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Discussions

Interactive comment on "Segmented flow coil equilibrator coupled to a Proton Transfer Reaction Mass Spectrometer for measurements of a broad range of Volatile Organic Compounds in seawater" *by* Charel Wohl et al.

Anonymous Referee #1

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Review of Segmented flow coil equilibrator coupled to a Proton Transfer Reaction Mass Spectrometer for measurements of a broad range of Volatile Organic Compounds in seawater By Wohl, et. al. Ocean Sci. Discuss., https://doi.org/10.5194/os-2019-5

Please see attached pdf of formatted review.

In this manuscript, Wohl et. al demonstrate the application of a Segmented Flow Coil Equilibrator (SFCE) for VOC and OVOC online dissolved gas analysis using Proton Transfer Reaction Mass Spectrometry (PTR-MS). The performance of the combined

system is demonstrated through a comprehensive suite of calibration, background, and response time tests. This manuscript's main contribution to the field is the expansion of our knowledge behaviors of the SFCE dissolved gas sampling method and aspects and pitfalls of successful implementation. Of particular interest is the simplicity of the design combined with the extent and speed of equilibration of both low and high solubility gases. This information is of interest to both the ocean science community, but also air quality, ecology, and inland water quality applications, and represents simple alternative to other equilibrator designs. Additionally, there is a lot of interesting data regarding the operation of the PTR-MS, including ion source and drift tube tuning that are valuable insights to the PTR-MS user and science community. Overall, this documentation of a sound instrument development project and the results are very exciting and well demonstrated. Additionally, the authors have thoughtfully included detailed appendixes/SI that clearly lays out many details of their work.

There are several broad areas where the manuscript could use improvement. (1) Nomenclature. Many colloquialisms are used that imprecisely describe materials and processes at in question, which obfuscates the discussion but also harms communication across fields. a. Using the IUPAC Glossary of Terms Related to Solubility (10.1351/pac200880020233) as a reference i. Instead of 'airside' use 'gas phase' ii. Instead of 'waterside' use 'dissolved gas concentration' b. While softer/harder ionization is technically correct, it's a lot more illuminating to discuss proton affinity differences and effective temperatures, which are the forces at play in the PTR-MS drift tube and ion optic system. c. The protonated target molecule is the "primary ion". A charged fragment of dissociation should be called a "product ion" or "fragment ion".

(2) Uncertainty. Consistently state and propagate uncertainty and significant figures. a. Section 3.2 needs attention. The reader cannot determine the input concentrations for the evasion experiments with the information provided. Are the purge factors really known to the stated (per-mil) precision?

(3) Harmonize section 3 and 4. These sections seem a bit repetitive and scattered, con-

ceptually jumping back and forth between PTR-MS and SFCE tests. I suggest moving the theoretical/math into Section 3, and calling it “Derivation of Dissolved VOC concentrations from SFCE/PTR-MS measurements”. The experimental/operational work (3.1 Determination of System Background and 3.2 Estimation of Equilibration Efficiency) could be moved into section 4. Section 3.2 and 4.2 seem like they could be combined. Another thought is that the SFCE testing is largely disconnected from the PTR-MS humidity and calibration testing, so those phases could each get their own sections (Section 3: “PTR-MS operation”, Section 4 “SFCE testing and operation”)

(4) Since the manuscript deals with both gas phase mixing ratios and dissolved concentrations, I suggest using “ppbv” instead of “ppb”, as gas mixing ratios are typically by molar volume while aqueous mixing ratios are often by mass.

(5) Instead of a long series of appendixes, could that information just be put in the supplemental material? Using the PTR-MS at 160 Td yields some unusual data, but in this case PTR-MS is fundamentally just the detector and the main focus of the manuscript is the SFCE application.

Specific comments and suggestions:

Line 16: 1 min instead of 1min.

Line 43-60: Are the authors aware of any investigators using hollow fiber membrane contactors for online dissolved gas analysis in seawater? (I am not aware of any example, but they are popular in inland surface water, groundwater, and industrial settings. So perhaps there is an example that escapes my limited search and knowledge?)

Line 90: Consider rephrasing to “In this paper we extend the application of the segmented flow coil equilibrator. . .” The core design is substantially similar, but the target analytes are hitherto undocumented. 120-135 and 195-220: I note that the inlet water is warmed to 20 °C. I wondered how much N2 would exsolve from the water and add to the total gas flow, as this would effectively dilute the measured VOCs. Air is about 25%

less soluble at 20 °C than at 0 °C, and using the solubilities of O2 and N2 as proxies, it seems like the amount of air exsolved from a 100 cm3/min flow of water warming from 0 to 20 °C would be about 0.5 sccm: so the temperature change is not causing enough off gassing to measurably modify the mixing ratios measured in the equilibrator.

Line 197: It would be more clear to write “R=8.314 ïĆť 10-3 dm3 Pa mole-1 K-1” or similar.

Line 260-270: PTFE has a measurable permeability to many gases, and at thin cross-sections, is used as a membrane material, leveraging that property. Looking at some manufacturer datasheets, acetone and methanol are among the most permeable gases in PTFE. It seems like switching to the PTFE tee fitting improves the situation by reducing residence times of gas/fluid and minimizing unswept volumes. Would you recommend stainless steel or glass for future designs?

Line 260: Can you give us an idea of what volume of water was in the PTFE jar and tee at steady state here? That would help give us an idea of water residence time in the entire system. (Figure 1 gives a hint about the tee seems like about 10 cm3, but the jar is unknown.)

Line 285-295: Can you include some more detail, or perhaps expand the appendix/SI to include more specific information about how the evasion standards were made and used. How much MilliQ water was used? What was the pipette volume/precision? What was the dilution volume/mass and precision? How many dilutions were done to get to the final stock? How long was the SFCE purged before measurement? Line 305-310: Are the solubilities known to a level of accuracy that allow for 5 significant figures? If not, perhaps the uncertainty should be clarified.

Line 354: “100cm3 n: 100cm3” should this be restated as “air and water at equal flow rates of 100 cm3 at 20 C”?

Line 370: Peristaltic pumps are notoriously bad actors in dissolved gas sampling, and

require assiduous attention to maintain constant flow over time. Would you recommend another pump, perhaps a magnetically coupled stainless steel gear pump, to others?

Line 376: “Our aim is to build an equilibrator that fully equilibrates for the very soluble OVOCs”. This sentence succinctly describes the manuscript. Consider if it can be placed somewhere in the abstract or introduction (perhaps around line 93).

Line 516: Hollow cathode DC plasma discharge

Line 528: Instead of (H218O+)H2O (which would be m/z 39) you probably mean (H216O)H3O+.

Line 530: A great deal is written here about how much effort is put into managing humidity to achieve consistent results. Getting a handle on these relationships is a curcial aspect for achieve maximal PTR-MS performance and is both widely recognized and documented from a very early point in the PTR-MS methods arrival. The implementation as described basically has a PTR-MS with a heated inlet and vacuum system, in a conditioned space aboard a ship, drawing a gas/water mixture through a temperature-controlled coil (the SFCE) at 20C. The vapor pressure of water at this temperature is around 17 torr. The flow rate of water vapor through the PTR-MS ion source was essentially constant (3 sccm). One might surmise these measurements benefited from an extremely predictable and stable input of water relative to air quality and biogeochemical measurements. How much variation in drift tube humidity was there? Can you show us a plot of % m/z 37 over time? How about %m/z 55? What’s the return of this tweaking vs running the PTR-MS in a more conventional manner?

Line 544: “ionization by water clusters is lower energy and. . .”

Line 544-560: Running the instrument at 160 Td is unusual, as is the water flow (5 sccm) and discharge current (3mA). Most investigators report a sweet spot between 100 and 140 Td, with resulting uncertainties in the range of 5-25% RSD. While discharge conditions are not as commonly reported (to my dismay), the latest HS-PTR-

MS user manuals up to 2011 (the last I have access to) suggest water flow rates between 6-15 sccm and discharge of 4-6 mA. While it does have the effect of reducing the abundance of hydrated clusters in the drift tube, it also decreases the reaction time and greatly increases fragmentation, both of the target analytes and of higher mass molecules, from whom the fragment ions can then interfere with the measurements. There are basically two selection criteria of the PTR-MS method (1) Only molecules with a proton affinity higher than water are detected (2) Those protonated ions can be uniquely detected at a specific m/z ratio either directly or by some signal deconvolution. By operating the PTR-MS in this configuration, it’s likely that those conditions are only true for a select set of compounds. I would surmise that performance with monoterpenes, acetic acid, and anything with a terminal hydroxyl group to be especially problematic. The high degree of fragmentation of isoprene observed here is emblematic of these operating conditions. The authors should emphasize that in seeking to suppress cluster formation in the drift tube, they are making substantial performance tradeoffs in other areas.

Line 570-603: I’m a bit confused: how much of the background signal of OVOCs are being attributed to humidity and how much do you think is from OVOCs in the water can? Can you comment on the background signal of these other OVOCs over time? Water held under dynamic vacuum preferentially degases, so one would expect any dissolved gases to be removed from the water can after a prolonged period of PTR-MS operation, especially in a warm instrument cabinet on a rocking ship, turning over the water. Reviewing several years of my own PTR-MS datasets, I see elevated backgrounds immediately after the instrument is turned on after service/water can fills, but they quickly recede to a stable signal (usually a few hundred CPS) with an extremely weak relationship between m/z 37 and m/z 45 or m/z 63.

Line 651: I suggest calling Appendix E: “Compilation of published solubilities for methanol, acetone, and acetaldehyde”.

Table 3: (and throughout). For consistency, I suggest sticking with nmol/dm-3 through-

out, and using scientific notation for isoprene instead of pmol dm-3. i.e. 9.96 * 10-3 +/- 1.25 * 10-3 nmol dm-3)

Figure 3 (a): Typo “assuming” not “assuning”.

Figure 4: I suggest either using all black or using some color variation. It’s hard to tell the 1:1 line and the fit to the measurement lines.

Figure 5: This plot and caption could use some clarification. This is a comparison of range solubilities observed with the SFCE-PTR-MS system and values predicted from literature. The meaning of the numbers in the legends (1-44) of Figure 5 are not immediately clear. To help, each line could be “Ref. x” (x=1-44), with “This work” as the thick red line and “S. P. Sander” as the thick blue one. In the caption, please write what you want the reader to take away from this demonstration. It seems like you are seeing lower solubility than the literature values.

Figure 7: Can this be remade as a full page plot? The horizontal axis is extremely tight. If size is an issue, plot gases of similar magnitude on the same subplot and use the right axis. I suggest adding to the x axis “Sample Date & Time (HH:MM DD/MM/YYYY)”.

Figure B-1: Are there error bars (like the caption says) in these plots? They are not rendering on my printer or pdf.

Please also note the supplement to this comment:
https://www.ocean-sci-discuss.net/os-2019-5/os-2019-5-RC1-supplement.pdf

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