

Review of amt-2017-201 manuscript: “An aircraft gas chromatograph-mass spectrometer System for Organic Fast Identification Analysis (SOFIA): design, performance and a case study of Asian monsoon pollution outflow”, by Efstratios Bourtsoukidis, Frank Helleis, Laura Tomsche, Horst Fischer, Rolf Hofmann, Jos Lelieveld, and Jonathan Williams

This article describes the technical design and first application of a fast preconcentration – gas chromatography/mass spectrometry (GC/MS) system for analysis of ambient organic trace gases from the HALO aircraft platform.

This manuscript is in general well written. The engineering of the instrument is impressive. The system builds on a cryogenic preconcentration technique on an open tubular micro-trop with a second focusing step on a cooled GC column section. GC separation is achieved on a commercial column that is contained in a low thermal mass and fast response heater. Detection relies on mass spectrometry with an Agilent MSD. These all are more or less established analytical principles and technical approaches that have been demonstrated in previous research and publications. The most remarkable accomplishment is the fast time resolution that can be achieved with this system, allowing a full analytical cycle in 2-3 min. But again, this has also been accomplished before, for instance with the TOGA instrument (see summary in Table 2). Therefore, overall, I see relatively little novelty in this work.

For a paper describing a new analytical development, I would have liked to see a more in depth characterization of the analytical system through analytical testing. The application examples unfortunately in my opinion do not serve that purpose. Examples of such analytical experiments are for instance:

- Demonstrate neglect of water vapor effects by running test series at varying humidity.
- Demonstrate robustness against CO₂ interference. Under the chosen trapping conditions most of the CO₂ is expected to be focused. Upon desorption this will replace carrier gas and alter the chromatography. That’s why cryogenic focusing systems used by other groups often use CO₂ removal agents. It doesn’t seem like this was tested here?
- Show linearity of the system.
- Compare response in synthetic versus whole air standards.
- Investigate interference from ozone.
- Demonstrate how detection limits were determined.

My most severe concern is the lack of addressing interferences from ozone in the sample air. Given that this is an aircraft instrument with a high ceiling altitude (15 km, page 12/line 6), significantly higher (than surface) ozone levels will be regularly sampled. Problems from co-collection of ozone have been recognized some 20+ years [Goldan *et al.*, 1995]. There are multiple effects that can occur, such as artifact formation from reaction of ozone in the sampling system, as well as loss of analytes during the prefocusing from oxidation by ozone. Consequently, there is potential for positive and negative artifact effects. Ozone interference has been well documented in the peer-reviewed literature, see for instance [Bates *et al.*, 2000; Plass-Duelmer *et al.*, 2002; Pollmann *et al.*, 2005; Lee *et al.*, 2006; Apel *et al.*, 2008;

Arnts, 2008; Hellen *et al.*, 2012]. Modern analytical systems relying on VOC preconcentration systems followed by GC analysis take the ozone interferences into account, and mitigate this problem by selective removal of ozone in the sample air. Analytical protocols and standard operating procedures developed through ACTRIS and by the WMO/GAW program (i.e. https://www.wmo.int/pages/prog/arep/gaw/documents/4thGAWVOC_DWD_ACTRIS-GAW_RecomRequire.pdf; https://www.wmo.int/pages/prog/arep/gaw/documents/5thGAW-VOC-Plas-Dulmer_OVOC.pdf; and WMO-GAW VOC Measurement Guidelines, in prep.) recommend use of ozone scrubbing techniques.

Given this plethora of information on this interference, and the obvious analytical biases that can occur, I think at this point in time enrichment/GC analytical systems need to consider ozone management for achieving good measurement quality. I recommend against publishing analytical GC VOC analysis work that neglects addressing the important issue of ozone management.

Other comments:

Figure 1:

- I find this figure hard to read and recommend enlarging it. Further, even after studying it for a while I had a hard time following the flow pathways. I recommend adding in a supplement further versions of this figure that show highlighted with color the most important flow paths during important analytical sequence steps.
- For the zero/cal unit, shouldn't the zero supply gas be air, and shouldn't be the flow arrow go the other direction?
- How does the system get sufficient flow at the very low outside cabin pressures at 15 km altitude? I don't fully understand the purpose of the 'Inlet FC' when there is another 'Sample FC' downstream in the path?

Page 3/Line 30: Define MuPo when first mentioned.

3/34-38: The figure is lacking this detail?

4/4: Is the catalyst indeed Pt or platinum oxide?

4/10-12: Provide full detail on the standard that was used, i.e. components, compound mole fractions, and preparation date.

4/11: 5 ml min⁻¹

4/27: Shouldn't one use a 'vacuum pump' rather than a 'sampling pump' for this application?

4/27: NTC sensor is not shown in schematic.

4/31: Please provide pressure sensor specs.

5/17: ...converter.

6/8-9: Please provide more detail on the pressure controller fabrication.

7/25-30: The plumbing diagram does not show how dilution series can be done with the system.

8/19: Please explain the 'in-flight pressure calibration curve'.

8/21: Please be more clear with the wording here. I recommend using the term 'precision error'. A low precision would actually reflect a high standard deviation, so a 'high' value.

11/12: I would not necessarily agree with this statement. In proper configuration the MSD is probably as fast as a GC detector as any other GC detection method.

11/37: Replacement of the carrier gas by CO₂ released into the flow path during sample desorption could be a major chromatographic interference.

Table 1: The precision result needs to be reported with the mole fraction at which it was determined.

Figure 4: A figure showing an ambient sample would be more valuable. Synthetic standards are usually easier to measure.

Figure 8: Mole fraction scale on y-axis in lower graph is missing.

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