



Open-Path FTIR spectroscopy of CO₂, CH₄ & CO: Experimental accuracy evaluation for ambient to highly polluted concentrations.

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Abstract

When compared to established point-sampling methods, OP-FTIR spectroscopy can measure different gases simultaneously, in situ and near-continuously, providing path-integrated concentration retrievals. However, few studies have investigated the accuracy of the retrieval process for CO₂, CH₄ and CO, particularly across a broad range of concentrations found in ambient air, as well as those found in highly polluted plumes (from fires or industry). In this work, a field-portable FTIR spectrometer was placed at one end of a one-metre IR-transparent cell filled with the gas of interest. The spectrometer was used to observe the signals from an IR lamp placed at the other end of the cell. Gas concentrations were retrieved from the measured IR spectra using the MALT forward model and a non-linear least squares fitting procedure. CO₂, CH₄ and CO target concentrations ranged from ambient to 100x ambient, yet with optimisation of the retrieval parameters all retrievals were accurate to within 6% of the true gas cell concentration. Sensitivity to model inputs (instrument field-of-view, temperature and pressure) were also investigated. CO retrievals were shown to be most sensitive to these parameters. The findings suggest that good quality temperature measurements and sound knowledge of instrument FOV are required when retrieving gas concentrations.

Keywords: OP-FTIR, greenhouse gases, accuracy, MALT

1. Introduction

In many applications, remote sensing of gas species presence and concentrations offer advantages over established point-sampling and/or laboratory analysis methods. Open-path (OP) Fourier Transform Infrared (FTIR) spectroscopy can be used to detect and quantify a wide range of gases simultaneously; can operate in situ, eliminating contamination from tubing or sample handling; can operate continuously, providing real-time data at a relatively high temporal resolution (seconds); and can be used over long path lengths, providing path-integrated gas concentrations less prone to artefacts induced by point-based sampling and which cannot easily be acquired using alternative approaches.

A variety of analysis techniques are available to retrieve trace gas concentrations from measured single-beam spectra acquired by FTIR instrumentation. These generally involve comparing the measured spectra with reference spectra of the gas of interest under known conditions of temperature, pressure and concentration. Reference spectra may come from laboratory measurements of gases, or may be synthetically generated (e.g. Griffith, 1996) from molecular absorption databases, such as HITRAN (Rothman et al., 2009). One retrieval technique involves fitting the reference spectra to measured spectra using classical least squares (CLS) or partial least squares methods over a spectral window within which the gas of interest has significant features. Alternatively, single-beam reference spectra may be forward modelled and iteratively fitted to the measured spectra using nonlinear least squares (NLS) (e.g. Griffith et al., 2003). The accuracy of both methods is generally derived via a goodness-of-fit measure between the measured and modelled or reference spectra. However, only a few published studies have assessed absolute retrieval accuracies via independent accuracy assessments based on experimental methods using cells containing known gas concentrations (e.g. Horrocks et al., 2001). This is surprising given the sensitivity of retrieval methods to analysis parameters such as spectral window selection, temperature, pressure and instrument line functions.

OP-FTIR spectroscopy is being used increasingly as a method for monitoring key carbonaceous greenhouse and tracer species such as carbon dioxide (CO₂), methane (CH₄) and carbon monoxide (CO) across an ever-increasing range of applications, including volcanology (e.g. Oppenheimer et al., 2002); urban and aircraft pollution monitoring (e.g. Grutter, 2003) agricultural emission estimation (e.g. Childers et al., 2001); and biomass burning investigations (e.g. Yokelson et al., 1997), it is important that the true accuracy of the various retrieval techniques is established over the wide range of potential concentrations found in these applications. Here we use an experimentally-based laboratory setup to determine the absolute accuracy of OP-FTIR retrievals of CO₂, CO and CH₄ across a concentration range encompassing both ambient air and highly polluted plumes emanating from, for example, biomass fires, vehicle pollution and biogenic sources.

2. Methodology

In this study, undertaken at the UK's Natural Environment Research Council's Molecular Spectroscopy Facility (part of the Rutherford Appleton Laboratory, RAL), a stainless steel gas cell (length = 1.05 m; window diameter = 135 mm; cell diameter = 160 mm) fitted with IR transparent KBr windows was used to contain a series of sample gases. The spectrometer used was a MIDAC Corporation FTIR air monitoring system fitted with a mercury cadmium telluride (MCT) detector and ZnSe optics. The spectrometer was optically coupled to a 76 mm Newtonian telescope, and a MIDAC infrared source, a SiC glow bar operating at 1,100 K with a 150 mm collimator, was placed at the opposite end of the gas cell to act as the IR source (Figure 1). This setup is very similar to that used by Horrocks et al. (2001), with a total pathlength of ~1.5 m, ~0.5 m consisting of free air between the cell and spectrometer and cell and source, and air inside the spectrometer housing. CO₂ and H₂O concentrations in the ambient air outside of the cell were monitored using a calibrated LICOR 840 NDIR gas analyser. An attenuator was fitted to the FTIR spectrometer telescope to avoid MCT detector saturation. Internal cell gas temperature was monitored using a PRT.

The process used to estimate the trace gas concentration from the FTIR spectra retrieves the total number of gas molecules in the optical path (molecular number concentration; [molecules cm⁻²]), a metric that can be simply converted to a so-called pathlength concentration [ppm.m] measure that represents the product of trace gas volumetric concentration [ppmv] and optical pathlength [m]. The range of gas cell volumetric concentrations used here were chosen to represent molecular number concentrations ranging from those of clean air to those characteristic of highly polluted atmospheres (e.g. from industrial sources or biomass burning) that would be measured over pathlengths from ~10 to 1000 m. Gas mixtures were prepared barometrically using high purity (99.9%) component gases. For each mixture, the cell was evacuated before the sample gas was slowly released into the cell until the desired mixing ratio was reached. The cell was then filled with nitrogen to ambient pressure (~1,000 hPa) and allowed to stabilise. Six different CO₂ cell concentrations were used, spanning pathlength concentrations of 12,500-360,000 ppm.m, whilst five different CH₄ and CO concentrations were used, spanning 55-520 ppm.m and 20-6,400 ppm.m respectively. After stabilisation, ten IR spectra were measured with the FTIR spectrometer, each consisting of 8 co-added scans in order to increase signal-to-noise.

To retrieve sample concentration from the measured spectra, MALT (Griffith, 1996), a forward model used to generate synthetic absorbance spectra, was coupled with an iterative NLS fitting procedure (Griffith et al., 2003), which is used to fit the synthetic spectra to the measured spectra. MALT requires the user to select a suitable spectral window for the retrieval procedure. After testing numerous spectral windows (detailed in Smith *et al.*, *submitted*), three spectral windows were selected for each target gas (shown in Figure 2); 2150-2310 cm⁻¹ for CO₂, 2980-3090 cm⁻¹ for CH₄. Two spectral windows were used for CO (2000-2230 cm⁻¹ for

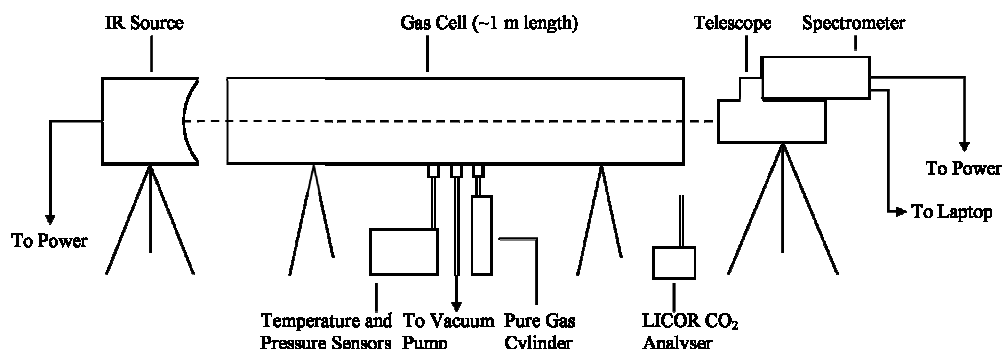


Figure 1: Schematic of the physical instrumentation used during this study.

concentrations <500 ppm.m and 2039-2057 cm^{-1} for greater concentrations). The forward model also requires a number of atmospheric (*e.g.* sample temperature and pressure) and instrumental (*e.g.* spectral resolution, field-of-view etc.) parameters, therefore, as well as finding the absolute accuracy of this retrieval process, a sensitivity analysis was performed in order to determine the influence of parameter uncertainty on retrieval accuracy. Uncertainties in temperature, pressure and spectrometer field-of-view (FOV) were considered, which may result from field situations where the measurements conditions are less tightly controlled than in the laboratory.

3. Results and Discussion

Table 1 summarises the results of the absolute accuracy assessment (the mean percentage difference between the retrieved and actual trace gas concentrations) as well as the results of the sensitivity analysis (the mean increase in retrieval error when using incorrect assumed temperature, pressure or FOV). A full description of retrieval errors for individual gas concentrations and sensitivities to parameterisation uncertainties is provided in Smith *et al.* (submitted). When using optimum parameterisation of the forward model, the nonlinear least squares fitting procedure was able to retrieve gas concentrations to within 5.7% of the true values for all gases and concentrations tested (Figure 3). Mean retrieval errors were 1.5%, 1.4% and 3.1% for CO_2 , CH_4 and CO, respectively.

Retrievals for all three gases showed a systematic reliance upon assumed spectrometer FOV, with retrieved concentrations generally increasing with FOV. CO demonstrated the greatest sensitivity to FOV. This may be explained by the inability of the FTIR spectrometer to fully resolve the narrow CO absorption lines at the 0.5 cm^{-1} spectral resolution used here, thus increasing the sensitivity of CO retrievals to FOV.

Retrieval sensitivities to assumed pressure showed a similarly systematic relationship, with concentrations being overestimated when pressure is underestimated, and *vice versa*. As was the case with the FOV parameter, the forward modelled absorption line widths are affected by the assumed pressure; when a lower pressure is assumed, narrower lines than are actually present in the measured spectrum are modelled due to inadequate pressure broadening. Calculating the best-fit spectrum from these narrower lines results in the overestimation of gas concentrations, whereas the reverse is true when pressure is overestimated. CO_2 showed the greatest sensitivity to assumed pressure. This sensitivity may be explained by the strength of CO_2 absorption lines. For all concentrations tested here, CO_2 demonstrated strong (deep) absorption lines (Figure 2). Deeper absorption lines cause any line shape inaccuracies due to incorrect pressure specification to be exacerbated.

For most retrievals, temperature increases lead to increasing retrieved concentrations (except for the high CO concentration retrievals made using the 2039-2057 cm^{-1} spectral window). These findings are best explained by the temperature dependence of the spectral absorption band shape, with higher temperatures causing more absorption in the weaker lines that lie towards the edge of the band, and reduced absorption in the stronger lines located towards the middle of the band. Therefore, for spectral windows containing strong absorption lines, when temperature is overestimated, higher gas concentrations are required for the forward modelled spectrum to best-fit the measured spectrum. When a narrower spectral window is used, the

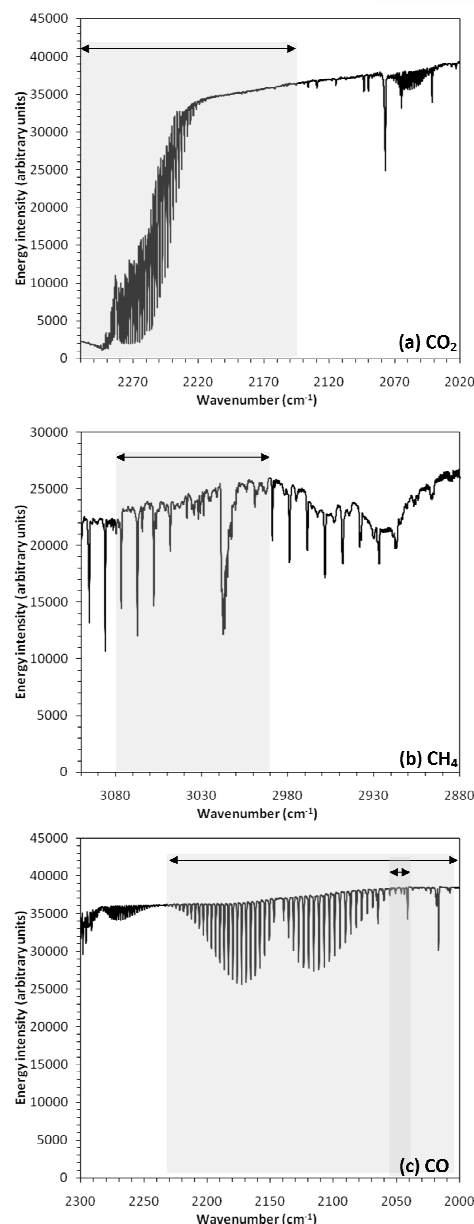


Figure 2: Measured FTIR single-beam spectra for CO_2 , CH_4 and CO. The locations of the spectral windows used in the analysis are indicated by the grey boxes and arrows.

Source of Error	Mean Retrieval Error for all concentrations of each gas (%)			
	CO ₂ (2150-2310 cm ⁻¹)	CH ₄ (2980-3090 cm ⁻¹)	CO (2000-2230 cm ⁻¹)	CO (2039-2057 cm ⁻¹)
Field-of-view (10% change)	2.13	1.58	4.63	4.75
50 hPa error in assumed pressure	2.70	0.48	1.23	1.05
10°C error in assumed temperature	2.85	2.10	0.6	11.80
Total (added in quadrature)	4.47	2.67	4.83	12.76
Line intensity uncertainty (HITRAN)	5.0-10.0	5.0-10.0	1.0-2.0	1.0-2.0
Accuracy of retrieved:true (best parameters)	1.45	1.44	2.87	3.55

Table 1: Summary of trace gas concentration retrieval errors associated with parameter uncertainty

magnitude and direction of the temperature sensitivity depends on the relative position of the spectral window within the absorption band. The 2039-2057 cm⁻¹ CO window lies towards the edge of the absorption band, where overestimated temperatures result in lower retrieved concentrations, and where the sensitivity to the assumed temperature is greater than for a window encompassing the entire absorption band.

4. Conclusion

Our study collected single-beam OP-FTIR spectra of a wide set of concentrations of CO₂, CH₄ and CO, representing a range equivalent to the ambient atmosphere to highly polluted plumes of biomass fires, volcanoes and industrial sources measured over the equivalent of pathlengths of tens to hundreds of metres.

The results from this study confirm that a forward modelling approach coupled with a nonlinear least squares fitting routine can be a viable and accurate method for retrieving gas concentrations from OP-FTIR spectra, in this case using an MCT detector covering a wide spectral range (1.6 – 15 μm; 6000 - 650 cm⁻¹). The concentrations of the three most abundant carbonaceous gases in the atmosphere were able to be retrieved to better than 6% accuracy over a pathlength concentrations ranging over four orders of magnitude. Results from this study provide confidence for future retrievals using this method in the natural environment.

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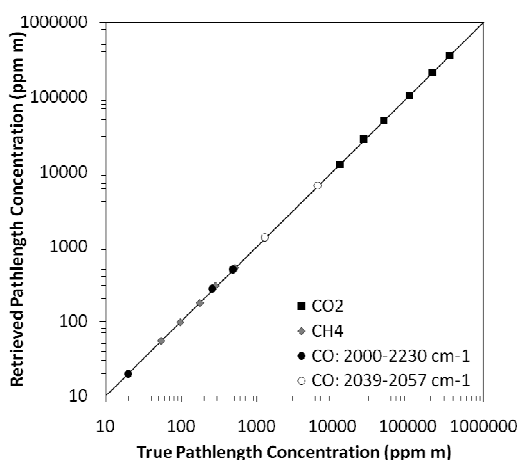


Figure 3: Relationship between mean retrieved pathlength gas concentrations and true gas-cell concentrations. The 1:1 line is shown and all retrieved concentrations are within 5.7% of true concentrations (note logarithmic axes).