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Atmospheric Measurement Techniques Discussions

Interactive comment on "Assessment of a multi-species in-situ FTIR for precise atmospheric greenhouse gas observations" *by* S. Hammer et al.

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Review for amtd-5-3645-2012

Assessment of a multi-species in situ FTIR for precise atmospheric greenhouse gas observations
by S. Hammer *et al*

Vanessa Sherlock, 3 September 2012

General comments

It was a pleasure to review this paper. While entirely technical in scope, it represents and exhaustive study of the performance of the FTIR trace gas analyser developed by the University of Wollongong and now commercialised by Ecotech. The paper is dense in detail, but I am sure it will serve and be widely cited as a leading reference for FTIR analyser measurement and calibration procedures for some time to come. I do have some suggestions which I would encourage the authors to consider/implement to assist a general reader to access the information in the paper more efficiently:

- A short section providing a brief overview of the sample data acquisition, analysis (retrieval through cross-sensitivity correction) and the calibration procedure should be added immediately after the introduction. This should give the reader a clear steer on aspects of the instrument hardware and analysis that are key or limiting factors governing measurement precision and accuracy. This will enable the reader to make better sense of the multitude of technical details they encounter from Section 2.1 onwards!
- Similarly, it would help if the first paragraph (up to l15 of p3673) in section 6 was moved to section 2, and that the hardware and Standard Operating Conditions for the current Heidelberg setup were all discussed in a dedicated subsection. Once again, it would help the reader to have the key instrument changes required to meet the performance requirements clear at the outset so they can more readily appreciate the relevance of the subsequent results and discussion. A single terminology should be adopted to refer to original and current configurations (the text uses new/modified/Heidelberg/current, and is sometimes difficult for the reader to follow).
- The flow of the presentation of the results would be clearer if the material in Section 2.4 (and figure 2) were moved to an appendix. The discussion of the homogeneity of the temperature distribution within the cell in the introduction to

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Section 3 is sufficient lead-in to the presentation of the temperature sensitivity results (and the reader can be referred to the appendix for futher details). The flush/evacuation sample exchange methods are only mentioned once again themselves in passing in Section 6, and reference there to the Appendix would also suffice.

Specific comments

Section 2.3

I struggled with this section, which covers a lot of measurement concepts which have not been explicitly introduced (air and tank sample types (calibration procedure requiring reference gases); spectrum acquisition in static and flow modes of operation, flow and evacuation methods sample exchange . . .) and further mixes details specific to original and current configurations of the analyser and its operation.

The reasons behind the choice to flow both air and calibration tank samples are never described explicitly (although systematic biases between static and flowing measurements are mentioned in Section 3.5). I believe the unresolved issue of static/flow biases is as important (and potentially related to) the measurement temperature dependencies, and should be discussed more fully.

Section 2.4

In addition to the recommendation above to make this section an appendix:

- p3652 l1-2 Reword? e.g. 'Sample measurement and calibration accuracy depend both on the intrinsic instrument performance (SNR) and on the complete exchange of the gas sample in the cell without memory effects.
- p3653 paragraph 2 Surely some mention of the RTD sensor response time needs to be made here? Details of the calculation of the Reynolds number for the cell should be given (e.g. in a second appendix).

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Section 3

I feel the introductory discussion does not distinguish clearly enough between systematic retrieval biases which depend on sample properties (e.g. the retrieved target gas concentration may vary with cell pressure due to errors in spectroscopic parameters describing line broadening) and errors in the measured values of the sample properties (pressure, temperature) and their propagation into the estimated dry air mole fraction. In principle, sensor errors are 'unknowable' random errors which cannot be corrected (systematic biases should be eliminated in hardware).

The systematic retrieval biases can in principle be characterised by sensitivity experiments of the type described here, provided the errors in the measurements of the sample properties themselves are sufficiently small. Alternatively, the empirical sensitivity characterisation can be considered to comprise contributions from the retrieval and sample parameter measurement errors, and this may be useful when considering the temporal stability of a sensitivity correction multiplier: the spectroscopic errors are unchanged, but measurement sensitivity may alter due to changes e.g. in instrument ILS or drifts in the calibration of sample parameter sensors. One would assume the latter (drifts) would small, but for these high-end applications this probably needs to be checked routinely: significant drifts have been found in the pressure sensors (MKS 902 series piezo transducer) used in some prototype FTIR analysers.

Given the comments above, the 'Temperature disequilibrium sensitivity' merits careful presentation. The error in the estimated gas temperature can only be considered to be a correctable cross-sensitivity if the error is reproducible i.e. a systematic bias which depends on some other system variable (e.g. flow rate) and the error can be reliably estimated i.e. the error can be characterised, but for some reason, the method used to characterise the error cannot be applied in data acquisition (or at least not retro-actively). The multiplier dX/dT in the Taylor series expansion for the tracer dry air mole fraction X as a function of temperature error ϵ_T can be derived by perturbing the temperature assumed in the Malt retrievals and the associated calculation of the

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molar concentration of dry air in the cell. The temperature error ϵ_T is common to all tracer retrievals, so the empirically determined tracer sensitivity to cell temperature (in this case) ΔX divided by dX/dT should give a consistent estimate of ϵ_T for all tracers. The signs and magnitudes of the slopes of the curves in Figure 4 are consistent with a common temperature error which is $\sim$directly proportional to the cell temperature for CO_2, CH_4 and CO but not for N_2O (I did not do the calculation for $\delta^{13}CO_2$). Given the magnitude of the corrections applied ($\sim$2 ppm/C for CO_2), this is cause for further thought, particularly as there is no clear mechanism for the inferred temperature error.

If I interpret the room temperature bars at the top of Figure 4 correctly (i.e. assuming that the cell temperature range shown for each box is the true range for the given site/instrument deployment), then the data set forms three disjoint clusters (in cell temperature), and in many cases, the temperature dependence of a given cluster is a lot less marked than the impression given by the ensemble. I assume (the authors should state explicitly in the text and figure legend) that the measurements shown are not calibrated. If the mean difference between air and calibration tank sample temperatures (ΔT) is $\sim$0, then would calibration not eliminate the first order site dependent differences? Residual variability of the order of e.g. $\pm$0.1 ppm full range in CO_2would remain for each sub-ensemble, but this is arguably a more realistic estimate of the measurement reproducibility, at least in the configuration using the PT100 RTD temperature sensor. If the mean ΔT is not $\sim$0 and/or this varies from deployment to deployment, then the situation is more complicated and would suggest to me, as the authors discuss, that the problem is fundamentally related to cell conditioning and/or temperature sensor response post-evacuation.

Finally, I recommend the discussion of the different TDS with RTD and J-type thermocouple temperature sensors in paragraph 2 of section 6 (l15-24 of p3673) is moved to Section 3 (e.g. create a subsection 3.3 Temperature sensitivity with subsections 3.3.1 and 3.3.2 containing the material currently in sections 3.3 and 3.4 respectively; add the material from section 6 as a third subsection (3.3.3)).

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Section 5.1

Had the PT100 RTD temperature sensor been replaced when the short-term stability test was run? If so, the text on p3667 l4-7 appears to contradict the statements in Section 6. Please clarify in the manuscript.

Section 6

Do you think the conclusions regarding the merits of evacuation and flushed sample exchange depend on the temperature sensor employed in the experiment i.e. do you think a similar conclusion holds for the PT100 RTD sensor or not? It would be worth noting in the manuscript.

Conclusions

I think the conclusions definitely need to recap. the instrument modifications and operating conditions (flowing calibration etc) that were needed to fulfil the requirements for precision, accuracy and stability.

I would add static/flow bias to current outstanding issues: as you say, flowing calibrations require a lot of precious cal gas, and this is a significant drawback particularly for deployments at remote field stations.

Technical corrections

- in situ should not be hyphenated
- write out demo-experiment in full i.e. demonstration experiment
- does two-daily mean twice daily or every two days? please revise thoughout

Abstract

- There is a mix of tenses used in the abstract.

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- p3646 l2 suggest reword as 'The FTIR analyser is shown to measure . . . '
- p3646 l7-9 suggest reword as 'Residual dependencies between . . . thermodynamic properties of the sample and the cross-sensitivities . . . constituents are quantified and minimised where possible.'
- p3646 l11 suggest reword 'investigated by' as 'characterised using'

Section 1

- p3647 move paragraph 'Another benefit of optical spectroscopy ...' after the paragraph ending line 24 of that page?
- p3647 l21 cut Especially
- p3648 l1 'Especially' should be replaced by 'In particular'
- p3648 l18 reword 'and their benefits' as 'and the resulting benefits'

Section 2

- p3648 l23 reword 'Further on' as 'Hereafter'
- p3649 l5-6 reword as 'the transfer optics between the interferometer, the multipass cell and the interferometer housing ...'
- p3649 l22 Should original be added for clarity in 'For additional stabilization ... in the cell, the original Heidelberg configuration used an add-on ...'?
- p3651 l17 reword as 'Measurements of ambient air . . . still differ with respect to . . . however.'
- p3651 l21-22 Suggest cutting sentence 'Possible disadvantages . . . later on.'

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Interactive Comment

Section 3

- p3655 l3-4 The reference to 'current FTIR setup' here is ambiguous: the sample injection is the same for original and modified versions of the instrument right?
- p3661 l16 reword 'linearity disappeared' as 'linearity broke down'

Section 6

- p3675 l28 reword to clarify that CO_2 refers to CO_2 cross-sensitivity

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Interactive comment on Atmos. Meas. Tech. Discuss., 5, 3645, 2012.