

Review of EGUSPHERE-2024-2049-revised Manuscript

Overview and general comments

I have reviewed this manuscript before, and I will focus on my previous review comments in this re-review as discussed below. The authors addressed some of the comments in my initial review, but I still have reservations about the overall quality of the work as described in my updated list of my initial review comments below.

Overall, my main concerns are:

- The description of the gas-equilibration model was moved from the main text to the appendix, but the model itself was not modified substantially and still suffers from the same physical misconceptions.
- The description and discussion of the data processing and uncertainty assessment are not fully adequate for a methods paper.
- The work uses design concepts that are covered / protected by a patent. I believe it would be wise to clarify the rights to use these concepts before moving forward.

I recommend to resolve these points before moving forward.

Details and specific comments

This is a list of my initial review comments with follow-up comments related to the revised manuscript (*in italics*). I removed the comments that were sorted out by the revision from this list.

1. Introduction

Line 67 The dynamic steady state in a conventional MIMS is controlled by many more factors than just the dissolved gas concentrations and the MS pumping rate. The water flow rate, the geometry of the membrane system, water salinity, temperature, aging of the membrane material and its gas permeation properties, etc. play a crucial role.

The authors' revision fails the point. My comment was aimed at discussing the numerous parameters that control the operation and measurement results (and their uncertainties!) of the MIMS technique.

2.1 Membrane equilibrator

Appendix A, line 117/118 Using a pressure sensor to determine the total gas pressure and to quantify the partial pressures of the different gas species in the membrane equilibrator has been previously described in patent EP 4 109 092 A1, which should be referenced here. *The authors' system clearly does use a pressure sensor to determine the total gas pressure, which in turn is needed to quantify the partial pressures of the various gas species. I'd advise to consult an expert to avoid any potential for patent conflicts.*

Line 112 How “negligible” is the gas removal? This is a crucial control for the accuracy of the analytical results and calls for a quantitative argument.

The authors argue that this is “...a minor effect and applies to the calibration and measurements as well.” However, the effect does not apply to the calibration measurements because the calibration gas is not taken from the membrane module.

Line 114 and 115 Why would a clogged capillary pose a risk for the MS? I'd rather argue that the clogging protects the MS from accidents with too much water.

The authors now argue that the clogging of the pores of the membrane material by particles could be an issue. This has nothing to do with water in the capillary. I don't understand and am unsure about this revision.

Line 116 and 117 Is this a confusion between accuracy and precision?

The authors revised this to indicate the precision of the temperature sensor, but I think the information on accuracy would be much more relevant, because it is needed to determine the dry-gas pressure.

Line 121 and 122 Why would the depressurization in the outflow tubing have an effect on the gas/water equilibrium in the membrane module? Please explain.

The authors' response makes sense, but they did not add their explanation to the revised manuscript.

2.2 Mass spectrometry

Line 139/140 The Faraday cup and SEM are likely used not only for detection, but rather for quantification.

It seems the authors did not mention the SEM in their revision.

Line 140–142 One might expect a better signal/noise ratio from the SEM, in contrast to the observation reported here. Why is this? Please elaborate.

I agree with the authors' response, but it would still be useful to add a comment to the manuscript to avoid confusion with readers.

Line 143/144 Quantification of the partial pressures must be based on the peak heights in the mass spectrum. To determine the peak heights, the baseline values therefore need to be subtracted from the peak-top values measured at the indicated m/z positions. Were the baseline values measured? At which m/z values?

At m/z = 3 the signal is governed by the peak of H-3 molecules in the mass spectrometer, so this does not seem like a suitable position in the spectrum to determine the base line.

Lines 150–154 Why 60 repetitions for averaging? Why a 6 h long test period? The usual approach is to optimize the signal/noise ratio while minimizing the effect of drift. This is commonly done using an Allan plot. Is this what the authors did? Please explain. *The Allan plot seems incomplete, as it only shows the increasing trend of the Allan deviation corresponding to drift. The plot is missing the short-term range where the Allan deviation shows a decreasing trend corresponding to random noise. It is therefore impossible to determine the optimal integration time corresponding to the minimum Allan deviation at the transition between these two regimes (random noise vs. drift). I believe the the averaging/integration chosen by the authors is not optimal.*

3.1 Accuracy and Precision

Line 168/169 Estimating the water vapor pressure by assuming saturation in the GE-MIMS equilibrator has been described in patent EP 4 109 092 A1, which should be referenced here.

I'd recommend to consult an expert to avoid any potential for patent conflicts.

Lines 173–180 Using Henry's Law to convert the partial pressures to dissolved gas concentrations has been described in previous GE-MIMS work, which should be referenced here (see previous comments).

My comment is aimed at referencing previous GE-MIMS work, not Henrys Law.

Lines 182–188 Air-equilibrated water (AEW) is a good reference to assess the analytical performance, but fabrication of AEW is notoriously difficult. I would recommend comparison and validation of their GE-MIMS system with other (validated and established) methods for dissolved-gas quantification.

*The authors claim the "stability of the measurement values shown in Figure 2". This indicates the precision of their measurements, not the **accuracy** of their AEW reference used to assess the analytical performance.*

192/193 The RSD is normalized relative to the concentration value. A lower concentration value should therefore not result in a lower RSD.

The authors seem to agree, but did not revise the manuscript accordingly.

3.2.1 Theory of equilibration kinetics

I am not convinced that this section adds much value to the manuscript. On the one hand, it assumes that the water is stagnant inside the membrane module (it is not), and it assumes that the membrane provides the bottleneck for the gas transfer between the water and the gas phase. However, the resistance of the membrane material to the gas transfer is marginal (the authors can convince themselves about this by blowing into the water inlet of a dry module while blocking the water outlet, and observe how the air easily escapes through the membrane material into the gas headspace). In contrast, the main bottleneck for the transfer of gas species between the water and the gas headspace is expected to result from the gas exchange mechanisms at the gas/water interface (see for example [?]). The main outcome of section 3.2.1 is that the partial-pressure equilibration follows an exponential function, which comes to no surprise given the assumption of a first-order exchange kinetic, and which does not warrant any mathematical derivation. A second result is equation (27), which provides a formula to calculate the equilibration time. However, this equation relies on incorrect model assumptions (stagnant water, membrane as bottleneck for gas/water transfer) and therefore does not provide much insight.

The authors (i) moved the model to the appendix and they (ii) argued that gas exchange was modeled assuming stagnant water. I do not understand how these points would be related to my comment, or how the revision would improve the manuscript.

Lines 285–286 This seems like a trivial finding since the removal of gas from a finite, stagnant volume of water will result in a lower dissolved-gas concentration, and hence in a lower partial pressure at equilibrium. In reality, there's a continuous flow of water through the membrane module, which means there's a (virtually) infinite amount of water available for equilibration with the gas headspace. Again, this shows that the model concept and equations are based on inappropriate assumptions.

*The authors argue that “the purpose of using a model that examines gas exchange with stagnant water was to provide a simplified representation for understanding the fundamental principles of gas dynamics. This approach was intended to help readers, especially those less familiar with the topic, grasp the essential mechanisms at play.” However, the stagnant water assumption does **not** represent the mechanisms at play and also makes the mathematical treatment overly complicated. Assuming a high flow of (non-stagnant) water with defined (constant) dissolved-gas concentrations would reflect the true GE-MIMS mechanisms much better and would make for much simpler maths.*

3.2.2 Measurement of τ

This section provides robust information on the time needed to attain gas/water equilibrium in the membrane module, and provides a useful basis to estimate the spatial resolution of the dissolved-gas data recorded on a moving ship. The measured equilibration times τ are approximately 50 % higher than those calculated from the model in Sec. 3.2.1, which supports my impression that the model is inaccurate and seems inappropriate to optimize the operation of the GE-MIMS method for the dissolved gas monitoring described in the manuscript. To this end, the experimentally determined τ values are more suitable, and the model could be removed from the manuscript entirely. *The authors added a note to the manuscript acknowledging the discrepancy of the observed τ relative to those expected from their model, but they did not attempt to revise (or remove) their inadequate model.*

Lines 340 I don't see the need for 29 equations simply to state that the partial pressures evolve exponentially towards their equilibrium value. This seems like a trivial result of the assumed first-order gas-exchange kinetic.

The authors argue that the extensive set of equations is necessary to provide the theoretical background of their model. However, the theoretical background is based on a number of physical misconceptions as described previously.

Fig. 4 The right panel seems unnecessary, as it shows the same data as the one on the left. I'd suggest to show only the left panel and add the fitted exponential curve.

The authors argue that the two panels do not show the same data, but at the same time they also indicate that the right panel presents part of the data in the left panel – so it is the same data. I still think this figure could be simplified a lot.

Lines 349–351 The ratios of the measured and modeled τ values are $4.8/4.3 = 1.1$ (N_2), $3.2/2.2 = 1.5$ (O_2), and $3.0/2.0 = 1.5$ (Ar). In other words, the true (measured) values are up to 50 % higher than those estimated from the model. I don't see how this large discrepancy can be explained by non-ideality of the gas or “impurities” of the membrane. As mentioned before, there are more fundamental flaws in model assumptions.

The observed data simply show that the model is not adequate (as pointed out before).

Lines 357–360 The membrane module used in this work is rather large and therefore exhibits long equilibration times of 12–20 min. Why did the authors not use much smaller membrane modules that would allow equilibration within about 3 min [?], which would in turn also provide approximately 5× better spatial resolution in their dissolved-gas monitoring?

The authors argue that the large size of the volume helps to prevent disturbing the solubility equilibrium. However, the equilibrium disturbance of the headspace

gases is mainly controlled by the dynamic balance of (i) the gas consumption to the mass spectrometer and (ii) the re-supply of gas from the water. Again, the authors' conceptual model of how the GE-MIMS technique works seems incomplete.

Lines 424–425 This has been demonstrated with a GE-MIMS instrument in previous work (Weber et al.).

*The Weber et al. work **did** use the GE-MIMS technique to determine the gas exchange, and I'd suggest to acknowledge that.*