Accurate stable carbon isotope ratio measurements with rapidly varying carbon dioxide concentrations using the Picarro $\delta^{13}CO_2$ G2101-*i* gas analyzer

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Summary: Stable isotope analysis relies on the simultaneous or near-simultaneous measurement of two individual species. In the case of the Picarro G1101-*i* and G2101-*i* gas analyzers, these two species are $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$, which we denote ^{12}C and ^{13}C for simplicity. In the G1101-i, alternate measurements of ^{12}C and ^{13}C are made with a period of about eight seconds; the fact that the two gas measurements are not made simultaneously leads to systematic errors in the reported delta in certain conditions when the gas concentration is varying significantly. In this white paper, we report on improvements that we have made in the G2101-i to reduce these systematic errors by more than a factor of eight.

Performance of the G1101-i

The Picarro G1101-i is a laser-based analyzer that employs cavity ringdown technology to measure the $\delta^{13}CO_2$ 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}C one for ^{13}C. The ratio of the peak heights of the lines is a measure of the ratio of the concentrations of each of the two isotopologues. In the G1101-i, the two lines are not measured simultaneously; the laser alternates between measurements of these two features every eight seconds. In static conditions, when the concentrations are not changing, the fact that the measurements are not made at the same time does not affect the measurement of the isotope ratio. However, when the concentration is varying, the measurements at different times can lead to an error in the reported isotope abundance.

The first-order variability is corrected in the G1101-i by using a linear interpolation process to predict the simultaneous concentrations, as shown in Figure 1 below.
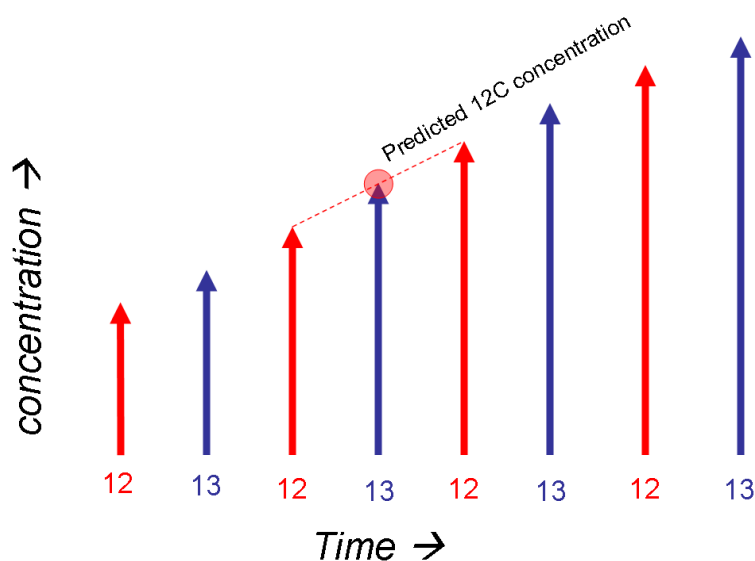
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Figure 1: measurement sequence in the G1101-i. The time between successive ^{12}C measurements is about 8 seconds.

Employing this first-order interpolation process delivers acceptable results under most practical circumstances. However, in cases of large, fast concentration fluctuations, the methodology breaks down, causing unwanted systematic errors in the reported isotope ratio.
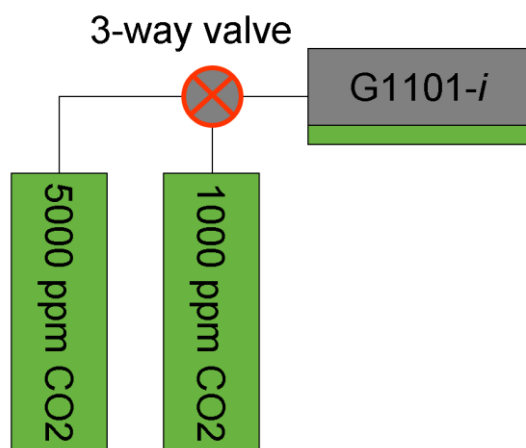

Figure 2: setup for providing step concentration challenges to the instrument.

To investigate these issues, we applied varying carbon dioxide concentrations to the inlet of the instrument, as shown in Figure 2. The three-way valve was switched every five minutes. The instrument flow was about 25 sccm, the standard flow for the G1101-i. We used two bottles with very different concentrations (1000 ppm and 5000 ppm) to simulate possible worst-case conditions for transient concentration dependence.

The resulting concentration profile can be seen in Figure 3. At the standard flow rate of 25 sccm, the maximum concentration change we observed was 200 ppm / second.
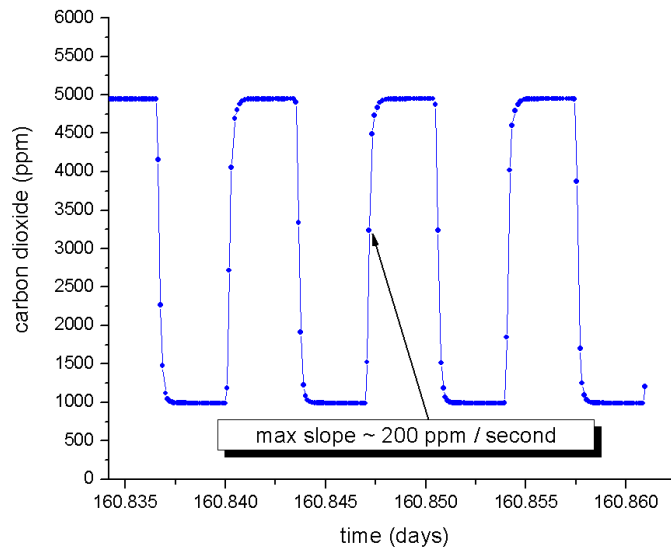
Figure 3: concentration profile on the G1101-i with two bottles. The measurement interval of 8 seconds is indicated by the small blue dots.

In Figure 4, we show the reported delta during these concentration steps. At each transition, there is a fast transient error in the reported delta, followed by a more gradual (minutes scale) relaxation of the reported delta to an equilibrium value. The scale of these errors is very large (10s of permil or more).
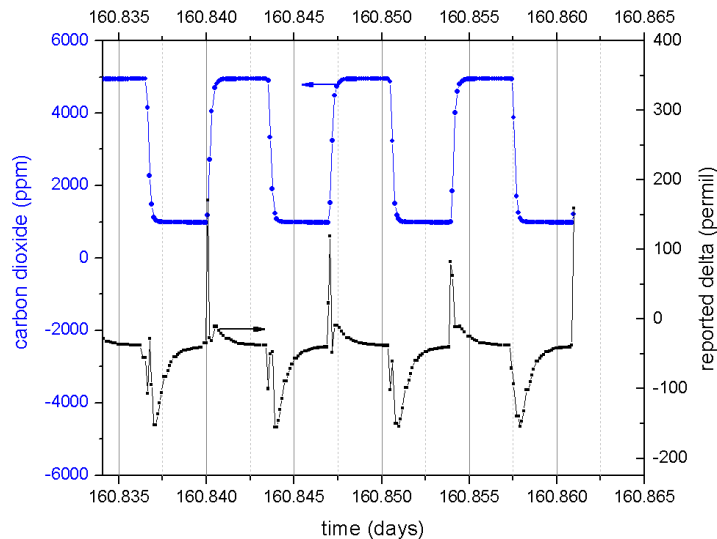
Figure 4: reported (unaveraged) delta during concentration step challenges. The reported delta does not recover for several minutes after the transient event. Each concentration step is 5 minutes long.

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Further analysis of the data reveals the following sources of transient response error in the G1101-*i*:

- o **Slow response of the internal background absorption tracking**: In the G1101-i, there 4is a thirty-second averaging loop on the background absorption loss of the cavity. This is a parameter that does not vary substantially with varying carbon dioxide concentration. However, there is a small variation in this parameter with concentration, which leads to a slow relaxation of the reported isotope ratio to its equilibrium value, caused by slow response of the average of the background absorption loss.

- o **Higher-order (i.e., nonlinear) concentration response in time**: The simple linear interpolation feature in the instrument breaks down if the concentration does not depend linearly with time. Clearly from the figure, the eight second measurement interval is long compared to the gas exchange time in the instrument of about 30 seconds; the linear approximation is no longer valid.

- o **Cross-talk between $^{12}CO_2$ and $^{13}CO_2$**: The two spectral features for 12C and 13C are largely independent of each other, but there is a small but significant cross-talk of the 12CO2 concentration to the 13CO2 concentration. This small cross-talk, combined with the fact that in the G1101-i fitting engine, the linear interpolation method is *not* available. Instead, the *previous* 12CO2 measurement is used as a fixed parameter in the subsequent 13CO2 spectral analysis, thus leading to a small systematic error in the reported isotope ratio.

Improvements in the G2101-i

The G2101-i was redesigned to address applications in which the concentration is varying quickly. Improvement to this performance was accomplished in the G2101-i using three separate techniques.

#1: Removal of the internal background absorption tracking

As part of the G2101-i development, we investigated removal of the internal background absorption tracking average. This average was originally designed to reduced the short term variability in reported isotope ratio, and it does improve the fast (8 second) noise by about 30-40%[a]. However, the loops have a clearly undesirable (and more unpredictable) effect on the transient response. In Figure 5, we compare the performance both with and without the baseline

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[a] Removing these averaging loops has essentially no effect on the performance of 2 minutes and longer averages.

average included. The transient response is clearly dramatically improved, especially in the relaxation of the reported isotope ratio to equilibrium during the pulse.
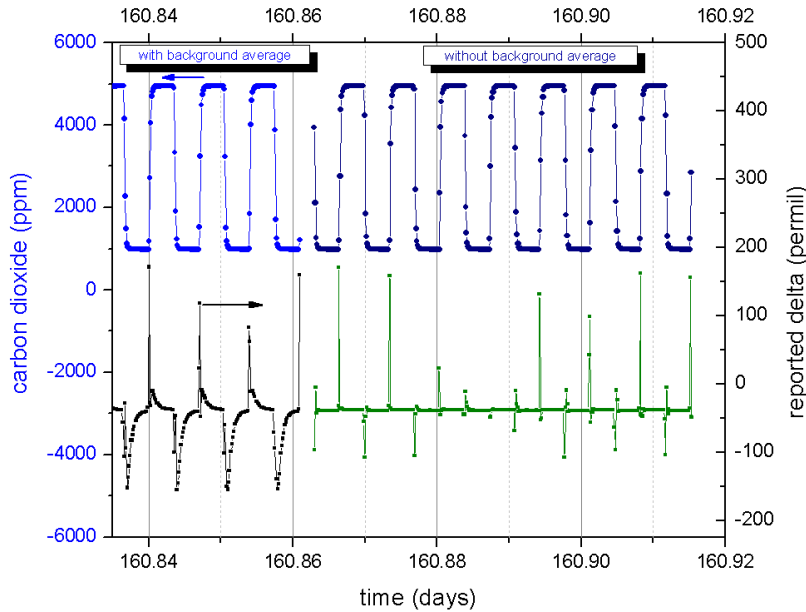
Figure 5: Comparison of the transient response both with and without background absorption tracking.

In the next figure (Figure 6), we zoom in to a finer scale in reported isotope ratio. Other than a short period immediately in the vicinity of the switch, there is clearly a dramatic improvement in the performance of the instrument.
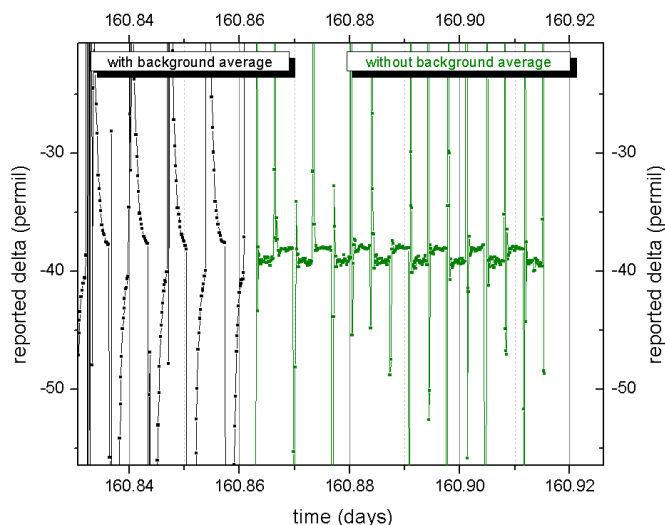
Figure 6: detailed view of the reported isotope ratio in time, both with and without background absorption tracking.

#2: Faster measurement rate

The next step in the development of the G2101-i was to increase the measurement rate. Making 12C and 13C measurements as nearly simultaneously as possible will reduce the effects of fast changes in concentration.   As a result of this development, the measurement period was decreased eightfold, from 8 seconds to about 1 second. The resulting performance is shown in Figure 7. The peak transient signals have decreased roughly in proportional with the decrease in scanning time, indicating a primarily linear dependence of the reported delta on the rate of change of concentration. Any higher order errors are reduced with an even bigger factor – a systematic error that depends on the 2nd derivative would be improved by a factor of $8^2 = 64$.
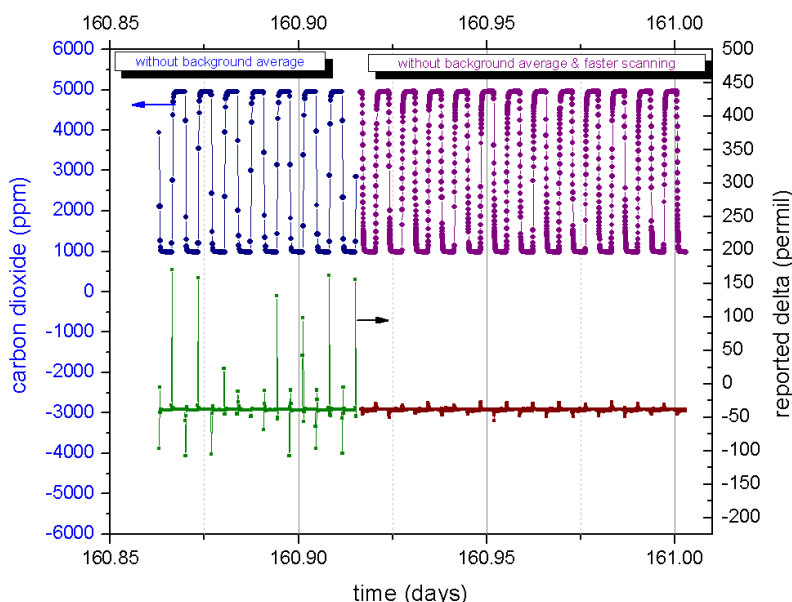
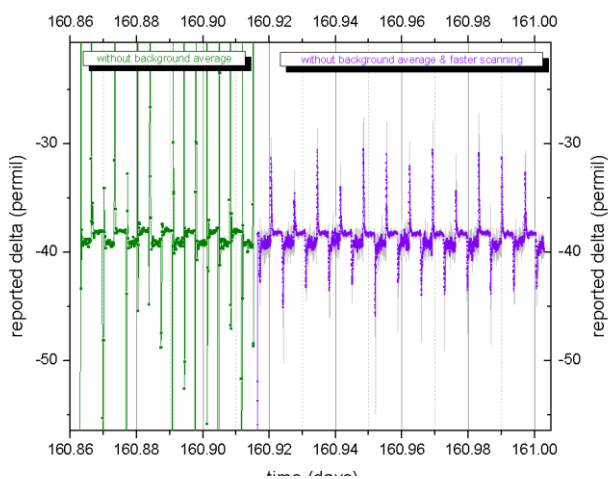**Figure 7: performance comparison between slower and faster scanning**

**Figure 8: detailed view of reported delta for different measurement intervals.**

If we look on a detailed view (Figure 8), we see that the reported isotope ratio has larger noise for faster scanning, as expected, due to the shorter acquisition time (gray data). An eight-second moving window average applied to this data (violet data in the figure) reduces the noise to essentially that of the slower measurement (green data points). This indicates that the fundamental performance of the instrument has not been affected substantially by this change, other than to increase the overall measurement rate and decrease the systematic reporting errors under transient measurements.

#3: Concentration derivative correction

There is still some small residual error still present in the data in Figure 8. It has a dependence that is proportional to the time derivative of the concentration, and not the second- or higher-derivative of the concentration, indicating that the source of the residual error with the faster scanning is cross-talk between 12C and 13C (the third bullet, above), and not higher order
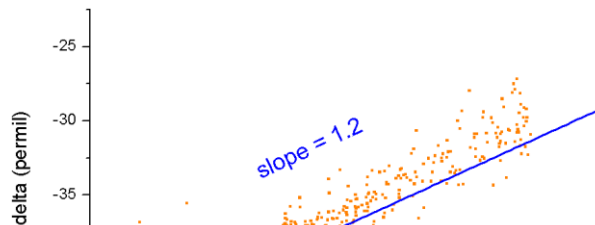
concentration response. In Figure 9, we show a detailed view of the reported data, together with the time derivative of the concentration data.
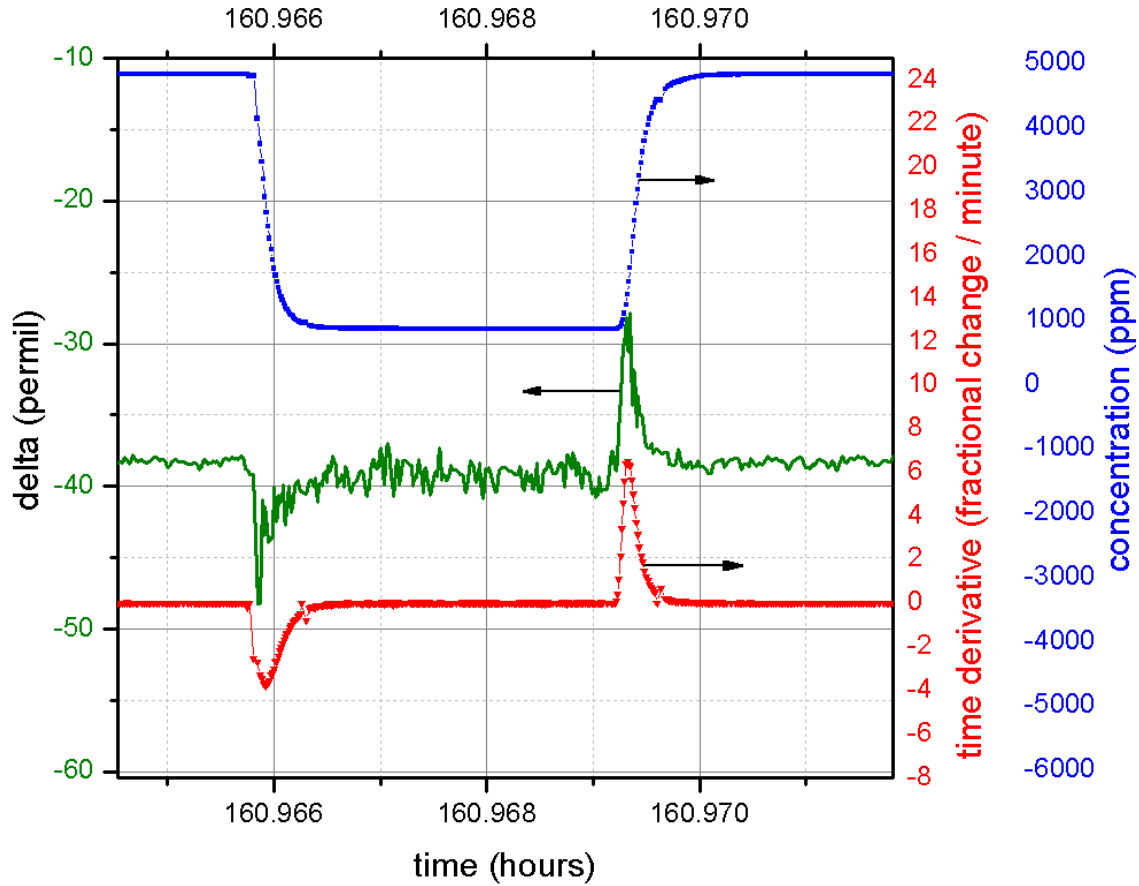
Figure 9: detailed view of the transient response (with faster scanning and without background absorption tracking). Note the good correlation to the time derivative.

Here, we define the fractional time derivative of the concentration using the following expression:

$$f = \frac{1}{c}\frac{dc}{dt} \tag{1}$$

Figure 10 displays these data in a different manner, plotting reported delta against measured fractional concentration time derivative as defined above. The clear linear dependence of the data is clear, with a slope

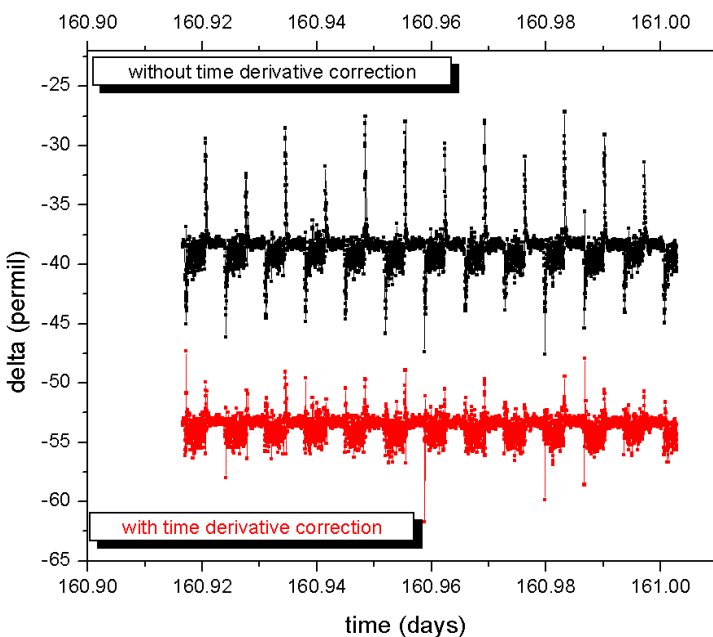**Figure 10: reported delta as a function of the fractional concentration time derivative. (Note: the slight offset in delta between positive and negative time derivatives is due to the real offset in delta between the 1000 ppm and 5000 ppm bottles used in the experiment)**

of 1.2 (in units of permil per fractional change / minute).

This simple dependence means that the data can be post-corrected for this effect. The results of this correction are shown in Figure 11. Clearly, there is very little residual error in the reporting of the isotopic abundance

Figure 11: reported delta after correction by the fractional time derivative. The red data have been offset for clarity.

We may view this final correction factor another way, using a Keeling plot that displays the reported delta as a function of the inverse concentration (Figure 12). This final correction factor brings the data to the point that it is well represented by a simple two-component mixing model (a simple line without hysteresis).
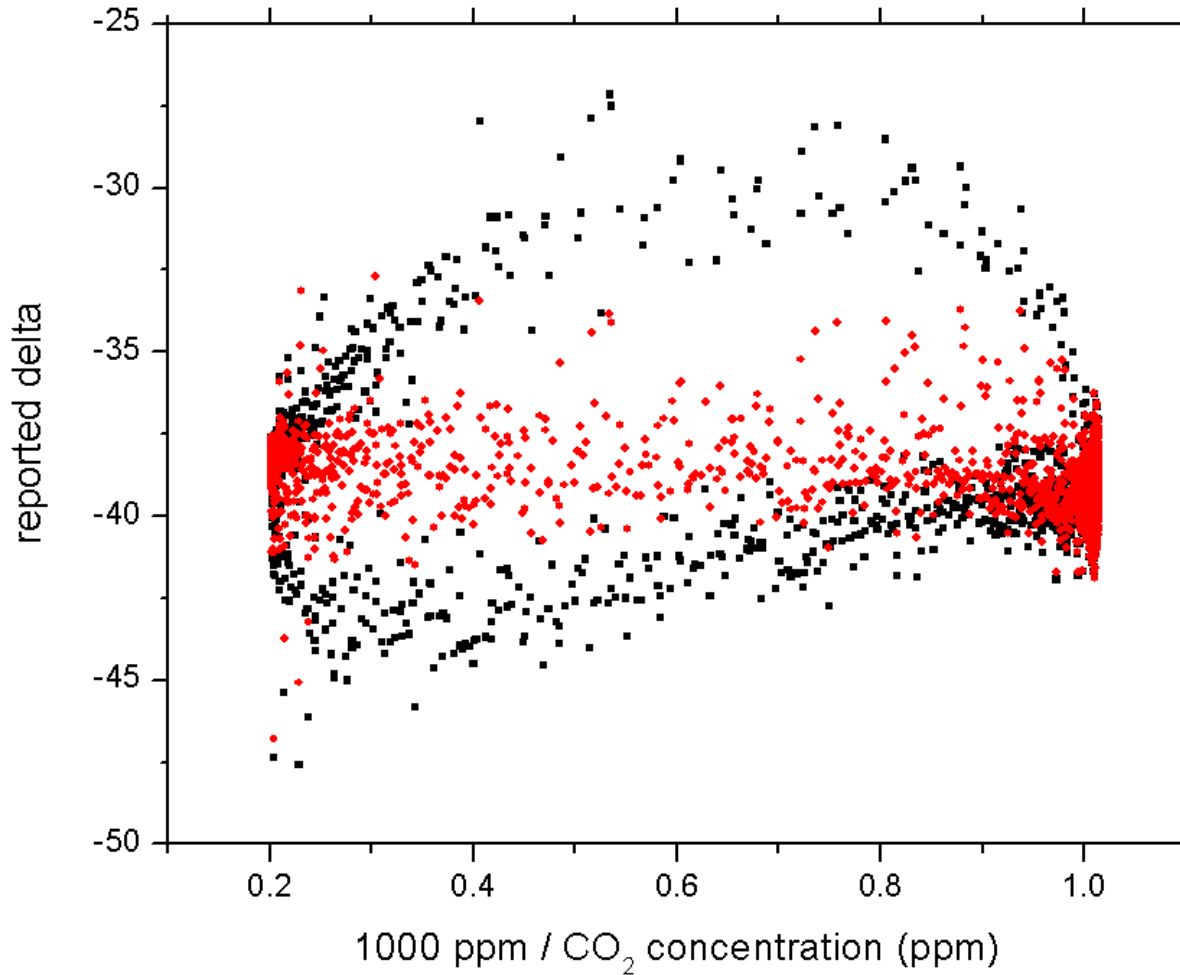
Figure 12: Keeling plot of the reported delta with (red) and without (black) correction for the fractional time derivative of the concentration. These are the same data shown in Error! Reference source not found.**, plotted against concentration rather than time. The corrected data better represent simple two component mixing.**

Summary

In the chart below, we summarize the performance of the G1101-i and the G2101-i.

condition	$\dfrac{1}{c}\dfrac{dc}{dt}$ (max)	maximum error in delta (in permil) *all errors proportional to fractional derivative*			
		standard G1101-i	+ removal of background tracking	+ faster scanning	+ correction for fractional derivative (G2101-i)
source switching: instrument response limited step change: 400 → 450 ppm CO_2	0.1 / minute	2.5 permil + 3 minute waiting time for equilibration	~ 2.5 permil, <1 minute wait for equilibrium	0.25 permil, <1 minute wait for equilibrium	<0.1 permil, dynamics determined by 2-component mixing model
chamber measurements: concentration slope of +400 ppm over 5 minutes (400 → 800 ppm)	0.15 / minute	3.75 + 3 minute waiting time for equilibration	~ 3.75 permil, <1 minute wait for equilibrium	0.375 permil, <1 minute wait for equilibrium	<0.15 permil, dynamics determined by 2-component mixing model

The errors are all proportional to the fractional time derivative of the concentration f (defined in Eq. 1), so it is a simple matter to use the table above to calculate the expected maximum error of the reported delta. It is important to note that these changes have essentially no effect on the stable concentration performance of the instrument. As a result of these improvements, the G2101-i is extremely well-suited to making isotope measurements, even in applications in which the concentration is varying rapidly.