

Low-pressure gas chromatography with chemical ionization mass spectrometry for quantification of multifunctional organic compounds in the atmosphere – Vasquez et al.

This paper will be an important contribution to the literature. It is mostly well-written although occasionally too indirect and not descriptive enough in describing key features of the instrument. The introduction is excellent – spot on. An excellent discussion is given in Section 4 regarding the field deployment of the instrument and its utility in ambient air measurements in forested environments. The instrument is very impressive and the authors did some fantastic work in developing this technique.

However, after the introduction, the paper loses focus and does not accomplish the objective of properly describing an analytical instrument. It is stated that the novelty of the paper comes from the “field-hardened design” implying that the paper is focused on that. The reader is presumably supposed to look back at previous publications from the group to fill in the gaps and missing details from this paper and be satisfied that the description of the field – hardened instrument is sufficient. This reviewer is too lazy to scour through those previous publications and would like this paper to stand-alone. I think that’s a reasonable expectation that could be met fairly easily by the authors

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.

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.

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.

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.

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.

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?

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

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 (~10 slm) ?????

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.

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?

Figures:

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

Fig 2. Enlarge drawing and add heaters on solenoid positions

Figures 3-13 are good and appropriate

Small thing...

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