Improvements in short-term atmospheric O$_2$ measurement precision by faster sample-reference switching

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Introduction

High-precision, atmospheric O$_2$ measurement employing the lead fuel cell technique involves switching sample and reference gases between two fuel cells, in order to improve measurement precision and accuracy (Stephens et al., 2007; see Figure 1). The switching frequency of the two gases is typically on the order of 1 minute, of which the first ~30 seconds of data are ignored (known as the sweep-out time). This is to account for flushing of the fuel cells and tubing, and the fuel cell response time (not particularly fast owing to the need for diffusion of sample/reference across a gas-permeable membrane). We have investigated the effect of changing the switching frequency on the short-term precision and accuracy of atmospheric O$_2$ measurements, using two atmospheric O$_2$ measurement systems that employ Oszilla II (Sable Systems Inc.) lead fuel cell analysers.

Methodology

- The Allan standard deviation of the differential O$_2$ signal with no switching indicates that the optimum averaging time is about 14 seconds (see Figure 2). This optimum averaging time represents a trade-off between improved precision from averaging the signal noise and reduced precision owing to the inclusion of longer-term drifts in the differential O$_2$ signal.

- As shown in Figure 1, a single double differential O$_2$ measurement consists of three jogs. Hence, in order to achieve the optimum averaging time, the reference and sample gases would need to switch every 4.5 seconds.

- Owing to the response time of the fuel cells (up to 15 seconds for 90% response time), it is not possible to switch every 4.5 seconds.

- Figure 2 demonstrates, however, that any reduction in sample-reference gas switching time should improve the short-term O$_2$ precision.

- We found that reducing the sample-reference gas switching frequency from 60 to 30 seconds with a sweep-out time of 15 seconds reduced the mean O$_2$ mole fraction standard deviation by up to 81% while measuring cylinder air (see Table 1), and by 25% while measuring ambient air (not shown).

- To mitigate compromising the accuracy of the O$_2$ measurement when reducing the sweep-out time, we minimised the residence time of air in the tubing between the switching valve and the fuel cells, by installing the switching valve as close as possible to the fuel cells and using 0.04" internal diameter tubing.

- We found no change in O$_2$ accuracy as a result of reducing the sweep-out time to 15 seconds (from 30 seconds). Reducing the sweep-out time to 10 seconds, however, did result in a bias in the O$_2$ mole fraction values.

Conclusions

- We demonstrate improvements in short-term atmospheric O$_2$ precision gained by faster sample-reference switching, using two high-precision continuous O$_2$ and CO$_2$ measurement systems.

- Reducing the sample/reference gas switching frequency from 60 to 30 seconds with a sweep-out time reduced from 30 to 15 seconds improved the mean O$_2$ mole fraction standard deviation by up to 81% while measuring cylinder air.

- No change in O$_2$ accuracy was detected as a result of reducing the sweep-out time to 15 seconds. Reducing the sweep-out time to 10 seconds, however, did result in a bias in the O$_2$ mole fraction values.

- Potential biases in the O$_2$ mole fraction values were mitigated by reducing the residence time of air in the tubing between the switching valve and the fuel cells.

References


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Table 1: Improvements in the standard deviation of the O$_2$ measurement of ‘Target’ and ‘Zero’ cylinders made by two different Oszilla II analysers. All values are in ppm units. The standard deviation values for the Antarctic measurement system are lower than those for the Shipboard measurement system owing to the greater number of cylinder runs included in the Antarctic measurement system tests.

<table>
<thead>
<tr>
<th>Shipboard measurement system</th>
<th>Antarctic measurement system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switching time/sweep-out time</td>
<td>60/30 secs</td>
</tr>
<tr>
<td>Target cylinder</td>
<td>± 7.02</td>
</tr>
<tr>
<td>Zero calibration cylinder</td>
<td>± 5.91</td>
</tr>
<tr>
<td># of cylinder runs in analysis</td>
<td>11 Zero, 3 Target</td>
</tr>
</tbody>
</table>

Figure 1: Typical Oszilla II response during sample/reference gas switching. An O$_2$ measurement, indicated by the red (J1) and orange (J2) vertical lines, consists of three switching periods known as ‘jogs’, where sample (S) and reference (WT) gas are switched between cell 1 (red points) and cell 2 (dark blue points). The mean difference between the two cells (after discarding the first 30 seconds of each switch as sweep-out) for a, b, and c (ΔO$_2$; green points) is used to calculate the double differential O$_2$ signal (ΔΔO$_2$) from ΔΔO$_2$ = (a + c – 2b)/2, where overbars denote means. The bottom panel shows the ΔΔO$_2$ measurement in ppm units.

Figure 2: Allan standard deviation plot showing the optimum averaging period of about 14 seconds (black dot). The Allan standard deviation for ΔΔO$_2$ with a standard jog time of 1 minute is indicated by the pink dot.

Figure 3: Red dots show (sample – reference) ΔO$_2$, uncalibrated values, and blue dots show (reference – sample) ΔO$_2$, uncalibrated values. Black dots are data that are not used when calculating ΔΔO$_2$, as these points are when the tubing and fuel cells are being ‘swept-out’. In this example, the sweep-out time is 15 seconds. The calibrated difference in δ(O$_2$/N$_2$) ratio between the reference and sample gases is about 150 ppm meg.