

## THE UOW FTIR TRACE GAS ANALYSER: COMPARISON WITH LOFLO, AGAGE AND TANK MEASUREMENTS AT CAPE GRIM AND GASLAB

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### Abstract

Accurate baseline measurements of clean air composition are technically demanding, and benefit from advances in instrumentation which improve accuracy and lower the cost and effort of ownership. The University of Wollongong FTIR trace gas analyser for determination of atmospheric trace gas concentrations has been significantly refined in the past decade since its initial development, providing improved accuracy and greater ease of operation. From October 2008 to February 2009 we operated a new analyser at Cape Grim, parallel to the CSIRO LoFlo CO<sub>2</sub> analyser and AGAGE automated GC system. The FTIR analyser drew air from the 70-m tower inlet and operated continuously and autonomously for 110 days measuring 10-minute average concentrations of CO<sub>2</sub>,  $\delta^{13}\text{C-CO}_2$ , CH<sub>4</sub>, CO and N<sub>2</sub>O. Here the measurements are compared with LoFlo for CO<sub>2</sub>, AGAGE for the other gases and isotope ratio mass spectrometry for  $\delta^{13}\text{C}$  in CO<sub>2</sub>. The FTIR analyser provided precisions significantly better than those provided by AGAGE for all co-measured species, but less than that of LoFlo for CO<sub>2</sub>. In March and April 2010 we also operated the same analyser at CSIRO's Global Atmospheric Sampling Laboratory (GASLAB), making measurements of 36 standard calibration cylinders with well-characterised concentrations. We present the results of this comparison, in which the FTIR shows good precision and linearity over all measured concentration ranges. The FTIR analyser provides a cost-effective, low maintenance solution for the simultaneous measurement of the target species.

### 1. Introduction

Atmospheric trace gas analysis techniques with the accuracy and precision required to follow secular trends and variability in the clean background atmosphere require extraordinary care and attention to maintain and verify data quality and calibration. They are generally labour-intensive and hence expensive to operate and calibrate. Measurement programs such as the Advanced Global Atmospheric Gases Experiment (AGAGE) and others that form the World Meteorological Organisation's Global Atmospheric Watch (GAW) programme and include baseline stations such as Cape Grim, thus benefit from new techniques which provide either improved precision, and/or lower cost and effort of operation and calibration. New and emerging optical techniques such as laser absorption or cavity ringdown spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy, have much to offer because absorption of radiation is a more fundamental quantitative basis for measurement than chemical and separation methods such as gas chromatography. Optical methods usually provide continuous data and with current performance (determined by sources, detectors, stability and noise) provide precision and calibration accuracy generally on a par with or better than chemical or separation methods.

Since the early 1990s, at the University of Wollongong we have developed and operated a multi-species analyser for high precision measurements of trace gases in clean air based on

FTIR spectrometry. The original instrument is described by Esler *et al.* [2000a; b], including a 2-week trial at Cape Grim in 1995. From October 2008 to February 2009 we operated a new analyser incorporating several improvements at Cape Grim, parallel to the CSIRO LoFlo CO<sub>2</sub> analyser and AGAGE automated GC system. In March-April 2010 the same analyser was located in CSIRO Marine and Atmospheric Research's Global Atmospheric Sampling Laboratory (GASLAB) in Aspendale and used to make measurements of all target gases in 36 calibration tanks. This paper briefly describes the instrument and presents the results of these comparisons.

### 2. Experimental methods

#### 2.1. FTIR analyser

The new FTIR analyser contains several improvements over the earlier version described by Esler *et al.* [2000a; b], and will be described in more detail in a paper in preparation for *Atmospheric Measurement Techniques*. In summary, the analyser consists of a commercially-available FTIR interferometer (IRcube, Bruker Optics, Germany), coupled to a multi-pass sample gas cell (IRanalysis, Anaheim CA) with 24 m optical pathlength and 3.5 L volume, all contained in a thermostatted enclosure to improve stability. Sample and calibration gas handling is via an integrated manifold of Dekabon<sup>®</sup> tubing, 8 solenoid valves and an oil-free 4-stage diaphragm pump. Air samples are dried to < 20  $\mu\text{mol}$

mol<sup>-1</sup> H<sub>2</sub>O with a Nafion<sup>®</sup> dryer followed by Mg(ClO<sub>4</sub>)<sub>2</sub> trap. Recorded spectra are analysed in real time and the resultant trace gas concentrations and other data logged and displayed after each spectrum is recorded. Operation is fully automated via a single program ('OSCAR') written in Visual Basic and running on a standard laptop PC computer running Windows XP. At Cape Grim the PC was connected to the internet, allowing remote control via Windows Remote Desktop from Wollongong after installation.

Recent improvements to the instrument include the new Bruker FTIR interferometer, incorporating a thermoelectrically-cooled Mercury Cadmium Telluride (MCT) detector which does not require liquid nitrogen, and general improvements in signal:noise, stability, purging, sample and calibration gas handling, and spectrum quantitative analysis. The only consumables required are a small N<sub>2</sub> purge of 0.1-0.2 L min<sup>-1</sup>, Mg(ClO<sub>4</sub>)<sub>2</sub> replacement (typically 2-4 months), and calibration gas. The instrument operated over the trial period with only minimal intervention from Cape Grim staff (exchange of N<sub>2</sub> purge cylinder).

Unlike laser-based (e.g. Los Gatos, Picarro) or filter-based (e.g. NDIR such as LoFlo and LI-COR) optical instruments, the FTIR spectrometer records the broadband absorption spectrum (1800-5000 cm<sup>-1</sup>) of the sample air; the same spectrum can be analysed in different spectral regions to retrieve concentrations of several trace gases simultaneously. Spectra are archived and can be reanalysed at a later date with improved methods as they may become available. In clean, dried air, the species available with useful precision are CO<sub>2</sub>, CH<sub>4</sub>, CO and N<sub>2</sub>O. In addition, <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> are determined independently, allowing a continuous determination of δ<sup>13</sup>C in CO<sub>2</sub>. In this study spectra were analysed by nonlinear least squares fitting of portions of the measured spectrum with a modelled spectrum calculated from the HITRAN database of absorption line parameters [Rothman *et al.*, 2005]. The spectrum model calculation (MALT) is described in detail elsewhere, with the original Classic Least Squares (CLS) method replaced by non-linear least squares fitting of calculated to measured spectra [Griffith, 1996; Griffith *et al.*, 2003]. Three separate spectral regions were fitted for each spectrum: 2150-2320 cm<sup>-1</sup> for <sup>13</sup>CO<sub>2</sub>, <sup>12</sup>CO<sub>2</sub>, CO and N<sub>2</sub>O, 3001-3150 cm<sup>-1</sup> for CH<sub>4</sub> and 3520-3775 cm<sup>-1</sup> for CO<sub>2</sub> (all isotopomers) and residual H<sub>2</sub>O. From the spectrum analysis, we determine true concentrations (*C* mol m<sup>-3</sup>) of each gas species; the concentrations are converted to mixing ratios (mole fractions, *χ*) by dividing by the concentration of air

$$\chi_{wet} = \frac{C}{P/RT} \quad (1)$$

where *P* is the total cell pressure, *T* the absolute temperature and *R* the universal gas constant, and

corrected to dry air using the water vapour amount determined from the FTIR spectrum:

$$\chi_{dry} = \frac{\chi_{wet}}{1 - \chi_{H_2O}} \quad (2)$$

## 2.2. Precision and calibration

Precision of the FTIR measurements was determined by analysis of Allan variance [Werle *et al.*, 1993] in laboratory work prior to the Cape Grim comparison. For 10-minute averages, as used here, the 1σ precisions of repeated measurements of the target quantities of a single sample ('repeatability' as defined by GAW, [Klausen and Scheel, 2007]) are given in Table 1. The observed scatter in the 10-minute time series of measurements at Cape Grim is consistent with but slightly higher than these laboratory-determined repeatabilities.

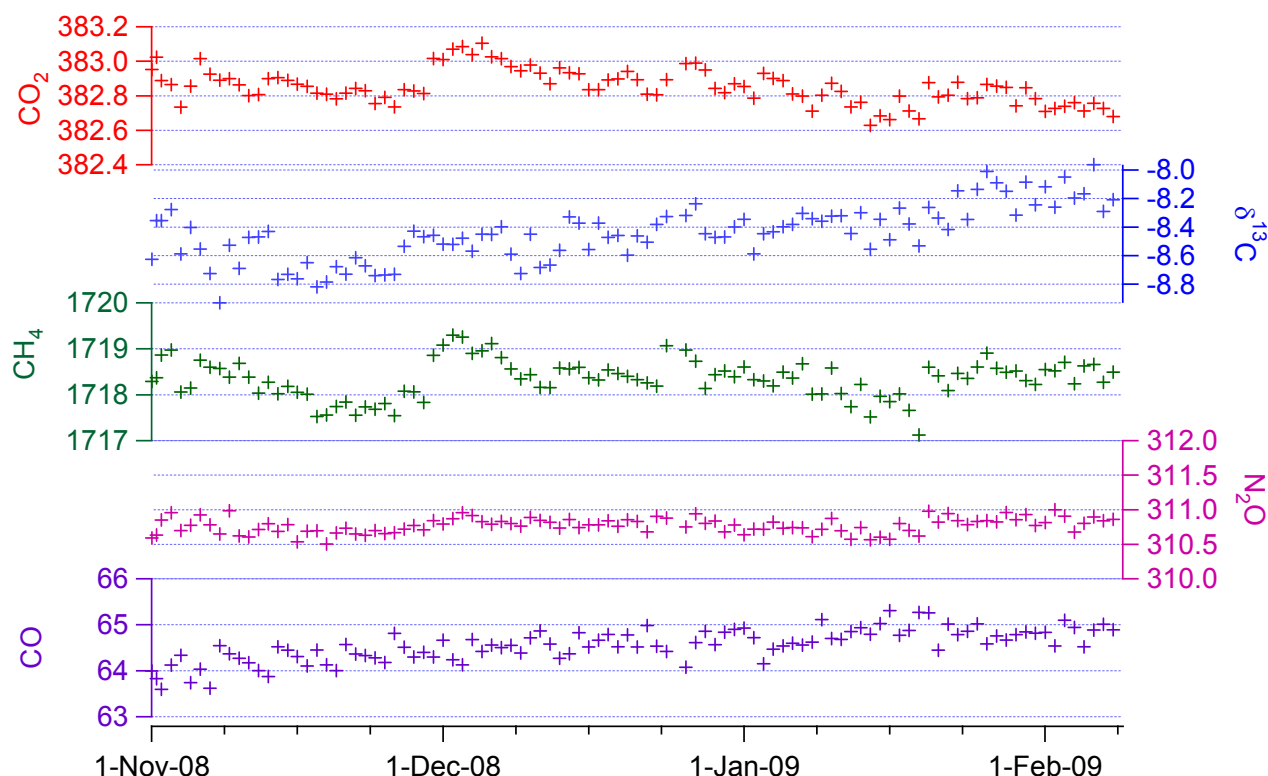
**Table 1.** Repeatability of trace gas determinations for the FTIR analyser. The precision values are the 1σ scatter in repeated 10-minute average measurements of a single air sample.

Species	Precision (1σ, 10 min)
CO <sub>2</sub>	0.02 μmol mol <sup>-1</sup>
δ <sup>13</sup> C in CO <sub>2</sub>	0.04 ‰
CH <sub>4</sub>	0.2 nmol mol <sup>-1</sup>
CO	0.2 nmol mol <sup>-1</sup>
N <sub>2</sub> O	0.06 nmol mol <sup>-1</sup>

For all species except CO<sub>2</sub> and CO, repeatability further improves with approximately the square root of the averaging time up to at least 1-2 hours. For CO<sub>2</sub> and CO repeatability did not improve beyond 5 minute or 20 minute averaging respectively due to slow drifts in the concentrations in the cell – CO<sub>2</sub> decreases slowly and CO increases. These drifts are chemical in origin, not due to the spectroscopy, and can in principle be addressed with different cell construction materials or treatment.

The FTIR analyser provides mixing ratios in its own raw 'FTIR scale' based on the spectral fitting technique and HITRAN spectroscopic data. This scale is precise as described above, but generally only accurate to within a few percent. The FTIR scale data were compared to AGAGE- and GASLAB-calibrated data by using daily FTIR measurements of a single calibrated reference gas cylinder. The daily FTIR measurements of the reference gas were used to generate a daily scale factor, by which the FTIR data were converted to the reference scales. The calibration gas measurement procedure is described in the following section.

The raw daily determinations of the reference gas on the FTIR scale are shown in Figure 1. The day-to-day measurement variability and drift over the 110 days of the trial is generally similar to the short-term measurement precision, illustrating the good stability of the instrument.



**Figure 1.** Time series of daily raw calibration gas FTIR measurements. All values are in the raw FTIR scale,  $\text{CO}_2$   $\mu\text{mol mol}^{-1}$ ,  $\delta^{13}\text{C}$  ‰, other species in  $\text{nmol mol}^{-1}$ .

The reference gas was collected on 22 October 2008 at Cape Grim under clean (but not baseline) atmospheric conditions in a 34 L stainless steel archive cylinder (G-166/S34L-H16, UAN 20100075) to ~6 MPa pressure following the standard Cape Grim archive gas cryogenic collection procedure. The reference cylinder was analysed using the AGAGE GC system while at Cape Grim and in GASLAB on 14 August 2009. Table 2 summarises the determinations of the mixing ratios of all trace gas species in the reference cylinder.  $\text{CH}_4$  and  $\text{N}_2\text{O}$  mixing ratios were assigned from AGAGE GC analyses at Cape Grim and  $\text{CO}$  and  $\text{CO}_2$  were assigned from GASLAB GC analyses.  $\text{CO}$  was calibrated in GASLAB because of uncertainty in the non-linearity correction for the AGAGE reduction detector GC and a high- $\text{CO}$  reference tank used at the time. (AGAGE analyses of  $\text{CO}$  have not yet been corrected for this non-linearity.)

These values were used in turn to convert the raw FTIR measurements to mixing ratios more

directly comparable to the respective AGAGE and LoFlo datasets. Previous work [Griffith and Steele, 2002, unpublished] and the GASLAB tank study described below show the FTIR analyser to have excellent linearity for all species to well above the range of mixing ratios observed at Cape Grim, but linear regressions of FTIR vs reference scales generally have small but non-zero intercepts. For practical reasons only a single calibrated reference gas was used for this study. For each day of measurement a scale factor between the raw FTIR determination of the reference gas (Figure 1) and the relevant assigned trace gas mixing ratio was calculated. FTIR air sample data were corrected to the relevant calibration scale using the daily calibration factors interpolated to the sample time grid. A more comprehensive FTIR calibration strategy would be required to provide fully validated FTIR data for the most rigorous comparison with accepted calibration scales.

**Table 2.** Determinations of the reference cylinder G-166/S34L-H16, UAN 20100075, filled at Cape Grim on 22 October 2008.  $\text{CO}_2$  and  $\text{CO}$  were analysed in GASLAB by gas chromatographic analysis, and  $\text{CH}_4$  and  $\text{N}_2\text{O}$  were determined at Cape Grim by the AGAGE GCMD system. \*  $\text{CO}$  showed some growth in the flask.

Species	Assigned value	units	Scale
$\text{CO}_2$	$382.36 \pm 0.05$	$\mu\text{mol mol}^{-1}$	WMOX2007
$\delta^{13}\text{C}$ in $\text{CO}_2$	$-8.22 \pm 0.05$	‰	VPDB
$\text{CH}_4$	$1755.56 \pm 1.19$	$\text{nmol mol}^{-1}$	Tohoku University, gravimetric
$\text{CO}$	$58.33 \pm 0.23$	$\text{nmol mol}^{-1}$	CSIRO
$\text{N}_2\text{O}$	$321.22 \pm 0.12$	$\text{nmol mol}^{-1}$	SIO-98

### 2.3. Comparison at Cape Grim

The FTIR analyser was installed in the main laboratory at Cape Grim on 23 October 2008 (Figure 2).



**Figure 2.** FTIR analyser installed in the Cape Grim main laboratory.

Air for analysis was drawn from the 70-m tower through a dedicated inlet line parallel to those for the LoFlo and AGAGE instruments. For 23.5 hours each day air was drawn continuously through the analyser at  $0.5 \text{ L min}^{-1}$ ; spectra were recorded continuously at  $80 \text{ scans min}^{-1}$ , averaged every 10 minutes and analysed to provide trace gas concentrations in real time. For comparison of FTIR with LoFlo measurements of  $\text{CO}_2$  10-minute means of the LoFlo 1-minute data were calculated to match each FTIR 10-minute measurement interval. For comparison with AGAGE measurements of  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$  the time-weighted mean of the two 10-minute FTIR measurements bracketing the AGAGE GC injection time was used.

The remaining 0.5 hour each day was used for the once-daily calibration with a single clean-air calibration standard. From 00:00 – 00:30 the cell was first evacuated and a background spectrum of the evacuated cell measured. The cell was then filled, after a short (5 s) purge and re-evacuation,

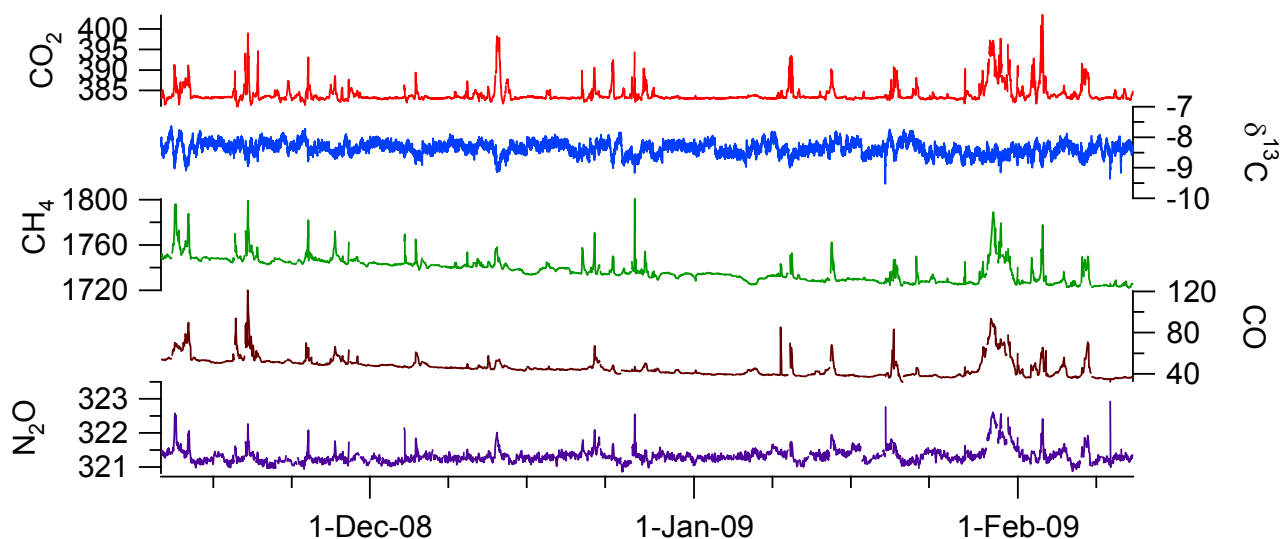
with gas from the reference cylinder and the spectrum of the reference gas was averaged for 10 minutes. To conserve reference gas, this measurement was made statically, i.e. the reference gas was not flowed through the cell but the cell was filled to the desired pressure (similar to the flowing air sample pressure) and the cell closed off for the measurement. During this calibration cycle sample air flow was maintained through the Nafion<sup>®</sup> and  $\text{Mg}(\text{ClO}_4)_2$  (but bypassed the cell) to avoid transient effects in the sampling lines and drier. After measurement of the reference gas the cell was evacuated and the air sample flow re-established in time for the next measurement period at 00:30.

### 2.4. Comparison with standard tanks

In March-April 2010 the same analyzer was operated in GASLAB to compare FTIR measurements of 36 primary calibration air standards and other tank gases with their assigned calibration values. As for the Cape Grim study, the target species were  $\text{CO}_2$ ,  $\delta^{13}\text{C}$  in  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{N}_2\text{O}$ . Tanks were connected to the undried inlet of the FTIR analyzer after purging the regulator and connecting tubing. In an automated sequence, the FTIR cell and inlet lines were first evacuated, the inlet lines and cell purged with target gas for 5 sec, the cell re-evacuated, then filled to 990-1000 hPa and the inlet and outlet valves closed. After a 30 sec settling time, the spectrum of the tank air in the cell was recorded for 10 minutes and analysed.

## 3. Results - Cape Grim

Figure 3 gives an overview of all FTIR measurements from 1 November 2008 after the instrument had stabilised and dried so that residual water vapour remained below  $20 \mu\text{mol mol}^{-1}$ . The slow decreases in  $\text{CH}_4$  and  $\text{CO}$  are due to the spring phase of the respective annual cycles.

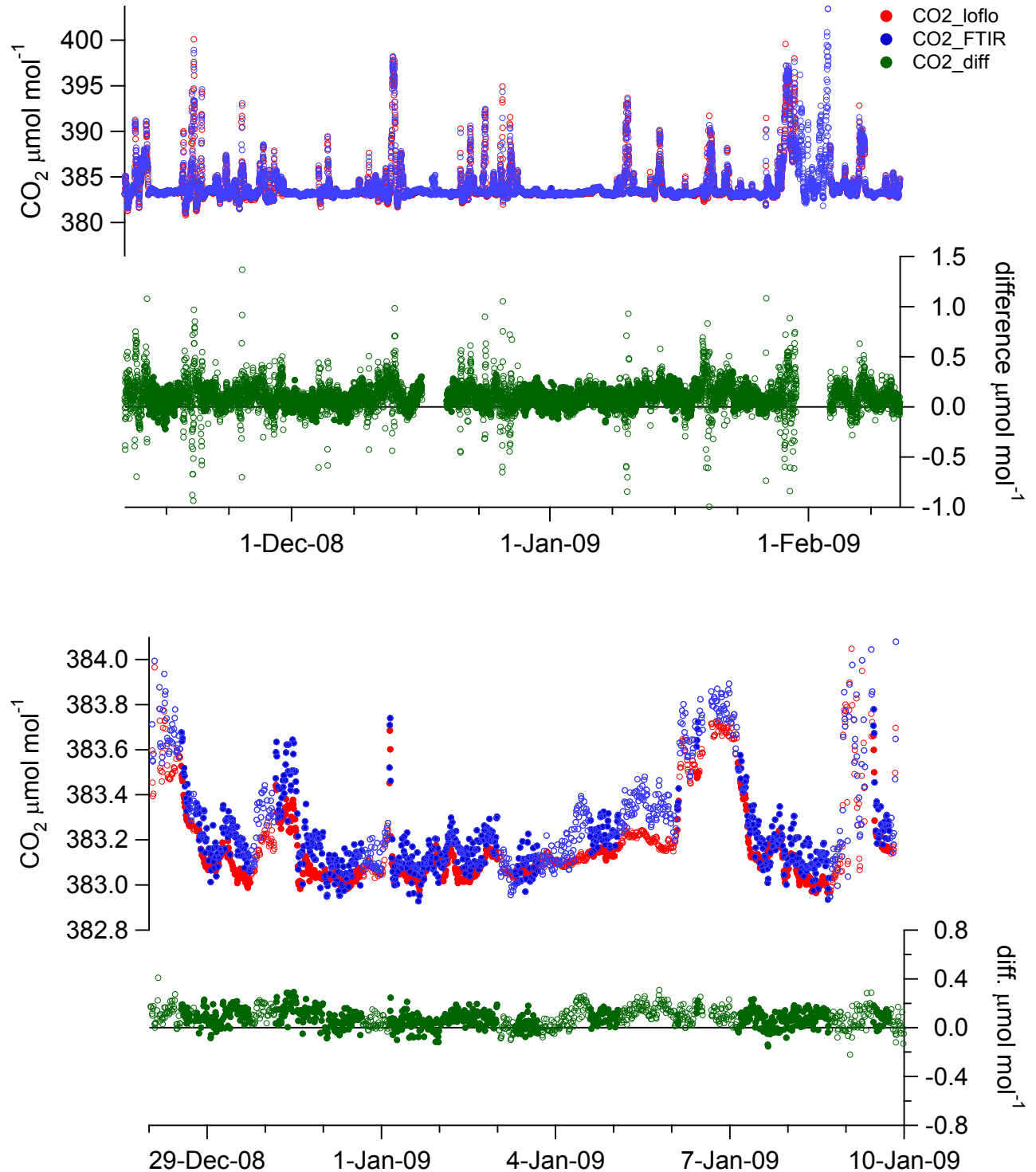


**Figure 3.** Overview time series of FTIR trace gas measurements from the comparison period.  $\text{CO}_2$  in  $\mu\text{mol mol}^{-1}$ ,  $\delta^{13}\text{C}$  in ‰, other species in  $\text{nmol mol}^{-1}$ .

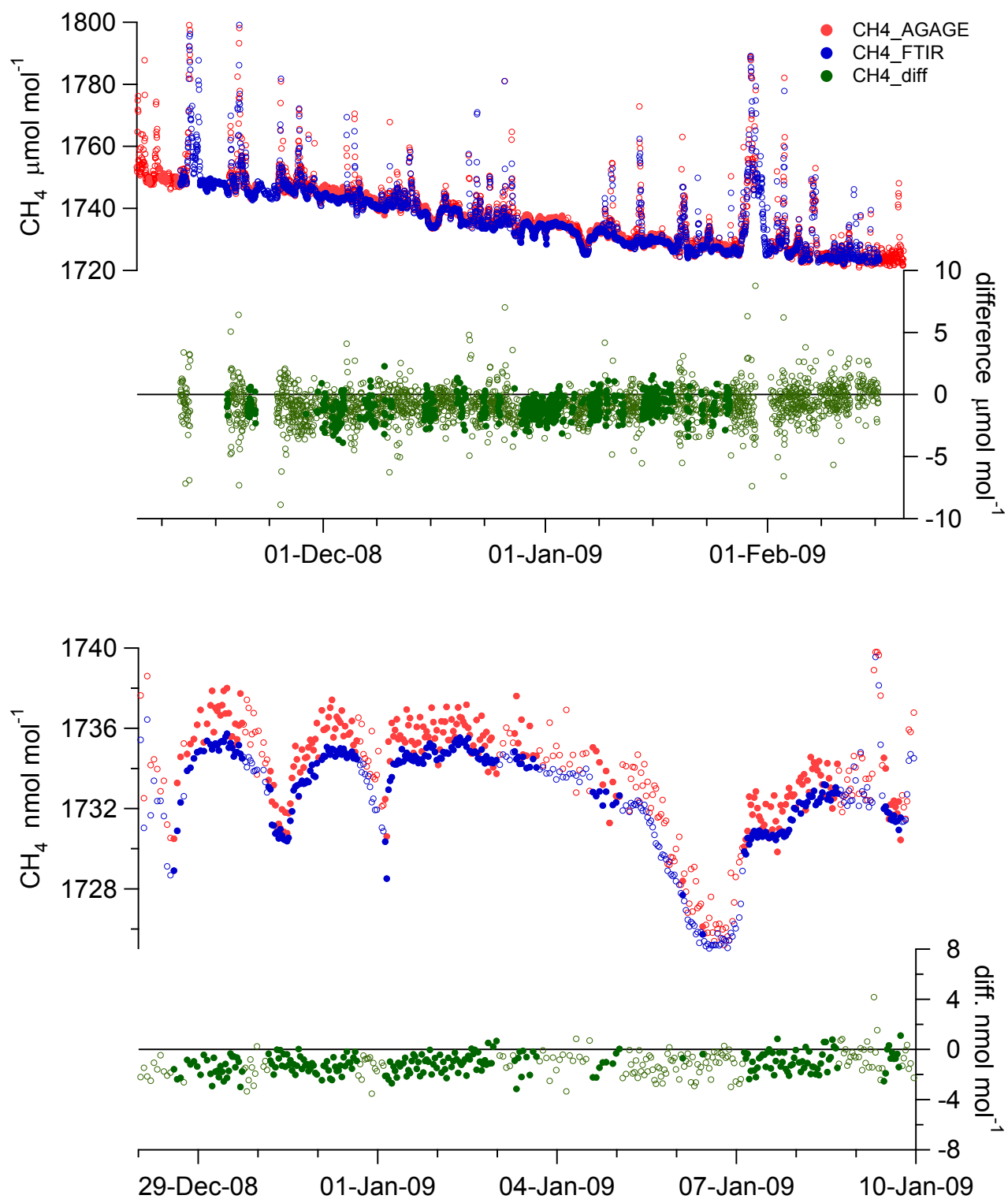
Figure 4-7 illustrate the comparisons of FTIR measurements for each species against the relevant LoFlo or AGAGE measurements. In all plots the closed symbols represent data collected during baseline periods and open symbols all other data. LoFlo measurements of CO<sub>2</sub> concentration show

higher precision (less scatter) than FTIR, but for the other gases FTIR precisions are significantly higher than those of the AGAGE GC measurements.

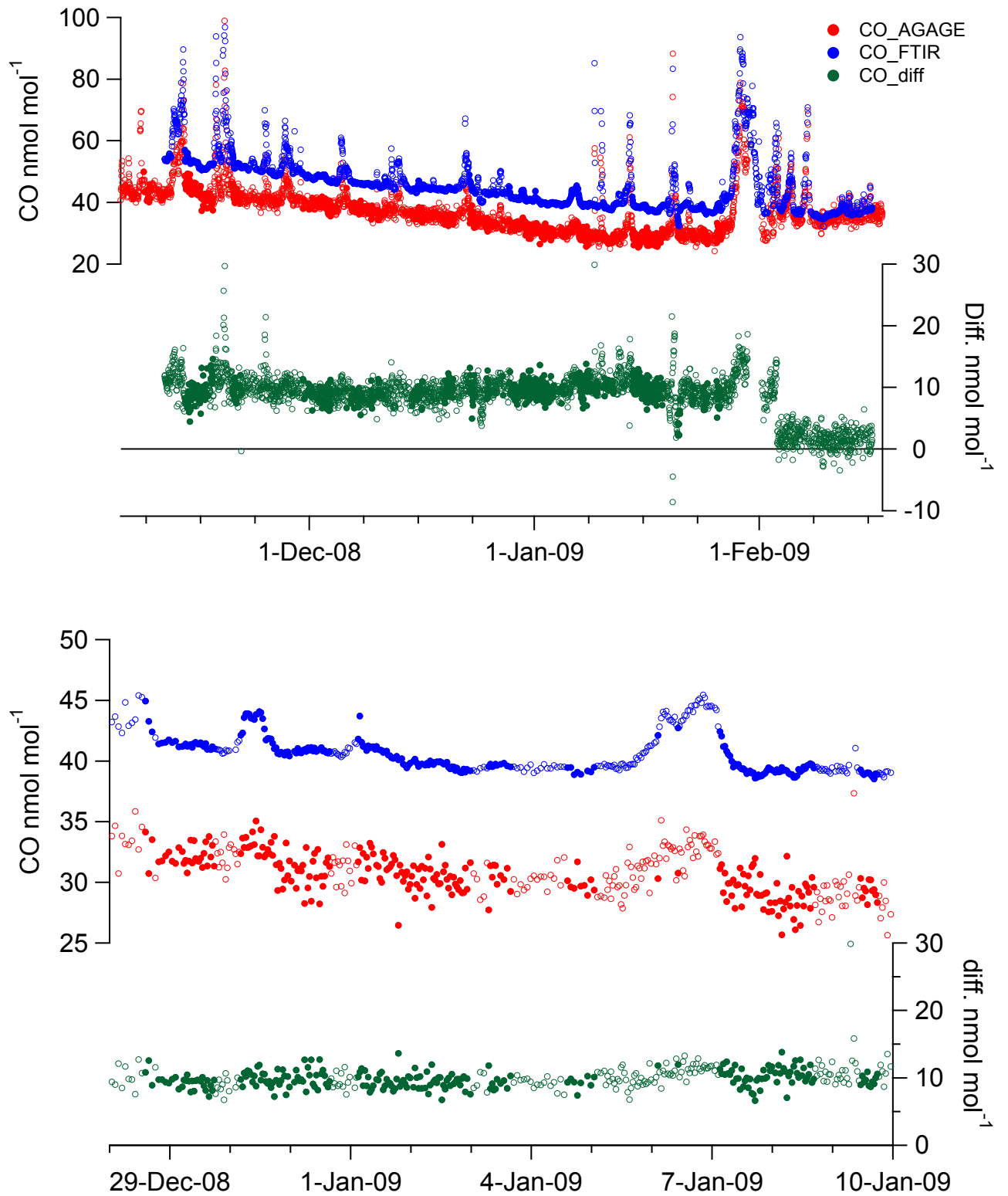
**Figure 8** shows an expanded view of the  $\delta^{13}\text{C}$  record.



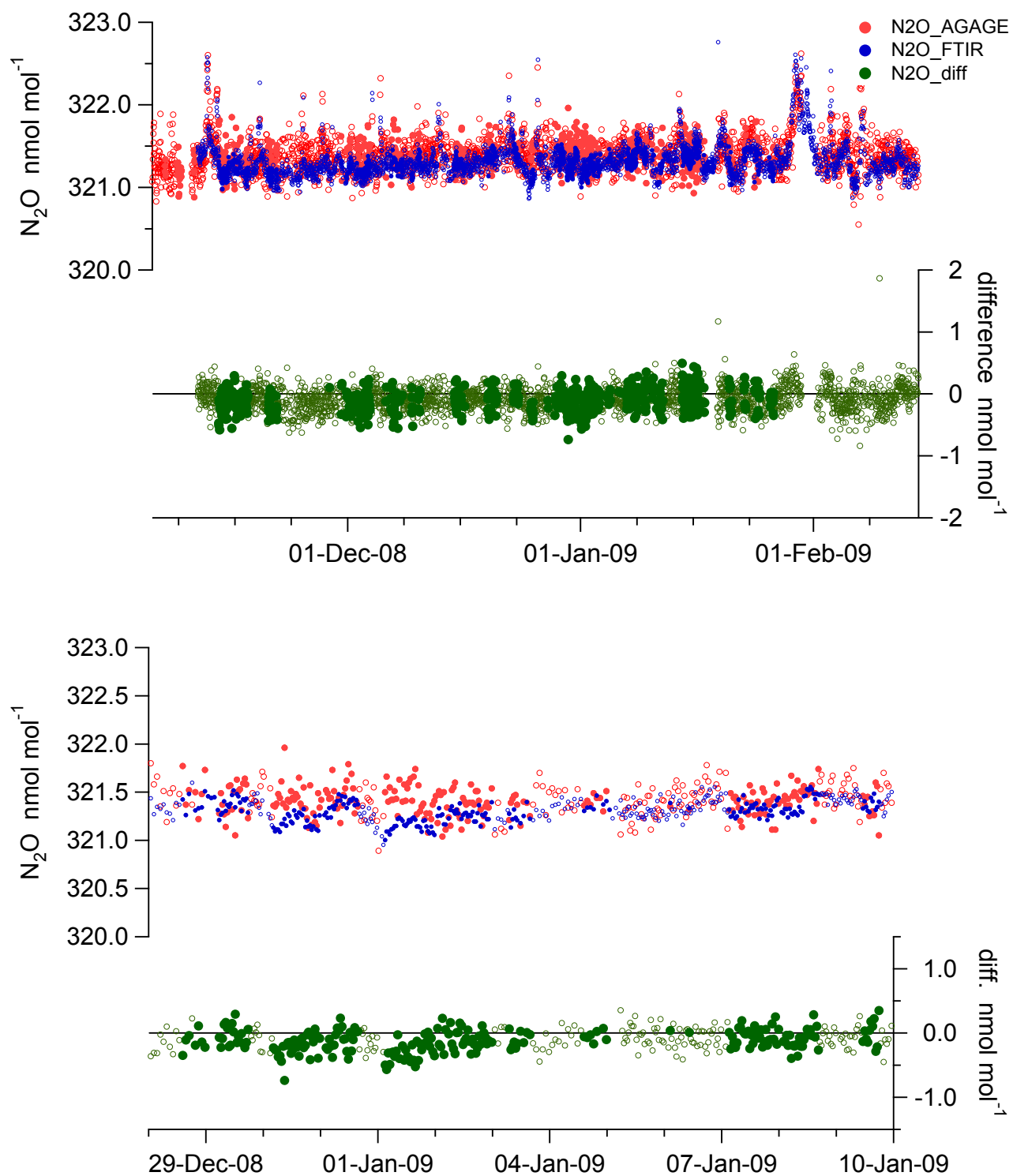
**Figure 4.** Comparison of FTIR and LoFlo measurements for CO<sub>2</sub>. Upper: Full comparison period. Lower: expansion of clean air period 29 December 2008 – 10 January 2009. LoFlo (red), FTIR (blue), difference (green), solid symbols denote baseline conditions.



**Figure 5.** Comparison of FTIR and AGAGE GC measurements for CH<sub>4</sub>. Upper: full comparison period. Lower: expansion 28 December 2008 – 10 January 2009. AGAGE (red), FTIR (blue), difference (green), solid symbols denote baseline conditions.

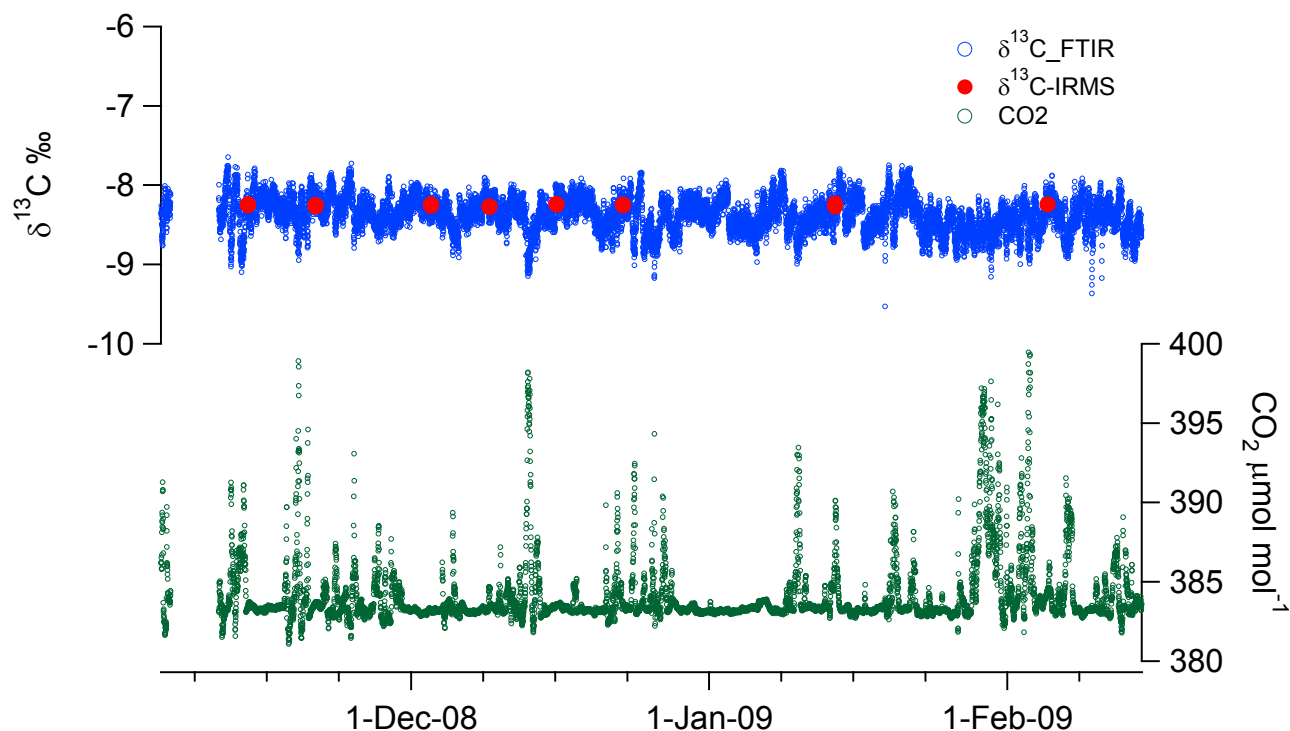


**Figure 6.** Comparison of FTIR and AGAGE GC measurements for CO. Upper: full comparison period. Lower: expansion 28 December 2008 – 10 January 2009. AGAGE (red), FTIR (blue), difference (green), solid symbols denote baseline conditions. AGAGE CO measurements have not yet been corrected for AGAGE GC detector non-linearity.



**Figure 7.** Comparison of FTIR and AGAGE GC measurements for  $\text{N}_2\text{O}$ . Upper: full comparison period. Lower: expansion 28 December 2008 – 10 January 2009. AGAGE (red), FTIR (blue), difference (green), Solid symbols denote baseline conditions.





**Figure 8.** FTIR measurements of  $\delta^{13}\text{C}$  in  $\text{CO}_2$  (blue) with flask-sample measurements collected during baseline episodes during the comparison period and analysed in GASLAB. The lower panel shows the  $\text{CO}_2$  record for comparison.

### 3.1. Discussion - errors and variability

Table 2 shows the mean differences (biases) and standard deviations of the differences between FTIR and the relevant LoFlo or AGAGE measurements for all baseline-selected data during the comparison. In all cases the mean bias is of the same magnitude or less than the scatter in the measurements (except for  $\text{CO}$  due to the uncorrected AGAGE non-linearity offset), and constant over the entire 3 months of the comparison.

**Table 2.** Mean differences (biases) and standard deviations of the differences for all baseline-selected measurements.

Species	Mean bias FTIR-LoFlo/AGAGE	Standard deviation	units
$\text{CO}_2$	0.078	0.085	$\mu\text{mol mol}^{-1}$
$\text{CH}_4$	-1.01	0.90	$\text{nmol mol}^{-1}$
$\text{CO}$	9.33	1.60	$\text{nmol mol}^{-1}$
$\text{N}_2\text{O}$	-0.12	0.22	$\text{nmol mol}^{-1}$

The small biases reflect the reliability and stability of all aspects of the measurement process – both the sampling of the airstream for measurement and the transfer of reference gas to the respective analysis instruments. Figure 4 - Figure 7 also illustrate that these biases remain largely constant in baseline conditions, only deviating significantly during large variations from clean conditions when concentrations may be changing rapidly.

### 4. Results - Calibration standards

Results for all tanks analysed are listed in Appendix 1. There are 45 analyses of 36 tanks with some replicates. The raw FTIR analyses have been corrected for variations in cell pressure and residual water vapour in the spectra between individual measurements – these corrections are small, generally of the order of the repeatability shown in Table 1, or less.

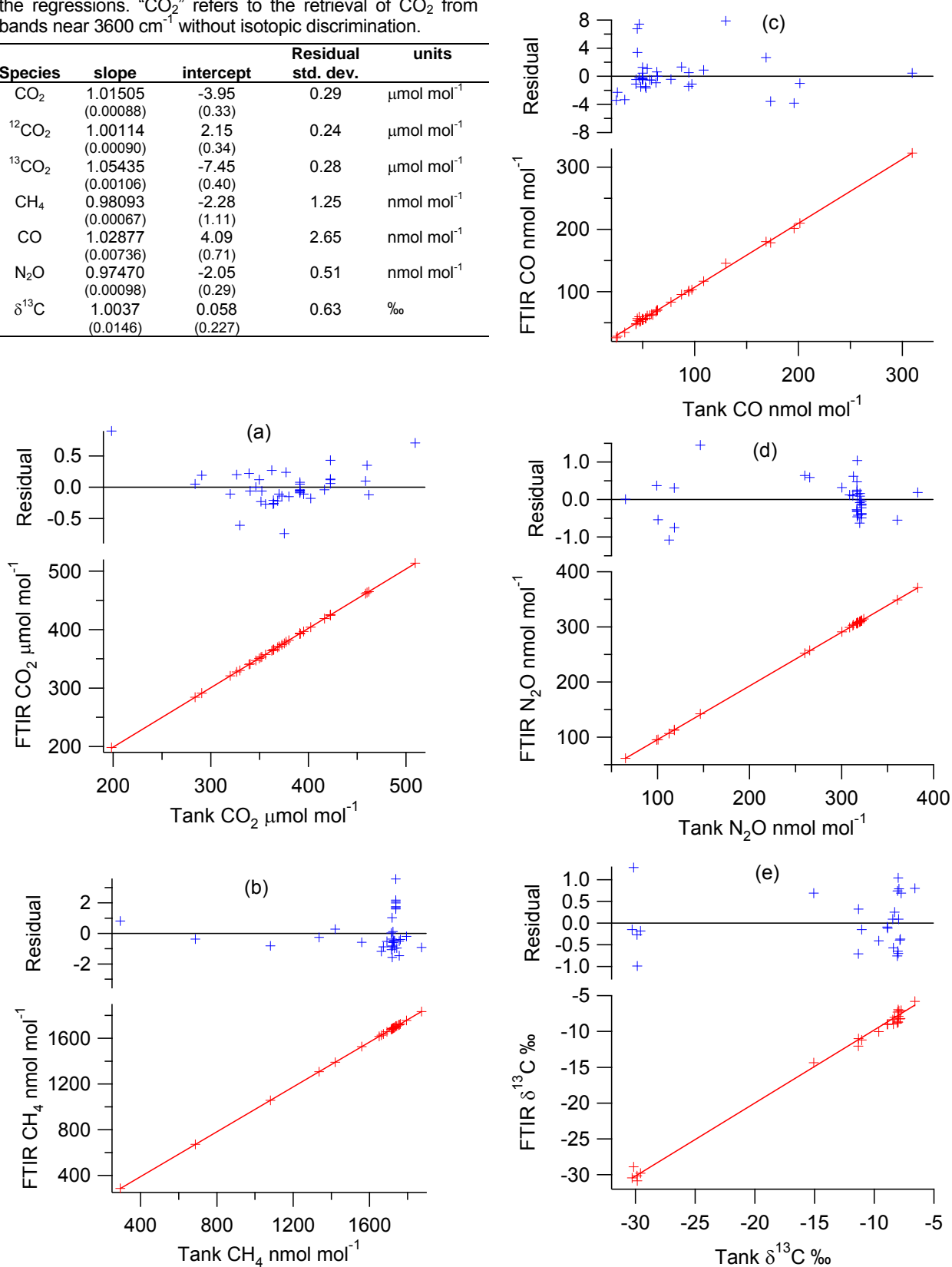
Figure 9 shows the regressions of FTIR against standard tank values for each species. The regressions are of the form

$$C_{\text{measured}} = a \cdot C_{\text{true}} + b \quad (3)$$

for each species, where  $C$  is used to mean either concentration or mixing ratio interchangeably if the context allows. The residuals are the differences between FTIR measurements and the regression line for each tank. **Table 3** summarises the regression parameters and standard deviations of the residuals about the respective regressions. The individual residuals are also listed in Appendix 1.

**Table 3.** Slope, intercept and standard deviation of residuals for regressions of FTIR vs tank standard values for all species. Values in parentheses are standard errors of the regressions. “CO<sub>2</sub>” refers to the retrieval of CO<sub>2</sub> from bands near 3600 cm<sup>-1</sup> without isotopic discrimination.

Species	slope	intercept	Residual std. dev.	units
CO <sub>2</sub>	1.01505 (0.00088)	-3.95 (0.33)	0.29	μmol mol <sup>-1</sup>
<sup>12</sup> CO <sub>2</sub>	1.00114 (0.00090)	2.15 (0.34)	0.24	μmol mol <sup>-1</sup>
<sup>13</sup> CO <sub>2</sub>	1.05435 (0.00106)	-7.45 (0.40)	0.28	μmol mol <sup>-1</sup>
CH <sub>4</sub>	0.98093 (0.00067)	-2.28 (1.11)	1.25	nmol mol <sup>-1</sup>
CO	1.02877 (0.00736)	4.09 (0.71)	2.65	nmol mol <sup>-1</sup>
N <sub>2</sub> O	0.97470 (0.00098)	-2.05 (0.29)	0.51	nmol mol <sup>-1</sup>
δ <sup>13</sup> C	1.0037 (0.0146)	0.058 (0.227)	0.63	‰



**Figure 9.** Regressions of FTIR vs standard tank values for each species (a) CO<sub>2</sub>, (b) CH<sub>4</sub>, (c) CO, (d) N<sub>2</sub>O, (e) δ<sup>13</sup>C in CO<sub>2</sub>. For (e), see notes in text.

For CO<sub>2</sub>, the concentration is measured independently in three bands: the (ν<sub>1</sub>+ν<sub>3</sub>)/(2ν<sub>2</sub>+ν<sub>3</sub>) combination bands centred at 3613 and 3715 cm<sup>-1</sup> and the ν<sub>3</sub> band near 2350 cm<sup>-1</sup>. In the combination bands the measured FTIR spectrum does not discriminate between isotopologues and the analysis assumes natural isotopic abundance, providing a single “whole CO<sub>2</sub>” measurement. In the ν<sub>3</sub> region the band of the <sup>13</sup>C<sup>16</sup>O<sub>2</sub> isotopologue (abbreviated 636) centred at 2283.5 cm<sup>-1</sup> is shifted 65.6 cm<sup>-1</sup> from the parent <sup>12</sup>C<sup>16</sup>O<sub>2</sub> (626) band at 2349.1 cm<sup>-1</sup> and these two isotopologues can be analysed as separate, independent species (regressions not shown in Figure 9 but included in **Table 3**). The reference cylinder concentrations for the isotopologues, C<sub>626</sub> and C<sub>636</sub> are calculated from the whole-CO<sub>2</sub> concentration C<sub>CO2</sub> and the isotopic ratio δ<sup>13</sup>C for each tank:

$$C_{626} = \frac{X_{626} \cdot C_{CO2}}{X_{626} + \sum_i (1 + \delta^i) X_i} \quad (4)$$

$$C_{636} = \frac{(1 + \delta^{13}C) X_{636} \cdot C_{CO2}}{X_{626} + \sum_i (1 + \delta^i) X_i} \quad (5)$$

(4) and (5) and other isotopic calculations are derived in Appendix 2. The index *i* refers to individual isotopologues, and the sum over *i* runs over all isotopologues except 626. X<sub>626</sub> and X<sub>636</sub> are the natural isotopologue abundances in CO<sub>2</sub> as defined in the HITRAN database [Rothman *et al.*, 2005] and listed in Appendix 2. Note that when all δ<sup>i</sup> are zero, (4) and (5) reduce to C<sub>626</sub> = X<sub>626</sub> · C<sub>CO2</sub> and C<sub>636</sub> = X<sub>636</sub> · C<sub>CO2</sub>, the absolute concentrations of <sup>12</sup>C<sup>16</sup>O<sub>2</sub> and <sup>13</sup>C<sup>16</sup>O<sub>2</sub> in natural abundance.

δ<sup>13</sup>C in CO<sub>2</sub> is calculated for each tank measurement from

$$\delta^{13}C = \frac{C_{636} / X_{636}}{C_{626} / X_{626}} - 1 \quad (6)$$

where C<sub>636</sub>/C<sub>626</sub> is the sample isotope ratio and X<sub>636</sub>/X<sub>626</sub> is the standard ratio. If δ<sup>13</sup>C in CO<sub>2</sub> is calculated from uncalibrated FTIR concentrations of <sup>12</sup>C<sup>16</sup>O<sub>2</sub> and <sup>13</sup>C<sup>16</sup>O<sub>2</sub> over the range of tanks measured, the resultant δ<sup>13</sup>C is not linearly related to the true δ<sup>13</sup>C because it also depends in general on C<sub>CO2</sub>, which is variable (see Appendix 2). Thus in Figure 9e the FTIR values of δ<sup>13</sup>C on the y-axis are calculated using equation (6) and calibrated FTIR concentrations (equation (3)) and the residuals are the differences between standard tank values of δ<sup>13</sup>C determined by mass spectrometry and the calibrated FTIR values.

The raw FTIR scales are within 5% of the relevant tank standard scales, but have significant y-axis intercepts. There is no measurable deviation from linearity over the measured concentration

ranges. The scatter about the regressions summarised in **Table 3** is in general somewhat larger than the repeatabilities given in Table 1 for measurements of a single air sample in the FTIR cell, and reflect the (lack of) consistency and repeatability in the cell-filling and purging procedures relative to that of the actual spectroscopic measurement.

## 5. Discussion and conclusions

The UoW FTIR analyser provided reliable, continuous and simultaneous measurements of 5 trace gas species (CO<sub>2</sub>, δ<sup>13</sup>C in CO<sub>2</sub>, CH<sub>4</sub>, CO and N<sub>2</sub>O) for the 3 months of the Cape Grim trial, delivering excellent precision (Table 1) and minimal drift throughout. Measurement precision, judged from relative scatter during baseline periods, was 2 (N<sub>2</sub>O) to 4 (CH<sub>4</sub>, CO) times better for 10 minute average FTIR measurements relative to grab samples taken every 40 minutes and analysed by AGAGE, but approximately 5 times lower for CO<sub>2</sub> relative to 10 minute LoFlo averages (~0.05 vs 0.01 μmol mol<sup>-1</sup>). In general scatter in the FTIR measurements reduces with longer averaging times. Shorter averaging times to a practical limit of less than 1 minute are possible at the cost of lower precision, decreasing with the square root of the averaging time.

Further development of the instrument since this study has improved precision by a factor of 2-3 or better from the values in Table 1. This improvement comes about largely through improved detector specifications, higher energy throughput through the optical system, and consequent lower signal:noise ratio in the optical signal which feeds directly to reduced scatter in concentration measurements.

FTIR analysis of a suite of 36 calibration cylinders in GASLAB showed the FTIR analyzer to be linear over ranges of concentrations of all species well beyond those expected in Cape Grim and other baseline measurements. The precision of measurement of the tanks was somewhat less than the spectroscopic measurement repeatability, suggesting that sample introduction to the analyzer is the limiting factor in the precision of these measurements.

The designated GASLAB “primary” laboratory calibration suite has all but one cylinder with δ<sup>13</sup>C in CO<sub>2</sub> near -30‰, significantly different from that of clean air near -8‰. This should be considered in analysis of air using these standards with any FTIR or laser analyser for which the analysis is isotopologue-specific. The calibration strategy described above and in Appendix 2 provides a consistent approach to isotopic calibration.

Maintenance requirements for the analyzer are low, and the analyzer could be managed remotely via the controlling PC connected to the internet. Calibration with a single calibrated clean air standard once per day was more than sufficient given the observed lack of drift and good linearity.

The FTIR analyser should provide a cost-effective solution in a number of potential applications which exploit its mobility, high precision, low maintenance requirements and multiple gas advantages. These include:

- Automated monitoring at fixed sites such as those of the GAW, AGAGE and emerging European ICOS (Integrated Carbon Observing System) networks.
- Initial assessment of new air sampling sites.
- Mobile platforms such as trains and ships [Deutscher *et al.*, 2010]. The analyser has not yet been tested on aircraft.
- Tall tower profiling measurements.
- Micrometeorology and flux measurements.
- Calibration propagation for air standards.

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## Appendix 1. Table of all tanks analysed

Tank no.	UAN	Description	CO <sub>2</sub> / $\mu\text{mol mol}^{-1}$			CH <sub>4</sub> / $\text{nmol mol}^{-1}$			CO / $\text{nmol mol}^{-1}$			N <sub>2</sub> O / $\text{nmol mol}^{-1}$			$\delta^{13}\text{C}$ / ‰		
			tank	FTIR	resid	tank	FTIR	resid	tank	FTIR	resid	tank	FTIR	resid	tank	FTIR	resid
CA06847	997925	LoFlo low	363.92	365.17	-0.27	1714.4	1679.5	0.0	43.78	48.65	-0.48	319.62	308.86	-0.63			
CA06863	997929	LoFlo High	402.28	404.21	-0.18	1715.1	1679.0	-1.1	43.46	47.70	-1.11	319.78	309.57	-0.08			
CA04974	994435	LoFlo medium	369.91	371.42	-0.11	1719.3	1682.7	-1.6	53.26	57.22	-1.67	316.84	306.48	-0.30	-8.07	-8.83	-0.76
CA04983	994431	Isotope STD-B	364.53	365.81	-0.26	1724.1	1688.3	-0.6	94.39	101.71	0.52	317.9	307.39	-0.42	-8.89	-9.01	-0.12
CA04924	994429	Isotope STD-C	461.93	464.81	-0.12	1723.4	1688.4	0.1	108.66	116.76	0.88	360.68	348.96	-0.55	-11.33	-11.01	0.32
CA04904	994443	Isotope STD-A	329.68	330.08	-0.61	1420.2	1391.1	0.3	44.81	56.95	6.75	260.05	252.07	0.64	-6.6	-5.80	0.80
CQB06584	960035	Japan synthetic standard	340.25	341.36	-0.06												
CA08001	20100303	Picarro low	364.21	365.53	-0.21	1651.2	1616.6		50.42	55.23					-8.46	-8.37	0.09
CA08027	20100304	Picarro High #1															
CA08025	20100513	Picarro Iso	509.44	513.87	0.71	1752.5	1715.5		59.61	62.46		324.05	314.30		-15.07	-14.38	0.69
CA08015	20100277	Picarro High #2															
CA06831	997930	loflo #6 new GC std	422.53	425.37	0.43	1718.5	1684.5	1.0	46.65			320.01	310.03	0.16			
CA06831	997930	loflo #6 new GC std	422.53	425.06	0.13	1718.5	1683.1	-0.4	46.65	59.51	7.42	320.01	309.96	0.09			
CA06831	997930	loflo #6 new GC std	422.53	425.06	0.12	1718.5	1682.6	-0.9	46.65	51.84	-0.24	320.01	309.85	-0.01			
CA08219	20100747	Picarro hi co2/ch4															
CA01689	970829	Primary	422.45	424.91	0.06	1719.9	1684.0	-0.8	77.17	83.06	-0.43	312.98	303.63	0.62	-11.06	-11.21	-0.15
CC106607	920539	Primary	362.39	364.16	0.27	1662.9	1627.7	-1.2	52.73	56.88	-1.46	118.22	113.49	0.31	-29.87	-30.14	-0.27
CC106592	920547	Primary	377	378.96	0.24	1873.0	1834.1	-0.9	195.73	201.63	-3.82	99.03	94.85	0.37			
CC106605	920542	Primary	198.29	198.21	0.90	293.4	286.3	0.8	25.72	28.28	-2.27	118.33	112.54	-0.75			
CC106596	920543	Primary	290.68	291.29	0.19	687.0	671.3	-0.4	24.58	25.95	-3.43	112.56	106.58	-1.08	-30.16	-28.88	1.28
CC106611	920549	Primary	326.47	327.63	0.20	1080.6	1056.9	-0.8	32.74	34.43	-3.34	100.62	95.48	-0.54	-29.59	-29.77	-0.18
CC106598	920548	Primary	339.15	340.52	0.22	1755.9	1718.7	-1.5	97.28	103.05	-1.12	65.16	61.48	0.01	-30.29	-30.44	-0.15
CC106614	920544	Primary	349.49	350.92	0.12	1559.6	1526.9	-0.6	48.16	52.14	-1.50	146.47	142.17	1.45	-29.85	-30.84	-0.99
CC64041	880001	GASLAB STD	346.12	347.37	0.00	1691.6	1656.5	-0.5	201.18	210.05	-1.01	300.36	291.04	0.32	-8	-8.70	-0.70
CA04518	994030	NIES Std C	460.14	463.47	0.35	1717.9			168.67	180.28	2.67	382.74	371.20	0.19	-11.34	-12.05	-0.71
ALVZ864	900005	GASLAB STD	352.22	353.51	-0.06	1672.9	1637.8	-0.9	64.37	70.30	-0.01	308.8	299.06	0.12	-7.82	-8.19	-0.37
CC113587	950554	GASLAB STD	283.94	284.31	0.05	1335.7	1307.7	-0.3	54.48	61.24	1.10	265.41	257.24	0.59	-8	-6.96	1.04
CA01642	950123	GASLAB STD	368.48	369.86	-0.22	1743.4	1706.9	-1.0	309.38	322.82	0.45	312.3	302.45	0.10	-8.4	-8.97	-0.57
CA01672	995479	CLASSIC STD	356.07	357.20	-0.27	1577.1			44.93	53.68	3.37	317.07	306.54	-0.46	-8.91	-9.00	-0.09
CA01660	951539	CLASSIC STD	375.41	376.37	-0.74	1689.0			129.91	145.62	7.88	409.34			-9.62	-10.03	-0.41

Continued

Tank no.	UAN	Description	CO <sub>2</sub> / $\mu\text{mol mol}^{-1}$			CH <sub>4</sub> / $\text{nmol mol}^{-1}$			CO / $\text{nmol mol}^{-1}$			N <sub>2</sub> O / $\text{nmol mol}^{-1}$			$\delta^{13}\text{C}$ / ‰		
			tank	FTIR	resid	tank	FTIR	resid	tank	FTIR	resid	tank	FTIR	resid	tank	FTIR	resid
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.27	0.08	1737.8	1704.5	2.2	49.83	55.81	0.45	321.6	311.30	-0.12			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.14	-0.05	1737.8	1704.4	2.1	49.83	54.91	-0.45	321.6	311.27	-0.15			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.12	-0.06	1737.8	1704.3	2.0	49.83	54.89	-0.47	321.6	311.36	-0.05			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.11	-0.08	1737.8	1704.0	1.6	49.83	55.09	-0.27	321.6	311.02	-0.40			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.24	0.05	1737.8	1705.9	3.6	49.83	54.99	-0.37	321.6	310.92	-0.49			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.15	-0.04	1737.8	1704.0	1.6	49.83	54.86	-0.50	321.6	311.20	-0.22			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.13	-0.06	1737.8	1704.1	1.7	49.83	55.29	-0.06	321.6	311.04	-0.38			
CA04918	20100280	ex-LoFlo2B-ref	391.25	393.09	-0.09	1737.8	1704.1	1.7	49.83	56.62	1.27	321.6	311.04	-0.38			
CA04984	994870	LoFlo2B-320	319.99	320.74	-0.11	1762.0	1725.7	-0.4	94.28	99.65	-1.43	316.71	306.33	-0.32	-8.05	-7.31	0.74
CA04928	994238	LoFlo2B-350	351.49	352.60	-0.23	1731.2	1694.9	-1.0	56.82	62.03	-0.51	316.54	306.22	-0.27	-8.03	-8.68	-0.65
CA04902	994868	LoFlo2B-370	372.89	374.41	-0.14	1793.3	1756.7	-0.2	173.17	178.67	-3.57	317.4	307.46	0.14	-8.3	-8.05	0.25
CA04966	994236	LoFlo2B-380	380.04	381.66	-0.15	1731.2	1695.5	-0.5	58.47	63.69	-0.55	316.57	306.72	0.21	-7.97	-7.88	0.09
CA04952	994263	LoFlo2B-395	395.05	396.93	-0.11	1727.5	1691.8	-0.5	62.77	67.74	-0.93	316.73	307.14	0.47	-7.94	-7.15	0.79
CA04930	994264	LoFlo2B-415	416.51	418.79	-0.04	1726.4	1690.7	-0.5	63.58	70.12	0.62	316.86	307.04	0.25	-7.86	-8.25	-0.39
CA05297	994871	LoFlo2B-460	458.51	461.55	0.10	1755.7	1719.4	-0.5	87.36	95.28	1.32	317.01	307.99	1.04	-7.76	-7.07	0.69

Table A1. Assigned tank concentrations, measured FTIR concentrations and residuals from the FTIR vs standard value regressions for each species. The FTIR values for the four trace gases are the raw retrieved values from MALT-fitting of the spectra, corrected for small variations in residual water vapour in the cell and cell pressure. The FTIR  $\delta^{13}\text{C}$  values are calculated from the *calibrated* FTIR values for  $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$  (not shown).

## Appendix 2. Calibration and calculation of $\delta^{13}\text{C}$ for isotopologue-specific FTIR analysis

Optical techniques such as FTIR and tuneable laser absorption spectrometry determine the absolute concentrations of individual trace gas species from the quantitative analysis of selected absorption bands or lines in the measured spectrum. The FTIR spectrometer records a broadband spectrum which is analysed in selected regions for several trace gases. For  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$  combination bands near  $3600\text{ cm}^{-1}$ , the low resolution FTIR spectrometer does not resolve individual isotopic species, and the relevant whole absorption bands are fitted assuming that the isotopologues are present in natural abundance. For these determinations natural variations in isotopic abundances do not significantly affect the FTIR measurements.

For the particular case of  $\text{CO}_2$  in the  $\nu_3$  band near  $2350\text{ cm}^{-1}$ , the  $^{13}\text{C}^{16}\text{O}_2$  isotopologue band centred at  $2283.5\text{ cm}^{-1}$  is shifted almost  $70\text{ cm}^{-1}$  from the parent  $^{12}\text{C}^{16}\text{O}_2$  band at  $2349.1\text{ cm}^{-1}$  and the low resolution FTIR spectrum easily resolves the two so that they can be quantified as independent species. The individual isotopologue bands are strong enough to provide precise independent concentrations, from which the usual isotopic ratio  $\delta^{13}\text{C}$  can be calculated as described below.

The same principles apply to isotopic calibration of laser diode spectrometer measurements, which are also normally isotopologue-specific [Loh *et al.*, 2010].

### Terms and definitions

Following IUPAC recommendations [Cohen *et al.*, 2007], [Coplen, 2008] we distinguish the following quantities:

- $C$  concentration, eg  $\text{mol m}^{-3}$
- $\chi$  mixing ratio or mole fraction of trace gas eg.  $\mu\text{mol mol}^{-1}$ , ppmv
- $X$  isotopic abundance of an isotope or isotopologue,  $\text{mol mol}^{-1}$
- $R$  isotope ratio

Where the distinction is unimportant, we use  $C$  to mean either concentration or mixing ratio.

Spectroscopic techniques measure absorption of radiation from which *concentration* is determined directly; mixing ratios are calculated by dividing the concentration  $C$  by the concentration of air:

$$\chi = \frac{C}{P/RT} \quad (\text{A.1})$$

where  $P$  is sample pressure,  $T$  sample temperature and  $R$  the gas constant. In the HITRAN database of absorption line parameters on which the analysis is based [Rothman *et al.*, 2005], linestrengths for each isotopologue are scaled by the natural isotopic abundance of the isotopologue. For  $\text{CO}_2$  these abundances are given in Table A.1. As a consequence, in the FTIR analysis of individual

isotopologues, concentrations or mixing ratios are quoted scaled by their natural abundances:

$$C' = \frac{C}{X} \quad \text{or} \quad \chi' = \frac{\chi}{X} \quad (\text{A.2})$$

where  $C$  is the actual concentration (or mixing ratio  $\chi$ ) of an isotopologue,  $X$  is its natural abundance, and  $C'$  is the scaled concentration. Thus if a sample of  $\text{CO}_2$  in air with natural isotopic abundance of  $^{13}\text{C}$  ( $\delta^{13}\text{C}=0$ ) is analysed by FTIR, the reported concentration of  $^{13}\text{CO}_2$ ,  $C_{636}$ , will be equal to that reported for  $^{12}\text{CO}_2$ ,  $C_{626}$ .

Isotopologue	Notation	Abundance
$^{12}\text{C}^{16}\text{O}_2$	626	0.98420
$^{13}\text{C}^{16}\text{O}_2$	636	0.01106
$^{12}\text{C}^{18}\text{O}^{16}\text{O}$	628	0.0039471
$^{12}\text{C}^{17}\text{O}^{16}\text{O}$	627	0.000734

Table A.1 HITRAN isotopologue abundances for  $\text{CO}_2$ .

With these definitions the calculation of  $\delta^{13}\text{C}$  follows as

$$\delta^{13}\text{C} = \frac{C'_{636}}{C'_{626}} - 1 = \frac{C_{636}/C_{626}}{X_{636}/X_{626}} - 1 \quad (\text{A.3})$$

where  $C_{636}/C_{626}$  is equivalent to the usual sample isotope ratio  $R_{\text{sample}}^{13}$  and  $X_{636}/X_{626}$  is the standard isotope ratio  $R_{\text{std}}^{13}$ . The reference scale is thus that of HITRAN. Calibration of isotopologue concentration measurements against standard isotopologue concentrations calibrated to VPDB corrects for both the difference between HITRAN and VPDB scales and scale factors in the individual FTIR determinations of  $C_{636}$  and  $C_{626}$ .

### General calibration considerations

The analysis of calibration standards over the range of concentrations studied shows that the raw FTIR measurement is generally linear with respect to the assigned mixing ratios within the measurement precision (see for example Fig 9 in the main text). Thus calibration assignment of whole species (without isotopic discrimination) and individual isotopologues is based on a regression of measured against standard concentrations or mixing ratios:

$$C_{\text{meas}} = a \cdot C_{\text{std}} + b \quad (\text{A.4})$$

### Calculation and calibration of isotopic quantities

In applying equation (A.4) to isotopologues, we require the individual isotopologue concentrations or mixing ratios of the standards. For parent and  $^{13}\text{C}$  isotopologues of  $\text{CO}_2$  these can be calculated from the (assumed known) total  $\text{CO}_2$  concentration and isotopic  $\delta$  values as follows:

The total CO<sub>2</sub> concentration is

$$\begin{aligned} C_{CO_2} &= C_{626} + C_{636} + C_{628} + C_{627} + \dots \\ &= C'_{626} X_{626} + C'_{636} X_{636} + C'_{628} X_{628} + \dots \end{aligned} \quad (A.5)$$

From the definition of  $\delta$ , equation (A.3)

$$\begin{aligned} C'_{636} &= (1 + \delta^{13}) C'_{626} \\ C'_{628} &= (1 + \delta^{18}) C'_{626} \\ C'_{627} &= (1 + \delta^{17}) C'_{626} \end{aligned} \quad (A.6)$$

and (A.5) can be written

$$C_{CO_2} = C'_{626} \cdot (X_{626} + \sum_i (1 + \delta^i) X_i) \quad (A.7)$$

where the index  $i$  runs over all isotopologues except 626. Thus

$$C'_{626} = \frac{C_{CO_2}}{X_{626} + \sum_i (1 + \delta^i) X_i} \quad (A.8)$$

and from (A.6)

$$C'_{636} = \frac{(1 + \delta^{13}) \cdot C_{CO_2}}{X_{626} + \sum_i (1 + \delta^i) X_i} \quad (A.9)$$

To compute (A.8) and (A.9), all values of  $\delta^i$  must be known – for calibrated standards  $\delta^{13}$  and  $\delta^{18}$  are usually measured, and with sufficient accuracy for FTIR calibrations we can assume  $\delta^{17} = 0.5 \cdot \delta^{18}$  and all  $\delta = 0$  for multiply-substituted isotopologues since their contributions to the sums are very small.

In the calibration regressions described in the main text, the standard tank mixing ratios for 626 and 636 isotopologues are calculated from (A.8) and (A.9).

If uncalibrated  $C'_{626}$  and  $C'_{636}$  are used to calculate  $\delta^{13}$ , the result is not simply a linear relation to the true  $\delta^{13}$ , because it also in general depends on the concentration of CO<sub>2</sub> in the sample as follows from (A.3):

$$\begin{aligned} \delta_{meas}^{13} &= \frac{C'_{636,meas}}{C'_{626,meas}} - 1 \\ &= \frac{a_{636} \cdot C'_{636} + b_{636}}{a_{626} \cdot C'_{626} + b_{626}} - 1 \end{aligned} \quad (A.10)$$

which rearranges to

$$\delta_{meas}^{13} = \frac{a_{636} C'_{626}}{a_{626} C'_{626} + b_{626}} \delta_{true}^{13} + \frac{(a_{636} - a_{626}) C'_{626} + b_{636} - b_{626}}{a_{626} C'_{626} + b_{626}} \quad (A.11)$$

If the intercepts  $b$  are zero, this relationship reduces to a linear form

$$\delta_{meas}^{13} = \frac{a_{636}}{a_{626}} \delta_{true}^{13} + \frac{(a_{636} - a_{626})}{a_{626}} \quad (A.12)$$

from which the two  $\delta$  scales are related by the isotopologue calibration scale factors only. But if  $b_{626} \neq 0$  the slope and intercept are concentration dependent and the regression over a range of tank concentrations is not linear. Thus to compare  $\delta$  determined from FTIR with standard values,  $\delta$  is calculated using the true, calibrated values of  $C'_{626}$  and  $C'_{636}$  in (A.3).