Optimize the Precision and Accuracy of Seawater and High-Saline Water Stable Isotope Measurements

PICARRO

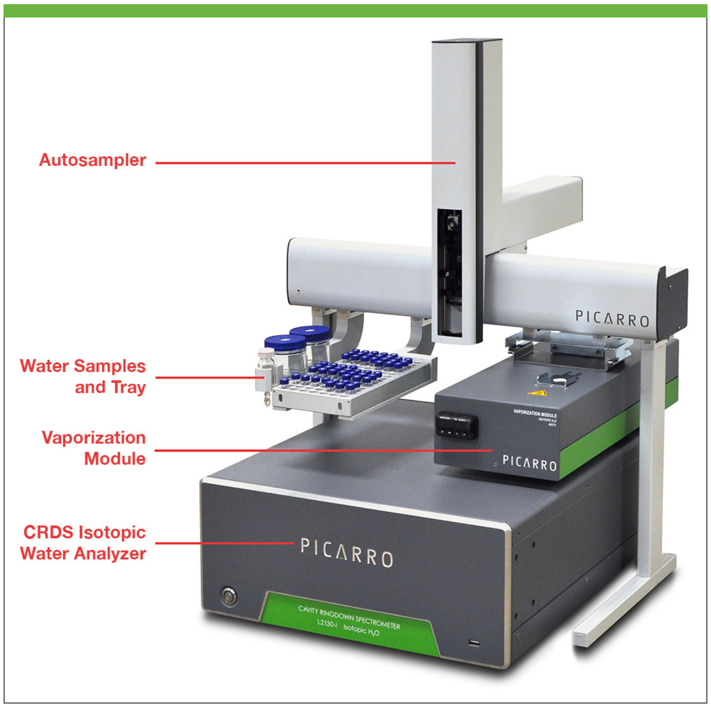
APPLICATION NOTE (AN039)
SALT LINER ACCESSORY FOR CRDS ISOTOPIC WATER ANALYZER SYSTEMS

Summary

Applications in the fields of hydrology and oceanography require precise, accurate measurement of stable water isotopes, $\delta^{18}O$ and $\delta^{2}H$, in seawater and high-saline water. Cavity ring-down spectroscopy (CRDS) analyzers produce high-precision measurements of water isotopes in gas phase. High levels of total dissolved solids (TDS) in water samples can foul laser-based spectroscopy analyzers and peripherals, adversely affecting performance and requiring frequent cleaning with extended downtime. The Picarro Salt Liner is an easy-to-use, inexpensive accessory that protects the isotopic analyzer system from salt build-up in the vaporizer. It can be removed, cleaned, and replaced in a few minutes to reduce downtime. Picarro recommends cleaning and replacing the salt liner after every 24 hours of seawater analysis.

Stable Isotope Water Analysis System

For discrete water sample analysis, the Picarro stable isotope water analysis system (right) is composed of an autosampler (A0325), a high-precision vaporizer (A0211), and a L2130-*i* or L2140-*i* cavity ring-down spectroscopy (CRDS) isotopic water analyzer. The autosampler automatically draws less than 2 μL of liquid water from the sample tray, using a syringe, and injects it into the vaporizer chamber. There it is vaporized into a gas phase and blended with a gas carrier (N_2 or zero air) to produce a precise, optimum water vapor concentration. The vapor is then slowly released to the CRDS analyzer for analysis. This produces a less-expensive, easier-to-use, higher-throughput solution than an isotope ratio mass spectrometer (IRMS) for precise, accurate isotopic measurements in a range of research applications including hydrology, ocean science, and paleoclimatology.



Salt Liner Accessory

The Picarro stable isotope water analysis system has proven its ability to produce precise, accurate measurements of seawater (up to 3.46% salt)[1] and high-saline water samples (339.4 g/L).[2] However, there is a potential for salt accumulation to affect the precision, drift, and memory effect of laser-based spectroscopy analyzer systems. This application note describes how the Picarro salt liner accessory (left) protects the isotopic analyzer system from excessive salt build-up in the vaporizer to maintain optimum performance and precise, accurate measurements.

[1] S.A. Walker et al., *Oxygen isotope measurements of seawater: A comparison of CRDS and IRMS*, Limnology and Oceanography: Methods
[2] Grzegorz Skrzypek and Douglas Ford, *Stable Isotope Analysis of Saline Water Samples on a CRDS Instrument*, Environmental Science & Technology

Easy-to-Use Stainless-Steel Mesh Insert

The Picarro salt liner is an inexpensive, stainless-steel mesh insert that can be placed quickly and easily into the Picarro high-precision vaporizer (right). The mesh liner catches up to 80% of salt precipitates as the injected high total dissolved solids (TDS) water sample is evaporated in the vaporizer chamber. This significantly reduces salt build-up in the vaporizer to extend operating time up to 24 hours for seawater analysis. It can be removed, cleaned, and reinserted within minutes.

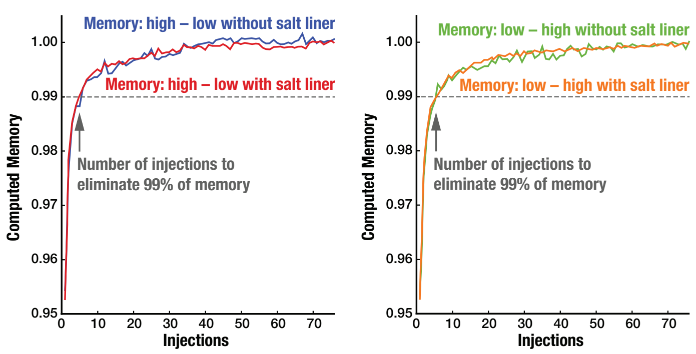
Test Sample Solutions

Tests were conducted to determine memory effect, precision, and drift with and without salt liners using 1) deionized water and 2) a seawater solution with 4% salinity. Sample solutions were prepared with 100% deionized water and with deionized water, Kona Deep bottled water, and Instant Ocean sea salt mixed to produce a 4% salinity solution. Specific test methods are described with each test and result.

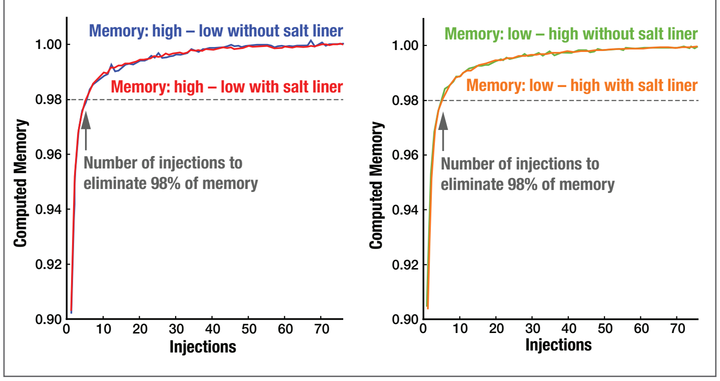
Test 1: Deionized Water With and Without Salt Liner

Memory test graphs show that it takes the same number of injections to eliminate 99% of the memory in $\delta^{18}O$ (below left) and 98% of the memory in $\delta^{2}H$ (below right) with and without the salt liner inserted in the vaporizer. Overall, performance for sample injections are fundamentally unaffected with the salt liner inserted.

Memory effect on $\delta^{18}O$ With and Without Salt Liner



Memory effect on $\delta^{2}H$ With and Without Salt Liner



Test Method

76 consecutive injections of a first sample with a known low isotopic value were followed by 76 consecutive injections of a second sample with a high isotopic value. The 100% value of each graph (computed memory = 1.00) is calculated from the average of the final 30 injections (47 – 76). This calculation method minimizes memory effect from early injections and retains a relatively large sample size.

Memory: high – low is the percent difference between the measured value of the first sample (d_1m), a known low isotopic value, and the calculated value of the second sample (d_2c) divided by the difference between the calulated value of the first (d_1c) and second (d_2c) samples. Percent Memory = $(d_1m - d_2c)/(d_1c - d_2c) \times 100\%$.

Memory: low – high is the percent difference between the measured value of the second sample (d_2m), a known high isotopic value, and the calculated value of the first sample (d_1c) divided by the difference between the calulated value of the second (d_2c) and first (d_2c) samples. Percent Memory = $(d_2m - d_2c)/(d_2c - d_1c) \times 100\%$.

Table 1 (below) shows that precision and drift are identical for δ18O with and without the salt liner inserted. Precision also is identical for δ2H with and without the salt liner inserted and slightly better for δ2H with the salt liner.

Table 1 – Precision and Drift Test of Deionized Water With and Without Salt Liner Inserted						
	Specifications		Measured without salt liner		Measured with salt liner	
	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$
Precision (‰)	>0.025	>0.1	0.01	0.05	0.01	0.05
Drift (‰)	>0.2	>0.8	0.06	0.33	0.06	0.2

Test Method

A deionized water sample of known isotopic value was measured over the course of 160 successive injections.

Test Result 1: Measurement performance of deionized water is unaffected by the salt liner insert as precision, drift, and memory performance remain fundamentally unchanged.

Test 2: 4% Seawater Solution With Salt Liner

Table 2 (below) shows that precision and drift, while higher than the measurements of deionized water with the salt liner, remain within or very close to isotopic water system specifications.

Table 2 – Precision and Drift Test of 4% Seawater Solution With Salt Liner Inserted				
	Specifications		Measured with salt liner	
	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$
Precision (‰)	>0.025	>0.1	0.03	0.08
Drift (‰)	>0.2	>0.8	0.13	0.33

Test Method

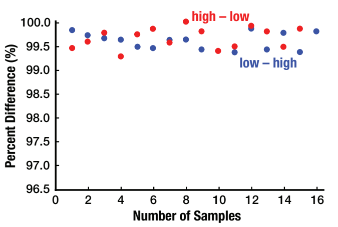
A seawater water sample of 4% salinity was measured over the course of 160 successive injections.

Test Result 2: Precision and drift performance of a 4% seawater solution with a salt liner insert remain within or very close to isotopic water system specifications.

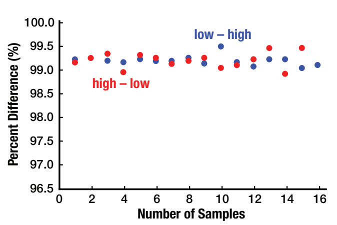
Test 3: Memory Performance Evaluation With the Salt Liner

Memory performance evaluation graphs (below left) show the percent difference between two low-salinity water samples for δ^{18}O and δ^{2}H. For low-salinity water, the memory performance with the salt liner inserted is stable. Memory performance evaluation graphs (below right) show the percent difference between two seawater samples for δ^{18}O and δ^{2}H. For seawater with 4% salinity, the memory performance starts to degrade after 200 total injections (about 30 hours of continuous operation).

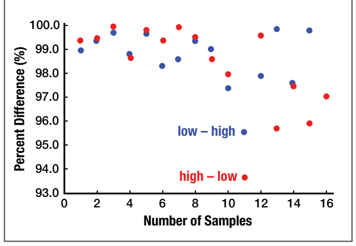
4th Injection Memory of δ^{18}O – Low-Saline Water



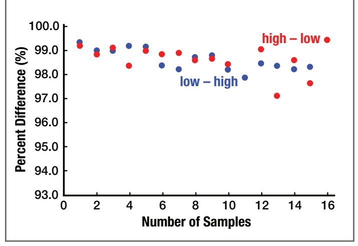
4th Injection Memory of δ^{2}H – Low-Saline Water



4th Injection Memory of δ^{18}O – Seawater



4th Injection Memory of δ^{2}H – Seawater



Test Method

10 injections were taken alternating between two low-salinity water samples of δ^{18}O and δ^{2}H and two seawater samples of δ^{18}O and δ^{2}H. The percent difference between the 4th injection of each 10 is displayed for low-salinity water samples of δ^{18}O and δ^{2}H (above left) and seawater samples of δ^{18}O and δ^{2}H (above right).

See Test Method 1 for an explanantion of the percent difference of **high – low** and **low – high** measurements.

Test Result 3: For low-salinity water, the memory performance with the salt liner inserted is stable. However, for seawater with 4% salinity, the memory performance starts to degrade after 200 total injections (about 30 hours of continuous operation). This indicates that the salt liner needs to be cleaned and replaced.

Cleaning Recommendations for the Picarro Salt Liner Accessory

The salt liner traps up to 80% of salt precipitates (by weight) protecting the vaporizer chamber from salt buildup. This maintains memory, precision, and drift specifications. **Picarro recommends cleaning and replacing the salt liner after every 24 hours of seawater analysis** to prevent deterioration of the isotopic water analyzer system performance due to salt buildup in the vaporizer.

Cleaning and replacing the salt liner involves minimum downtime (a few minutes), compared with the time required to clean the vaporizer chamber (about 24 hours). Recommended cleaning steps follow:

1. Remove the salt liner from the vaporizer using the same procedure as replacing the vaporizer septum.
2. Soak the salt liner in hot water for 5 minutes to allow the salt build-up to dissolve.
3. Rinse the salt liner with deionized water.
4. Dry the salt liner.
5. If salt particles are still visible, repeat the first steps.

If the primary cleaning procedure does not completely dissolve the salt residue, try the following.

Option 1: Sonicate the salt liner in deionized water bath.

Option 2: Soak the salt liner 3 minutes in a mild acidic solution (pH ~2), and rinse it with deionized water.

PICARRO
3105 Patrick Henry Drive, Santa Clara, CA 95054 | 408-962-3900 | sales@picarro.com | picarro.com

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