Improvements in short-term atmospheric O_2 measurement precision by faster sample-reference switching

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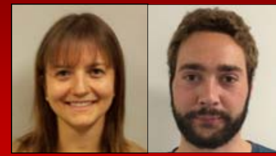

Introduction

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 Oxzilla II (Sable Systems Inc.) lead fuel cell analysers.

Methodology

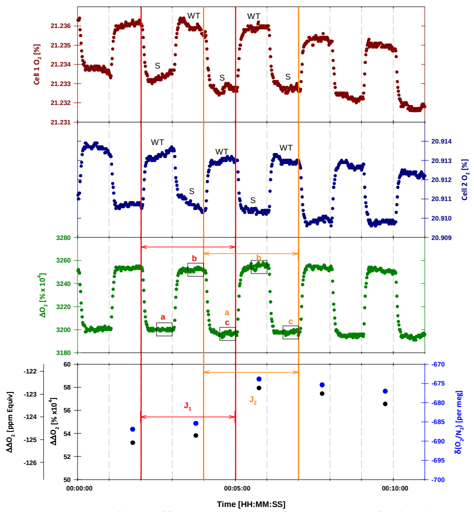

Figure 1: Typical Oxzilla II response during sample/reference gas switching. An O_2 measurement, indicated by the red (J1) and orange (J2) vertical lines, consists of three switching periods known as 'jogs', where sample (S) and reference (WT) gas are switched between cell 1 (red points) and cell 2 (dark 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 ($\Delta\Delta O_2$) from $\Delta\Delta O_2 = (\bar{a} + \bar{c} / 2) - \bar{b}$, where overbars denote means. The bottom panel shows the $\Delta\Delta O_2$ measurement in % x 10^4 and ppm equivalent units (black symbols), as well as $\delta(O_2/N_2)$ ratio in 'per meg' units once calibrated (blue symbols), where a 4.77 per meg $\delta(O_2/N_2)$ change is equivalent to a 1 ppm change in trace gas mole fraction.

- 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.

Results

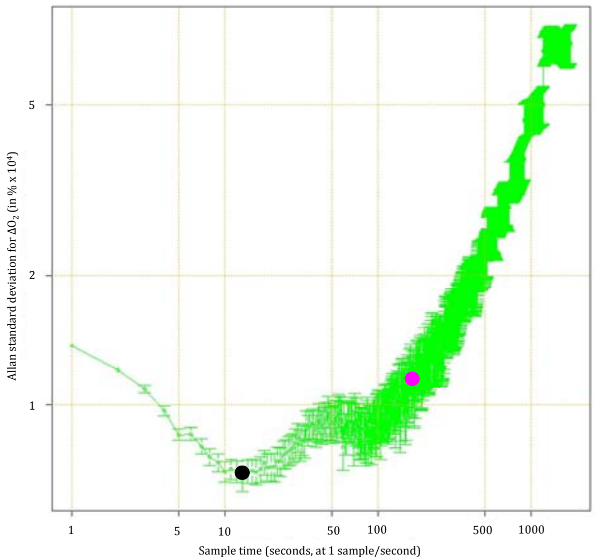

Figure 2: Allan standard deviation plot showing the optimum averaging period of about 14 seconds (black dot). The Allan standard deviation for ΔO_2 with a standard jog time of 1 minute is indicated by the pink dot.

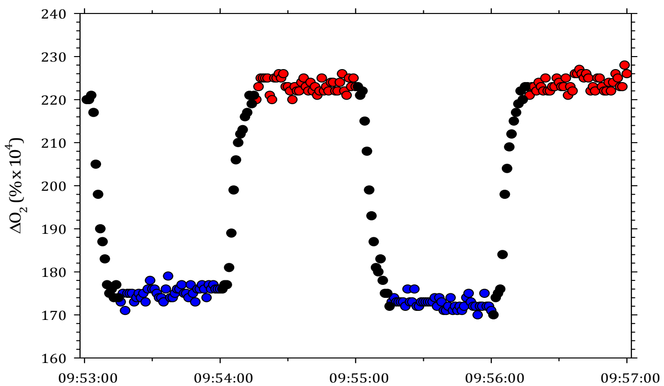

Figure 3: Red dots show (sample –reference) ΔO_2 uncalibrated values, and blue dots show (reference – sample) ΔO_2 uncalibrated values. Black dots are data that are not used when calculating $\Delta\Delta O_2$, as these points are when the tubing and fuel cells are being 'swept-out'. In this example, the sweep-out time is 15 seconds. The calibrated difference in $\delta(O_2/N_2)$ ratio between the reference and sample gases is about 150 per meg.

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

	Shipboard measurement system		Antarctic measurement system	
Switching time/sweep-out time	60/30 secs	30/15 secs	60/30 secs	30/15 secs
'Target' cylinder	± 7.02	± 1.31	± 1.18	± 0.90
'Zero' calibration cylinder	± 5.91	± 1.22	± 1.63	± 1.17
# of cylinder runs in analysis	11 Zero, 3 Target		43 Zero, 25 Target	

Table 1: Improvements in the standard deviation of the O_2 measurement of 'Target' and 'Zero' cylinders made by two different Oxzilla II analysers. All values are in per meg 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.

References

Stephens, B. B., Bakwin, P. S., Tans, P. P., Teclaw, R. M., and Baumann, D. D.: Application of a differential fuel-cell analyzer for measuring atmospheric oxygen variations, Journal of Atmospheric and Oceanic Technology, 24, 82-94, 10.1175/jtech1959.1, 2007.

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