

Supplementary Information

Speciation analysis of both inorganic and organic ^{129}I in seawater and its application in the study of marine iodine cycle

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A complete protocol is presented for the speciation analysis of ^{129}I for both inorganic and organic iodine in seawater using coprecipitation and solid-phase extraction (SPE) combined with accelerator mass spectrometry (AMS). The coprecipitation method for inorganic ^{129}I analysis used in this study was modified based on Luo et al.¹ and Xing et al.², while the SPE-DO ^{129}I method was developed according to a SPE dissolved organic matter (DOM) analytical method³⁻⁵. It is worth mentioning that during the oxidation of dissolved organic iodine (DOI) using $\text{K}_2\text{S}_2\text{O}_8$ ⁶, iodide and DOI in solution undergoes an intermediate stage in the form of I_2 and is then oxidized to iodate, and Cl^- will also be oxidized to Cl_2 . Under the acidic experiment environment, the solubility of Cl_2 is very low, and the release of gaseous Cl_2 from the solution to the air will carry a certain amount of I_2 to cause the loss of iodine. Therefore, to avoid the loss of iodine, a sealed environment is necessary during the oxidation process, and after the oxidation, the inner wall of the headspace part of the container should be fully infiltrated by shaking the solution to ensure that the escaped I_2 is redissolved into the liquid sample. The detailed experimental procedures are shown as follows:

1. Separation of iodide (I^-) from seawater by coprecipitation
 - a. Transfer seawater sample (0.5 ~ 2 L) to a beaker, and add 0.6 mg or 1.0 mg of $^{127}\text{I}^-$ carrier.
 - b. Add AgNO_3 (0.03 mol/L, up to the Ag^+ as 100 mg/L) slowly under stirring to coprecipitate iodide as AgI with AgCl and AgBr .
 - c. Stir for 45 min.
 - d. Settle the precipitate with seawater overnight in the dark, followed by decanting of the supernatant and centrifuging of the remaining slurry.
 - e. Wash the slurry with 3 ml 3 mol/L HNO_3 , 10 ml of Milli-Q water, 10 ml of 10% NH_4OH , and 10 ml of Milli-Q water step by step. After each washing step, a centrifugation process (3000 rpm for 10 min) is adopted to separate the precipitate and supernatant.
 - f. Dry the precipitate at 70 °C for 24 h, ground, add Nb powder with the $\text{AgI}:\text{Nb}$ mass ratio of 1:4, and finally press them into the aluminum holder for AMS measurement.
2. Removal of remaining iodide from seawater by coprecipitation (Reduce the cross-contamination)
 - a. Transfer the supernatant obtained from the previous step to a beaker, and add 2.0 mol/L Na_2SO_3 to the concentration of 0.3 mM.
 - b. Adjust the pH of seawater to about 4.0 by HNO_3 (0.5 mol/L).
 - c. Add AgNO_3 (0.03 mol/L, up to the Ag^+ as 100 mg/L) slowly under stirring to coprecipitate

iodide as AgI with AgCl, AgBr, and Ag₂SO₃.

- d. Stir for 45 min.
 - e. Settle the precipitate with seawater overnight in the dark, followed by decanting of the supernatant.
3. Separation of iodate (IO₃⁻) from seawater by coprecipitation
- a. Transfer the supernatant obtained from the previous step to a beaker, add 0.5 mL of 2.0 mol/L Na₂SO₃ and add 0.6 or 1.0 mg ¹²⁷I⁻ carrier.
 - b. Adjust the pH of seawater to about 1~2 by HNO₃ (60%) to accelerate the reduction of iodate to iodide.
 - c. Add AgNO₃ (0.03 mol/L, up to the Ag⁺ as 100 mg/L) slowly added under stirring to coprecipitate iodide as AgI with AgCl, AgBr, and Ag₂SO₃.
 - d. Stir for 45 min.
 - e. Settle the precipitate with seawater overnight in the dark, followed by decanting of the supernatant and centrifuging of the remaining slurry.
 - f. Wash the slurry with 3 ml 3 mol/L HNO₃, 10 ml of Milli-Q water, 10 ml of 10% NH₄OH, and 10 ml of Milli-Q water step by step. After each washing step, a centrifugation process (3000 rpm for 10 min) is adopted to separate the precipitate and supernatant.
 - g. Dry the precipitate at 70 °C for 24 h, ground, add Nb powder with the AgI:Nb mass ratio of 1:4, and finally press them into the aluminum holder for AMS measurement.
4. Separation of total inorganic iodine (TII) from seawater
- The treatment procedure for total inorganic iodine is the same as for iodate.
5. Separation of total iodine (TI) from seawater
- a. Transfer seawater sample (0.2 ~ 0.6 L) to a container, and add 0.6 mg of ¹²⁷I⁻ carrier.
 - b. Add K₂S₂O₈ to the sample to the concentration of 10 mg/g of seawater.
 - c. Adjust the pH of seawater to about 1~2 by HNO₃ (60%).
 - d. Seal the sample container.
 - e. Incubate the sample at 60 °C for 20 h.
 - f. Shake the sample to fully infiltrate the inner wall of the headspace part of the container.
 - g. Add Na₂SO₃ to the Na₂SO₃:K₂S₂O₈ mass ratio higher than 1:2.
 - h. The following steps are the same as the steps b ~ g of the separation of iodate from seawater.
6. Separation of dissolved organic iodine (DOI) from seawater

- Isolate DOI by the PPL SPE-DOI method developed in this study.
- Transfer an appropriate amount of aqueous DOI isolate to a glass centrifuge tube.
- The following steps are the same as the steps b ~ h of the separation of total iodine from seawater.

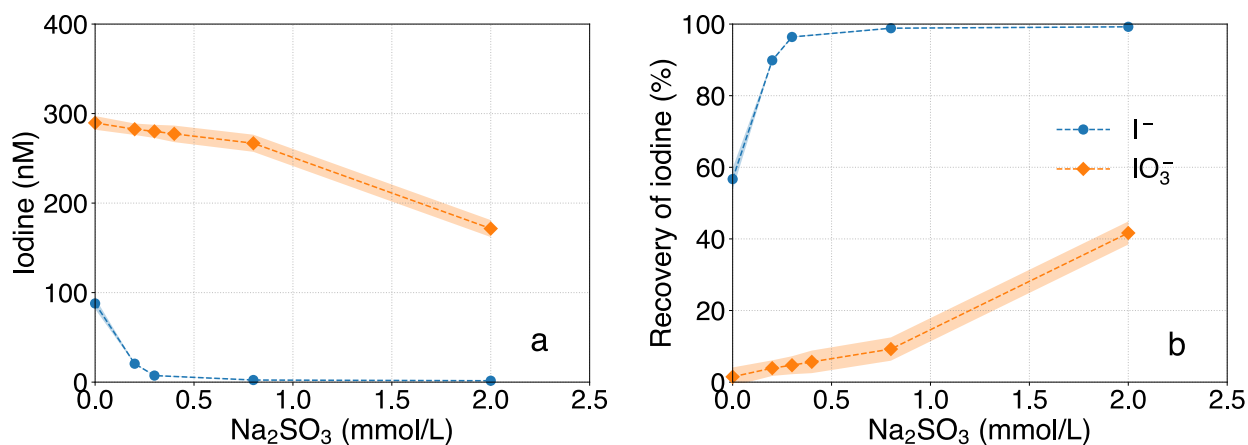


Figure S1. Influence of the Na_2SO_3 concentration on coprecipitation of iodine. (a) Iodine concentration in the supernatant and (b) calculated recovery of iodine in the precipitate. Experiment condition: ASW with pH ~ 5.0; 100 mg Ag^+ per liter of seawater. The x-axis represents

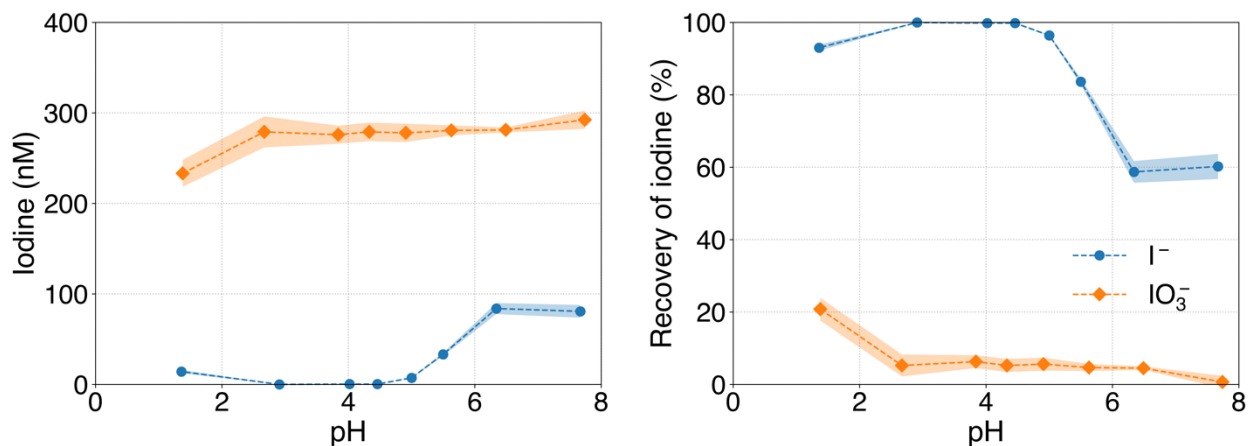


Figure S2. Influence of the pH on coprecipitation of iodine. (a) Iodine concentration in the supernatant and (b) calculated recovery of iodine in the precipitate. Experiment condition: 100 mg Ag^+ per liter of seawater; 0.3 mmol/L Na_2SO_3 . The shaded areas show the 1σ interval of variation curves based on the triple measurement of iodine in the supernatant.

Table S1. Iodine speciation results of surface seawater in the Tokyo Bay

Station	TI (nM)	T ¹²⁹ I (× 10 ⁷ atoms/L)	T ¹²⁹ I/T ¹²⁷ I (× 10 ⁻¹²)	TII (nM)	TI ¹²⁹ I (× 10 ⁷ atoms/L)	TI ¹²⁹ I/TI ¹²⁷ I (× 10 ⁻¹²)
St.61	400.6 ± 2.6	2.21 ± 0.07	92 ± 3	389.3 ± 2.6*	2.00 ± 0.09*	85 ± 4*
St.J	387.8 ± 2.1	2.43 ± 0.08	104 ± 3	366.5 ± 2.2*	2.28 ± 0.09*	103 ± 4*
TB09	400.3 ± 2.6	2.12 ± 0.08	88 ± 3	381.0 ± 2.6*	1.95 ± 0.10*	85 ± 4*
TB13	360.7 ± 3.0	2.29 ± 0.08	105 ± 4	311.1 ± 3.2*	2.10 ± 0.08*	112 ± 4*

Table S1. Continued

Station	I ⁻ (nM)	¹²⁹ I ⁻ (× 10 ⁷ atoms/L)	¹²⁹ I ⁻ / ¹²⁷ I ⁻ (× 10 ⁻¹²)	IO ₃ ⁻ (nM)	¹²⁹ IO ₃ ⁻ (× 10 ⁷ atoms/L)	¹²⁹ IO ₃ ⁻ / ¹²⁷ IO ₃ ⁻ (× 10 ⁻¹²)
St.61	188.6 ± 1.9	1.33 ± 0.03	117 ± 2	200.6 ± 3.2*	0.72 ± 0.02*	60 ± 1*
St.J	178.1 ± 1.9	1.46 ± 0.08	136 ± 7	188.4 ± 2.9*	0.68 ± 0.03*	60 ± 3*
TB09	191.0 ± 1.8	1.38 ± 0.03	120 ± 3	190.0 ± 3.2*	0.60 ± 0.03*	52 ± 2*
TB13	146.2 ± 2.4	1.36 ± 0.04	154 ± 4	164.9 ± 4.0*	0.60 ± 0.03*	60 ± 2*

Table S1. Continued

Station	SPE-DOI (nM)	SPE-DO ¹²⁹ I (× 10 ⁵ atoms/L)	SPE-DO ¹²⁹ I/DO ¹²⁷ I (× 10 ⁻¹²)	TI ¹²⁹ I + DO ¹²⁹ I/0.6 (× 10 ⁷ atoms/L)	¹²⁹ I ⁻ + ¹²⁹ IO ₃ ⁻ (× 10 ⁷ atoms/L)
St.61	6.8 ± 0.4	4.13 ± 0.32	101 ± 5	2.07 ± 0.09	2.06 ± 0.03
	7.1 ± 0.3	4.07 ± 0.26	96 ± 4		
St.J	7.7 ± 0.4	5.19 ± 0.35	113 ± 4	2.36 ± 0.09	2.14 ± 0.08
	8.2 ± 0.4	5.24 ± 0.39	106 ± 6		
TB09	6.9 ± 0.4	4.80 ± 0.30	115 ± 6	2.03 ± 0.10	1.98 ± 0.04
TB13	17.9 ± 0.9	9.53 ± 0.49	89 ± 4	2.26 ± 0.08	1.96 ± 0.05

* represents the evaluated value based on assuming the extraction efficiency of PPL SPE to be 60%

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