et al. describes a new instrument that performs sensitive in-situ measurements of important trace gases in regions of the atmosphere that are under-sampled and difficult to access. These new measurements will provide valuable insights into UTLS processes. The instrument capabilities are clearly illustrated with results from an instrument flying in the upper troposphere. Considerable effort has been invested in calibrations and characterizing measurement sensitivity. The in-flight calibrations and background determinations are critical diagnostics for achieving accurate measurements, and the in-depth descriptions of these efforts represents a substantial advancement. Though

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the instrument clearly works and provides unique and useful results, there are several aspects of the paper that need to be clarified for these findings to be useful to other researchers. In particular, the instrument duty cycle, time response, background, and precision needs to be better quantified.

The instrument time response is confusing, and this further confuses the interpretation of the results. I recommend making a single section that details the time response for each compound. The abstract states 1 s time resolution, Table 1 uses 1 s for some species and 20 s for others, and section 6.2 characteristic times are listed as 500 s for HNO₃ and 150 s for HCl. The timeseries in figures 5 and 7 do not state the time averaging. Is it 1s, 20s, 500s? I don't understand the precisions listed in Table 1 and I don't think the precision should be represented as a percentage. At low mixing ratios, counting statistics should cause a large fractional imprecision that diminishes with larger mixing ratios. HNO₃ is listed with a 20% precision, but the data shown in Figure 7 look far better than that. On the other hand, if the inlet integrates for 500s, then determining a precision with a 20 s average isn't meaningful. Table 1 should also include a column that lists time response, especially if it varies between compounds.

The background levels are determined several ways and they are discussed qualitatively, but they are never quantified. What are the background levels? Are they the same for all compounds? What is the magnitude and time constant for the exponential decrease in background (pg 13587, line24)? Is this decrease the same for all compounds? Is it the backgrounds that establish the detection limits in Table 1? Given the instrument's high sensitivity, the detection limits could be much better in principle. It would be helpful to understand what determines the detection limit. Nylon wool is used to determine instrument background sometimes. This should remove HNO₃, but will it remove HONO SO₂ and HCl from an airstream? Has this been tested? It isn't clear how the background determinations are used in the data analysis. How is the background subtracted? Do you interpolate between all the backgrounds?

Some of the fundamental properties of the instrument are not detailed adequately. For

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example, what is the mass resolution of the spectrometer (give the FWHM of the mass peaks)? P13578 L 14 notes that peaks separated by 1 amu contribute less than 10% to the adjacent mass. But the results look much better than this. For example, Figure 5 shows HNO₃ (m82) of a couple ppbv, and SO₂ (m83) less 0.04 ppbv. Please give a more specific and accurate description of the mass resolution. Figure 3 could help by showing only from m50-m150.

Please describe the duty cycle. I don't understand how the instrument operates. How much time is spent at each mass? How much time is spent calibrating and zeroing? The paper states that backgrounds are performed hourly, but for how long? Comparisons between CIMS measurements and other measurements that integrate continuously can be complicated by the differing measurement cycles, so this detail is important. Further, it may help explain the detection limits in Table 1.

There are an appropriate number of graphs, and they demonstrate the important points. But they could be made clearer with some simple adjustments.

Figure 1: Instead of using part numbers for the pumps, please give their pumping speed. Or, if the part numbers are important, describe them in the text. Show the important flows at the bypass and into the ion source. What is the flow into the ion source? What is the optional dilution flow used for? Either discuss in text, or remove.

Figure 3: Plot to 1 or 10 Hz – this may give an idea of the instrument background. Why do the 2 peaks at ~M46 increase during a background? If this is unimportant, plot from 5-150.

Figure 4. In a), plot left axis from 0 to 0.1, so the linear relationship between cal and response can be seen more easily.

Figure 5. With log scale, plot to at least the detection limit (0.015), since there should be information there. Alternatively, use linear scale and plot to zero.

Figure 6. Too many panels. I don't think b) is necessary.

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Figure 5 and 7. State time averaging of the data. HNO₃>NO_y at the beginning – is this a problem from measuring at higher water mixing ratios?

Smaller points:

P13568 L15: replace generating a characteristic ionization scheme with “for selective generation of reagent ions”

L16 change permanently to continuously

L25 change “allow to draw” to yields P13569 L18: change is similarly affecting to affects

L20 change in to of

L25 Huey 1998 doesn't describe aircraft measurements. Please choose appropriate reference

P13570 L5-6. I don't understand sentence. Change to “The time resolution and accuracy of CIMS can be sufficient to characterize atmospheric processes from an aircraft platform.

L22 change trace to identify

L24 Neuman 1999 doesn't describe a CIMS instrument. Please choose appropriate reference

P13571, L18 remove while

L24 remove the

P13572 L1 change laid to place

L7 change adhesive molecules to reactive gases

L19 change continues to continuous

L15 what is the inlet temperature?

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L23 change “no stainless. . . is touched” to “all wetted parts are PFA”

L24 what is total inlet flow? How is this measured?

P13573 I2 remove potential, replace characterized by “accounted for”

L13 custom

L14 replace steered with drives

L21 descent

P13574 I24 Are all the ions really detected simultaneously? I think they are more likely detected sequentially. A discussion of the measurement cycle is needed.

P13575 I4 The reduction of the HNO₃ background is an important advancement. The paper should quantify this reduction and compare with published values of instrument backgrounds in order to highlight this improvement.

I11 replace instantly with rapidly

P13576 I5. I don’t understand sentence. Do you mean that sensitivity to HONO is the same as HNO₃? Or within an order of magnitude?

P13577 I3 remove “reducing the reaction efficiency, e.g.”

P13579 I15 I don’t what reservoir tank means.

L21 remove in a defined manner

L23 is nitrogen mass flow controlled?

L24 is pressure in permeation ovens measured? How much does it vary with altitude?

L28 change to “the pressure inside the oven is independent of the inlet pressure”

P13580 I3 You need to know the total inlet flow to determine calibration mixing ratios. What is it?

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L9 what is at 3 bar? Earlier, perm ovens were said to be held at 2 bar. Flow through perm oven isn’t important – instead, give total inlet flow.

L10 remove standardized to. And is this the total HCl concentration, or the concentration for the ³⁵Cl isotope?

L28 Description of calibration is confusing. The point of calibrating is to account for inlet and other losses, and the important parameter is the calibration mixing ratio in the inlet. How does flow through dilution oven and inlet loss affect the inlet calibration mixing ratio?

13581 I1 to be 12-%

I2 remove thermal. The ovens should reach thermal equilibrium very rapidly. Changing concentrations are probably from surface effects.

L3 replace it is pursued to remove it with they are removed

L4 is flow also kept constant?

L19 replace inevitable rest amount with impurity

L20 delete any kind of

P13582 I29 replace strong with large

13583 I9 How do you know the reaction rates for the differing isotopes? Please reference

P13584 section 5: the mass spectrometry tutorial isn’t necessary in this instrument paper. Instead, reference earlier work (e.g. Arnold or Viggiano from early 1990s), and this section can be shortened or entirely removed

P13586 I17. Why can’t noise be determined just as well in flight? This seems particularly important, since part of the value of this paper is demonstrating operation on a high altitude aircraft at reduced pressure and reduced water.

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P13587 I4 For what count rates is this true? The statistical noise should go as square root of number of counts. I am not clear what noise the discharge ion source adds. Is it a constant count rate at all masses?

L23 please explain how and why you use the nylon filter backgrounds. Do they agree with dry air flushes?

P13588 I2 from the calibration procedure

L15 replace despite with although

L20 this is an interesting idea to passivate the inlet lines with HNO₃. How long does this passivation last? Has this been tested (I wasn't sure from the text)? This must also increase the backgrounds. Further, if inlet passivation changes HNO₃ transmission, the instrument may have a nonlinear response, where HNO₃ transmission increases when HNO₃ mixing ratios are larger. A figure that shows improved time response before and after passivation would be helpful, or at least this statement should be supported by some quantification.

P13589 I7 How do you account for the changing sensitivity with water? Line 26 states that water vapor dependencies can be corrected. Are all the data corrected for water?

P13590 I1 I'm not sure what is meant by occasional evaluation of measurements at higher water vapor concentrations. Please be clearer about the range of water vapor that can be sampled. Perhaps discuss the utility of a dilution flow as shown in Figure 1 (if the dilution flow can be used to sample at high water vapor).

L23 what is the water vapor concentration at 4 km altitude?

P13591 I3. Were measurements really obtained in a thunderstorm cloud? And why doesn't HNO₃ change in the cloud?

L13 what is NO₂ (calculated)?

L17 how is the time from the lightning event known? Does this factor of 7 difference

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assume only photolysis and no dilution at all?

L29 I don't know what is meant by the derivatives of the stratospheric tracers. Fewer panels here may be less confusing.

P13592 – nearly all of this discussion can be removed. The use of correlations of tracers to understand atmospheric sources is well established. The discussion of NO_x and HNO₃ as markers of air mass age has appeared in many papers (e.g. Bertram et al., Science 2007). I recommend removing this material to shorten the manuscript.

P13593 I12 custom

L17 replace allow to identify the origin of. . . with "enable identification of air mass origin"

P13594 I8 remove naturally and e.g.

References: several typos

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 13567, 2015.