Eight years of in situ measurements of CH\textsubscript{4}, N\textsubscript{2}O and CO made with a prototype Fourier Transform gas analyser at Lauder, New Zealand

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1. Introduction
A prototype in situ Fourier transform infra-red spectrometer trace gas analyser (IFTS, Griffith, 2012) has been operating at Lauder, New Zealand (45\textdegree S, 170\textdegree E, 370m) since August 2006. Prior GGTM presentations have focussed on characterising the performance of the IFTS CO measurements to investigate the performance of the Lauder (LAU) IFTS at measuring CH\textsubscript{4}, CO and N\textsubscript{2}O and then comparing these measurements to similar measurements made at Baring Head, New Zealand (41\textdegree 35, 175\textdegree E, 87m).

How the IFTS works:
Continuous measurements of CO\textsubscript{2}, CH\textsubscript{4}, CO and N\textsubscript{2}O are made from air drawn from a 10 metre mast. The air sample is dried to <20 ppm H\textsubscript{2}O with a Nafion drier and Mg(ClO\textsubscript{4})\textsubscript{2} trap. The IFTS consists of a Bruker Optics iRCube interferometer coupled to a multi-pass sample gas cell (optical path 24 meters, column 3.5 L). The IFTS is thermally controlled, and since 2013 the sample cell temperature is actively stabilized (Braithwaite, 2012). The 34.5 minute absorbance spectra (1750-6750\textsuperscript{cm\textsuperscript{-1}}) are recorded and averaged over ten minute intervals as air flows continuously through the sample cell.

2. IFTS precision and accuracy

Precision:
The repeatability of the IFTS measurements is calculated from Allan variance analysis (Allan, 1966) for the measurement averaging time (10 minutes, see Table 1).

Corrections:
Prior to an instrument upgrade in mid-2013 the IFTS had a large operational cell pressure range (815mB–950mB), with differences between sample and calibration cell pressures of up to 50mB. Under such conditions it is necessary to apply a residual pressure sensitivity (RPS) correction (Hammer, 2013) to the retrieved dry mole fraction. After the upgrade cell pressure is kept at 1100Pa +/- 0.5Pa, dramatically reducing RPS correction.

Accuracy:
RPS corrected CH\textsubscript{4}, CO and N\textsubscript{2}O mixing ratios of a routinely measured single working tank (WT) are scaled by the assigned WT dry mole fraction to give a scale factor (SF). The SF is applied to sample measurements to place them on the WMO/NOAA trace gas calibration scales. WT’s are prepared by NGA-Gaslab with a dry mole fraction of 0.5%

4. Introduced bias when using a single WT

Aniwanua suite measurements confirm that the IFTS response function is linear with a zero-y intercept (Griffith, 2012 & Hammer, 2013). Linear calibration with a single WT (operational cell pressure and FTIR offsets) cannot account for a zero-y intercept term. The resultant calibration bias by assuming a zero offset has a dependence on the difference between the WT assignment and atmospheric baseline abundance. Due to a minimum concentration dependent bias in all three species when the single WT is of similar composition to the expected sample measurement abundance.

5. Monitoring long term instrument stability

Since 2012, a target tank (TT) has been routinely measured by the IFTS system to monitor short term and long term instrument stability (reproducibility). Additionally it provides a check on WT calibration with respect to the sample cell. The target tanks are kept at a constant pressure of up to 50mB. Under such conditions it is necessary to apply a residual pressure sensitivity (RPS) correction (Hammer, 2013) to the retrieved dry mole fraction. After the target tank upgrade cell pressure is kept at 1100Pa +/- 0.5Pa, dramatically reducing RPS correction.

6. Lauder IFTS CO-flask comparison

Fig 3. IFTS measurements are compared to trace gas concentration retrievals from gas chromatography (GC) of flask samples acquired routinely in baseline conditions (see section 7 for definition) at LAU since May 2009. IFTS-flask bias and 1-σ uncertainties are given for the measurements. The bias is defined as the difference between IFTS and the reference GC-flask baseline average.

7. Lauder - Baring Head comparison

Fig 4. A comparison of baseline concentrations at LAU (rural inland site) against Baring Head (BHD, coastal southern New Zealand) for CH\textsubscript{4}, CO and N\textsubscript{2}O. The "clean air" baseline is defined as the lowest seasonal concentration measured at the site. These seasonal cycle extremes are used as a representative of the background level for baseline comparison.

8. Summary

Operation of the IFTS over the past eight years has shown the instrument repeatability and reproducibility to be stable over the entire measurement range of 0-1 ppm.

Concentration dependent bias arising from using a single working tank is minimized when the composition of the working tank is similar to that of the expected atmospheric baseline abundance.

Comparison of the IFTS and GC-flask measurements show that the bias in CH\textsubscript{4} of -0.7ppb +/- 2.3 (IFTS - flask) and CO (-0.2ppb +/- 1.7) are within the recommended IFTS Inter-Laboratory comparability limits of 2ppb respectively. Whilst the bias in N\textsubscript{2}O (0.05ppb) is bordering on the accepted limit of 0.1ppb, the spread of 0.8ppb is outside the current recommended GC limits.

The IFTS time series captures the seasonal variations in CH\textsubscript{4} and CO, the secular rise in CH\textsubscript{4} since 2006, an increase in the upward trend in N\textsubscript{2}O since mid-2009 and the downward trend in CO.

Outlook:
Lauder IFTS and GC-flask CH\textsubscript{4} measurements have been submitted to the WDCCG. We are now approaching the point where we will be able to provide a secular CO2 baseline from 1965.

References