Supporting Information for "An Ultra-high precision, Highfrequency Dissolved Inorganic Carbon Analyzer based on Dual Isotope Dilution and Cavity Ring-Down Spectroscopy"

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1. Calculating [DI¹³C]_{spike} and [DIC]_{sample}

According to Eq. 1 in the maintext, when a CRM is measured, there is

$$\frac{[DI^{13}C]_{spike} + MR \cdot [DI^{13}C]_{CRM}}{[DI^{12}C]_{spike} + MR \cdot [DI^{12}C]_{CRM}} = R_{spiked_CRM}$$
(1)

The ratio of ${}^{13}C/{}^{12}C$ of the DIC in the CRM is defined as $R_{natural CRM}$:

$$\frac{[DI^{13}C]_{CRM}}{[DI^{12}C]_{CRM}} = R_{natural_CRM}$$
(2)

From Eq. (2) there are:

$$[DI^{12}C]_{CRM} = \frac{[DIC]_{CRM}}{1 + R_{natural_CRM}}, [DI^{13}C]_{CRM} = \frac{R_{natural_CRM} \cdot [DIC]_{CRM}}{1 + R_{natural_CRM}}$$
(3)

Since the spike is made of deionized water and NaH¹³CO₃, there is

$$[DI^{12}C]_{spike} = R_{NaH^{13}CO_3} \cdot [DI^{13}C]_{spike} + [DI^{12}C]_{DI_Water}$$
(4)

where $R_{NaH13CO3}$ is the molar ratio of the NaH¹²CO₃ and NaH¹³CO₃ of the ¹³C-enriched NaHCO₃ that is used to make the spike. The product we use has an $R_{NaH13CO3}$ of 1/49. The $[DI^{12}C]_{DI_Water}$ stands for the $[DI^{12}C]$ (~10 µmol kg⁻¹) of the deionized water that is used to dissolve the NaH¹³CO₃ crystal and make the spike solution. $[DI^{13}C]_{DI_Water}$ is negligible compared with other two terms ($[DI^{13}C]_{spike}$ and $[DI^{12}C]_{DI_Water}$), and is not included in the equation.

Combining Eq. (1), (3) and (4), there is

$$[DI^{13}C]_{spike} = \frac{MR \cdot (R_{spiked_CRM} - R_{natural_CRM}) \cdot [DIC]_{CRM}}{(1 + R_{natural_CRM})(1 - R_{spiked_CRM} \cdot R_{NaH^{13}CO_3})} + \frac{R_{spiked_CRM} \cdot [DI^{12}C]_{DI_Water}}{1 - R_{spiked_CRM} \cdot R_{NaH^{13}CO_3}} (5)$$

When a sample is measured, there is a relationship similar to that shown by Eq (1) and (2) and (3), i.e.,

$$\frac{[DI^{13}C]_{spike} + MR \cdot [DI^{13}C]_{sample}}{[DI^{12}C]_{spike} + MR \cdot [DI^{12}C]_{sample}} = R_{spiked_CRM}$$
(6)

$$\frac{[DI^{13}C]_{sample}}{[DI^{12}C]_{sample}} = R_{natural_sample}$$
(7)

and

$$[DI^{12}C]_{sample} = \frac{[DIC]_{sample}}{1 + R_{natural_sample}}, [DI^{13}C]_{CRM} = \frac{R_{natural_CRM} \cdot [DIC]_{sample}}{1 + R_{natural_sample}}$$
(8)

Combing Eq. (4), (6), (7) and (8), the [DIC] of the sample can be solved as

$$[DIC]_{sample} = \frac{1}{MR} \cdot \frac{1 + R_{natural_sample}}{R_{spiked_sample} - R_{natural_sample}} \cdot$$

$$\left\{ \left(1 - R_{spiked_sample} \cdot R_{NaH^{13}CO_3} \right) \cdot [DI^{13}C]_{spiked} - R_{spiked_sample} \cdot [DI^{12}C]_{DI_Water} \right\}$$
(9)

in which $[DI^{13}C]_{spike}$ has already been calculated from Eq. (5).

2. Calibration and Corrections

We mixed seawater and the spike at different mixing ratio to create a suite of standards to calibrate the δD_{spiked_sample} measurements. The results are shown in Figure S1.



Figure S1. Relationship between the measured δD_{spiked_sample} and the true δD_{spiked_sample} calculated from the known δD_{spiked} , δD_{sample} and the gravimetrically determined MR.

3. Stability and response time of the $\delta D_{\text{spiked sample}}$ measured in the Water-Line

To test the precision of the water isotope measurements, a mixture of spiked water was prepared by mixing deionized water and the spike at the MR of 40:1, and stored in a Cali-5-bond bag. The mixture was then run into the Water-Line at ~10 ml/min. Results of a ~6 hour run indicate high precision of δD and $\delta^{18}O$. With constant temperature of the sample (T_L) and that of the carrier gas (T_{WEC}), the extracted vapor concentration was very stable during the run (mean = 6942.3±7.8 ppm). The average δD was 2785.45 ‰. Calculation following the method of Allan¹ indicates that the precision of the raw δD (~1 s intervals) was ±2 ‰, and for the 2-minute integrated average, ±0.29 ‰ (Figure S3a). The relative precision is comparable to the reported specifications of the analyzer, indicating the noise mainly stemmed from the analyzer, and the uncertainty introduced by the water isotope fractionation at the Water vapor Extraction Chamber was small.

The response time of the Water-Line to change in Mixing Ratio was tested by running sequential samples of spiked water with the δD changing by ~200 ‰ increments/decrements within the range of ~2700 to 3100 ‰. The data for transitions were fit to an exponential function, i.e.,

 $\delta D(t) = \delta D_0 + (\delta D_{end} - \delta D_0) \cdot (1 - e^{-t/\tau_{Water-Line}})$

where δD_0 and δD_{end} represent the initial and end δD of each switch, and $\tau_{Water-Line}$ the efolding response time of the Water-Line. The average $\tau_{Water-Line}$ calculated from these experiments was 0.9 minute (Figure S3b).



Figure S2. Performance of the water isotope measurements. **a.**) The deviation of the δD_{spiked_sample} measurements at various integrated average intervals; and **b.**) Response time of the Water-Line. The grey dots show the raw measurements of δD_{spiked_sample} at various levels. The red line indicates the curve fitting results to determine the e-folding response time ($\tau_{Water-Line}$), which are shown in minutes at each transitional periods (from 0.8 -1 minute).

4. Natural δ^{13} C of DIC and δ D of water

Natural δ^{13} C of DIC and δ D of water were measured during the last day of the cruise onboard of *R/V Hugh Sharp*, and their relationships with salinity are used to estimate natural carbon and water isotopes ($\delta^{13}C_{sample}$ and δD_{sample}) of the samples collected during the first two and half days of the cruise (Figure S4).



Figure S3. The relationship between the natural δD of water vs. salinity **a**.) and the natural $\delta^{13}C$ of DIC vs. salinity **b**.) in the Delaware River and Bay. The grey dots show the measured values, and the blue lines show the fitting results. For the dD vs. salinity relationship is divided into 3 sections (salinity <5, 5≤salinity<25, and salinity≥25). The standard deviation of the residuals is 0.14, 0.39 and 0.23‰, respectively. The exact reason for the step-like behavior is still being studied with other data. The gap at S= 5.5 is most likely caused by the impact of the water from the Chesapeake Bay via the C&R Canal that merges into the Delaware estuary. Chesapeake Bay water likely has a slight different δD value from that of the Delaware River. The very small step at S>25 may reflect the mixing of the incoming seawater with that in the Delaware Bay. It is also possible a result of signal coming from saltmarshes surrounding in the lower bay.

The δ^{13} C was fitted as a square root function of salinity, and the standard deviation of the residuals is 0.13‰.

5. Summary of the sample comparisons

Table S1. Summary of the cruise data. Dissolved inorganic carbon concentration ([DIC] in μ mo kg⁻¹) of the discrete samples ([DIC]_{discrete}) and the corresponding [DIC] measured by the Dual Isotope Dilution-Cavity Ring-down Spectroscopy (DID-CRDS) method ([DIC]_{DID-CRDS}) are summarized in Table S1. All discrete samples were collected from the flow-through system of the ship. The codes in the station names are in the format of "the station name-method-sample number", where "Coul" and "NDIR" stand for the coulometry- and Non-dispersive Infra-red (NDIR)-based methods, respectively. The mean [DIC] is calculated wherever a pair of samples was collected and analyzed. For each station, mean [DIC] measured by the DID-CRDS method during the time of discrete sample collections is calculated. The differences of the [DIC] measured by the DID-CRDS method and the discrete methods are shown in the last column.

Station	Date	Time	Lat.	Lon.	SSS	SST	$[DIC]_{discrete}$	Mean	$[DIC]_{DID-CRDS}$ Difference	
		(GMT)	(N)	(W)		$(^{\circ}C)$		$[DIC]_{discrete}$		
B1-Coul-1	19-Nov	6:10	38.821	75.104	29.81	10.97	1975.3	1972.83	1972.81	0.02
B1-Coul-2	19-Nov	6:12	38.821	75.104	30.02	11.13	1970.35	-	-	-
B1-NDIR-1	19-Nov	6:23	38.821	75.104	29.57	10.71	1979.73	1978.33	1973.34	4.99
B1-NDIR-2	19-Nov	6:26	38.821	75.104	29.59	10.72	1976.94	-	-	-
B2-Coul-1	19-Nov	7:43	38.821	75.107	29.48	10.48	1974.5	1975.5	1976.36	-0.86
B2-Coul-2	19-Nov	7:46	38.821	75.107	29.48	10.48	1976.5	-	-	-
B2-NDIR-1	19-Nov	7:59	38.821	75.107	29.48	10.48	1968.15	1967.36	1973.82	-6.46
B2-NDIR-1	19-Nov	7:59	38.821	75.107	29.48	10.48	1966.56	-	-	-
B3-NDIR-1	19-Nov	9:58	38.821	75.109	29.49	10.46	1970.14	1971.9	1972.23	-0.33
B3-NDIR-2	19-Nov	10:00	38.821	75.109	29.49	10.46	1973.67	-	-	-
B3-Coul-1	19-Nov	10:03	38.821	75.109	29.48	10.43	1966.3	1970.53	1971.99	-1.46
B3-Coul-2	19-Nov	10:06	38.821	75.109	29.48	10.43	1974.75	-	-	-
B4-Coul-1	19-Nov	17:45	39.114	75.209	28.38	10.53	1933.4	1938.45	1942.31	-3.86
B4-Coul-2	19-Nov	17:47	39.114	75.209	28.38	10.53	1943.5	-	-	-
R17-Coul -1	19-Nov	12:02	38.784	74.936	31.5	12.08	1972.7	1976.6	1987.08	-10.48
R17-Coul -2	19-Nov	12:04	38.784	74.936	31.5	12.08	1980.5	-	-	-
R17-NDIR-1	19-Nov	12:10	38.783	74.938	31.52	12.08	1985.31	1985.31	1987.38	-2.07
R18-NDIR-1	19-Nov	20:42	39.262	75.344	19.95	9.61	1727.34	1727.34	1707.66	19.68
R18-Coul-1	19-Nov	20:51	39.259	75.342	19.74	9.67	1704.55	1704.55	1704.13	0.42

6. Recipe for the dual isotope spike

Table S2. Recipe for every 1 Liter (25 $^{\circ}$ C) of the dual isotope spike.

98 ¹³ C atom % NaH ¹³ CO ₃	0.36 g
pH 8.5 Trizma HCl pre-set crystal	6.6 g
99.9 atom% D ₂ O	27.7g
NaCl crystal	33g

Reference

1. Allan, D. W. Statistic of atomic frequency stadards. Proc. IEEE 1966, 54, 221-230.