ISOTOPIC SEAWATER ANALYSIS USING CAVITY RING-DOWN SPECTROSCOPY: METHOD FOR REDUCING THE EFFECT OF SALTS ON THE MEASUREMENT

PICARRO

David Kim-Hak (1), Kuan Huang (1), Renato Winkler (1), Claire Normandeau (2), Elizabeth Kerrigan(2),D.W.R Wallace (2)

(1) Picarro, Inc., 3105 Patrick Henry Drive, Santa Clara, California

(2) Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada

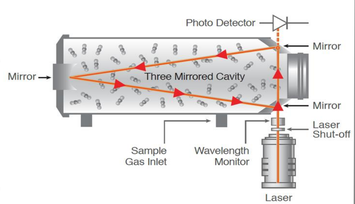
Introduction

- **Stable isotopes of water, $\delta^{18}O$ and $\delta^{2}H$, are unique tracers for studying hydrological and associated processes.**
- **CRDS analyzer produces high-precision measurements of water isotopes in the gas phase.**
- **High total dissolved solids (TDS) waters can foul the vaporizer affecting the memory performance and requiring more frequent cleaning and greater downtime[1].**
- **The Salt Liner is an accessory that protects the analyzer system from fouling while maintaining optimum performance**

CRDS Analyzer: L2130-*i and L2140-i.*

Cavity Ring-Down Spectroscopy (CRDS) Technology:

- **Laser-based technique to measure the stable isotopes of water, $\delta^{18}O$ and $\delta^{2}H$.**
- **Time-based measurement rather than absolute absorbance.**
- **Robust, compact and field-deployable.**
- **Highest precision and lowest drift.**



Salt Liner (SL)

- **Stainless Steel mesh insert for the High-Precision Vaporizer(A0211)**
- **Catches salt precipitates as the injected High-TDS water sample is evaporated in the Vaporizer chamber**
- **Cleanable and reusable**

Test Method

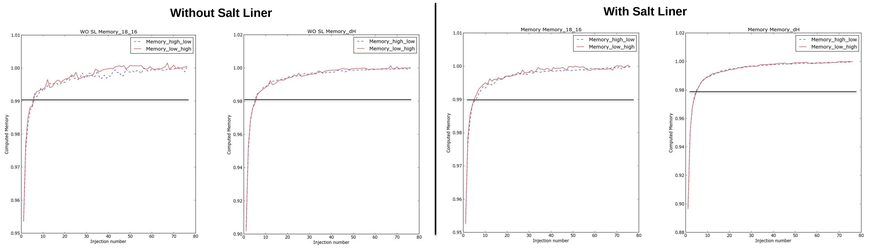
- **Precision test: 160 injections of a sample**
- **Memory test: 76 injections per sample. Two samples of different isotopic composition used.**
- **Sample to Sample Measurements: alternating 10 injections of two samples**

- **Sample Solutions:**
  - **DI water**
  - **Kona Deep Bottle Water**
  - **Instant Ocean mixed with DI water and Kona Deep (4% Salinity)**

Results

1) Drift, Precision, and Memory Test of DI water: with SL vs without SL

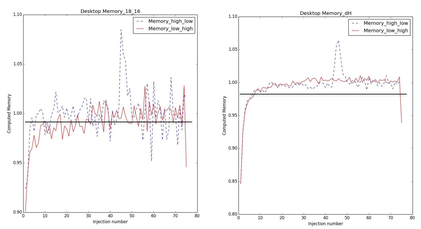
Without Salt Liner | **With Salt Liner**



	Specifications		Measured w/o SL		Measured with SL	
	d18O	dD	d18O	dD	d18O	dD
Precision (permils)	>0.025	>0.1	0.01	0.05	0.01	0.05
Drift (permils)	>0.2	>0.8	0.06	0.33	0.06	0.2

- **It takes 4 injections to get rid of 99% of the memory in $\delta^{18}O$ and 98% memory in δD**
- **Measurement performance of DI water is unaffected by the SL insert as Precision, Drift and Memory performance remain unchanged.**

2) Drift, Precision, and Memory Test of 4% Seawater Solutions with SL

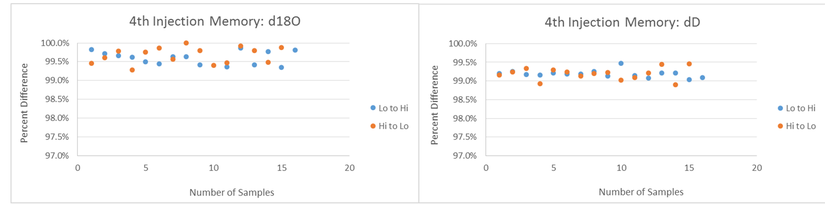


	Specifications (with DI)		Measured with SL	
	d18O	dD	d18O	dD
Precision (permils)	>0.025	>0.1	0.03	0.08
Drift (permils)	>0.2	>0.8	0.13	0.33

- **For water with high TDS, it takes 5-6 injections to get rid of 99% of the memory in $\delta^{18}O$ and 98% memory in δD;**
- **Although the Precision and Drift measurement performance of the 4% seawater solution is inferior, it remains within the specifications of the instrument.**

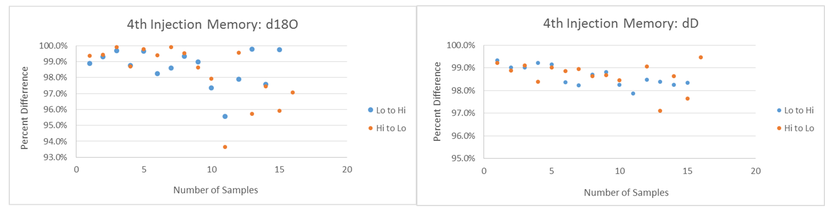
3) Memory performance evaluation with the SL

On DI Water



For DI water, the memory performance is stable, just as in the case when no SL is implemented.

On Seawater



For 4% TDS seawater samples, the memory performance starts to degrade after 200 injections(~ 30 hr of continuous run), suggesting that the SL needs to be replaced or cleaned. The replacement of the SL takes minimum down-time (a few minutes) compared with the time needed to clean the vaporizer chamber (24 hours).

By weighing the SL, we determine that 80% of the salt from the seawater solution is caught by the SL bringing the salinity of the water vapor <1000 ppm.

Conclusions

- **Precision and Drift performances are preserved for seawater isotopic analysis with the Salt Liner.**
- **Salt Liner effectively catches salt precipitates protecting the Vaporizer chamber from rapid salt buildup.**
- **Because of the decline of the memory performance caused by the salt build up in the SL, we recommend replacing and cleaning SL every 24 hr.**

References

[1] Walker et al. (2015), Oxygen isotope measurements of seawater (H218O/H216O): A comparison of cavity-ring down spectroscopy (CRDS) and isotope ratio mass spectrometry (IRMS), Limmol. Oceanogr.

Interested in learning more?

- Contact David Kim-Hak (dkimhak@Picarro.com)
- Visit www.picarro.com