Demonstration of High-Throughput Water Isotopologue Measurements Using Cavity Ring-Down Spectroscopy

PICARRO

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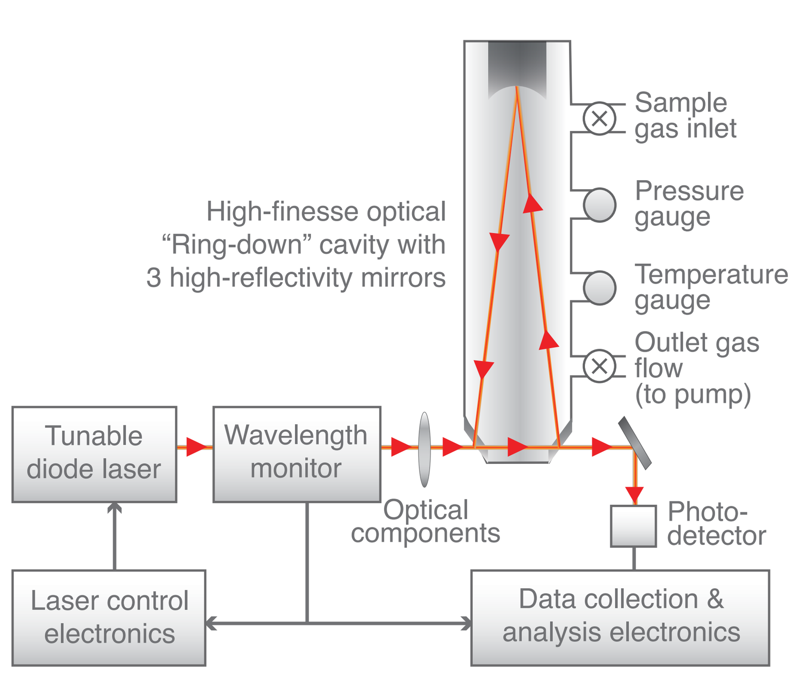
Abstract

The ability to measure the $\delta^{18}O$ and $\delta^{2}H$ isotopic content of water has long relied on cumbersome methods that require well equipped laboratories, highly qualified technicians and frequently calibrated instruments. The advent of commercial analyzers based on Cavity Ring-Down Spectroscopy (CRDS) for isotopic water measurements has opened up new possibilities for mobile laboratory and field deployable isotopic instruments. For many laboratories, sample throughput has been a major bottleneck – either real-time sampling of stream flow or simply the number of samples gathered during a campaign can be a daunting challenge. It is not uncommon for users to have a huge backlog on the water samples that need to be analyzed within a short period of time.

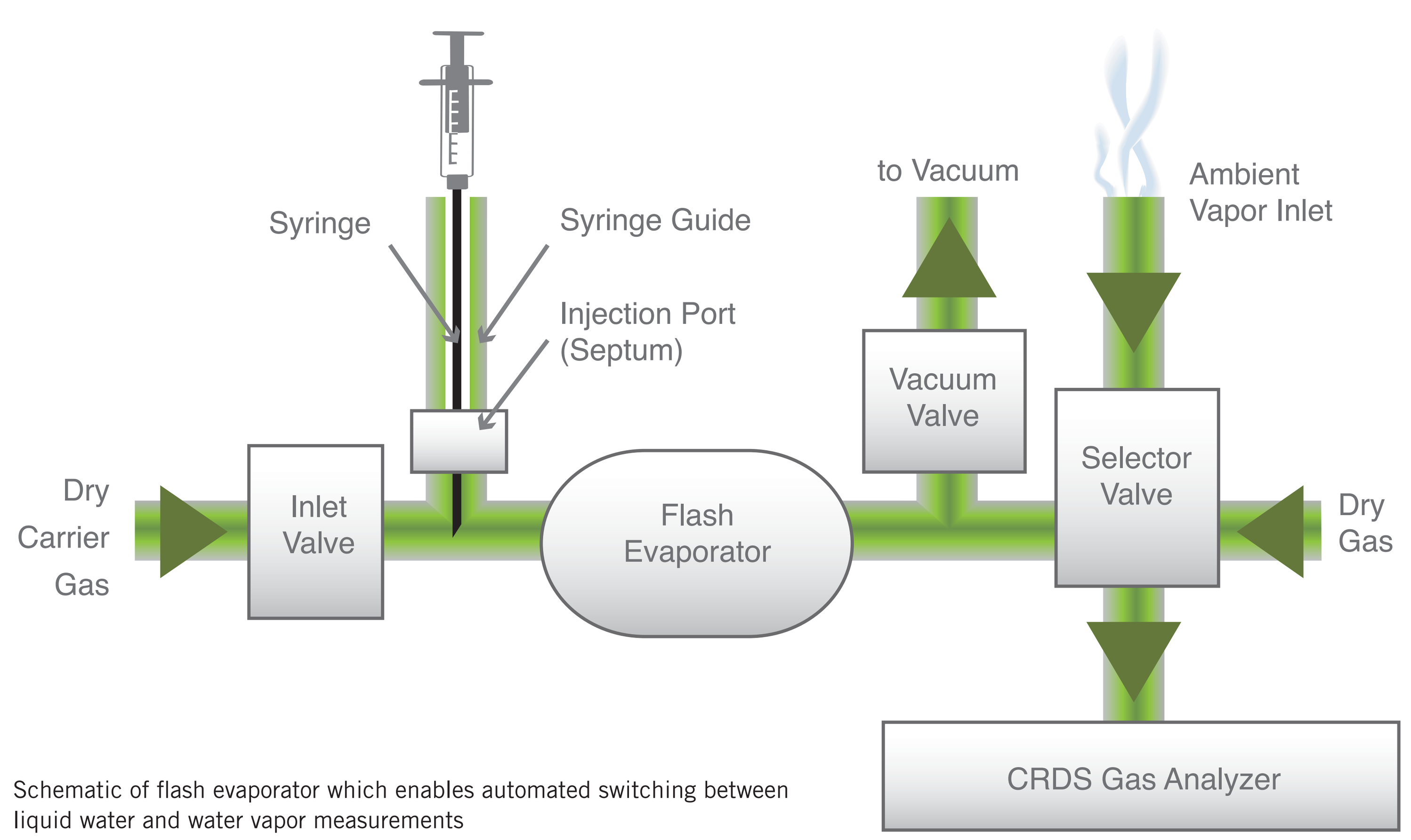
We present results of a new high throughput method for an isotopic water analyzer based on CRDS technology. This high throughput method comes with negligible impact on the precision and memory and absolutely no impact on the drift characteristics of the analyzer. In order to provide confidence in the data collected, even in the most challenging environments, there can be no comprise on the consistency or reproducibility of the instrument performance. The new high throughput method measures isotopologues of water with a typical precision of better than 0.15‰ for $\delta^{18}O$ and better than 0.6‰ for $\delta^{2}H$ and can execute over 380 injections per day. The analyzer has extremely low drift of < ±0.3‰ for $\delta^{18}O$ and < ±0.9‰ for $\delta^{2}H$. This presentation demonstrates these capabilities of the high throughput isotopic water analyzer. This water isotope analyzer can be configured to analyze water vapor, liquid, or alternate between vapor and liquid. The alternating configuration enables the periodic recalibration of water vapor measurements using liquid water isotopic standards. The results of this study clearly demonstrate that the precision of the analyzer is very high and the memory and drift are exceptional even with a high data acquisition rate.

Schematic of CRDS Analyzer



Schematic of Picarro CRDS analyzer showing optical cavity and sample gas flow.

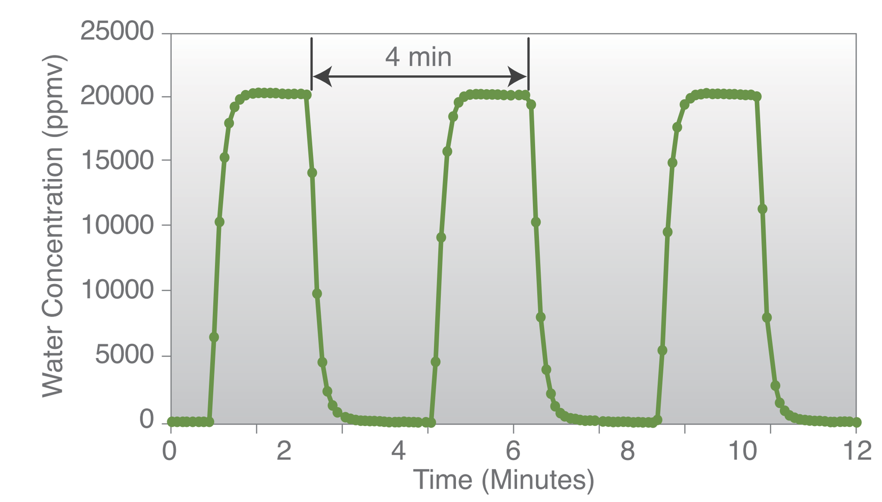
Instrument foot print: 54 cm x 60 cm
Instrument weight: ~ 40 Kg
Power consumption: 500 Watts @ 110V



Schematic of flash evaporator which enables automated switching between liquid water and water vapor measurements

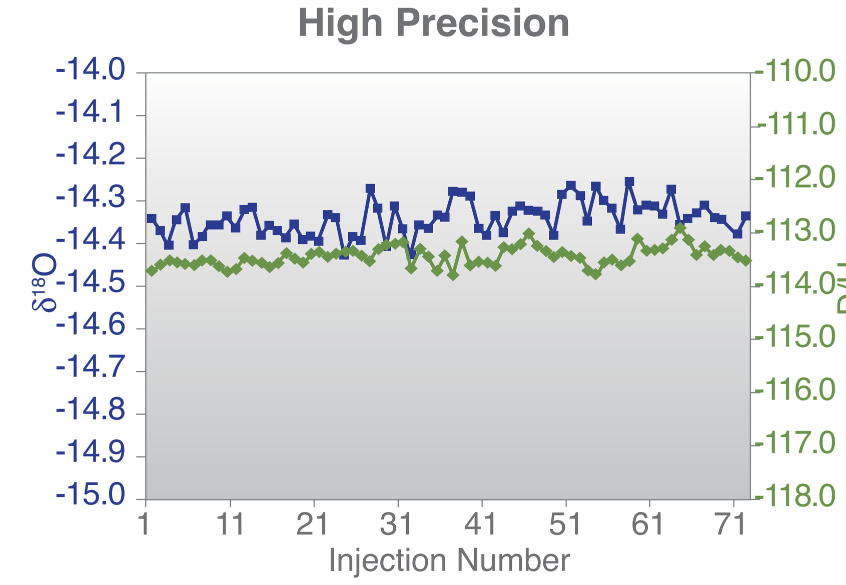
High Throughput Liquid Analysis

- Easily select between high precision and high throughput with one click
- High throughput mode delivers reliable measurements with a total cycle time of 4 minutes per injection
- No additional hardware needed

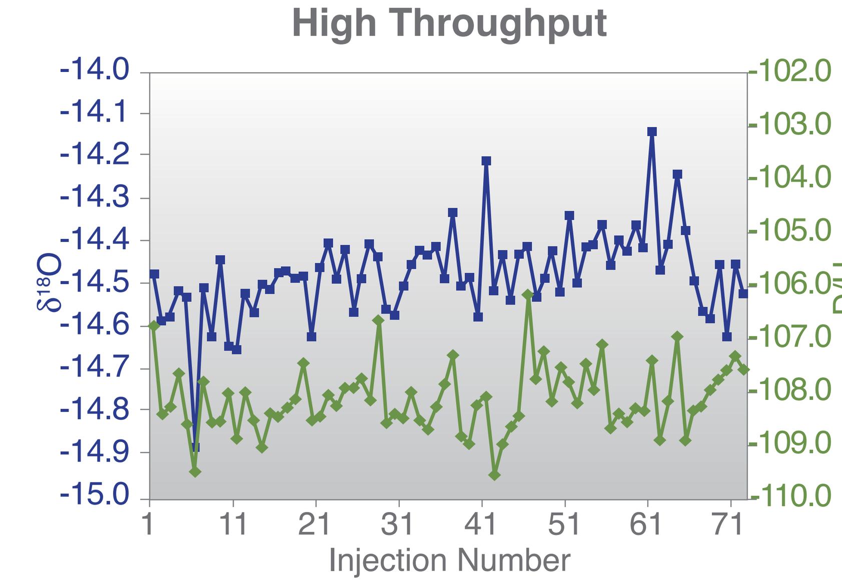


Fast Cycle Time from High Throughput Mode

High Precision



High Throughput

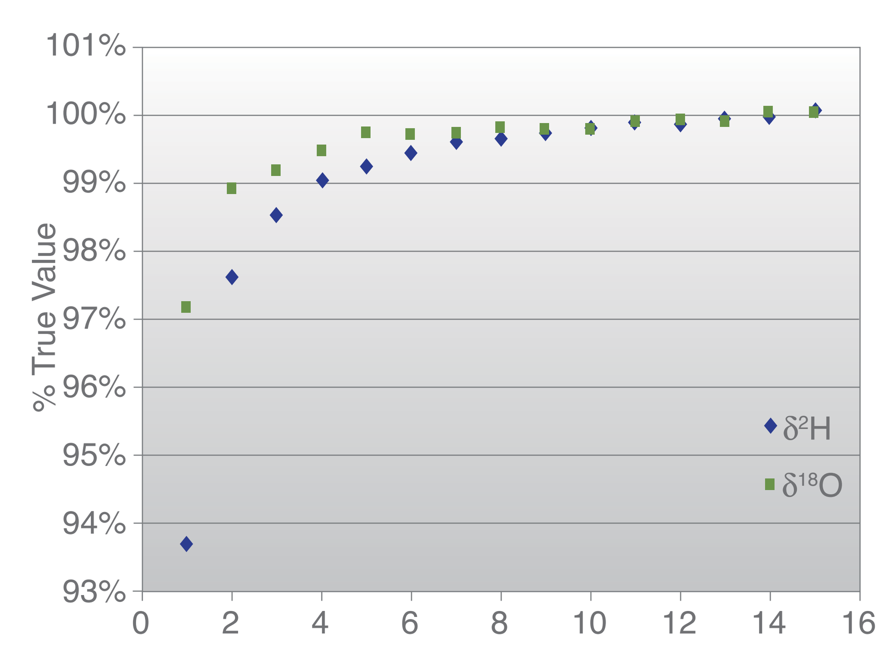


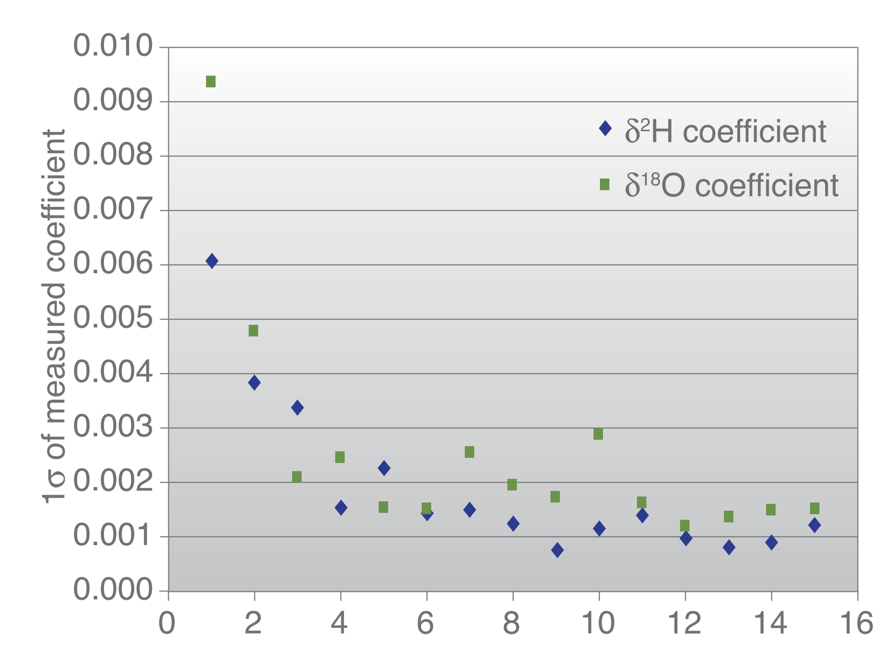
Software Mode	Cycle time	Std. Dev. $^{18}O/^{16}O$	Std. Dev. $^{2}H/H$
High Precision	9 min	0.04	0.18
High Throughput	4 min	0.10	0.63

Results of INSTAAR Evaluation

Consistent Memory, Fewer Injections, Faster Methods

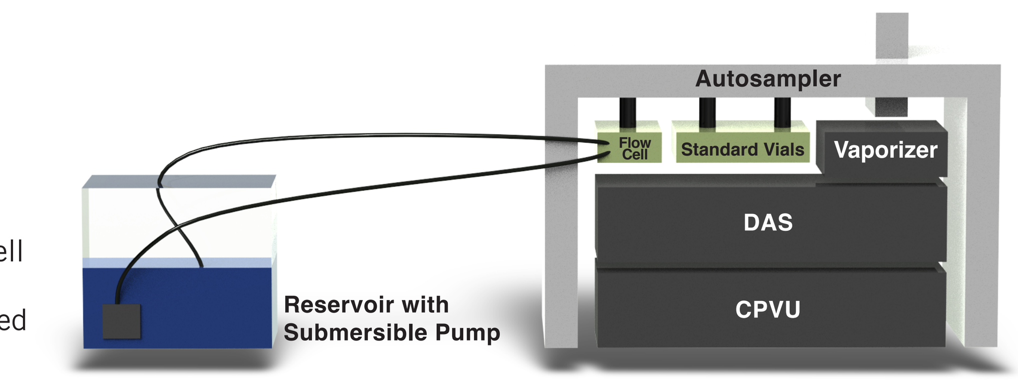
- Analyzer reading affected by traces of previous sample a.k.a. 'memory'
- Measured value will asymptotically approach true value with sequential injections, asymptote is reproducible
- Characterize memory and use to predict true value from fewer injections
- T=(M – (1 – X)P)/X where
  - T is true value of current injection
  - M is measured value of current injection
  - P is true value of immediately previous injection
  - X is memory coefficient
- Measured value ~99% true value by 3rd injection
- Excellent memory coefficient precision
- Correction can be applied as described in Rapid Commun. Mass Spectrom. 2009; 23: 2534–2542



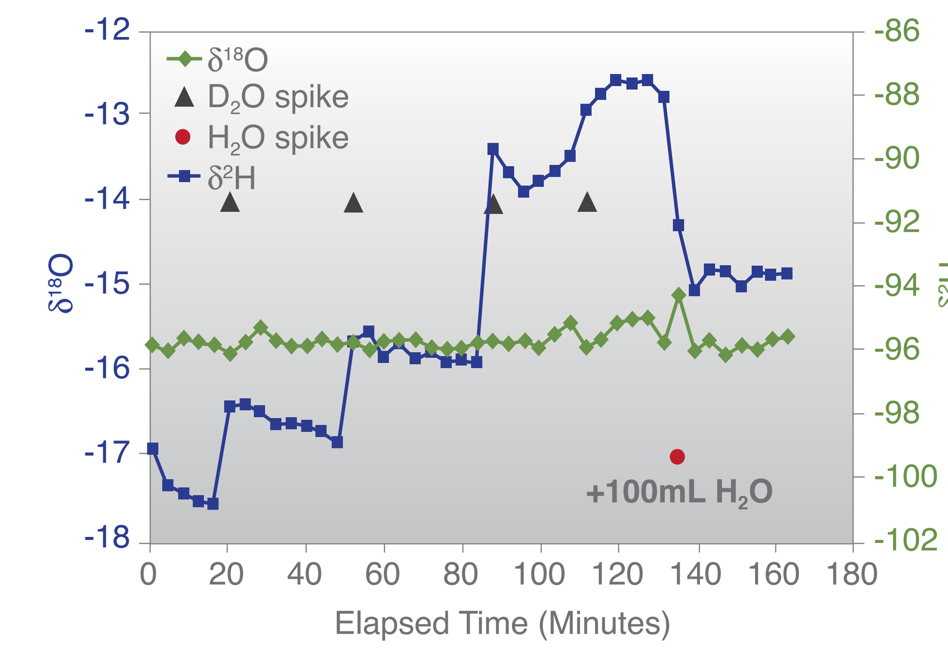


Real Time Analysis of Flowing Water Sources

- Water was circulated in a closed loop to simulate flowing water
- A small pump moved water from 550 mL reservoir through a flow cell at the autosampler
- High throughput mode was used to draw samples from the flow cell
- Periodic spikes of diluted deuterium oxide (75-200 μL) were added to the reservoir



- The flow cell is made of 316 stainless steel and accepts ¼" tubing
- Tubing connected to flowing water source
- Can be gravity fed or pumped
- Robust commercial off-the-shelf component



Laboratory Results

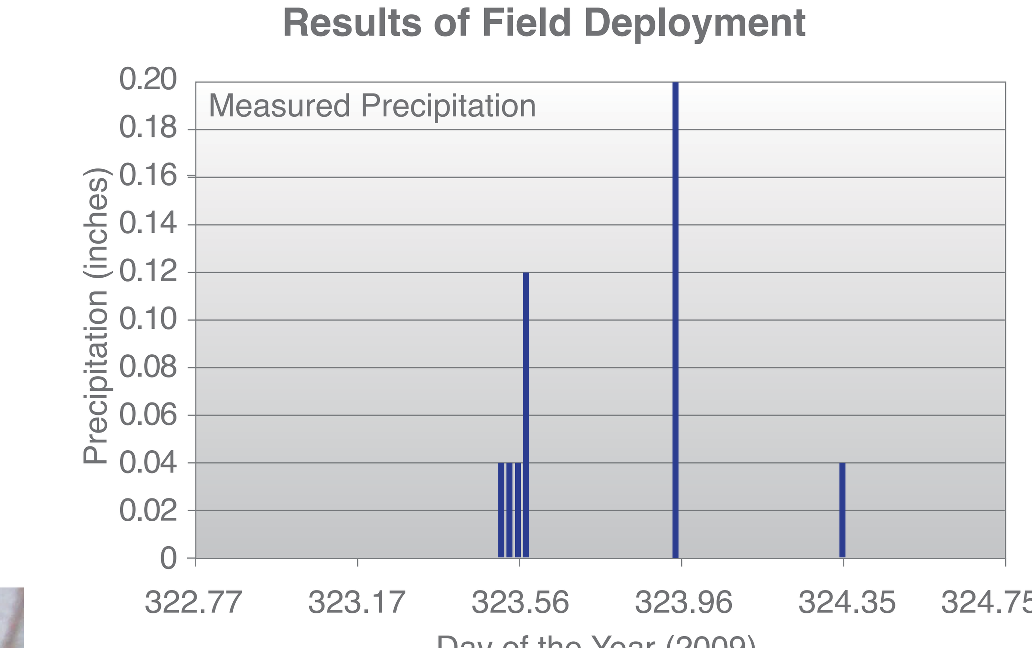
Discussion

- Samples were measured with a cycle time of 4 minutes
- $\delta^{2}H$ showed proportional stepwise increase when diluted D_2O solution was added to reservoir (at pump inlet)
- $\delta^{2}H$ decreased rapidly with addition of original H_2O solution
- Transient behavior due to long residence time in reservoir (~200 seconds) and poor mixing
- $\delta^{18}O$ remains steady throughout

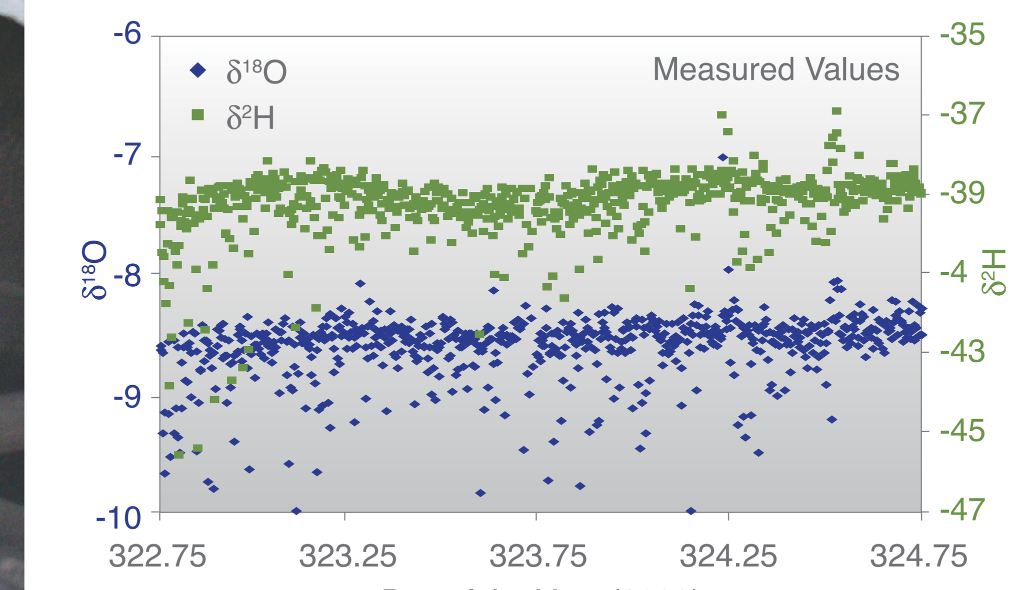
Field Deployment of Analyzer

- Private ranch in the Santa Cruz mountains
- Installed in a shed covering a filled but not flowing spring box
- Electrical power: Solar panel and batteries
- Dry air: Small aquarium air pump with Drierite

Results of Field Deployment



- Analyzer measured continuous for 48 hours
- δD and $\delta^{18}O$ virtually unchanged due to insufficient precipitation



- Each of the 700 injections plotted
- Data is raw and unfiltered, as was the water
- Achieved precision (1σ)
- 0.38‰ for $\delta^{18}O$
- 0.82‰ for $\delta^{2}H$