# Easier Analyzing of Stable Carbon Isotopes of Dissolved Inorganic Carbon in Water Samples or Solid Carbonate Samples: New Picarro Caddy Continuous Flow Interface + AutoMate Prep Device Pairing

**PICARRO**

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## 1. BACKGROUND

### Abstract

The Caddy Continuous Flow Interface has previously been used to connect available solid and liquid bulk sample preparation instruments—including the Picarro Combustion Module—to Picarro analyzers for high-precision carbon isotope ($13C$) measurements.

Picarro is happy to announce the AutoMate Prep Device from AutoMate FX as the Caddy's newest pairing. The Caddy's fully automated, low-cost, and simple operation will take advantage of the newest AutoMate Prep Device design improvements to bring together increased data quality and reduced interface complexity.

Here we present some results from tests done with the new Caddy +AutoMate Prep Device pairing, focused on assessing the system's precision at the lower end of our specification range for $CO_2$ concentrations. The results show the same or at times, improved precision levels and reduced memory effects otherwise associated with the previous interface device. All while making the pairing simpler to set up, easier to operate, and lower in cost.

## 2. OBJECTIVES

1. Determine how well the Caddy + AutoMate Prep Device pairing operates with $CO_2$ concentrations towards the lower end of our specification range (<380 ppm $CO_2$) by viewing precision values.

2. Assess memory effect between samples to confirm reduced memory effects seen during previous tests.

3. Confirm successful "proof-of-concept" tests previously conducted at Picarro HQ.

## 3. PICARRO CADDY + AUTOMATE PREP DEVICE PAIRING
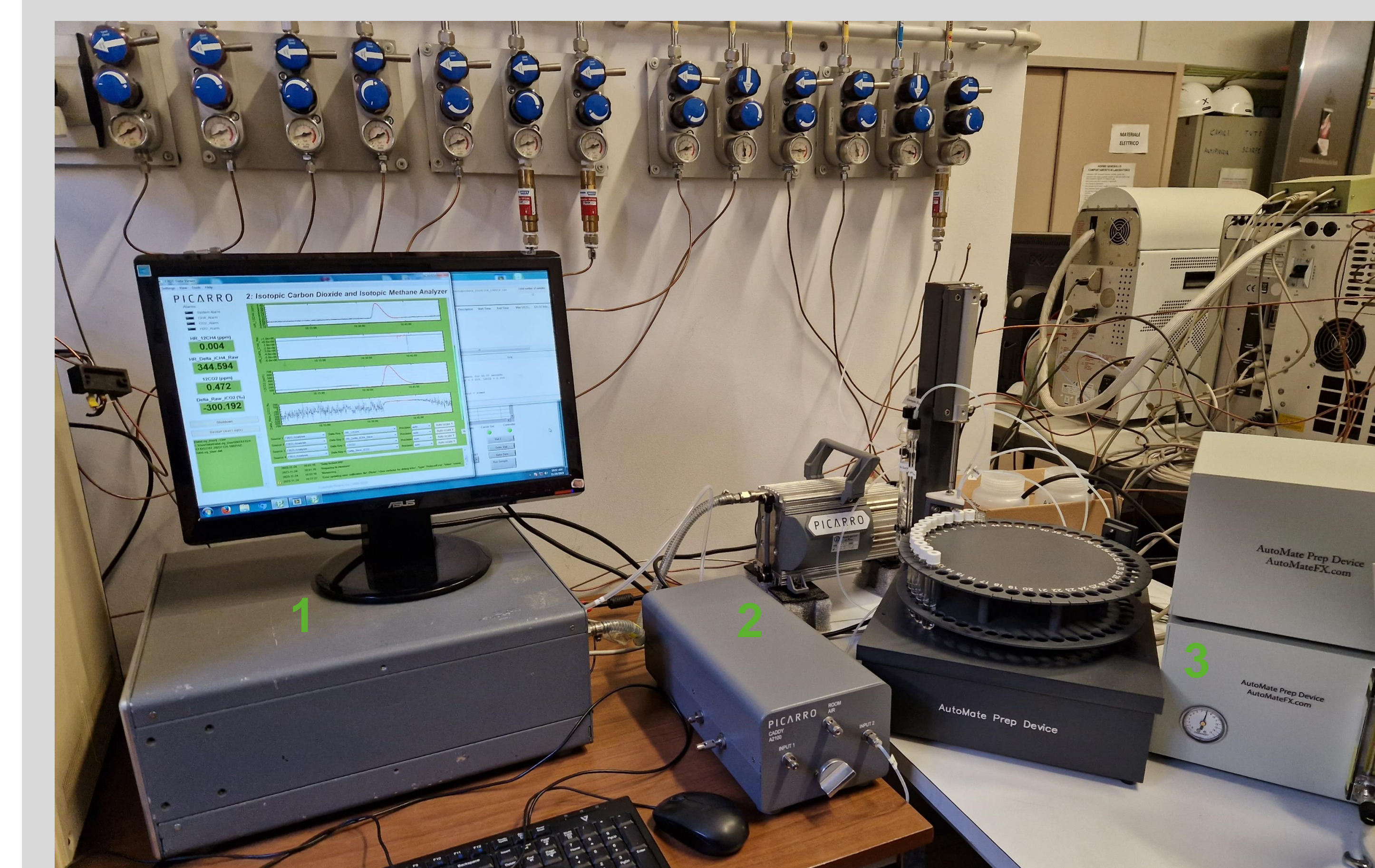


- The Picarro Caddy Continuous Flow Interface + AutoMate Prep Device system is composed of three components:

  1. Picarro isotopic analyzer (e.g., G2201-*i* or G2131-*i*)

  2. Picarro Caddy Continuous Flow Interface

  3. AutoMate Prep Device manufactured by AutoMate FX, Inc.

## 4. LOW CO₂ CONCENTRATION STUDY

### Overview

Dissolved inorganic carbon (DIC) solutions were made by mixing different weighted amounts of either sodium carbonate ($Na_2CO_3$) or sodium bicarbonate ($NaHCO_3$) to achieve $CO_2$ concentration values at or near the lower end of the analyzer's specification range. The AutoMate Prep Device adds phosphoric acid to samples to liberate $CO_2$, which flows to the Picarro for $\delta^{13}C$-$CO_2$ analysis. These ranged between $360 - 395$ ppm $CO_2$ for $Na_2CO_3$ solutions and between $330 - 360$ ppm $CO_2$ for $NaHCO_3$ solutions.
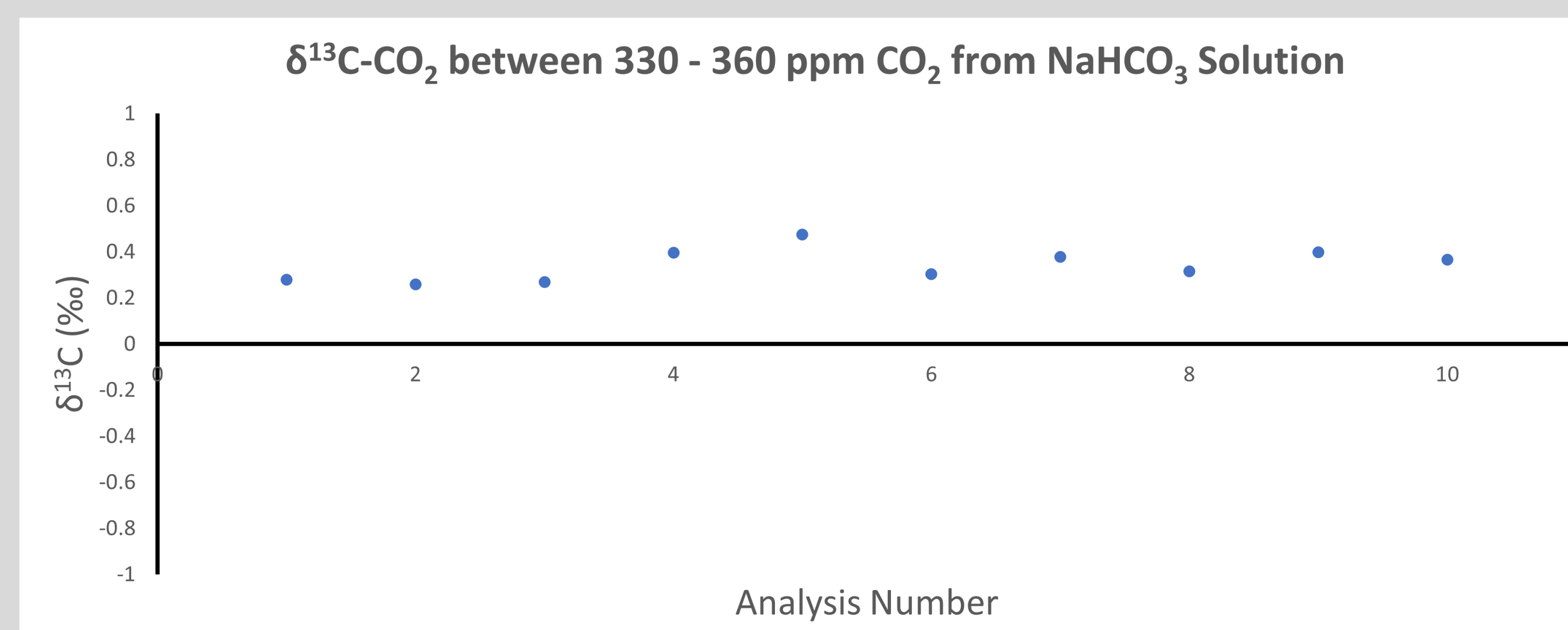
### Results – Na₂CO₃ Samples
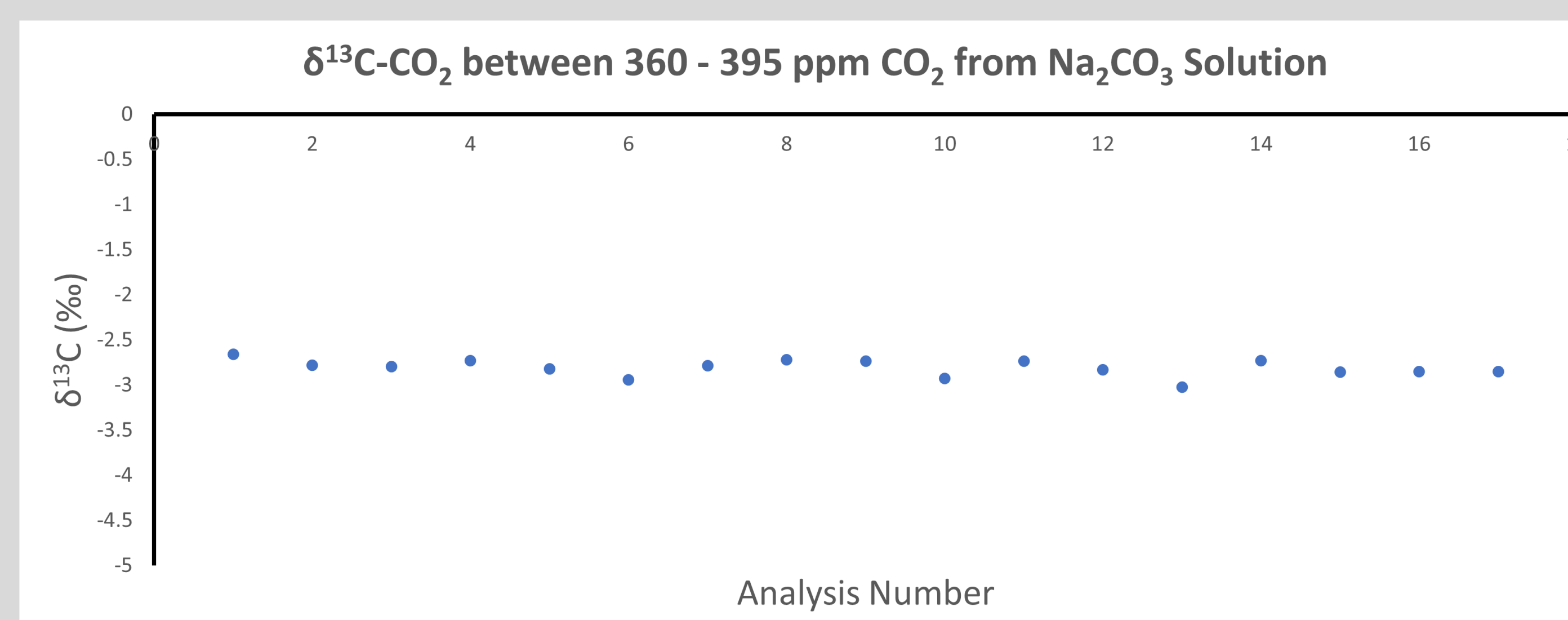


Each sample was analyzed three times. Below is a table showing the averaged results and precision per $Na_2CO_3$ solution sample.

| Sample | Avg $\delta^{13}C$ (‰) | Precision (‰, 1σ) | Avg [$CO_2$] (ppm) |
|---|---|---|---|
| Sample #1 | -2.747 | 0.075 | 377.3 |
| Sample #2 | -2.833 | 0.107 | 385.1 |
| Sample #3 | -2.749 | 0.035 | 370.1 |
| Sample #4 | -2.834 | 0.096 | 387.9 |
| Sample #5 | -2.871 | 0.148 | 388.8 |
| Sample #6 | -2.892 | 0.070 | 384.3 |

**Precision between 0.035 – 0.148‰**

### Results – NaHCO₃ Samples



Each sample was analyzed three times, except for Sample #1 due to an error (analyzed twice). Below is a table showing the averaged results and precision per $NaHCO_3$ solution sample.

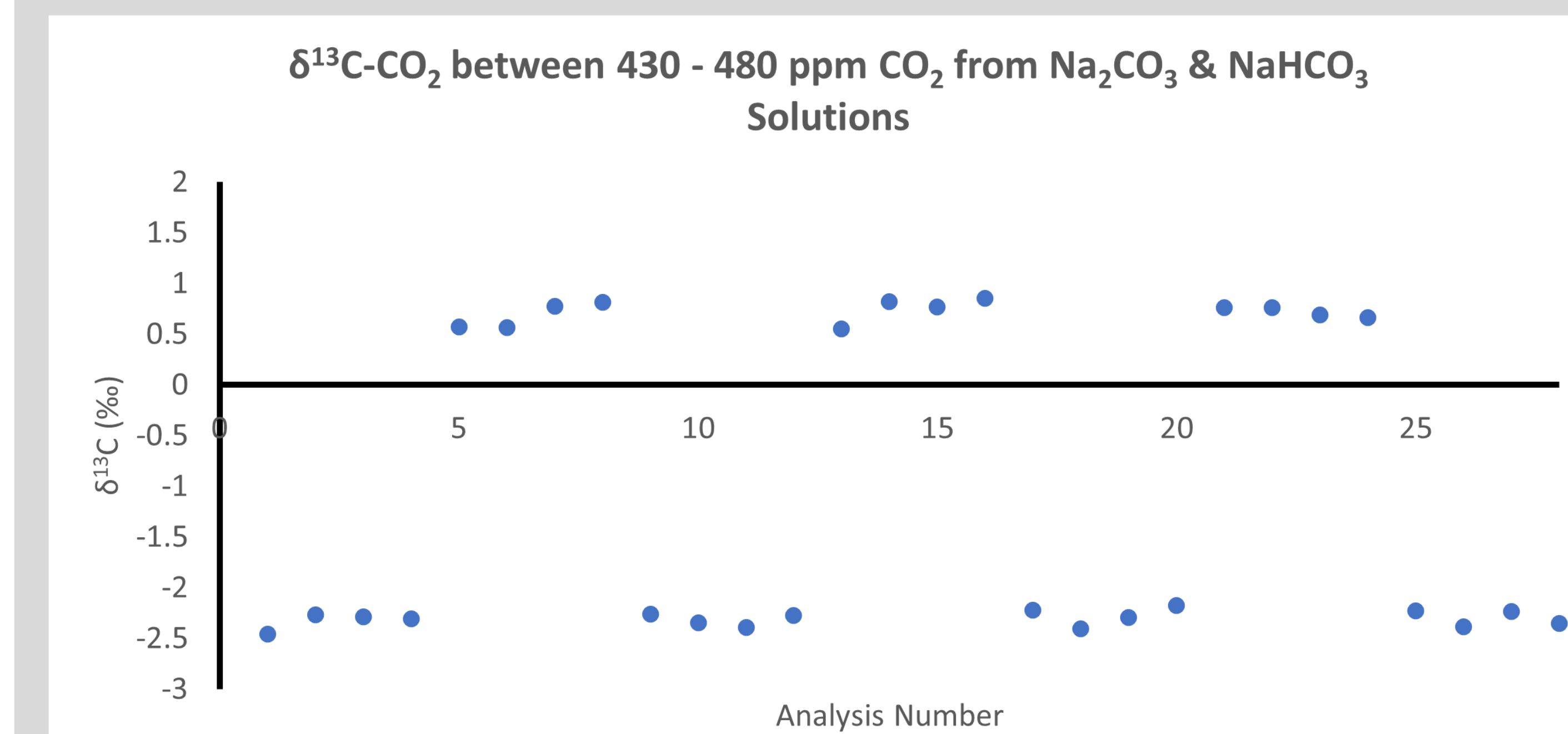| Sample | Avg $\delta^{13}C$ (‰) | Precision (‰, 1σ) | Avg [$CO_2$] (ppm) |
|---|---|---|---|
| Sample #1 | 0.2685 | 0.0134 | 343.2 |
| Sample #2 | 0.3797 | 0.1045 | 347.3 |
| Sample #3 | 0.3320 | 0.0394 | 339.3 |
| Sample #4 | 0.3867 | 0.0180 | 342.6 |

**Precision between 0.0134 – 0.1045‰**

## 5. ASSESSING MEMORY EFFECT

### Overview

Dissolved inorganic carbon (DIC) solutions were made by mixing weighted amounts of either sodium carbonate ($Na_2CO_3$) or sodium bicarbonate ($NaHCO_3$) to achieve $CO_2$ concentration values between $430 - 480$ ppm $CO_2$ for $Na_2CO_3$ and $NaHCO_3$ solutions. The AutoMate Prep Device adds phosphoric acid to samples to liberate $CO_2$, which flows to the Picarro for $\delta^{13}C$-$CO_2$ analysis. Each sample was analyzed four times in an interleaved sample series.

### Results



Below is a table showing the averaged results and precision per solution sample.

| Sample | Avg $\delta^{13}C$ (‰) | Precision (‰, 1σ) | Avg [$CO_2$] (ppm) |
|---|---|---|---|
| $Na_2CO_3$ – 1.86 mg #1 | -2.331 | 0.086 | 449.5 |
| $NaHCO_3$ – 0.9 mg #1 | 0.681 | 0.134 | 439.0 |
| $Na_2CO_3$ – 1.86 mg #2 | -2.318 | 0.062 | 466.7 |
| $NaHCO_3$ – 0.9 mg #2 | 0.749 | 0.135 | 446.8 |
| $Na_2CO_3$ – 1.86 mg #3 | -2.274 | 0.101 | 457.9 |
| $NaHCO_3$ – 0.9 mg #3 | 0.719 | 0.051 | 453.3 |
| $Na_2CO_3$ – 1.86 mg #4 | -2.302 | 0.080 | 452.8 |

**Precision between 0.062 – 0.101 for $Na_2CO_3$ samples**

**Precision between 0.051 – 0.135 for $NaHCO_3$ samples**

## 6. CONCLUSIONS



- The Picarro Caddy + AutoMate Prep Device pairing had precision values always better than **0.2‰**, and on average **~0.08‰.**

- The Picarro Caddy helps **remove memory effect**, otherwise associated with the sample bags inside the previous interface device.

- The Picarro Caddy + AutoMate Prep Device pairing is an **overall simpler set up** compared to the previous interface device, while also being **easier to operate** and **lower in cost.**