

## Removal of water vapour and CO<sub>2</sub> from background spectra

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### Preamble

Retrieved concentrations from the UoW FTIR trace gas analyser can depend on the background spectrum used to ratio the sample air spectrum before MALT fitting. This manifests itself most clearly as small changes in retrieved concentrations after recording a new background. It is most obvious in CO<sub>2</sub> retrieved from the 3600 cm<sup>-1</sup> window (and in δ<sup>13</sup>C, which is derived from it). This band is heavily overlapped by water vapour absorptions which, if variable, can lead to variable retrievals of overlapping species due to imperfect spectral water cancellation between sample and background spectra.

### Analysis of the problem

Sample and background spectra always contain some remnant water vapour absorption in the 3600 cm<sup>-1</sup> region (as well as CO<sub>2</sub> near 2350 cm<sup>-1</sup>). This water vapour absorption does not “ratio out” correctly when calculating a transmission spectrum to be fitted by MALT, for two reasons:

1. Because the sample and background spectra are recorded and apodised by the FTIR to 1 cm<sup>-1</sup> *before* being divided to calculate transmission, cancellation is not exact. This is a consequence of the well-known breakdown of Beer's Law at low resolution - see appendix for details.
2. The background water vapour spectrum actually has two components: water vapour at ~1mb total pressure in the sample cell, and water vapour at ~1000mb total pressure in the IRcube optics compartment. The low pressure absorption lines are narrower than those at 1000 mb, the spectral lineshapes are not identical and do not subtract cleanly from water vapour at ~1000 mb in the sample spectrum.

The result is that the calculated transmission spectrum calculated actually has three water components, which do not cancel fully. To account correctly for this behaviour, MALT must emulate it, in which case the water vapour amounts (in both 1mb and 1000mb layers) in the background must also be known or fitted independently – MALT can do this (see the manual) but it gives unstable solutions because of the strong correlations between the sample and background components of the composite water spectrum.

A better alternative, described here, is to remove the water vapour and CO<sub>2</sub> absorptions from the background spectrum altogether before division to form the transmission spectrum, so that water vapour and CO<sub>2</sub> absorption in the background is effectively zero and only sample water vapour and CO<sub>2</sub> need to be fitted.

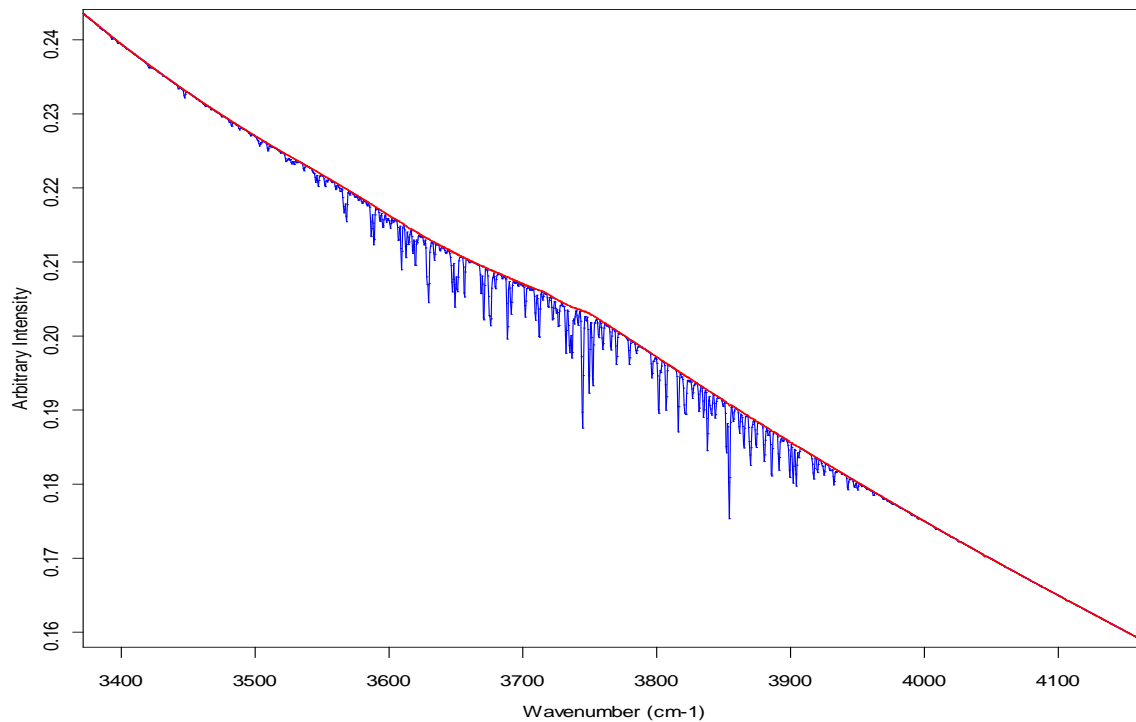
### Procedure outline

1. Fit the background spectrum with a 2-layer MALT model, one layer at 1mb total pressure, and one layer near 1000 mb. It is impossible to get a good fit with a single layer model, in a reasonably dry system there is approximately equal amounts of water vapour in each layer – approx 0.2 mb-m. The 2-layer fit is reliable, retrieving consistent partitioning of the total water between the 2 layers (water in the optics stays constant, that in the cell varies.)
2. Use the concentrations and ILS parameters from this fit as input to MALT in simulation mode to simulate the transmission spectrum of water vapour (2 layers) over the whole spectral region at the levels retrieved from the selected background spectrum.
3. Divide the measured (wet) background spectrum by this simulated water transmission spectrum. The result is a water-absorption free background spectrum.
4. Use the dried, or stripped, background when fitting sample spectra. The retrieved water vapour amount is now only that of the sample, and the fits are generally good with negligible residuals in the H<sub>2</sub>O lines.

5. Use this procedure wherever there are residual absorptions in the background spectrum – usually water vapour around 3500-3700  $\text{cm}^{-1}$  and  $\text{CO}_2$  near 2350  $\text{cm}^{-1}$ .

## Results

Figure 1 illustrates an unstripped (blue) and stripped (red) spectrum in the 3700  $\text{cm}^{-1}$  region.

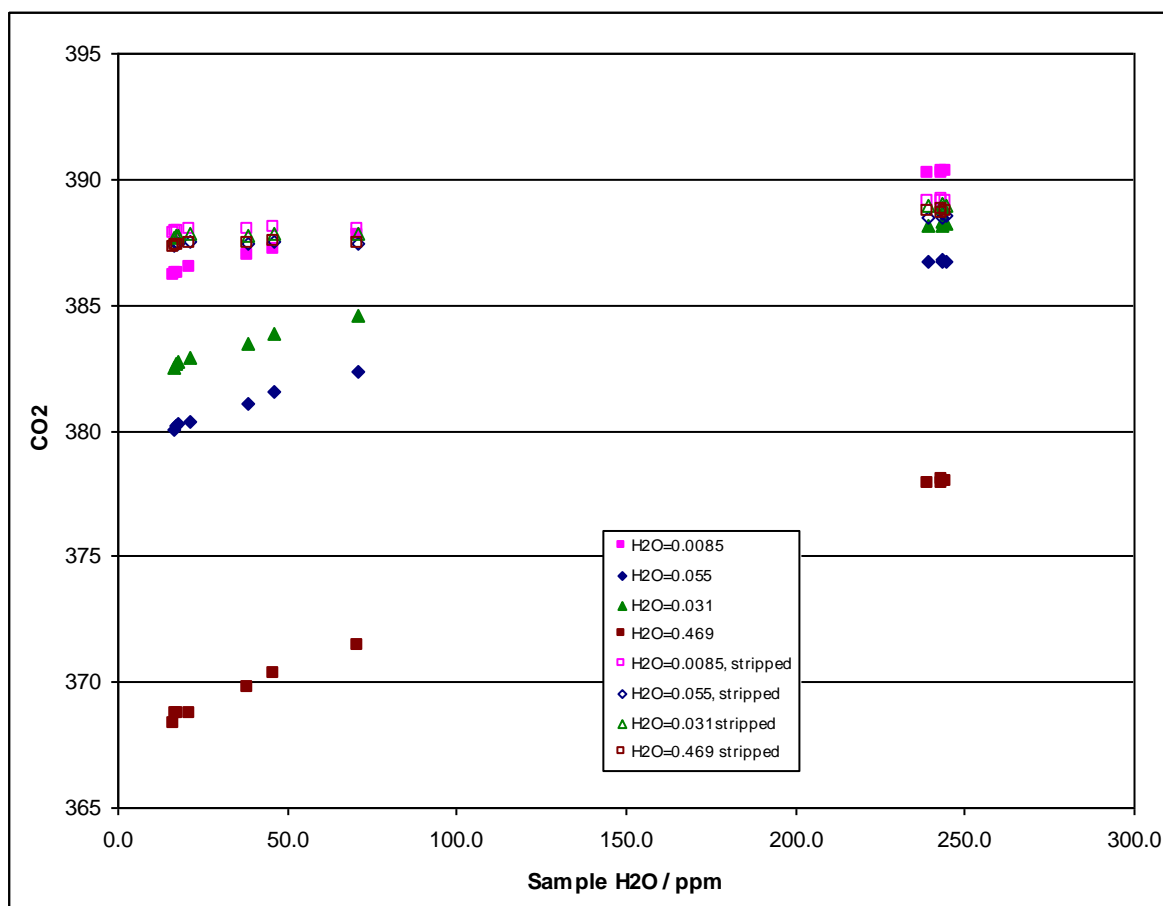


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**Figure 1. Original and stripped spectra in the 3600  $\text{cm}^{-1}$  region where water vapour absorption is strongest.**

Figure 2 shows an illustrative result for CO<sub>2</sub> retrieval near 3600 cm<sup>-1</sup>, where there is strong water vapour absorption, with stripped and unstripped background spectra. The measurements are of 11 spectra of a single tank of air, made over 8 days and having variable amounts of water vapour (10-250 ppm) in the sample (due to variable pre-conditioning of inlet lines and cell). The 11 spectra were ratioed to eight background spectra, four with water vapour at different levels\* (see legend, filled symbols), and the same four backgrounds with water stripped out by the procedure described above (open symbols).



**Figure 2. Retrieved CO<sub>2</sub> amounts with stripped and unstripped backgrounds and varying amounts of H<sub>2</sub>O absorption in the background spectrum. The levels given for water vapour in the legend are the amount of retrieved water vapour in the 24 m cell in hPa (assumed at 1 hPa total pressure) in the background spectrum. The water vapour amounts retrieved in the optics were of similar magnitude in each background spectrum and similar to the driest cell spectrum – 0.007 hPa over an equivalent 24 m path.**

There are two main observations:

1. For unstripped backgrounds, there is a strong dependence of retrieved concentration of CO<sub>2</sub> on both the amount of water vapour in the sample (X axis) and background water vapour (as given in the legend).
2. For stripped backgrounds, all four retrievals agree within 0.5 ppm, and the dependence of CO<sub>2</sub> on *sample* water vapour is reduced by more than a factor of ten relative to the wet backgrounds (to approx 0.0055 ppmCO<sub>2</sub>/ppmH<sub>2</sub>O).

The differences between the four stripped backgrounds reflect small changes in the overall response of the FTIR spectrometer, probably due mainly to temperature stability.

## Implementation

Stripping of water vapour and CO<sub>2</sub> from the measured background spectra is included automatically by the Strip Action in the Spectronus Task builder and included in the standard Background task.

## Revision history

V1	2010	Original description
V2	2018	Minor revisions for web site

## Appendix

The imperfect cancellation of water vapour features is due to the breakdown of Beer's Law at low resolution. Let  $\tau_S$  and  $\tau_B$  be the optical depth of the sample and background spectra at some frequency. Here  $\tau > 0$  due to water vapour concentrations in the sample and background:  $\tau = \alpha C$  is proportional to  $C$ , the water vapour concentration. The sample and background spectra are

$$I_S = I_0 \exp(-\tau_S) \quad \text{and} \quad I_B = I_0 \exp(-\tau_B)$$

The true, or monochromatic, transmission is

$$T_{\text{true}} = I_S/I_B = \exp(-(\tau_S - \tau_B)) = \exp(-\alpha(C_S - C_B))$$

This is exactly the same as the spectrum of a net water concentration  $C_S - C_B$ , the difference in concentrations between sample and background. This would also be true for measured spectra if the spectra were measured with infinite resolution. But in reality the spectra  $I_S$  and  $I_B$  are each apodised and convolved with an instrument lineshape (ILS) of  $1 \text{ cm}^{-1}$  resolution, significantly wider than the lines themselves, *before* being divided:

$$I_{S, \text{measured}} = I_S \otimes \text{ILS}$$

$$I_{B, \text{measured}} = I_B \otimes \text{ILS}$$

The convolution is not linear with respect to  $\tau$ , and

$$T_{\text{measured}} = I_{S, \text{measured}}/I_{B, \text{measured}} \neq I_S/I_B \neq T_{\text{true}}$$