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Discussions

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Interactive comment on "**An Improved, Automated Whole-Air Sampler and Gas Chromatography Mass Spectrometry Analysis System for Volatile Organic Compounds in the Atmosphere**" *by* **Brian M. Lerner et al.**

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This a very worthwhile paper describing a new GC-MS system for efficient analysis of multiple VOC species from whole air samples. This long-standing methodology remains heavily relied on in atmospheric chemistry research and continual improvements in technology are good to see. One paper can't cover every aspect of the measurement science and there are still major gaps in knowledge on how to best calibrate, storage, dry and data process VOC samples. In large part of the paper uses best practices when it is not suggesting new or improved ways of working. The core of the improved

capability here appears to be the Stirling cooler trapping system and a fast two-column separation – the improving ease of field operation and increasing sample throughput. With some additional information and clarifications that paper should be published.

The paper places most of the emphasis for external validation of the method against co-measurements made using PTR-MS. It is very understandable, since this instrument was available on the same campaigns. But when demonstrating a new GC system's measurement performance against a characterized reference then PTR doesn't really seem the best choice. Rather comparing to PTR seems to just add in a whole load of new uncertainties from that technique as well. Only a modest number of VOCs can be measured by both systems, and even then quite often it is a summation of compounds. GC-MS (and sometimes FID) remains the gold standard method, even if laborious and slow, so how does this new more efficient instrument compare against the previous WAS and GC method? Something in the paper on that would give a much better measure of 'progress'. Is this new system just faster, or is it faster, more sensitive and more precise? The authors have a huge track record of measurements going back many years, so it would be genuinely helpful to know how this system compares against notionally similar GC principles used previously. Is there a trade off between speed and precision, when compared to off the shelf instruments?

It was surprising that for an instrument where the new thermal desorption develop-ments are so central to that there is no demonstration of breakthrough volumes and trapping efficiency. The trapping volume is small and it relies primarily on cold brute force to achieve retention. Breakthrough volumes for say acetylene would be interest-ing. On P10 it was still a little unclear how much air was actually sampled on to each trap. 240 mL each or shared between two traps? There is some reference on P13 to changing trapping efficiencies suggesting that retention is not 100% for all species.

The very low temperatures necessitate both a water removal step and also one for CO_2. Whilst the general methods used are reported in other literature it would be interesting to have a comment on whether any hysteresis is introduced by either. Any

carry over for example on the coated beads of silica? Is there any residue if switching from a high ppb-level sample to a ppt sample. This is one of the big challenges for aircraft analysis systems since their samples can rapidally span a very wide dynamic range compared to surface-only sampling.

Whilst the focus of the paper is naturally on the GC-MS and component parts it would be valuable to have some additional information on tests conducted on the sampling system itself. A critical and often ignored part of a WAS is the air compression system pump itself – without that there is no sample to analyse. Whilst I couldn't find any details on-line for on the 28823-11 Senior Aerospace pump, most variants of this kind do not have completely sealed bellows systems, instead having pin-hole pressure relief holes in the bellows to prevent motor stall at low inlet pressures. Is this the case here, or was this relief welded shut? A consequence of this pump design can be that a proportion of the air delivered to the canisters is from the surrounds of the pump, not the inlet tubing.

What tests historically have been performed to show no contamination from this pump or losses – I appreciate this might already be published elsewhere in earlier work. It is an exceptionally difficult thing to do, but any insight that can be gained on testing of this kind would be valuable to other readers.

Reviewer 1 has already highlighted the need for an uncertainty budget and some further statistical details and I would also endorse these requests. Not only is this essential to understand how and where the data can subsequently be used, but it would provide a very helpful guide to where future instrumentation development is likely to yield the most beneficial gains.

P2. Line 17 – it is other detection methods for GC that are less sensitive, not that alternative chromatographic methods are used for VOC analysis.

P3 line 5. Lift capacity means needs defining here, not later on P8.

P6 line 16. What method, chemicals or technique is used to generate ultra zero air?

P7 line 22. What sort of valves and materials, were these externally purged?

P11 – can something more quantitative be said about the precision of the integration from the new automated software compared to previous methods? The text refers to improved precision and accuracy, but doesn't say anything else.

P13. Line 13. How are these reference gas dilutions achieved and do they include any reference materials that create traceability to other international standards? Can more information be given on how the 1 ppm PAMS 57 mix is diluted down to ambient levels, or is it used as is?

P13 Section 3.2 would be better titled calibration, since that is what the section is about and no sensitivities at actually presented. There is a discussion of a non-linear set of compound responses, and an undefined reference to linearity when mixing ratios are low compared high. Could this be sharped up with some quantitative numbers for various indicative compounds?

P14 The total uncertainty in the calibration method is given as 12%, which is quite high relative to the DQOs set out for example by GAW. Any comments on this? I found it noteworthy, if a little depressing, that commercial standards for C2-C5 NMHC gave difference up to 18%. Can any manufacturers be named and shamed.

P14 – for limits of detection it would be very helpful to the reader, and for future comparison against other researchers instruments, if an example chromatograms with trace level peaks could be included as a figure – perhaps in the Supplementary materials.

P15. The detection and precisions are given in section 3.3 and Table 2, but it is difficult to square these values with for example the inter-column comparison data in Figure 5. The quoted precision uncertainty of 7% clearly isn't appropriate to apply to the lowest abundance samples and an absolute value for each compound needs quoting. Figure 7 also suggests the quoted precisions for the method look a little generous. Giving explicit uncertainties at the lowest concentrations is really important, since this type

of VOC measurement often data ends up being (inappropriately) used in tracer-tracer ratios.

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Discussion paper