AN019

Automated Measurement of $\delta^{18}O$ and δD in Briny (Salty) Samples

A test spanning ca. 1200 separate injections over several days indicates no performance changes or other effects due to salt build-up.

Keywords:

Material: Briny samples, water, ocean water, salty water, mud logging samples
Process: Stable isotopes, $\delta^{18}O$ and δD, delta-18O, delta-D

Summary and Relevance:

Many real-world aqueous samples contain dissolved salts. Ocean water has a salt concentration of around 3.5% by weight. Samples at this concentration and higher are commonly referred to as "briny." A potential problem in any analytical instrument used with briny samples is build-up of salt crystals due to precipitation. With some techniques, this can quickly lead to physical clogging, in others it can impair optical or electronic performance. One of the recognized advantages of WS-CRDS isotope analyzers is their ability to obtain precise δD and $\delta^{18}O$ isotope ratios directly from aqueous samples without persistent memory effects and without resorting to distillation or any other time-consuming sample preparation methods. In this application note we present the results of an extended series of injections designed to investigate whether these advantages would also hold true for briny samples. The results of this study clearly confirm that large numbers of briny samples can be automatically processed with confidence. The ability to process raw briny samples in real-time is of relevance for scientists studying ocean water and salt lakes, and is also of particular advantage to petrochemical exploration efforts where it provides an extra dimension of information when analyzing the samples associate with mud logging.

Picarro Analyzer Used:

L1102-*i* equipped with autosampler option

Process:

4% (by weight) of table salt was added to three different water samples; a bottled water which has the characteristics of δD = -61.8 ‰, $\delta^{18}O$ = -9.6 ‰; an enhanced ^{18}O water and an enhanced D water.

A total of 1152 injections were then performed over a 7 day period of continuous testing. The sequence followed for this test was: 78 injections of briny bottled water; followed by 78 injections of briny enhanced ^{18}O water; followed by 78 injections of briny enhanced D water followed by 78 injections again of briny bottled water. This entire sequence was then repeated to the total number of injections. The purpose of cyclically measuring the enhanced waters was to check for any change in memory effects. The successive series of injections of the briny bottled water were used to check for any net drift in the measurement of δD and $\delta^{18}O$.

With *every* injection, the analyzer measured the water concentration in the analyzer chamber. This measurement confirms that the injection/evaporation process introduced a consistent amount (ca. 2 microliters) of water into the analyzer chamber, with no problems due to salt build up. In total, this 6 day test resulted in sampling 1618 microliters of water containing a total of 65 mg of salt.

Results:

The water concentration measurements made throughout the series shows that every injection is consistent even in the presence of growing salt concentration, see Figure 1.

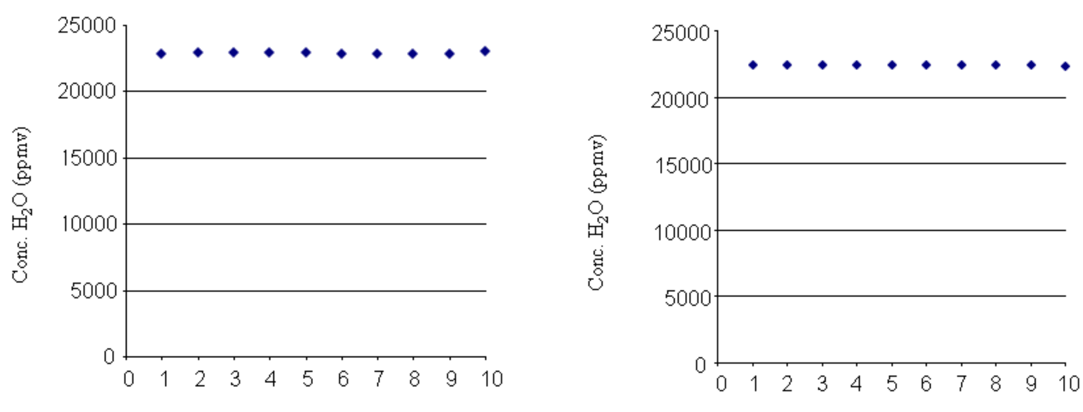

Figure 1. Left hand side data shows the water concentration of 10 injections from the 1st vial. Right hand data shows the water concentration of 10 injections from the last vial.

Figure 2 shows $\delta^{18}O$ and δD measurements from the beginning of the run and at the end of the run clearly shows that the precision and accuracy of the instrument is unaffected by the growing salt load. In addition, the data shows no drift (the instrument was not calibrated during the run).

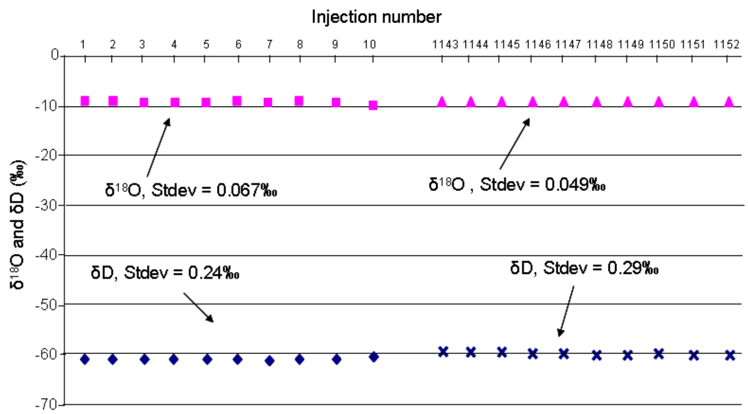

Figure 2. Left hand side data shows the values obtained for $\delta^{18}O$ and δD first 10 injections. Right hand data shows the values obtained for $\delta^{18}O$ and δD from the last 10 injections.

Figure 3 demonstrates that the memory effects when changing from the briny tap water to the enhanced ^{18}O and D waters remain very low throughout the run. Memory effects for the L1102-*i* are typically very low due to the volume of the vaporizer and the methods used to manage gas flow during a sample run.

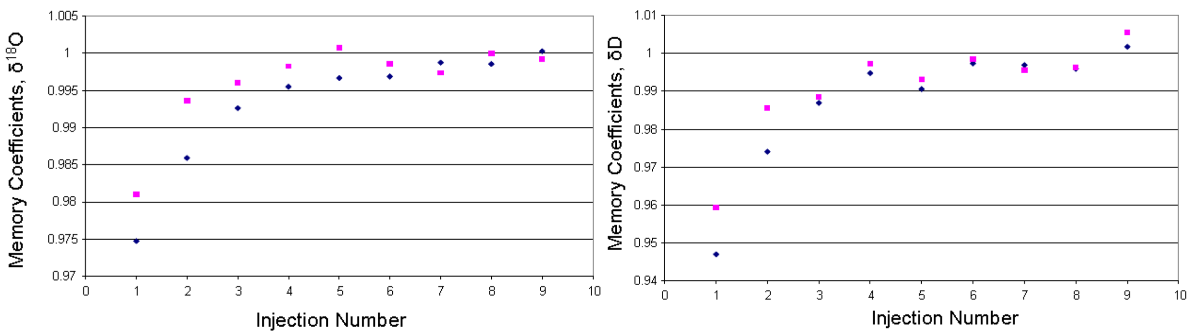

Figure 3. Left hand side data shows the values obtained for $\delta^{18}O$ memory. Right hand data shows the values obtained for δD memory. For both charts, the blue diamond ◆ represents the first transition from the tap water to the enriched sample and the pink square ■ represents the last transition, many hundreds of samples later. The memory is unaffected by the salts load.

Comments:

These tests confirm that large numbers of briny samples can be confidently processed to simultaneously yield δD and $\delta^{18}O$ ratios, with no negative effects on key performance parameters, including precision, memory, and concentration (i.e. injected volume).