Atomic Spectroscopy

Article

Carbon Isotopic Analysis of Dissolved Organic Carbon in High-Salinity Water Using a GasBench Plus coupled to an Isotope Ratio Mass Spectrometer

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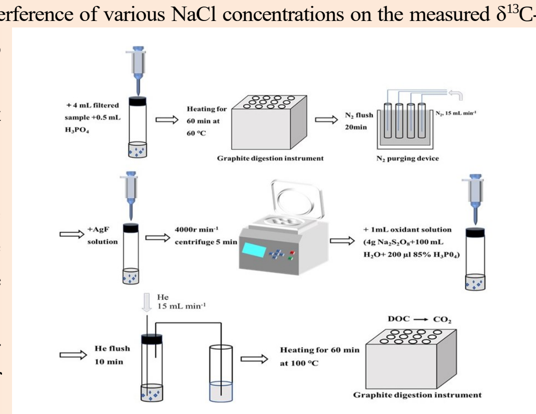
ABSTRACT: Analyzing the δ^{13}C-DOC in high-salinity water remains challenging due to significant differences in interfering ions and analyte concentrations. In this study, halide interference was eliminated using an AgF solution to generate AgCl precipitate, and the δ^{13}C-DOC was measured using a GasBench Plus preparation device coupled with isotope ratio mass spectrometry (IRMS), establishing an accurate and sensitive method to determine δ^{13}C-DOC in high-salinity water samples. The external accuracy of the method was 0.09‰, and the difference between the measured and certified δ^{13}C values of IAEA-601 was 0.14‰. When the carbon content of the sample was 2.0 μg (equivalent to 0.5 μg mL^{-1} DOC content in the sample), the precision was 0.11‰ with a 0.15‰ difference. The interference of various NaCl concentrations on the measured δ^{13}C-DOC was evaluated, and 200 g L^{-1} NaCl produced an approximately -13.97‰ difference between the stable isotope result and its true value. This difference was observed when we analyzed saline samples without any measures to deal with salt interference. However, this difference was overcome using the presented procedure. The δ^{13}C-DOC of twenty-one high-salinity water samples was determined using the proposed procedure and a total organic carbon analyzer with a high-temperature catalytic oxidation unit coupled to IRMS. The δ^{13}C-DOC results obtained using the two methods are consistent, with differences of -0.17‰ to -0.40‰, indicating that the influence of halides is completely overcome by the proposed procedure. Therefore, the proposed method enables the analysis of the δ^{13}C-DOC in high-salinity water regardless of the type and origin of the salt solution, provided the concentrations of DOC are between 0.5 to 50 μg mL^{-1}, and shows great promise in allowing many labs that are currently limited to analyzing freshwaters to expand their capabilities.



INTRODUCTION

The stable carbon isotopic composition of dissolved organic carbon (δ^{13}C-DOC) in water can provide insights into the carbon cycle as well as biogeochemical processes[1,2] and trace water movement and provenance in hydrogeochemistry,[3,4] making it a powerful tool for distinguishing sources and inputs of organic matter in aquatic systems. In natural water, the DOC concentrations are usually low, only tens or even a few milligrams per liter, and face matrix complexity. Therefore, methods for the accurate analysis of the δ^{13}C-DOC have faced many challenges, highlighting the need for professional equipment with high sensitivity and low background.

Currently, evaporation–combustion,[5-7] wet oxidation,[8-10] high-temperature combustion,[11-13] and high-temperature catalytic oxidation[14-16] are the major methods employed for the δ^{13}C-DOC. These methods convert DOC to CO_2, purify CO_2, and perform isotope ratio mass spectrometry (IRMS) on the CO_2 for δ^{13}C analysis. Nevertheless, there are certain limitations to these methods. The evaporation–combustion method requires multiple microliter aliquots of water to be evaporated or freeze-dried, potentially leading to large analytical blanks. Therefore, only up to 40 samples per week can be analyzed using this method, which is time-consuming and laborious. Wet oxidation and high-temperature combustion methods are based on total organic carbon (TOC) analysis coupled with IRMS and require multiple sets of peripheral equipment matching, leading to poor flexibility and complex operation. In addition, a significant instrument blank is the main drawback,[17] and the overall measurement error is approximately ±0.8‰.[11] The high-temperature catalytic oxidation method can be used for high-salinity samples. However, due to salt build-up, the samples could only be performed after cleaning the catalytic oxidation reactor, which limited the number of samples.

In recent years, a simple, accurate, and inexpensive method using a GasBench on-line gas preparation and introduction system coupled to IRMS has been developed, which does not require a separate TOC analyzer. This method has been successfully used for δ^{13}C-DOC analysis of in freshwater,[18] groundwater,[19] and surface water[20] samples and can analyze organic samples with carbon amounts as low as 1.2 µg.[18] The precision and accuracy of the δ^{13}C-DOC are better than 0.17‰ and 0.5‰, respectively, for samples containing carbon amounts larger than 5 µg.[21] Notably, this method is only applicable to water samples containing no salt because organics are oxidized to CO_2 using persulfate and heat, and incomplete oxidation is possible in the presence of a high Cl^- concentration.[20,22] To overcome the analytical problems of Cl^- interference, many methods have been employed in which 1) the salt is removed by ultrafiltration or cross-flow filtration,[23,24] 2) Hg salts are used to complex halides,[25] 3) $AgNO_3$ salt is used to decrease the Cl^- concentration,[8] and 4) the relative ratio of oxidant to sample volume is increased.[8,26] However, these methods are persulfate-based TOC analysis methods, and the daily sample analysis output is limited. Potential limitations of GasBench–IRMS for the analysis of the δ^{13}C-DOC in high-salinity water have not yet been evaluated.

Waters with salinities higher than that of seawater are widespread electrolytes, and natural aqueous fluids that contain NaCl are the most abundant.[27] For example, the NaCl concentration in water from the Dead Sea and evaporitic lakes of marine origin on the Crimea Peninsula reaches 200 g L^{-1}.[28] Therefore, in this study, we mainly focused on measuring the δ^{13}C-DOC in high-salinity water samples in the presence of a high halide concentration. An accurate, precise, and easily operated method to measure the δ^{13}C-DOC in high-salinity water samples was achieved using GasBench–IRMS-based persulfate wet oxidation. Halide interference on the δ^{13}C-DOC determination was evaluated and eliminated. Meanwhile, the δ^{13}C-DOC in actual high-salinity water samples was measured by the proposed method and verified by a total organic carbon analyzer with a high-temperature catalytic oxidation unit coupled to IRMS (TOC–HTC–IRMS).

EXPERIMENTAL

Instrument. A MAT253 Plus gas stable IRMS instrument equipped with a GasBench Plus on-line gas preparation and introduction system (Thermo Fisher Scientific, Bremen, Germany) and a CTC autosampler (CTC Analytics AG, Zwingen, Switzerland) were used for isotopic composition determination of the headspace CO_2. A PoraPlot Q fused-silica gas chromatography column (25 m×0.32 mm×10 µm, Agilent Technologies, America) was set at 70 °C and used to separate the CO_2 from the matrix gases. A Flash EA IsoLink CN/OH elemental analysis (EA) unit combined with an IRMS unit (Thermo Fisher Scientific, Germany) was used to estimate of the δ^{13}C value of the working standard. A multi N/C 3100 TOC/total nitrogen analyzer (Analytik Jena AG) was employed to determine the DOC content in the reagent blank. An ICS-1500 ion chromatograph (Thermo Fisher Scientific) was used to measure the Cl^- content in the water sample.

Standards and reagents. The organic carbon reference material IAEA-601 (benzoic acid) with a -28.81‰ and USGS65 (glycine) with -20.29‰ actual δ^{13}C value relative to Vienna Pee-Dee Belemnite was used to calibrate the isotopic composition of the samples. The actual sample data was normalized using two-point normalization, while the conditional experimental data was normalized using single-point normalization versus IAEA-601[29]. The potassium hydrogen phthalate (KHP, 99.99%), sodium chloride (NaCl, 99.99%), silver fluoride (AgF, 99%), and sodium persulfate ($Na_2S_2O_8$, 99.99%) were all obtained from the Shanghai Aladdin Bio-chem Technology Co., Ltd in China. KHP, which is difficult to oxidize, was used as the DOC working standard. The NaCl was pre-combusted at 650 °C for 2 h in a muffle furnace and then used for preparing different concentration salt solutions. The $Na_2S_2O_8$ solution was made within 24 h of use and was boiled on a hot plate for 45 min to remove the organic matter. 12 mol L^{-1} AgF solution was boiled on a hot plate for 45 min to remove the organic matter after 1 mL of $Na_2S_2O_8$ solution was added. Solid phosphoric acid (Thermo Fisher Scientific, America) was used to acidify samples for removing the inorganic carbon. Deionized water (18.2 MΩ cm^{-1}) containing 1.7 µg L^{-1} DOC was obtained from a water purification system (Millipore, France) and used for the preparation of different concentration salt solutions, working standards, $Na_2S_2O_8$ solution, and AgF solution. All glassware including the 12-mL borosilicate glass vials (Labco, Britain) and volumetric flasks were pre-combusted at 500 °C for 5 h to remove organic contaminants.

Sample preparation for determining the δ^{13}C-DOC. The wet

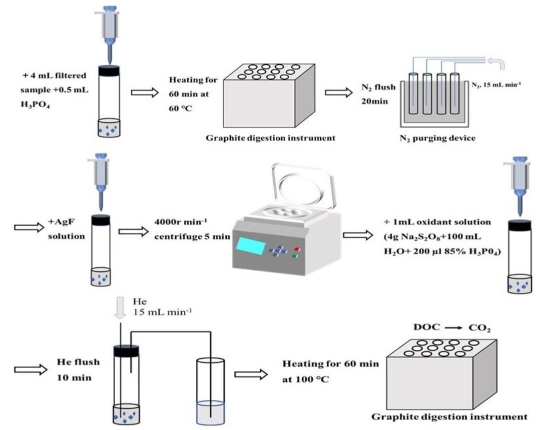


Fig. 1 Schematic representation of the sample preparation for the $\delta^{13}C$-DOC.

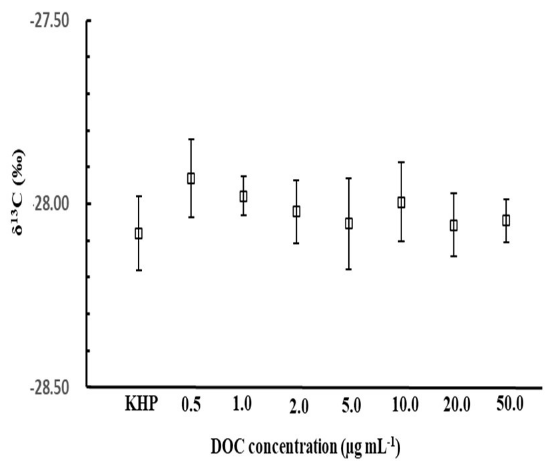


Fig. 2 $\delta^{13}C$ values of various KHP concentrations measured after wet oxidation, KHP on the X axis represents the value obtained using EA-IRMS.

oxidation method was carried out as described by Lang *et al.*[18] and Zhou *et al.*,[19] with the only differences being that we replaced the high-purity He with high-purity N_2 to remove the inorganic carbon, and Cl^- was pre-precipitated before the addition of oxidant solution. A schematic representation of the sample preparation procedure for measuring the $\delta^{13}C$-DOC is shown in Fig. 1. First, 4 mL of the filtered sample was transferred into a 12-mL borosilicate glass vial, and then 0.5 mL of 85% H_3PO_4 was added and reacted with the inorganic carbon by heating the vial at 60 °C for 60 min. After the reaction was complete, the samples were flushed with high-purity N_2 (99.999%) for 20 min at 15 mL min^{-1} to remove the inorganic carbon. Then, AgF solution (12 mol L^{-1}) was added, and the volume added depended on the Cl^- content in the sample, for example, 4 mL of 200 g L^{-1} NaCl solution required the addition of 1.14 mL of 12 mol L^{-1} AgF solution. After the AgCl precipitation reaction was complete, the samples were centrifuged for 5 min at 4000 r min^{-1}, and then, 1 mL of $Na_2S_2O_8$ oxidant solution (100 mL of H_2O + 4.0 g of $Na_2S_2O_8$ + 200 µL of H_3PO_4) was added to the vial with a disposable borosilicate pipette. Immediately after the addition of the oxidant, the samples were purged with high-purity He (99.999%) for 10 min at 15 mL min^{-1}, and the outlet was connected to copper tubing whose open end was submerged in water to prevent any backflow of atmospheric CO_2 into the sample. Finally, the mixture of sample and oxidant was heated to 100 °C for 60 min, and the DOC was oxidized to CO_2 gas. After oxidation, the samples were cooled to room temperature (about at 25 °C), the $\delta^{13}C$-DOC value of the CO_2 gas in the headspace was determined using a GasBench–IRMS instrument.

High-salinity samples collection and processing. We collected high-salinity water samples from Sanshan Island in Laizhou city, Shandong province, China. Samples were filtered through 0.7 µm glass fiber filters pre-combusted at 400 °C (Whatman@ GF/F) and stored for no more than 1 month at -18 °C in darkness until analysis. The samples were prepared according to the presented experimental procedure and subsequently measured by GasBench-IRMS. The $\delta^{13}C$-DOC of high-salinity samples was also directly determined by TOC-HTC-IRMS for comparison.

RESULTS AND DISCUSSION

Feasibility of the wet oxidation method. The wet oxidation method is based on the thermolysis of $Na_2S_2O_8$ to generate the sulfate radical anion oxidant. As recommended by previous studies,[18,19,21] the mixture of sample and oxidant needed to be heated at 100 °C for 60 min, which were the optimal oxidation conditions for oxidizing the DOC to CO_2 gas. To verify the feasibility of this method, an IAEA-601 (benzoic acid) with a $\delta^{13}C$ value of -28.81‰$_{VPDB}$ was used, and seven independent tests were carried out according to the experimental conditions, with one occurring every five days. The results are shown in Table 1. Using the recommended oxidation conditions, the internal accuracy of the analysis was 0.01–0.08‰, and the external accuracy of the analysis was 0.09‰, which are better values than the precision values of 0.2–0.4‰ reported in previous studies[18,31] and same as the precision of 0.1‰ reported by Suto and Kawashima.[32] The differences between the $\delta^{13}C$ values ($\Delta_{measured\text{-}certified}$) measured by the recommended wet oxidation method and the certified value of IAEA-601 were within 0.14‰ for all the tests, demonstrating an accuracy better than 0.5‰.[21] These results confirm that the recommended wet oxidation conditions were successful.

Effect of the oxidation condition on the DOC concentration. Although the recommended wet oxidation conditions are feasible, to determine whether high-concentration DOC can be completely oxidized or low-concentration DOC has a reagent blank effect requires further investigation. To evaluate the effect of the

Table 1. Verification of the feasibility of using the wet oxidation method for determining the δ^{13}C-DOC using IAEA-601 (‰$_{VPDB}$)

IAEA-601	Value	Internal accuracy (n=3)	External accuracy (n=7)	Standard deviation (±)	$\Delta_{measured-certified}$
Certified	-28.81	--	--	0.04[a]	--
1	-28.71	0.01	--	--	-0.1
2	-28.85	0.06	--	--	-0.04
3	-28.75	0.07	--	--	-0.06
4	-28.76	0.08	--	--	-0.05
5	-28.76	0.07	--	--	-0.05
6	-28.95	0.08	--	--	-0.14
7	-28.81	0.07	--	--	-0.0
Average	-28.80	--	0.09	--	-0.01

[a] Ref. [27]

Table 2. δ^{13}C-DOC measurements after eliminating Cl^- interference (‰)

NaCl concentration (g L^{-1})	Direct measurement of the δ^{13}C-DOC (‰)	δ^{13}C-DOC measurement after eliminating Cl^- interference (‰)
0	-28.03±0.04	-28.03±0.04
1	-28.88±0.12	-28.05±0.08
2	-29.13±0.18	-28.03±0.07
5	-29.93±0.17	-28.00±0.08
10	-31.16±0.15	-28.05±0.07
20	-31.87±0.18	-28.07±0.09
40	-32.90±0.14	-28.08±0.08
60	-33.68±0.13	-28.08±0.09
80	-34.34±0.17	-28.09±0.08
100	-35.36±0.12	-28.10±0.09
150	-39.93±0.16	-28.11±0.10
200	-42.00±0.13	-28.10±0.11

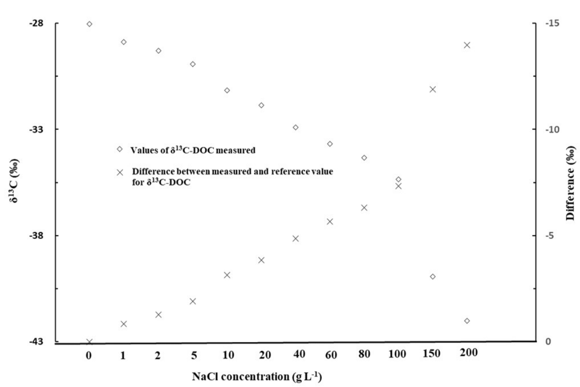


Fig. 3 The Interference effect of varying NaCl levels on δ^{13}C-DOC measured. The difference is the measured value of δ^{13}C-DOC minus the value obtained with EA-IRMS.

oxidation conditions on different DOC concentrations, KHP working standards with 0.5–50 μg mL^{-1} carbon contents were tested. The δ^{13}C value of KHP was -28.08±0.10‰ (Table S1), which was obtained by combustion at 960 °C to convert the organic materials into CO_2 without pretreatment and measured by EA–IRMS. The δ^{13}C values of different concentrations of KHP measured after wet oxidation are shown in Fig. 2. For 50 μg mL^{-1} of KHP (equivalent to 200 μg of carbon), the δ^{13}C value was -28.05±0.06‰, which was consistent with the δ^{13}C value measured by EA–IRMS, suggesting complete oxidation of high DOC contents without significant isotope fractionation during the pretreatment procedure. Furthermore, the conversion rate of KHP at 50 μg mL^{-1} was 99.8% (Table S2), which further supported the feasibility under oxidation conditions. For 0.5 μg mL^{-1} of KHP (equivalent to 2 μg of carbon), the δ^{13}C value was -27.93±0.11‰ with a 0.15‰ difference compared with the δ^{13}C value obtained by EA-IRMS. However, this difference is similar to the analytical error 0.14‰ of IAEA-601 and better than the 0.7‰ reported error[15], indicating that the effect of the reagent blank can be ignored. Notably, our reagent blank obtained from TOC analysis contained approximately 0.12 μg of carbon, which is lower than the values of 0.18-0.24 μg of carbon[18] and 0.5±0.06 μg of carbon[21] obtained in previous studies, The blank contribution to 0.5 μg mL^{-1} DOC was approximately 6%; therefore, blank correction was not necessary for DOC concentrations in samples greater than 0.5 μg mL^{-1}. The obtained results showed no significant difference regardless of the KHP concentration in the range of 0.5-50 μg mL^{-1}.

Interference of Cl^- on δ^{13}C-DOC measurement. The wet oxidation method is mainly uses the thermolysis of persulfate to generate a sulfate radical anion oxidant. However, in water samples, organics, bicarbonate, halides, and persulfate all compete for sulfate radical anions,[33] resulting in rapid radical consumption. In high-salinity water, halides are dominant and present in much greater abundance than organics. Therefore, the chance of sulfate radical anions reacting with organics is greatly reduced by the presence of halides. To evaluate Cl^- interference on δ^{13}C-DOC measurement, 10 μg mL^{-1} of KHP samples containing 0-200 g L^{-1} NaCl were studied, and the results are shown in Fig. 3. The δ^{13}C value clearly decreased with increasing salinity. Even at a low NaCl concentration of 1 g L^{-1} (equivalent to 0.61 g L^{-1} Cl^-), a -0.85‰ difference was observed. When the NaCl concentration reached 200 g L^{-1}, the effect of Cl^- ions produced an approximately -13.97‰ difference in the stable isotope result from its true value. These results suggest that δ^{13}C isotopic fractionation originated from effect

Table 3. Analysis of the δ^{13}C-DOC in actual high-salinity water samples by proposed method and TOC–HTC–IRMS methods

Sample	DOC (mg L^{-1})	Cl^- (g L^{-1})	Cl^-/ DOC	This method (‰)	TOC–HTC–IRMS (‰)	Difference (‰)
H-0	1.25	19.6	15680.0	-22.61±0.08	-22.92±0.13	-0.31
H-1	1.62	13.7	8456.8	-20.88±0.09	-21.20±0.15	-0.32
H-2	1.47	14.2	9659.9	-21.00±0.07	-21.34±0.20	-0.34
H-3	1.59	29.5	18553.5	-17.77±0.06	-18.17±0.18	-0.40
H-4	1.39	24.2	17410.1	-18.41±0.09	-18.85±0.22	-0.30
H-5	1.51	28.7	19006.6	-21.51±0.08	-21.82±0.18	-0.31
H-6	2.15	18.4	8558.1	-20.50±0.08	-20.90±0.20	-0.40
H-7	1.37	19.1	13941.6	-22.77±0.06	-23.05±0.16	-0.28
H-8	1.53	14.3	9346.4	-21.83±0.09	-22.05±0.16	-0.22
H-9	1.86	14.7	7903.2	-21.76±0.07	-22.07±0.20	-0.31
H-10	2.21	25.0	11312.2	-25.70±0.05	-25.90±0.24	-0.20
H-11	2.11	20.6	9763.0	-24.13±0.09	-24.30±0.19	-0.17
H-12	2.95	16.5	5593.2	-24.41±0.05	-24.60±0.17	-0.19
H-13	2.63	25.3	9619.8	-28.75±0.05	-28.97±0.24	-0.22
H-14	2.02	14.8	7326.7	-22.63±0.04	-22.91±0.14	-0.28
H-15	1.73	15.4	8901.7	-23.18±0.04	-23.48±0.15	-0.30
H-16	1.72	15.3	8895.3	-21.43±0.05	-21.68±0.17	-0.25
H-17	1.67	15.8	9461.1	-20.99±0.05	-21.23±0.11	-0.24
H-18	1.99	15.4	7738.7	-21.61±0.05	-21.85±0.20	-0.24
H-19	2.43	15.5	6378.6	-22.00±0.06	-22.19±0.20	-0.19
H-20	2.82	16.1	5709.2	-21.35±0.08	-21.53±0.12	-0.18
H-21	1.90	14.5	7631.6	-21.65±0.08	-21.91±0.24	-0.26

of Cl^- must be overcome when Cl^- concentrations are greater than 0.61 g L^{-1} in water samples.

Elimination of Cl^- interference. To eliminate Cl^- interference in the wet oxidation process, the addition of extra persulfate and extension of the reaction time[26] or increasing the relative ratio of oxidant to sample volume[8] can be employed in the TOC-wet oxidation-IRMS method. However, for GasBench-IRMS, these methods are not suitable. First, extension of the reaction time may increase the probability of gas leaking during the measurement, resulting in isotopic fractionation.[18] Second, the addition of extra persulfate means the blanks associated with this amount of persulfate would likely interfere with the δ^{13}C-DOC measurement signal, particularly the lower concentration δ^{13}C-DOC measurement signals.[21] Third, wet oxidation is carried out in 12-mL borosilicate glass vials and increasing the relative ratio of oxidant to sample volume would lead to a smaller sample size with reduced carbon content, resulting in poor analysis precision and accuracy.

However, an alternative strategy for eliminating Cl^- interference can be adopted by adding Ag ions to react with Cl^- forming AgCl precipitate. In our experimental studies, AgF reagent was selected because it causes AgCl precipitation, as well as CaF_2 and MgF_2 precipitation, bringing an additional positive desalting effect. In addition, The AgCl precipitate can be retrieved for chlorine isotope analysis. This stable chlorine isotope is a useful tool for tracing water evolution and exploring changes in the geological environment. It has a broad range of applications in earth science. After removing the Cl^- in 10 µg mL^{-1} KHP solutions containing different concentrations of NaCl, the δ^{13}C-DOC was determined by wet oxidation under the optimized experimental conditions, and the results are found in Table 2, which demonstrates that the analysis precision and accuracy of a 10 µg mL^{-1} KHP solution were effectively improved after eliminating Cl^- interference. The δ^{13}C-DOC analysis precision improved from within 0.18‰ to within 0.11‰, while the δ^{13}C-DOC analysis accuracy is improved from -42.00±0.13‰ to -28.10±0.11‰ for 200 g L^{-1} NaCl interference, indicating that the difference because of Cl^- improved from -13.97‰ to 0.07‰. Notably, a 0.07‰ difference is within the precision of 0.11‰ and can be ignored. To conclude, these results indicate that the use AgF to eliminate Cl^- interference is feasible and effective, and the method presented is precise and accurate for δ^{13}C-DOC measurements in high-salinity water.

Analysis of the δ^{13}C-DOC in actual high-salinity water samples. The δ^{13}C-DOC determination results of high-salinity water samples by presented method and TOC-HTC-IRMS method are presented in Table 3. As shown in Table 3, the high-salinity samples have a DOC concentration ranging from 1.25 to 2.95 mg L^{-1}, whereas the Cl^- ion concentration is 5593.2 to 19006.6 times higher. However, the δ^{13}C-DOC values obtained by the presented method ware -17.77±0.06‰ to -28.75±0.05‰, which are consistent with the values of -18.17±0.18‰ to -28.97±0.24‰ obtained by TOC-HTC-IRMS, and the differences between the two methods are only -0.17‰ to -0.40‰. These results suggest the complete oxidation of DOC in high-salinity samples, indicating that no significant carbon isotope fractionation occurs during sample preparation. Therefore, δ^{13}C-DOC determination by the presented method is considered to be effective for high-salinity sample.

CONCLUSION

In this study, the effect of Cl^- interference on the wet oxidation of DOC was eliminated by using AgF reagent, and a simple, accurate, and sensitive method for δ^{13}C-DOC determination in high-salinity water samples using a GasBench preparation device was established. The presented method can be successfully applied to various high-salinity waters and brines of different origins. Under the recommended sample preparation procedure, the isotopic composition of the samples is not fractionated, and the problem of Cl^- interference can be overcome. The presented method has application potential in measuring the δ^{13}C-DOC of seawater samples to aid in understanding the carbon cycle, and shows great promise in allowing many labs that are currently limited to analyzing freshwaters to expand their capabilities.

ASSOCIATED CONTENT

The supporting information (Table S1-S3) is available at www.at-spectrose.com/as/home.

AUTHOR INFORMATION

Wen-Jing Liu received her BSc in 2007 from China University of Geosciences, China, and M.A. in 2010 from Institute of Geochemistry, Chinese Academy of Sciences, and PhD in 2013 from the Institute of Geology and Geophysics, Chinese Academy of Sciences. She is a associate professor of geochemistry at the Institute of Geology and Geophysics, CAS. Her major research interests are chemical weathering and carbon cycling, Stable metal isotope (Li, Mg, Ca and Fe isotope systems) and cosmogenic nuclide (^{10}Be, ^{26}Al) applications in Earth's surface process (mainly continent weathering and erosion). She was awarded the International Postdoctoral Exchange Fellowship by the China Postdoctoral Council in 2014 and the Youth Innovation Promotion Association Fellowship by the Chinese Academy of Sciences in 2019. Wen-Jing Liu is author or co-author of over 40 articles published in peer-reviewed scientific journals.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. P. A. Raymond and J. E. Bauer, *Org. Geochem.*, 2001, **32**, 469–485. https://doi.org/10.1016/S0146-6380(00)00190-X
2. M. Zhao, H. Sun, Z. Liu, Q. Bao, B. Chen, M. Yang, H. Yan, D. Li, H. He, Y. Wei and G. Cai, *Sci. Total Environ.*, 2022, **812**, 152429. https://doi.org/10.1016/j.scitotenv.2021.152429
3. Y. S. Bong, J. S. Ryu, and K. S. Lee, *Anal. Chim. Acta*, 2009, **631**, 189–195. https://doi.org/10.1016/j.aca.2008.10.032
4. P. Amiotte-suchet, N. Linglois, J. Leveque, and F. Andreux, *J. Hydrol.*, 2007, **335,** 354–363. https://doi.org/10.1016/j.jhydrol.2006.12.002
5. H. Gandhi, T. Wiegner, P. Ostrom, L. Kaplan, and N. Ostrom, *Rapid Commun. Mass Spectrom.*, 2004, **18**, 903–906. https://doi.org/10.1002/rcm.1426
6. P. J. Polissar, J. M. Fulton, C. K. Junium, C. C. Turich, and K. H. Freeman, *Anal. Chem.*, 2009, **81**, 755–763. https://doi.org/10.1021/ac801370c
7. K. Selvaraj, K. Y. Wei, K. K. Liu, and S. J. Kao, *Quat. Sci. Rev.*, 2012, **37**, 48-60. https://doi.org/10.1016/j.quascirev.2012.01.009
8. C. L. Osburn and G. St-Jean, *Limnol. Oceanogr. Methods*, 2007, **5**, 296–308. https://doi.org/10.4319/lom.2007.5.296
9. A. Barber, M. Sirois, G. Chaillou and Y. Gélinas, *Limnol. Oceanogr.*, 2017, **62,** S71–S84. https://doi.org/10.1002/lno.10666
10. B. S. K. Kumar, V. V. S. S. Sarma, and D. Cardinal, *Estuar. Coast. Shelf S.*, 2022, **276**, 108004. https://doi.org/10.1016/j.ecss.2022.108004
11. S. Q. Lang, M. D. Lilley, and J. I. Hedges, *Mar. Chem.*, 2007, **103**, 318–326. https://doi.org/10.1016/j.marchem.2006.10.002
12. E. Federherr, C. Cerli, F. M. S. A. Kirkels, K. Kalbitz, H. J. Kupka, R. Dunsbach, L. Lange, and T. C. Schmidt, *Rapid Commun. Mass Spectrom.*,2014, **28**, 2559–2573. https://doi.org/10.1002/rcm.7052
13. F. M. S. A. Kirkels, C. Cerli, E. Federherr, J. Gao, and K. Kalbitz, *Rapid Commun. Mass Spectrom.*, 2014, 28, 2574–2586. https://doi.org/10.1002/rcm.7053

14. H. Ogawa and N. Ogura, *Nature*, 1992, **356,** 696. https://doi.org/10.1038/356696a0
15. R. J. Panetta, M. Ibrahim, and Y. Gélinas, *Anal. Chem.*, 2008, **80**, 5232–5239. https://doi.org/10.1021/ac702641z
16. M. C. Carvalho, *Rapid Commun. Mass Spectrom.*, 2023, **37**, e9451. https://doi.org/10.1002/rcm.9451
17. P. Albéric, *Rapid Commun. Mass Spectrom.*, 2011, **25**, 3012–3018. https://doi.org/10.1002/rcm.5212
18. S. Q. Lang, S. M. Bernasconi, and G. L. Früh-Green, *Rapid Commun. Mass Spectrom.*, 2012, **26**, 9–16. https://doi.org/10.1002/rcm.5287
19. Y. Zhou, H. Guo, H. Lu, R. Mao, H. Zheng and J. Wang, *Rapid. Commun. Mass Spectrom.*, 2015, **29**, 1827–1835. https://doi.org/10.1002/rcm.7280
20. R. S. Hindshaw, S. Q. Lang, S.M. Bernasconi, T. H. E. Heaton, M. R. Lindsay and E. S. Boyd, *J. Geophys. Res-Biogeo.*, 2016, **121**, 1073–1085. https://doi.org/10.1002/2015JG003303
21. W. Zhang, Y. L. Zhang, F. Cao, Y. Xiang, Y. Zhang, M. Bao, X. Liu, and Y. C. Lin, *Atmos. Chem. Phys.*, 2019, **19**, 11071–11087. https://doi.org/10.5194/acp-19-11071-2019
22. G. R. Aiken, *Environ. Sci. Technol.*, 1992, **26,** 2435–2439. https://doi.org/10.1021/es00036a015
23. B. Fry, E. T. Peltzer, C. S. Hopkinson, A. Nolin, and L. Redmond, *Mar. Chem.*, 1996, **54,** 191–201. https://doi.org/10.1016/0304-4203(96)00031-X
24. S. Bouillon, M. Korntheuer, W. Baeyens, and F. Dehairs, *Limnol. Oceanogr: Methods*, 2006, **4**, 216–226. https://doi.org/10.4319/lom.2006.4.216
25. J. E. Bauer, R. I. Haddad, and D. J. Desmarais, *Mar. Chem.*, 1991, **33,** 335–351. https://doi.org/10.1016/0304-4203(91)90076-9
26. J. H. McKenna and P. H. Doering, *Mar. Chem.*, 1995, **48,** 109–114. https://doi.org/10.1016/0304- 4203(94)00049-J
27. F. Martineau, F. Fourel, A. M. Bodergat, and C. Lécuyer, *Chem. Geol.*, 2012, **291**, 236–240. https://doi.org/10.1016/j.chemgeo.2011.10.017
28. A. Porowski, *Isot. Environ. Healt. S.*, 2019, **55,** 41–55. https://doi.org/10.1080/10256016.2018.1561449
29. D. Paul, G. Skrzypek, and I. Forizs, *Rapid Commun. Mass Spectrom.*, 2007, **21**, 3006–3014. https://doi.org/10.1002/rcm.3185
30. T. B. Coplen, W. A. Brank, M. Gehre, M. Gröning, H. A. J. Meijer, B. Toman, and R. M. Verkouteren, *Anal. Chem.*, 2006, **78,** 2439–2441. https://doi.org/10.1021/ac052027c
31. Y. Jiang, Y. Hu, and M. Schirmer, *J. Hydrol.*, 2013, **478,** 157–168. https://doi.org/10.1016/j.jhydrol.2012.12.001
32. N. Suto and H. Kawashima, *Rapid Commun. Mass Spectrom.*, 2018, **32**, 1668–1674. https://doi.org/10.1002/rcm.8240
33. D. A. House, *Chem. Rev.*, 1962, **62**, 185–203. https://doi.org/10.1021/cr60217a001