

Eight years of in situ measurements of CH₄, N₂O and CO made with a prototype Fourier Transform trace gas analyser at Lauder, New Zealand



[Poster presenter: Gordon Brailsford.]

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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 (45S, 170E, 370m) since August 2006. Prior GGMT presentations have focussed on characterizing the performance of the IFTS CO₂ measurements. Here we investigate the performance of the Lauder (LAU) IFTS at measuring CH₄, CO and N₂O then comparing these measurements to similar measurements made at Baring Head, New Zealand (41S, 175E, 87m).

How the IFTS works:

Continuous measurements of CO₂, CH₄, CO and N₂O are made from air drawn from a 10 metre mast. The air sample is dried to <20 ppm H₂O with a Nafion drier and Mg(ClO₄)₂ trap. The IFTS consists of a Bruker Optics IFCube interferometer coupled to a multi-pass sample gas cell (optical path 24 meters, volume 3.5 L). The IFTS is thermostatically controlled, and since 2013 the sample cell pressure is actively stabilised. The mid-infrared spectra (1750-6750cm⁻¹) are recorded and averaged over ten minute intervals as air flows continuously through the sample cell.

The retrieved gas concentrations (via MALT spectral fitting analysis, Griffith, 1996) are converted to dry mole fraction by dividing by the sample cell air concentration and correcting for H₂O in the sample.

(*mole fraction abbreviations: ppm => μmol mol⁻¹, ppb => nmol mol⁻¹)

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 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 upgrade cell pressure is kept at 1100hPa +/- 0.5hPa, dramatically reducing RPS correction.

Accuracy: RPS corrected CH₄, CO and N₂O dry 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 NIWA-Gaslab with a lineage to WMO-CCL scales.

Species	Precision (10 minute mean) [ppb]	RPS [ppb hPa ⁻¹]	Current working tank scale
CH ₄	0.2	0.034	WMOx2004A
CO	0.3	0.001	WMOx2014
N ₂ O	0.05	0.008	NOAA2006A

Table 1. IFTS precision 1-σ standard deviation (SD) for a 10-minute spectra average, empirically derived linear RPS and the current trace gas calibration scale for each species.

3. A customized IFTS calibration suite

A dedicated IFTS scale transfer standard gas tank suite (referred to as the *Aniwaniwa* suite) was designed by NIWA and prepared at NOAA ESRL-GMD. It has a customized trace gas composition matrix consisting of prescribed CO₂, CH₄, N₂O and CO mole fractions spanning the typical trace gas concentrations seen at LAU.

The composition matrix (see Table 2) is configured to minimize gas measurement cross sensitivity/covariance in the MALT retrieval algorithm. The MALT retrieval code performs spectra fitting across four independent micro-window bands. Preference for species concentration orthogonality is given to species retrieved in the same micro-window band (for example CO and N₂O).

Tank ID	CO ₂ [ppm] WMOx2007	CH ₄ [ppb] WMOx2004A	CO [ppb] WMOx2014	N ₂ O [ppb] NOAA2006A
CB09978	412.70	1733.24	95.90	339.02
CB10005	398.51	1687.32	131.01	320.08
CB10248	457.68	1742.82	51.32	307.38
CB10202	380.42	2019.30	107.77	338.94

Table 2. Species concentrations of the four tank calibration suite. The three coloured bands (orange, green, aqua) in the table cells correspond to the three independent MALT retrieval micro-window bands used in the retrieval of the four species. Table cell brightness is related to relative concentration, lighter the colour the lower the relative concentration.

4. Introduced bias when using a single WT

Aniwaniwa suite measurements confirm that the IFTS response function is linear with a non-zero y-intercept (Griffith, 2012 & Hammer, 2013). Linear calibration with a single WT (operational configuration to date) cannot account for a non-zero y-intercept term. The resultant calibration bias by assuming a zero offset has a dependence on the difference between the WT assignment and sample abundance. Figure 1. shows a minimal concentration dependent bias in all three species when the single WT is of similar composition to the expected sample measurement abundances.

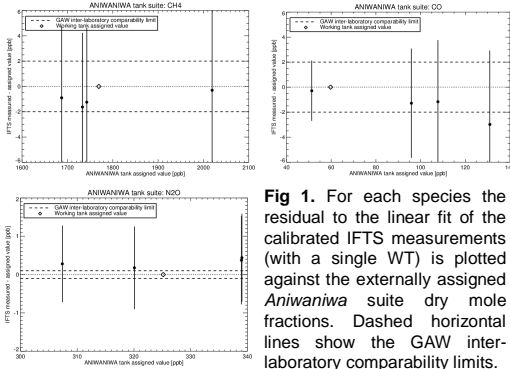


Fig 1. For each species the residual to the linear fit of the calibrated IFTS measurements (with a single WT) is plotted against the externally assigned *Aniwaniwa* suite dry mole fractions. Dashed horizontal lines show the GAW inter-laboratory comparability limits.

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 drift until a multi working tank suite is employed. It is advantageous to interleave TT and WT cylinder changes to minimize TT and WT correlations. Figure 2 displays measurements over the lifetime of one TT. Temporal drift in all three species concentrations is minimal. CH₄, CO and N₂O TT 1-σ SD are 0.65, 0.24, and 0.19 (ppb) respectively.

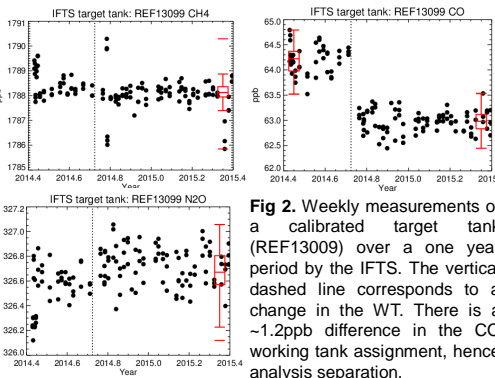


Fig 2. Weekly measurements of a calibrated target tank (REF13099) over a one year period by the IFTS. The vertical dashed line corresponds to a change in the WT. There is a ~1.2ppb difference in the CO working tank assignment, hence analysis separation.

6. Lauder IFTS GC-flask comparison

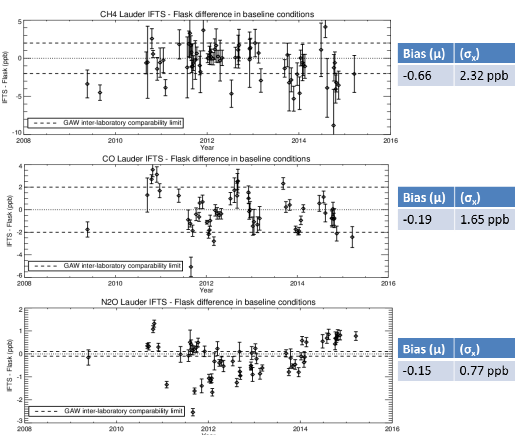


Fig 3. IFTS measurements are compared to trace gas concentrations derived from gas chromatography (GC) of flask air samples acquired routinely in baseline conditions (see section 7 for definition) at LAU since May 2009. IFTS-flask bias and 1-sigma SD are shown for each species. CH₄ and CO bias and SD meet GAW compatibility goals (dotted lines) whilst N₂O bias is more serendipitous, given the comparison SD.

7. Lauder - Baring Head comparison

Figure 4 shows a comparison of baseline concentrations at LAU (rural inland site) against Baring Head (BHD, coastal southern ocean site) GC-flask baseline measurements (Brailsford, 2012). Back trajectory modelling shows that in baseline conditions both sites have a considerable origin of air component from the Tasman sea and/or Southern ocean, but in addition LAU also sees air masses that have had last surface contact from the west of the South Island of New Zealand, an abundant temperate rain forest area.

In contrast to LAU-BHD CO₂ baseline measurement comparisons (Steinkamp, GGMT2015 poster) we do not see any seasonal drawdown or elevated levels at LAU for CH₄, CO and N₂O. Both sites show remarkably similar trends and season cycles for all three trace gases alluding to a lack of any large scale local terrestrial biogenic -or anthropogenic- sinks/sources. Both sites capture a curious decrease in N₂O during 2009.

Baseline definition: representative of a well-mixed planetary boundary layer with minimum trace gas variability.

- Lauder baseline: Measurements taken between 15:00-16:00 NZST when the mean wind speed > 5 m/s.
- Baring Head baseline: When CO₂ 1-σ SD (measurements via a continuous analyser) over a 6 hour interval is < 0.2ppm.

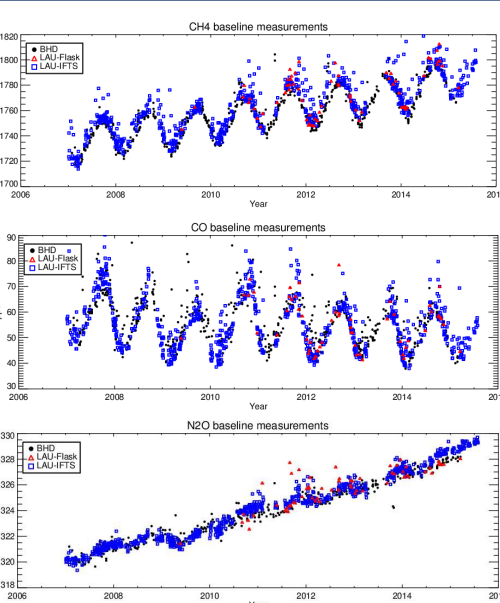


Fig 4. LAU IFTS (blue square) and GC-flask (red triangle) baseline measurements overlaying BHD (black circle) baseline GC-flask measurements for the three species. Linear trend for each species: CH₄, ~6ppb/year, CO: ~-1ppb/year, N₂O: 1ppb/year.

8. Summary

- Operation of the IFTS over the past eight years has shown the instrument repeatability and reproducibility to be stable over the long term.
- 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 abundances.
- Comparison of the IFTS and GC-flask measurements show that the bias in CH₄ of -0.7ppb +/- 2.3 (IFTs - flask) and CO (-0.2ppb +/- 1.7) are within the recommended GAW Inter-Laboratory comparability limits of 2ppb respectively. Whilst the bias in N₂O (of -0.15ppb) is bordering on the accepted limit of 0.1ppb , the spread of 0.8ppb is outside the current recommended GAW limits.
- The IFTS time series captures the seasonal variations in CH₄ and CO, the secular rise in CH₄ since 2006, an increase in the upward trend in N₂O since mid-2009 and the downward trend in CO.

Outlook:

- Lauder IFTS and GC-flask CH₄ measurements have been submitted to the WDCGG. We are now approaching the point where IFTS-CO can also be submitted.
- A multi-tank working tank suite is to be employed to allow characterisation of the non-zero linear offset. This will reduce the concentration dependent bias inherent in the current calibration scheme.

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