

## Accurate stable carbon isotope ratio measurements in humid gas streams using the Picarro $\delta^{13}\text{CO}_2$ G2101-*i* gas analyzer

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**Summary:** The Picarro G1101-*i* and G2101-*i* gas analyzers provide field measurements of the stable isotope ratio  $\delta^{13}\text{CO}_2$  with a precision of 0.3 permil in five minutes. In an isotope ratio mass spectrometry (IRMS) laboratory, it is customary to dry the samples to very low dew points ( $< -45\text{C}$ ) prior to isotope analysis. For field work, however, drying the samples is in many cases inconvenient or impractical. Water vapor can affect the reported delta via spectroscopic broadening or direct spectroscopic interference. In the G2101-*i*, the effects of the water vapor concentration, *including* its isotopes, has been characterized, and the reported isotope ratios have been corrected. Residual errors of less than 0.3 permil can be achieved in the G2101-*i*, even in very humid gas streams.

### Spectroscopy of the G1101-*i* and G2101-*i*

The Picarro G1101-*i* and G2101-*i* are laser-based analyzers that employ cavity ringdown technology to measure the  $\delta^{13}\text{CO}_2$  stable isotope abundance. The stable isotope abundance is measured by measuring two independent spectral absorption lines in the near-infrared region of the spectrum, one for  $^{12}\text{C}$  one for  $^{13}\text{C}$ . The ratio of the peak *heights* (not areas) of the lines is a measure of the ratio of the concentrations of each of the two isotopologs.

Water vapor can interfere with the measurement of the carbon dioxide concentration and isotope ratios in the following ways:

- **Dilution:** The dilution effect is simply the change in mixing ratio of carbon dioxide and methane caused by variability in the humidity. For example, a dry air mass traveling over warm water will accumulate humidity, and this additional water vapor will dilute the concentration of the other gases. Conversely, a humid air mass that becomes drier (as through precipitation) will cause an inverse dilution effect, increasing the mixing ratios of the other gases. Because it affects  $^{12}\text{C}$  and  $^{13}\text{C}$  equally, dilution affects *only* the concentration, not the reported isotope ratio. The magnitude of the effect is a 1% decrease in the reported fractional concentration for every 1% increase in water vapor

## White Paper

concentration. The dilution effect is largely due to the most abundant isotopolog of water ( $^1\text{H}_2^{16}\text{O}$ ), which is 99.8% of all the water in the world under most conditions.

- **Spectral broadening<sup>a</sup>:** The Lorentzian broadening of the spectral lines are affected by the presence or absence of water vapor. The magnitude of the effect on the reported concentrations is of the order of the dilution effect (though generally somewhat smaller). The effect on each of the two lines is not necessarily identical, leading to a systematic error in the reported isotope ratio as a function of water vapor concentration. The effect on delta is proportional to water vapor concentration and independent of carbon dioxide concentration. As with dilution, this effect is largely due to  $^1\text{H}_2^{16}\text{O}$ .
- **Direct spectral interference:** Direct spectral interferences are caused by any water vapor spectral lines that are in the immediate vicinity of either the  $^{12}\text{C}$  or  $^{13}\text{C}$  spectral lines. These can cause offsets to these two gas species which affect both the concentrations and the reported isotope ratio. The effect on delta is proportional to the product of the water vapor concentration and inversely proportional to the carbon dioxide concentration (as we will derive, below). Unlike dilution, this effect can depend on whichever isotopolog or isotopologs are interfering with the  $^{12}\text{C}$  and  $^{13}\text{C}$  measurements.

This white paper is organized in the following way. First, we summarize the spectroscopy of water and carbon dioxide in the region scanned by the Picarro instrument. We next report on calibration of the water vapor line against our reference method. Then, we present a summary of the interferences which affect the concentration reporting of  $^{12}\text{CO}_2$ , and finally, we present the effects of water vapor interference on the reported isotopic ratio. Finally, we present a summary of the correction factors, and the estimated errors associated with these correction factors over typical conditions.

### Near-infrared spectroscopy of water vapor and carbon dioxide

The G1101-*i* and G2101-*i* both operate in the same region of the near-infrared spectrum, in the vicinity of 1600 nm. In this region, there are a multitude of ro-vibrational overtones of carbon dioxide and water vapor. The situation is complicated by the fact that each isotopolog of water vapor and carbon dioxide all have distinct spectral features which can complicate the spectral

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<sup>a</sup> For a more complete treatment of the general theory of spectral broadening, please see the technical white paper, “Accurate Greenhouse Gas Measurements in Humid Gas Streams Using the Picarro G1301 Carbon Dioxide / Methane / Water Vapor Gas Analyzer,” available on the Picarro website: [http://www.picarro.com/assets/docs/White\\_Paper\\_G1301\\_Water\\_Vapor\\_Correction.pdf](http://www.picarro.com/assets/docs/White_Paper_G1301_Water_Vapor_Correction.pdf)

region and potentially confuse the nonlinear spectral fitting algorithm. Many of these spectral interferences must be addressed and accounted for to report a reliable  $\delta^{13}\text{C}$  isotope ratio.

In the figure below, we present the fingerprints of water vapor in the region of interest. The absorption data are presented on a logarithmic scale, so that even small spectral features can be seen. The locations of the key carbon dioxide absorption lines are also indicated in the figure. Three waters were injected into the instrument, each with a different isotopic mixture: a) Picarro00, which is a standard mixture with nominal abundances for the key isotopes, b) Picarro33, which has elevated levels of  $^2\text{H}$  and  $^{18}\text{O}$ , and two ultra-high enriched samples of  $^2\text{H}$  and  $^{18}\text{O}^b$ . These mixtures were used to identify the different spectral features.

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<sup>b</sup> a water vapor sample with an elevated level of  $^{17}\text{O}$  was not available for this study.

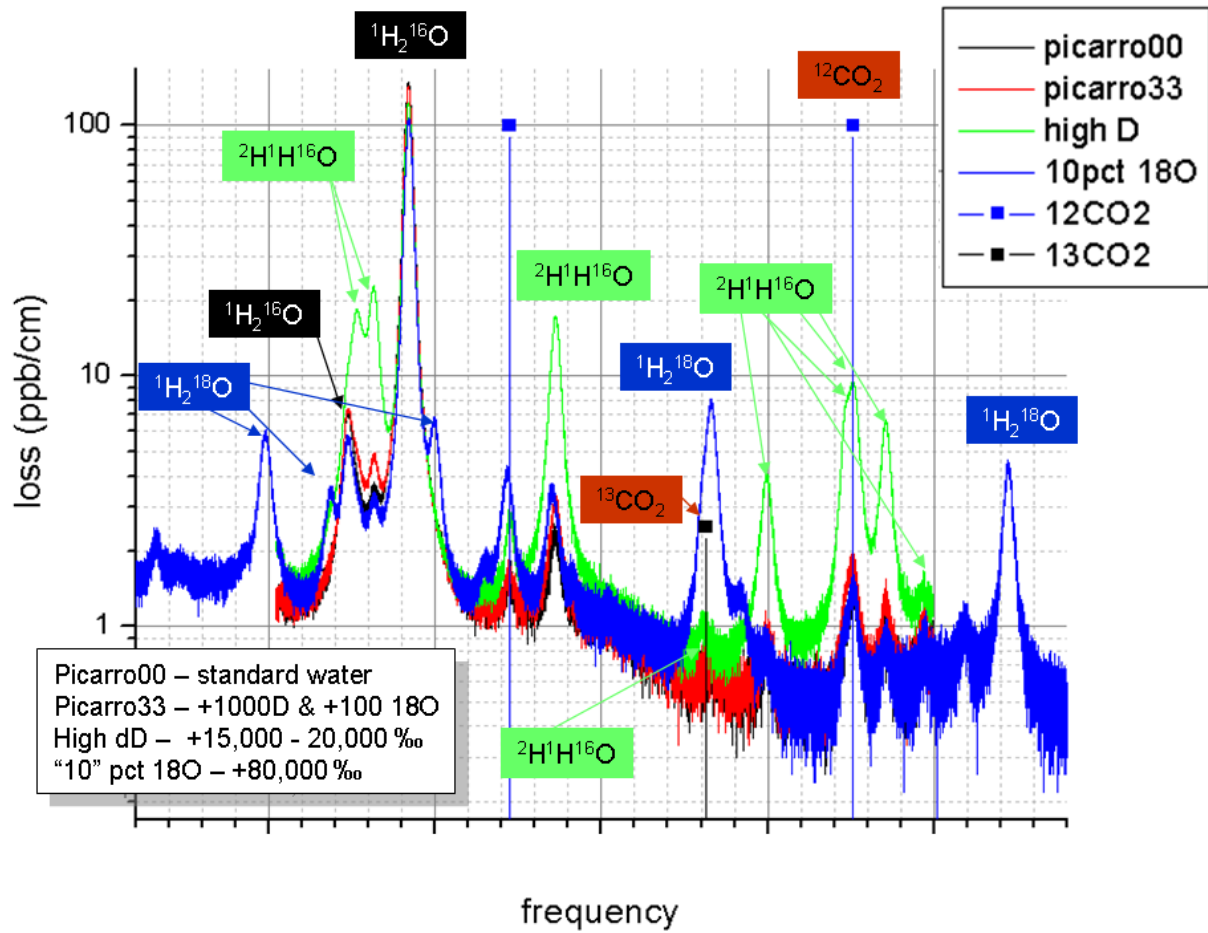


Figure 1: water vapor spectrum in the vicinity of the analyte spectroscopic features. The  $^{12}\text{CO}_2$  on the right side of the graph is used in the measurement of the isotopic ratio. The water vapor concentration is about 31,000 ppm, and the carbon dioxide lines correspond to a carbon dioxide concentration of about 200 ppm.

From this figure, we may draw several conclusions. Firstly, it is clear that the water vapor spectrum in this region is highly complex, and will require sophisticated spectroscopy and calibration algorithms. In addition, there is a substantial isotopic component to the interference, via  $^2\text{H}$  and  $^{18}\text{O}$ ; the abundance of these isotopes can vary in real-world conditions, and the instrument will need to deal with that variability. Finally, there are many small (but significant) directly interfering lines, which will mean that the correction factors for the reported carbon dioxide concentration and isotope ratio will be dependent not only on the water vapor concentration, but also on the carbon dioxide concentration.

Despite the apparent complexity of this spectral region, it is important to understand the scale of the problem. At 400 ppm of carbon dioxide, the water vapor correction factor is only about 5

permil / % H<sub>2</sub>O. Variability in isotope abundances under normal ambient conditions will be smaller adjustments to that correction factor. As we will demonstrate below, the spectroscopy is easily able to support carbon isotope measurements on a scale of a fraction of a permil, even over the full range of water vapor variability.

### Calibration of the <sup>1</sup>H<sup>16</sup>O<sub>2</sub> spectral line

We investigated the reported water vapor concentration from the G1101-*i* against the G1301, which in turn was calibrated against a traceable dew point meter at the Max Planck Institute in Jena, Germany. In a simple experiment, a single water vapor source (in this case, a source of zero air humidified with Picarro00 injected into the upstream side of a hydrophobic filter<sup>c</sup>) was directed into two instruments running side by side, a G1101-*i* and a G1301. The G2101-*i* uses the same water line, and the calibration should be identical between the two instruments. The reported water concentration is derived from the following expression:  $H_{reported} = a_h p_h$ , where  $H_{reported}$  is the water concentration and  $p_h$  is the peak height. The constant  $a_h$  is 0.0148, for the peak height in absorption units of ppb/cm and concentration in units of %v.

The two calibration curves only differ by a multiplicative factor of 0.989 between the two. This factor can be included in the calibration factor obtained at MPI-Jena for the G1301 to arrive at the absolute calibration of the G1101-*i* and G2101-*i*:

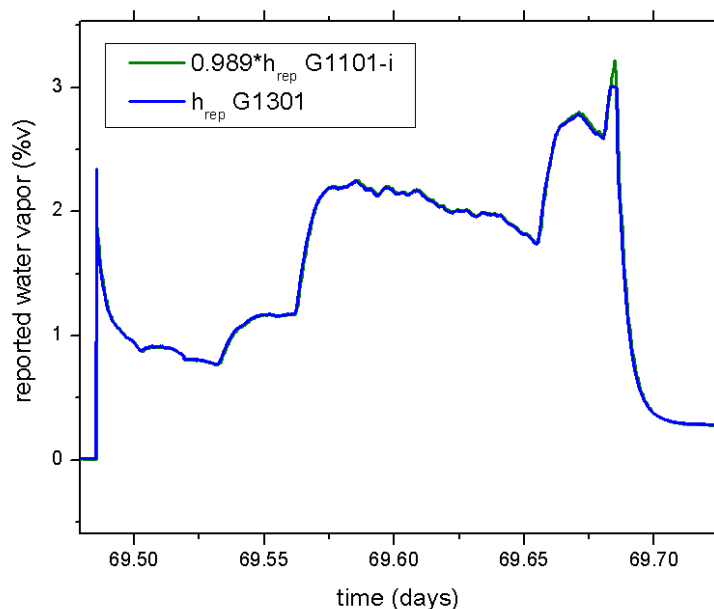
$$H_{actual} = 0.7635(H_{reported} + 0.02497H_{reported}^2)^d$$

The nonlinearity of this expression stems from the self-broadening of the water vapor line with increasing water vapor concentration.

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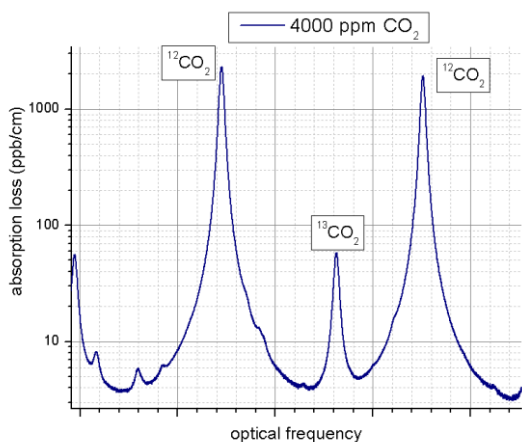
<sup>c</sup> See white paper on G1301 for more information.

<sup>d</sup> These water vapor measurements all use <sup>1</sup>H<sub>2</sub><sup>16</sup>O lines.



**Figure 2:** comparison of the *reported* (not actual) water vapor concentration from the G1101-i and the G1301. The disparity above 3%v is an artifact due to condensation in the line between the G1301 and the G1101-i.

### The <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> spectroscopic lines



**Figure 3:** Carbon dioxide spectrum at 4000 ppm

The figure at the left (Figure 3) shows the spectroscopy of carbon dioxide in this region. The G1101-i and G2101-i use the right-most <sup>12</sup>CO<sub>2</sub> peak and the pictured <sup>13</sup>CO<sub>2</sub> peak to perform the concentration and isotopic analysis. For both concentration and isotope ratio, the peak heights (rather than peak area) are used; the following expressions are used to calculate these results:

$$c_{12} = a_{12}p_{12}, c_{13} = a_{13}p_{13}, \text{ and } {}^{13}\text{C} \delta = 1000 \left( \frac{r - r_0}{r_0} \right),$$

where  $r = \frac{c_{13}}{c_{12}}$ .

$r_0$  is the concentration ratio of the primary reference standard, Pee Dee Belemnite. In the following, we will report on correction factors to  $p_{12}$  and  $p_{13}$  which then get transferred to the target analytical quantities of concentration and isotope ratio. For concentration in units of ppm and peak height in units of absorption (ppb/cm), the calibration factors for both the G1101-i and

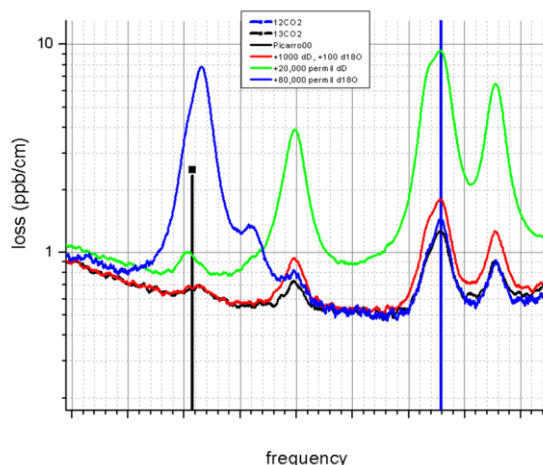
# White Paper

the G2101-*i* are  $a_{12} = 1.68307$  and  $a_{13} = 0.64382$ . It is important to remember that  $c_{12}$  and  $c_{13}$  are the raw reported concentrations, prior to the application of any correction factors.

## Corrections to the reported carbon dioxide concentration

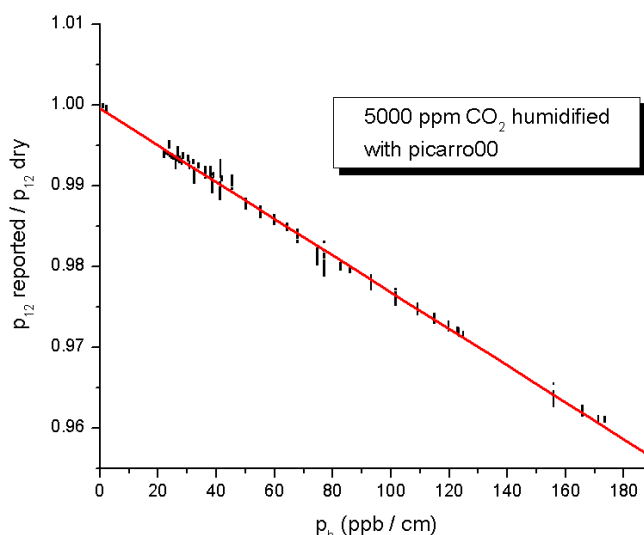
The figure below shows a close-up view of the spectral region near the primary  $^{12}\text{CO}_2$  peak. As is evident from the figure, the primary direct interference on this peak is a cluster of HDO lines. On the other hand, the dilution effect and spectral broadening will be dependent on the standard  $^1\text{H}_2\ ^{16}\text{O}$  concentration. There will therefore be an isotopically dependent correction factor to the reported concentration.

To investigate this correction factor, we have performed the following matrix of measurements. We have taken the gas from two bottles, containing 380 ppm and 5000 ppm of carbon dioxide, and humidified each with both standard Picarro00 water as well as water enriched to a  $\delta\text{D}$  of +15,000 – 20,000 ‰. We can then measure the overall water correction curve for this spectral line, including an isotopic correction.

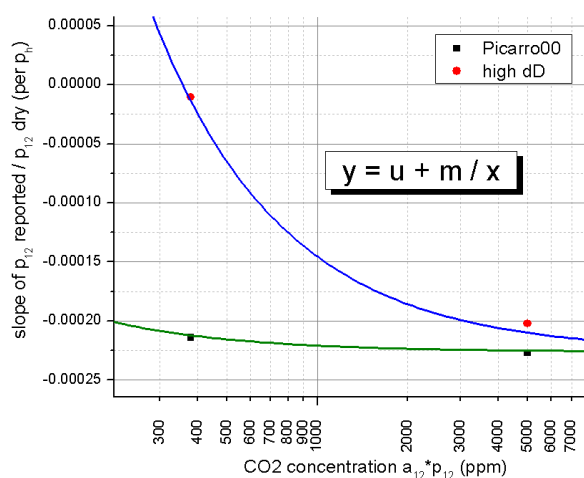


**Figure 4: close up of the water isotope spectra in the vicinity of the analyte carbon dioxide peaks.**

An example of one of these experiments (5000 ppm of carbon dioxide humidified with Picarro00 water) is shown below. The slope of the red line in the figure is  $-2.27 \times 10^{-4}$ , which corresponds to  $-0.01533 / \%v$  reported water ( $H_{reported}$ ); it also corresponds to  $-0.0187 / \%v$  actual water vapor concentration  $H_{actual}$ .



**Figure 5: ratio of the reported peak height to the dry gas peak height as a function of the water peak height.**



**Figure 6: slope of fractional change in carbon dioxide peak height with water vapor, vs concentration, for two waters.**

This experiment was repeated four times for each of the two gas bottles and humidification sources. We plot the slopes obtained from plots like that shown in Figure 5 and arrange them in a single graph, shown below.

For broadening and dilution, the slope should be independent of carbon dioxide concentration. For a direct spectroscopic interference (like the HDO lines underneath the <sup>12</sup>CO<sub>2</sub> line), the effect on the slope should be

stronger for lower concentrations, and should depend inversely with concentration. The two curves (green and blue) follow this  $y = u + m/x$  functional form. To first order, we presume

that  $m$  should be proportional to the HDO concentration (since the lines that directly interfere are HDO lines), and that  $u$  should be proportional to the <sup>1</sup>H<sub>2</sub><sup>16</sup>O concentration, because this species is the source of broadening and dilution.

The two curves were generated using the following values:  $u = -2.26 \times 10^{-4}$  and  $m = 5.3 \times 10^{-3}$  ( $1 + \delta D / 1000$ ), where we have assumed a  $\delta D = 14,200 \%$ . Analysis of the peak raw spectral peaks



## White Paper

in Figure 1 and Figure 4 indicates that the isotope ratio of the water used for these experiments is  $14,000 \pm 1000$  ‰, which is a good consistency check.

We may then summarize the results of the water vapor correction on the reported concentration in the following expression, where we have substituted  $H_{reported}$  for  $p_h$ :

$$\frac{c_{12\_wet}}{c_{12\_dry}} = 1 + \left( u' + \frac{m'}{c_{12\_dry}} \right) H_{reported}$$

where  $u' = -0.01527$  and  $m' = 3.58 \times 10^{-1} (1 + \delta D / 1000)$ . For computational simplicity, it is acceptable to replace the reported wet  $c_{12}$  value, rather than the dry value – the errors introduced by this process are small compared to the uncertainties in the analysis.

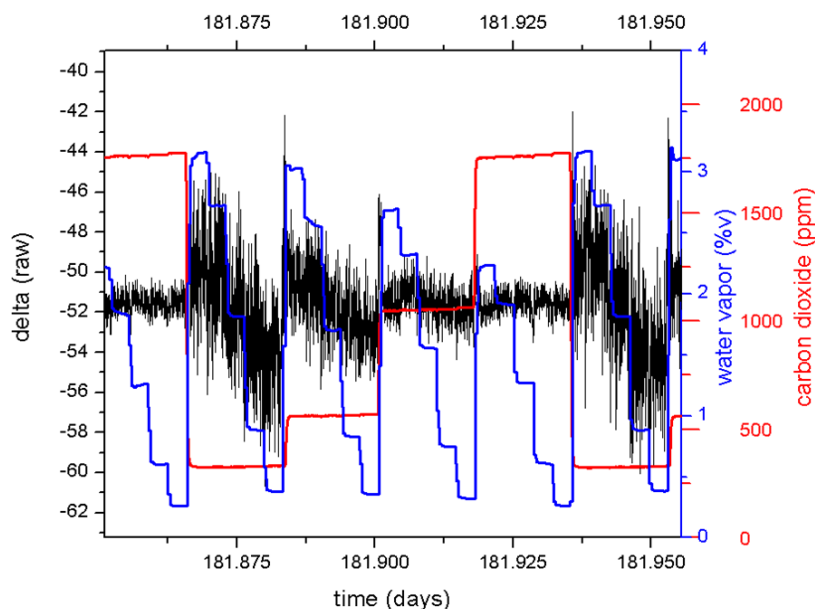
The correction factor is about 6.46 ppm / %v water (reported) at 400 ppm carbon dioxide, for a nominal water isotope content with a  $\delta D$  of 0‰. The error in this correction factor is about 35.8 ppb carbon dioxide / %v water (reported) @ 400 ppm carbon dioxide, for every 100‰ change in  $\delta D$  of the water vapor in the gas stream<sup>e</sup>.

### Corrections to the isotope ratio

We turn our attention to the corrections of the reported isotope ratio as a function of variable water vapor concentration. It is clear from Figure 4 that in addition to the corrections to  $c_{12}$  described above there will be additional adjustments to  $c_{13}$  that must be taken into account. Here, the primary direct interfering species is  $^1H_2^{18}O$ , although there are a couple smaller satellite HDO peaks in the vicinity that may have an effect on the reported delta. To investigate the effect of the measurement on the isotopic ratio  $\delta^{13}C$ , we performed a detailed experiment in which the concentration of both water vapor and carbon dioxide concentration was varied. A single 5000 ppm source of carbon dioxide and a humidified zero air source were used to generate the gases – the resulting isotope ratio should be constant. The results of this measurement on the G1101-*i* are shown in Figure 7, using the factor correction factor of -3.3 ‰ / %v water (reported). The correction factor clearly fails at lower carbon dioxide concentration levels – this is due to the fact that direct absorption interference (in the form of HDO lines under the  $^{12}CO_2$  line and the  $^1H_2^{18}O$  beneath the  $^{13}CO_2$  line) has an ever increasing effect on the delta with decreasing concentration.

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<sup>e</sup>  $\delta D$  varies over a range of 100 - 400 ‰ under nearly all conditions.



**Figure 7: measurement of delta as a function of water vapor concentration and carbon dioxide, using the standard G1101-i water vapor correction factor of -3.3 ‰ / %v water (reported).**

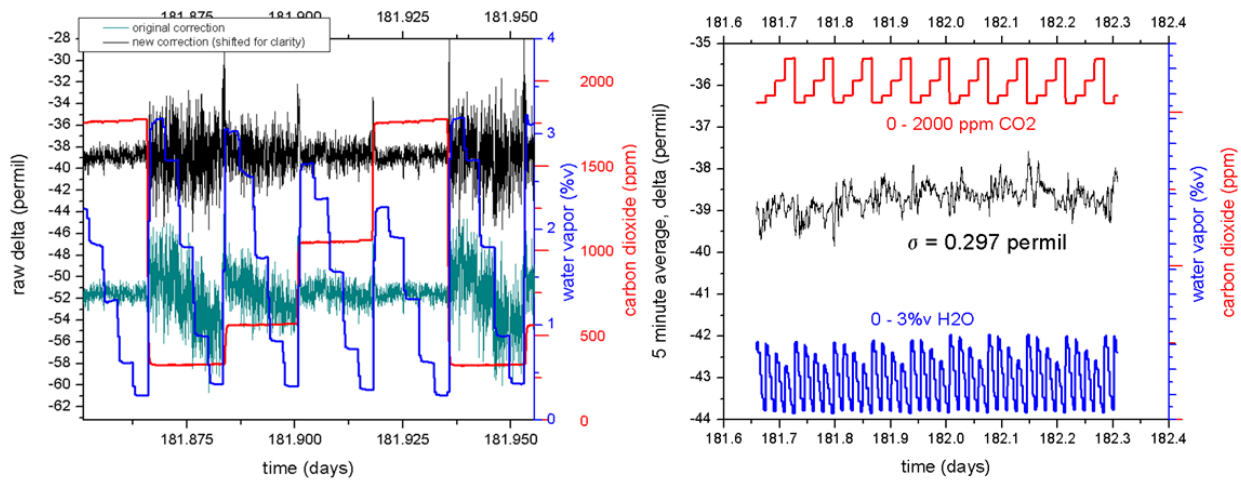
Given these two effects, we look for a correction factor with the following form<sup>f</sup>:

$$\delta_{corr} = \delta_{raw} + H_{reported} \left( d + \frac{e}{c_{12\_wet}} \right).$$

We have opted to use the reported value of the carbon dioxide concentration, rather than the dry value, for computational simplicity. The nonlinear errors associated with this substitution are not detectable outside the noise of the measurements. Using values of  $d = -3.1 \pm 0.3$  and  $e = -800 \pm 100$ , we reanalyze these data and plot it in the next figure. The corrected delta now shows no significant systematic error with water vapor concentration at any carbon dioxide concentration sampled during the experiment.

<sup>f</sup> In the G2101-i, the corrections to the isotope ratio for water vapor are applied directly to the measured peak heights, rather than as a delta correction as written here. We have elected to express the correction in terms of delta so that the effect of water vapor can be more transparently evaluated, and so that it is possible to use this equation to post-process existing data sets.

White Paper



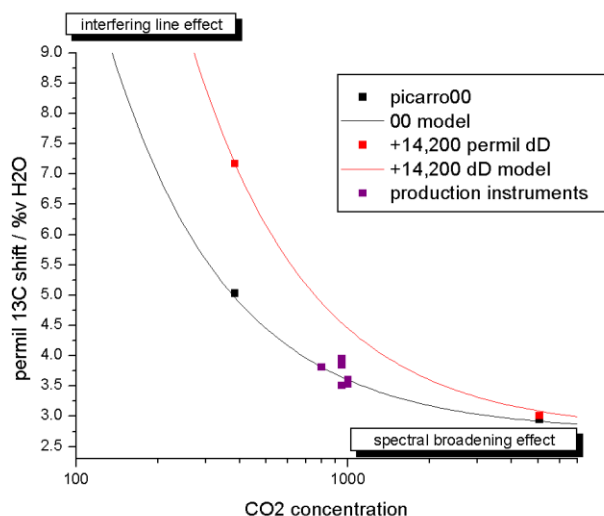
**Figure 8:** Left panel - corrected delta on the G2101-i (black) compared to the result from the G1101-i (teal). See text for the functional form of the correction. Right Panel – 5 minute average of the same data, repeated over about 12 hours, with the ~30 seconds around each water or carbon dioxide step removed. The standard deviation of the entire data set is 0.297 ‰.

It is important to note that the correction factor as expressed above is dependent on the  $^1\text{H}_2^{16}\text{O}$  concentration, even though the direct absorption interference is isotopically dependent (HDO under both lines and  $^1\text{H}_2^{18}\text{O}$  in the case of the  $^{13}\text{CO}_2$  line). There are therefore errors in this correction factor as the isotopic composition of the water vapor varies. We measured the error caused by deuterated water using the same data in Figure 6, by analyzing the shift in delta with increasing water vapor concentration at two different bottle concentrations and two waters with different deuterium isotopic compositions. These results are presented in Figure 9. The two

curves are generated from the following expression:

$$\frac{\delta_{corr}^{13}\text{C}}{H_{reported}} = 2.8 + \frac{850(1 + \delta D / 7100)}{c_{12}}$$

The observed small effect on the slope due to deuterated water of 0.03 ‰ / ‰v water (reported) for every 100 ‰ change in  $\delta D$  is caused primarily by the small HDO line beneath the  $^{13}\text{CO}_2$  peak, which is offset to some extent by the larger HDO line beneath the  $^{12}\text{CO}_2$  peak. Note that removing all



**Figure 9:**  $^{13}\text{C}$  isotopic shift with water vapor as a function of carbon dioxide concentration, for two different waters.

## White Paper

deuterium from the sample (by setting  $\delta D$  to  $-1000$  ‰ in the above equation) still leaves a substantial error due to direct interference, which is due to the  $^1H_2^{18}O$  line near the  $^{13}CO_2$  peak. Given that, we then can arrive at the following complete expression for the correction factor:

$$\frac{\delta_{corr}^{13}C}{H_{reported}} = (2.8 \pm 0.3) + \frac{(850 \pm 100) \left( 1 + \frac{(\delta D + 60)}{7100} + \frac{(\delta^{18}O + 15)}{1135} \right)}{c_{12}}$$

Here, we have included the offsets for the actual isotope abundance of the vapor that was used in this calibration effort, which were approximately  $\delta^{18}O$  of  $-10$  ‰ and  $\delta D$  of  $-60$ ‰. We have estimated the total uncertainty from the limited experiments we have done here – as we manufacture more instruments, we will be able to refine these uncertainties.

From this expression, we may estimate the magnitude of the errors due to unknown isotope composition. For the expected variation in  $^1H_2^{18}O$  of about  $40$  ‰ in typical applications, the error in the water correction is about  $0.2$  ‰ in the reported  $\delta^{13}C$  (at  $400$  ppm carbon dioxide and  $3\%$  v change in  $H_2O$ ). Similarly, for the expected maximum variation of about  $400$  ‰ in  $\delta D$ , the error in the reported  $\delta^{13}C$  is  $0.33$  ‰ (at  $400$  ppm carbon dioxide and  $3\%$  change in  $H_2O$ ). Under most conditions, these values are much smaller. Unfortunately, both corrections are in the same direction, so that for typical water vapor lying on or near the meteoric line, the contributions add. Still the total uncertainty is only about  $0.5$  ‰ over the complete range of expected ambient conditions, and usually much smaller than this. Thus, though our measurement of water vapor is based solely on the  $^1H_2^{16}O$  concentration, and despite the fact that the direct interferences on the spectral lines are due to less abundant isotopomers, the correction factor based on the  $^1H_2^{16}O$  line is quite good over normal conditions.

## Summary

The G2101-*i* can deliver accurate measurements of the  $\delta^{13}\text{C}$  of carbon dioxide, within 0.5 ‰ of the true value, even in humid gas streams. The following table estimates the errors caused by water vapor on the measurement:

	<b>concentration error (ppm @ 400 ppm / water vapor 0 – 3%)</b>	<b>isotopic error (‰ @ 400 ppm / water vapor 0 – 3%)</b>
No correction factor	19.2 ppm (12 ppm from dilution, 6.9 ppm from broadening, and 0.35 ppm due to direct interference)	15 ‰ (10 ‰ from spectral broadening and 5 ‰ from direct interference)
With correction factor. constant isotopes ratios	± 0.15 ppm estimated	0.3 ‰ (instrument drift limited)
With correction factor but variable isotope ratios	±0.25 ppm estimated	0.8‰ (0.3‰ drift, 0.5‰ isotopes worst case.)