

RESPONSE TO REVIEWER #2

The authors appreciate the reviewer's extensive and most helpful comments and recommendations for improvements. His suggestions for ways to clarify the paper are especially appreciated. All of the minor edits and suggestions not requiring discussion were accepted and incorporated into the re-submitted manuscript. For the rest of the comments, we offer the following specific responses and changes:

Abstract

We agree the abstract could be further clarified so all of the recommendations were adopted except for substituting the word "parameter" which we feel captures the intent that the model must be "tuned", i.e. parameters changed, to obtain the most accurate result. The abstract's reference to response trending in the text is strengthened by using the same formulation of the result (2%/week instead of 5% over 19 days as originally stated) in the text rather than relying on the reader to make the connection.

The abstract now reads:

A reliable method of sample introduction is presented for on-line gas chromatography with a special application to in-situ field portable atmospheric sampling instruments. A traditional multi-port valve is replaced with a valveless sample introduction interface that offers the advantage of long term reliability and stable sample transfer efficiency. An engineering design model is presented and tested that allows customizing this pressure switching device for other applications. Flow model accuracy is within measurement accuracy (1%) when parameters are tuned for an ambient-pressure detector and 15% accurate when applied to a vacuum based detector. Laboratory comparisons made between the two methods of sample introduction using a thermal desorption aerosol gas chromatograph (TAG) show that the new interface has approximately three times greater reproducibility maintained over the equivalent of a week of continuous sampling. Field performance results for two versions of the valveless interface used in the in-situ instrument demonstrate typically less than 2%/week response trending and a zero failure rate during field deployments ranging up to four weeks of continuous sampling. Extension of the valveless interface to dual collection cells is presented with less than 3% cell-to-cell carry-over.

Introduction, p. 7533

Lines 1-2: "low abundance". It's a relative term but really you refer to instrumental detection limits. Maybe you could state it more explicitly, like "...at abundances below the typical GC detection threshold range of xx-xxxppbv, ..." or something like that.

The "low abundance" phrase was replaced with "ppb or lower levels"

Line 7: I disagree that it MUST be isolated. Splitless injection with cryogenic focusing at continuous carrier gas flow in the analytical column's head works too, which is a separation but not from the analysis components.

The authors wish to emphasize that for semi-continuous sampling instruments, having the analysis and sampling conducted simultaneously minimizes gaps in measurement. The use of in-line cryo-trapping does not meet this goal. To clarify this key point we have replaced that line:

“For semi-continuous in-situ measurements, the analysis and sampling are ideally conducted simultaneously to minimize gaps in measurement. Regardless of the collection method employed, the pre-concentration sampling inlet should be isolated from the analysis components of the instrument.”

Line 18: "inevitably leads to leaking" - I understand what you are trying to say, but it's not always the case. What you might want to say is that it "inevitably bears the risk of leaking".

The authors do not consider the statement that moving seals eventually fail and create leaks (be they internal or external) to be controversial. However, we moderated the statement as suggested to appear less biased in the presentation.

GAS FLOW MODEL

p7537 line 10, 22: "assumed ideal gas behavior", "non-continuum, entrance and wall effects" - no surface interactions, no molecular mass dependency? Gas mixtures traveling through an orifice (or experiencing expansion) fractionate by molecular weight at varying escape velocities. This could be tested for using the existing data in Figure 6 (internal standards mentioned on p.7544 line 4, and line 25 are not typical SOA precursors, but at least vary in molecular weight enough to test for this. p.7545 lines 24-28 at least contain some reactive polar compounds). Secondly, if no wall interactions could be assumed then no coatings would be necessary in heated parts of the injection system. In practice, this has to be validated with each instrument using multi-component standards and recovery tests, which you did, routinely. Non-continuum behavior is discussed on p.7549 line 4.

For the purposes of predicting sample transfer across the valveless interface, molecular separation of the analytes is not important since we reintegrate the sample at the head of the column and thus do not require non-dispersive transfer of individual species. The flow mechanics are governed entirely by the helium carrier gas, with the stated assumptions, which is what our model aims to handle. If direct detection (i.e. no column) were employed then these effects the author raises would be important to consider but we are not in a position to evaluate such an extension. Nor can we separate inline losses of transfer between the point of collection and the detector. The interface certainly contributes to losses but in our experience the collection cell and sample size dominate transfer efficiency.

Line 24-25: I disagree with that sentence but it's up to you if you leave those statements C2849 in here. I would reformulate them by stating that such effects are controlled for using adequate multi-component standard runs.

Above response applies here too. We refer again to the gas flow modeling not the transfer of analytes which we agree has strong surface interactions. The Blumberg citation we provided persuasively supports this claim.

Line 26-27: "now employed in the TAG family of instruments" - what are you trying to convey? You mean in your lab, or with the company selling them? State it here, so the reader doesn't have to guess what you mean. In fact, you mention the same thing again on p.7541 line 14-17, so best to remove that statement here, since it's a paper not a brochure.

Line 28f: I am confused about this sentence, please clarify.

We address these two points with the following clarifying substitution:

"We present the theory of operation for the simpler interface configuration that uses a valve on the carrier gas line as shown in Figure 1. The original, more general configuration uses an additional flow control capillary instead of this valve and was used in the prototype. The theory of operation for this more general approach is presented in Appendix A."

Line 11: Your assumption of 0kPa, did you calculate that for values not equal to zero, but in the range of typical MS vacuums? I.e., a maximum pressure. I agree that your conclusion in the next sentence is still valid (lines 12-13), even if one is not assuming perfect vacuum. (same in p7539 line 16).

Using a typical MS source pressure ($\sim 10^{-6}$ kPa) gives the same result.

Line 23: "recondenses": cryogenic under continuous flow? Not sure I recall seeing that detail on how you do that.

Our application is semi-volatile organics which readily re-condense on a column at $\sim 40^\circ\text{C}$ a readily achievable oven temperature in the field. No cryo-focusing is needed but could be added if an extension to more volatile compounds was sought.

p.7540 line 10, 19, 27-28: No coating is perfect - what method did you use to validate survival of polar SOA precursors?

In general, polar compounds require derivatization to be detected by GC/MS as covered by the companion paper (Isaacman et al. AMTD, 7, 7495–7529, 2014). All evaluations are performed with liquid standard injections directly into the cell prior to thermal desorption and GC/MS analysis.

p.7541 line 6-7: were this SS block and further mentioned fittings coated as well, internally?

Yes, all SS surfaces coming in contact with sample was passivated as described.

p.7542 line 21: "encountered" - circular argument. You are introducing VLI-TAG here in this paper, but are now invoking typical VLI-TAG applications. Maybe reword this.

Agreed, substituting this more general contextual sentence:

"The range of control parameters used represents typical ranges encountered in the analysis of low volatility organics by capillary gas chromatography: ..."

p.7545 line 16: "metal fiber filter cell" - the previously invoked polar SOA precursors (Intro) might not experience degradation here?

Same answer as for p.7540 above. Yes, so evaluation of system with this element provides a lower limit of performance for the VLI alone as stated in the text.

p.7546 line 4: still not sure what you mean by "trending" here.

To help clarify we added the sub-phrase: "drifting response or trending". Naming aside, the mathematical expression Eq(5) is simple to understand and it is why T_r is used in the presentation of results.

RESULTS

p.7547 line 17,19,22: "ID" is lab prose unless defined

p.7548 line 9-10: here you spell out ID again... maybe mention it spelled out at first occurrence

and be consistent after (either acronym or spelled out, throughout)

Indeed. A combination of spelling out or the symbol *d* was substituted throughout.

p.7549 line 16-17: Maybe state calibration of what here (flow, volume, pressure...), to be clear.

Inserted *d* parameter to be explicit about what is usually calibrated

p.7552 line 20: are these 'contaminants' column bleed?

For clarification, we expand this sentence:

"Starred peaks are isolated compounds known to be present as internal contaminants that otherwise do not interfere with sample analysis."

These isolated peaks can arise from multiple sources such as residual decomposition products in the cell from prior thermal desorption cycles or internal plumbing contaminants that are not efficiently removed during sample injection and as a result can linger for extended periods. However, these are easily ignored during analysis of MS based data given unique retention time and *m/z* signal.