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Atmospheric Measurement Techniques Discussions

Interactive comment on "Low-pressure gas chromatography with chemical ionization mass spectrometry for quantification of multifunctional organic compounds in the atmosphere" *by* Krystal T. Vasquez et al.

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Thank you for the carful read of our manuscript. We have addressed the comments and modified our manuscript accordingly.

Instrument description section:

Suggest devoting significantly more time on the first paragraph describing the instrument and Figure 1. Even if the details of this are in previous papers. The title speaks of low pressure chromatography but the words "low pressure" are mentioned only two

times and with very little description of it, how it works, what pressures the GC operates under etc.

We agree and the following changes have been made in response to this comment:

* Fig. 1 has been updated and now differentiates different instrument flow paths including direct CIMS sampling, GC trapping and GC elution.

* The first paragraph of this section has been expanded and now briefly contrasts laboratory studies described in previous papers with this automated GC-CIMS design.

* We have included an additional paragraph under the GC subsection to further discuss the low pressure chromatography. This includes listing the pressure that the GC operates (< 260 mbar depending on if passing the GC output through the ion source or flow tube) at as well as the benefits that result from operating under these conditions. This passage reads: "As mentioned above, connecting the GC outlet directly to the mass spectrometer allows the entire column to remain at sub-ambient pressures during elution. . . low pressures support the use of short, large bore columns without significant loss in peak separation. This becomes especially advantageous during cryotrapping as this large I.D. column allows for a greater volume of analytes to be pulled through and trapped, beneficially impacting the instrument signal to noise. In addition, low pressure conditions also allow for faster analysis times and lower elution temperatures (Table 2). The decrease in analysis time provides this instrument with sufficient time resolution to capture diurnal variations in measured species (one GC cycle per hour), while lower elution temperatures allow this method to be used on thermally-labile species, extending the range of compounds that can be analyzed."

It is not clear at all how the cryofocusing is accomplished. Please clarify this section and take the time and space to describe the different parts of Figure 1 – particularly the cryofocus and low pressure aspects of the GC. The very high flow rates are an interesting aspect of the design and this should be highlighted and explained.

We have taken better care to better describe how cryofocusing is accomplished while referencing several components labeled in Fig. 1. Also, as mentioned above, further discussing the low pressure aspect of this GC also highlights the high flow rates of this instrument.

Since this paper is about the description of an automated field-hardened instrument, provide more details on how the various components of the instrument are fitted together and how the automation was accomplished. The description of the instrument is not concise and does not have a good flow.

More detail has been provided, particularly in the GC section. This section has also been rearranged to highlight key design components followed by a concise description of sample collection and elution operating parameters.

Often very indirect language is used which results in the manuscript being too wordy perhaps at the expense of not providing concise details.

An example: 5/11: "During the collection of analytes on the head of the column, it is important that the temperature remains stable, as sizable fluctuations in temperature adversely affects the chromatography. To control the trapping set point. . ."

Could be replaced by something like: A PID control loop using heaters and the resistance temperature detector (RTD, F3102, Omega) located on the GC column ring (Fig. 2, #2 on diagram) were used to maintain fine control over the temperature set points during cryofocusing. This is needed to obtain reproducible chromatography.

Suggest going through the Instrument description sections and make clear declarative statements where possible and appropriate of the instrument design. Provide details needed for the reader to grasp the primary design features and justification for them without having to refer to previous papers.

The specific example and other instances in the instrument description now use more direct language. Primary design features and justification for their use are now de-

scribed in more detail in both the instrument description and discussion sections

5/12: To control the trapping set point, we utilize the heaters and the resistance temperature detector (RTD, F3102, Omega) located on the GC column ring (Fig. 2, #2 on diagram)

Perhaps show the heaters on the diagram

We have updated Figure 2 and heater locations were added to the diagram.

5/14: In addition, during trapping we only use the solenoid valve connected to the 0.15 mm I.D. restrictor as this valve provides a CO2 flow that is adequate to maintain the GC temperature ($\sim$10 slm)

?????

We apologize for the confusion. We have reworded the passage to clarify the purpose of the different CO2 valves.

Calibrations and backgrounds:

7/15: However, as standards are not available for many species mentioned in this work, these calibration experiments were simultaneously performed on the c-ToF-CIMS to directly compare the compound sensitivities between these two instruments. On average, the c-ToF-CIMS was 1.4 times more sensitive. . .

I know what you mean here and it is explained further in the supplement but please rewrite more clearly in the main section as other readers will not get this on a quick read through.

We have rewritten this passage and incorporated some information that was provided in the supplement to make the calibration procedure clearer to the reader.

7/21: We use two methods to quantify the instrumental background signals caused by interfering ions present at targeted analyte masses. In the first method, the instrument

undergoes a "dry zero" where the CIMS flow tube is overfilled with dry nitrogen so that no ambient air is sampled during this time. In this method, the humidity within the instrument changes substantially compared with ambient measurements. The second method passes. . ..

How do the two methods compare?

The following text has been added to the section as a response to this comment: “The dry zero is most similar to the GC measurements and can assess the health of the instrument over the course of a campaign (i.e. these backgrounds should not change over time), while the ambient zero captures background signals that are adjusted for the water dependent sensitivity of the compounds measured during direct CIMS sampling.”

Discussion

8/16: The largest technical challenge in developing a field-deployable GC was the design of a sampling system capable of collecting and separating compounds with minimal analyte degradation.

Why is this true for a field-deployable system? Seems that you need those same characteristics for a laboratory based system. The difference in a field – deployable system one would think is in getting the sample undisturbed to the instrument which is not addressed – and possibly trivial if the right sampling manifold is used (also not discussed). Referring to my opening comments, the question here is whether more of the details of the system – or a similar prototype system are discussed in previous papers. I suggest that these details be repeated here for the reader. Address what was specifically done in the field-deployable GC versus the prototype laboratory system.

We agree. The goal of this section was to discuss the difficulty of minimizing losses while transmitting reactive compounds through this GC system, rather than the difficulty of constructing a field-deployable GC as a whole. As such we’ve rearranged this section to better reflect this. In addition, parallels between this GC system and the

laboratory prototype have been added to the Instrument Description section. This is necessary to highlight the automated nature of this instrument.

Field Performance:

10/9: “However, instrument upgrades performed prior to the Caltech study were able to greatly reduce GC downtime and significantly improved the chromatography, despite other operating conditions remaining mostly unchanged.”

This in a nutshell exemplifies the main problem with the paper. What were the instrument upgrades? Isn’t this what the paper is supposed to be about?

We have removed this passage from this section and it is now incorporated in Section 2 when we discuss features of the GC design. Additional information about these upgrades are also provided in the Supplement.

Figures:

Fig 1. Enlarge the LP-GC portion of the drawing with better detail on the valving and cryofocusing aspects

The authors have updated Fig. 1 as described in a previous comment. We have also included better detail on some of the valves (e.g. the 4-port valve at the head of the column)

Fig 2. Enlarge drawing and add heaters on solenoid positions

Fig 2. has been updated to include more information, including heater position on the assembly.

Small thing. . .

4/22: For the studies detailed in this paper. . .unnecessary to start the sentence with this. Check paper for other such incidences

This text was removed and other instances in this paper were corrected as well.

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