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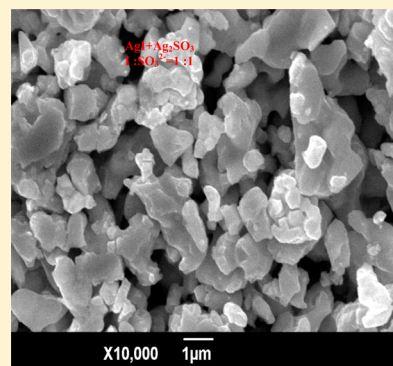
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Speciation Analysis of  $^{129}\text{I}$  in Seawater by Carrier-Free AgI–AgCl Coprecipitation and Accelerator Mass Spectrometric MeasurementMaoyi Luo,<sup>†,‡,||</sup> Xiaolin Hou,<sup>\*,‡,§</sup> Chaohui He,<sup>†</sup> Qi Liu,<sup>§</sup> and Yukun Fan<sup>§</sup><sup>†</sup>Department of Nuclear Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China<sup>‡</sup>Center for Nuclear Technologies, Technical University of Denmark, Risø Campus, 4000 Roskilde, Denmark<sup>§</sup>Xi'an AMS Center and SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

## Supporting Information

**ABSTRACT:** A rapid and simple method was developed for speciation analysis of  $^{129}\text{I}$  in seawater by selective coprecipitation of carrier-free iodide and accelerator mass spectrometry (AMS) measurement of  $^{129}\text{I}$ . Iodide was separated from seawater and other species of iodine by coprecipitation of AgI with  $\text{Ag}_2\text{SO}_3$ , AgCl, and AgBr by addition of only 100 mg/L  $\text{Ag}^+$  and 0.3 mmol/L  $\text{NaHSO}_3$  at pH 4.2–5.5. The separation efficiency of iodide was more than 95%, and crossover between  $^{129}\text{IO}_3^-$  and  $^{129}\text{I}^-$  fractions is less than 3%. Iodate and total inorganic iodine were converted to iodide by use of  $\text{NaHSO}_3$  at pH 1–2 and then separated by the same method as for iodide.  $\text{Ag}_2\text{SO}_3$  in the coprecipitate was removed by washing with 3 mol/L  $\text{HNO}_3$  and the excess AgCl and AgBr was removed by use of diluted  $\text{NH}_3$ , and finally a 1–3 mg precipitate was obtained for AMS measurement of  $^{129}\text{I}$ . The recovery of iodine species in the entire procedure is higher than 70%. Six seawater samples collected from the Norwegian Sea were analyzed by this method as well as a conventional anion-exchange chromatographic method; the results from the two methods show no significant difference ( $p = 0.05$ ). Because only one separation step and fewer chemicals are involved in the procedure, this method is suitable for operation on board sampling vessels, as it avoids the transport of samples to the laboratory and storage for a longer time before analysis, therefore significantly improving the analytical capacity and reliability of speciation analysis of  $^{129}\text{I}$ . This improvement can stimulate oceanographic tracer studies of  $^{129}\text{I}$ .



Chemical species of iodine play a key role in the geochemical cycle of iodine, which is related to the interaction of iodine between seawater and atmosphere and transfer of iodine among different environmental media. Meanwhile, iodine species are also related to climate changes and Earth's radiation budget, linking to the formation of primary particles in the marine boundary layer<sup>1,2</sup> and depletion of ozone in the troposphere through reaction between active iodine species and ozone.<sup>3</sup> Due to the multiple sources of iodine and conversion among iodine species in the environment, chemical speciation analysis of stable iodine cannot provide sufficient information for the investigation of geochemical cycle of iodine, which needs a new approach to identify and monitor the conversion of iodine species in the environment.

$^{129}\text{I}$  is a naturally occurring long-lived radioisotope of iodine ( $15.7 \times 10^6$  years) with a natural ratio of  $^{129}\text{I}/^{127}\text{I}$  less than  $1.5 \times 10^{-12}$  in marine system.<sup>4–6</sup>  $^{129}\text{I}$  in the current earth surface environment mainly originates from nuclear activities, including nuclear weapons testing, nuclear accidents, and discharges from nuclear facilities, and the  $^{129}\text{I}/^{127}\text{I}$  ratios have elevated to  $10^{-10}$ – $10^{-4}$  in the present environment.<sup>7–10</sup> Of all anthropogenic sources, marine discharges of  $^{129}\text{I}$  from reprocessing plants at Sellafield (U.K.) and La Hague (France) account for more than 90% of the total inventory of environmental  $^{129}\text{I}$ .

Due to long residence time ( $4 \times 10^5$  years) of iodine in the ocean, relatively long half-life, and continuous releases of  $^{129}\text{I}$  from two European reprocessing plants,  $^{129}\text{I}$  provides a unique tracer to study the circulation of seawater masses.<sup>11–19</sup> The specific species of  $^{129}\text{I}$  from the source make the anthropogenic  $^{129}\text{I}$  an ideal field tracer to investigate the conversion of chemical species of iodine, fluxes, and release mechanism of marine iodine to atmosphere.<sup>20,21</sup> Combined with knowledge obtained from stable iodine, comprehensive information on iodine biogeochemical behavior can be extracted from the information provided by  $^{129}\text{I}$  speciation analysis.

In open sea water, iodine predominantly exists as iodide ( $\text{I}^-$ ) and iodate ( $\text{IO}_3^-$ ) and minor organic iodine,<sup>22</sup> while organic iodine can be an important species in estuarine and coastal water.<sup>23</sup> Differential pulse polarography<sup>24,25</sup> and cathodic stripping voltammetry<sup>26</sup> are often used to measure iodate and iodide in seawater, respectively. Neutron activation analysis (NAA) combined with selective precipitation of iodide with silver and active charcoal trapping<sup>27</sup> and anion-exchange chromatography for separation of iodine species<sup>28</sup> have also

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been used for speciation analysis of stable iodine. Ion chromatography (IC) in combination with inductively coupled plasma mass spectrometry (ICP-MS) has recently been used for the measurement of iodide, iodate, and total iodine.<sup>29,30</sup> However, due to 4–12 orders of magnitude lower  $^{129}\text{I}$  concentration compared to stable iodine ( $^{127}\text{I}$ ) in environmental samples, all these methods cannot be directly used for speciation analysis of  $^{129}\text{I}$ .

A method for speciation analysis of  $^{129}\text{I}$  in environmental water samples has been reported. In this method, iodide and iodate were separated from water and from each other by anion-exchange chromatography based on the different affinities of iodide and iodate on anion-exchange resin. The separated iodide and iodate in each fraction were purified by solvent extraction, and  $^{129}\text{I}$  was finally measured by accelerator mass spectrometry (AMS) or radiochemical neutron activation analysis (RNAA).<sup>31</sup> This method is effective and has been successfully applied for the speciation analysis of  $^{129}\text{I}$  in seawater and rainwater samples.<sup>11,18–21,23,32</sup> However, the separation procedure of this method is time-consuming (4–20 h depending on the sample size) and not practically suitable for operation on board sampling vessels because of the complex and time-consuming procedures needed. Furthermore, purification and enrichment of iodine by solvent extraction requires adding  $^{127}\text{I}$  carrier, which might introduce a small amount of  $^{129}\text{I}$  to the samples. This therefore raises the analytical uncertainty, especially for samples with low  $^{129}\text{I}$  concentration, such as those collected in the deep sea and from the southern hemisphere with  $^{129}\text{I}/^{127}\text{I}$  close to or lower than  $1 \times 10^{-12}$ . A method that uses derivation of iodide and gas chromatography/mass spectrometry (GC-MS) measurement has recently been reported for speciation analysis of  $^{129}\text{I}$  in groundwater, but the method is only for samples with high  $^{129}\text{I}$  levels ( $^{129}\text{I}/^{127}\text{I}$  ratios as high as  $10^{-2}$ ) and small volumes (<50 mL), and it is also time-consuming.<sup>33</sup> To our knowledge, no simple method has been reported for rapid separation of carrier-free  $^{129}\text{I}$  species in environmental water samples with low  $^{129}\text{I}$  levels for  $^{129}\text{I}$  measurement that is suitable and convenient to be used on board sampling vessel. This work aims to develop a single-step procedure to separate carrier-free iodine species for speciation analysis of  $^{129}\text{I}$  in seawater.

## ■ EXPERIMENTAL SECTION

**Samples and Chemicals.** Seawater samples (100 L) were collected from the Kattegat (56°10' N, 11°50' E) on 10th December 2011 for method development. Six seawater samples were collected from the Norwegian Sea in May 2011 (Table S-1, Supporting Information) and analyzed for species of  $^{129}\text{I}$  for method validation. The collected seawater samples were filtered through a 0.45  $\mu\text{m}$  membrane and stored in polyethylene containers in the dark under normal laboratory conditions until analysis. Strongly basic anion-exchange resin (AG1-X4, 50–100 mesh, converted to  $\text{NO}_3^-$  form by use of  $\text{NaNO}_3$  before use) was purchased from Bio-Rad Laboratories (Richmond, CA).  $^{127}\text{I}$  carriers in NaI and  $\text{KIO}_3$  forms were from Merck KGaA (Germany); these two iodine reagents have been analyzed for  $^{129}\text{I}$  via AMS, and the measured  $^{129}\text{I}/^{127}\text{I}$  atomic ratios were lower than  $2 \times 10^{-13}$ . Another  $^{127}\text{I}$  carrier was prepared by dissolving iodine crystal ( $\text{I}_2$ ) (Woodward Company) in 0.4 mol/L NaOH solution. All other chemical reagents used were of analytical reagent grade, and all solutions were prepared with deionized water (18.2 M $\Omega$ ·cm).

## ■ Separation of Iodide from Seawater by Coprecipitation.

Seawater (100–1500 mL) was transferred to a beaker, and 0.01–30 mL of 1.0 mol/L  $\text{NaHSO}_3$ , 0–1000  $\mu\text{g}$  of [ $^{127}\text{I}$ ]iodide carrier (NaI), and 200 Bq of  $^{125}\text{I}^-$  and/or  $^{131}\text{IO}_3^-$  (for checking separation efficiency of iodide or iodate) were added.  $\text{HNO}_3$  (0.5 mol/L) was added to adjust the pH to 1.2–8.  $\text{AgNO}_3$  (46 mmol/L, 10–150 mg of  $\text{Ag}^+$ ) was slowly added under stirring to coprecipitate iodide as AgI. After the mixture was stirred for 0.1–2 h, the precipitate was separated by centrifugation or left to settle overnight in the dark, followed by decanting of the supernatant and centrifuge of the remaining slurry. The precipitate was rinsed with  $\text{H}_2\text{O}$  and the wash was combined with supernatant for iodate separation. The precipitate was sequentially washed with  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ , and 7.5%, 2.5%, and 1%  $\text{NH}_3\cdot\text{H}_2\text{O}$  to remove  $\text{Ag}_2\text{SO}_3$  and most AgCl and AgBr until 1–3 mg of precipitate remained.

## ■ Separation of Iodate and Total Inorganic Iodine by Coprecipitation.

To the supernatant and water washes from the iodide separation described in the previous section, or to 100–1000 mL of original seawater (for total inorganic iodine separation), 0–1000  $\mu\text{g}$  of [ $^{127}\text{I}$ ]iodate carrier ( $\text{KIO}_3$ ), 200 Bq of  $^{131}\text{IO}_3^-$ , and 0.01–20 mL of 1.0 mol/L  $\text{NaHSO}_3$  were added.  $\text{HNO}_3$  (6 mol/L) was added to pH 1–1.5 to convert iodate to iodide. A certain volume of 46 mmol/L  $\text{AgNO}_3$  (10–150 mg  $\text{Ag}^+$ ) was slowly added under stirring to coprecipitate iodide as AgI, and then the same procedure as for iodide separation was followed to remove  $\text{Ag}_2\text{SO}_3$  and most AgCl and AgBr in the precipitate to reduce the final coprecipitate to 1–3 mg. Figure S-1 (Supporting Information) shows a schematic diagram of the procedure for speciation analysis of  $^{129}\text{I}$ .

**Measurement of  $^{125}\text{I}$  and  $^{131}\text{I}$  by  $\gamma$  Spectrometry.**  $^{125}\text{I}$  and  $^{131}\text{I}$  in <20 mL of solution and precipitate were measured by NaI  $\gamma$  spectrometry (Canberra Industries Inc.) against the corresponding  $^{125}\text{I}$  or  $^{131}\text{I}$  standard prepared in the same geometry and sample medium. The NaI  $\gamma$  spectrometer consists of a  $3 \times 3$  in. well-type NaI(Tl) detector, a multichannel analyzer, and Genie 2000 software. The resolution of this system is about 55 keV for 662 keV  $\gamma$  ray of  $^{137}\text{Cs}$ , and a absolute counting efficiency of 30% for  $^{125}\text{I}$  (all X- ray and  $\gamma$  peaks together from 26 to 36 keV).

**AMS Measurement of  $^{129}\text{I}$ .** The separated iodine species as AgI or AgI–AgCl in the coprecipitate form were dried at 60–70  $^\circ\text{C}$ , ground to fine powder, and mixed with Nb powder (325 mesh) at a mass ratio of 1:3, which were then pressed into a copper holder for AMS measurement of  $^{129}\text{I}/^{127}\text{I}$  in a 3 MV AMS system (HVEE) in the Xi'an AMS Center. A detailed description of the AMS system and measurement method for  $^{129}\text{I}/^{127}\text{I}$  ratio has been reported elsewhere.<sup>34,35</sup>

## ■ RESULTS AND DISCUSSION

A coprecipitation method has been reported to separate carrier-free iodine from trap solution from combustion of solid sample and fresh water.<sup>34,35</sup> In this case, iodine was converted to iodide and coprecipitated as AgI–AgCl after addition of a suitable amount of chloride and an excess amount of  $\text{AgNO}_3$ . For seawater, due to high concentrations of chloride and bromide (up to 19.9 g/L and 68.9 mg/L, respectively), a huge amount of precipitate will be formed when  $\text{AgNO}_3$  was added. For 1 L of seawater, more than 95 g of  $\text{AgNO}_3$  has to be added to completely precipitate  $\text{I}^-$  with  $\text{Cl}^-$  and  $\text{Br}^-$ , and up to 81 g of coprecipitate will be formed. This makes it impossible to effectively separate a tiny amount of AgI from the huge amount of AgCl to prepare a few milligrams of coprecipitate of AgI with

AgCl for AMS measurement of  $^{129}\text{I}$ . Meanwhile, this method is also not practically useful for separation of iodine from seawater for radioiodine (e.g.,  $^{131}\text{I}$ ,  $^{133}\text{I}$ ) measurement, because of the high cost of large amounts of  $\text{AgNO}_3$ .

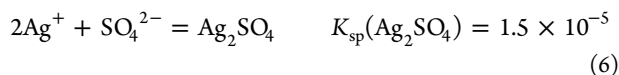
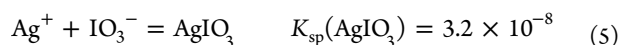
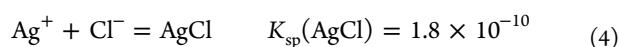
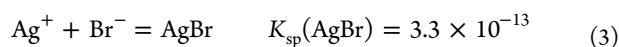
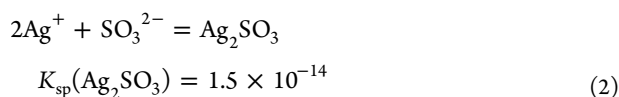
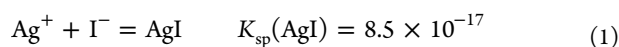
Due to much lower  $K_{\text{sp}}$  of AgI compared to AgBr and AgCl, a prior precipitation of AgI compared to AgCl and AgBr might occur when  $\text{AgNO}_3$  was added to seawater. The experiment showed that less than 50% of iodide was precipitated when 50 mg of  $\text{Ag}^+$  was added to 500 mL of seawater, and increasing  $\text{Ag}^+$  to 100 mg and reducing the pH of the solution from 6 to 1 could not significantly increase the recovery of iodide in the precipitate (Table 1). The major reactions involving in the

**Table 1. Effects of Concentrations of  $\text{NaHSO}_3$  and  $\text{Ag}^+$  on the Separation of Iodine by Coprecipitation of AgI–AgCl–AgBr<sup>a</sup>**

	$\text{NaHSO}_3$ (mmol/L)	$\text{I}^-$ added ( $\mu\text{g}$ )	$\text{Ag}^+$ added (mg)	pH	recovery <sup>b</sup> (%)
1	0	0	50	6.0–7.0	$37.29 \pm 4.16$
2	0	0	50	1.0–2.0	$43.00 \pm 3.79$
3	0	0	100	1.0–2.0	$39.09 \pm 4.96$
4	0	20	50	1.0–2.0	$42.73 \pm 3.15$
5	0	100	50	1.0–2.0	$55.45 \pm 4.88$
6	0	500	50	1.0–2.0	$78.93 \pm 2.86$
7	0	1000	50	1.0–2.0	$84.99 \pm 3.41$
8	0.30	0	10	1.0–2.0	$18.90 \pm 2.12$
9	0.30	0	30	1.0–2.0	$92.45 \pm 2.33$
10	0.30	0	50	1.0–2.0	$97.23 \pm 2.92$

<sup>a</sup>Values are average  $\pm$  SD,  $n = 3$ , 500 mL of seawater. <sup>b</sup> $^{125}\text{I}^-$  was spiked to the seawater, and the recoveries were obtained by measurement of  $^{125}\text{I}$  in the supernatant and seawater before precipitation.

coprecipitation processes when  $\text{Ag}^+$  is added to seawater and their corresponding solubility products ( $K_{\text{sp}}$ ) are listed in eqs 1–6:

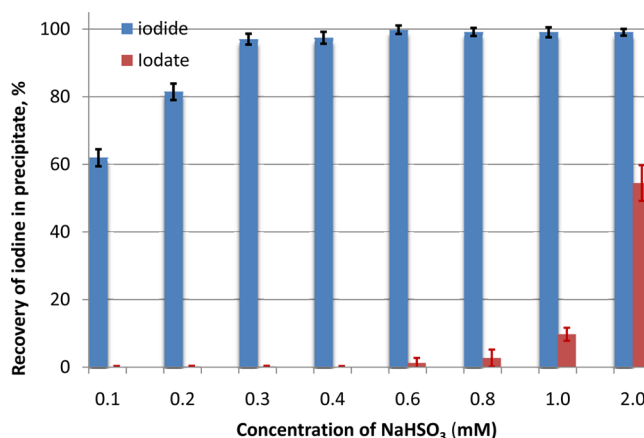


A simulation using Visual MINTEQ (an equilibrium speciation model, <http://www2.lwr.kth.se/english/OurSoftware/vminteq/index.html>) also showed that less than 50% of iodide can be precipitated from seawater when  $\text{Ag}^+$  concentration is lower than 1000 mg/L (Figure S-2, Supporting Information). With the addition of iodide carrier ( $^{127}\text{I}$ ) to the seawater, the recovery of iodide in the precipitate increased, and up to 85% of iodide could be precipitated when 1000  $\mu\text{g}$  of iodide was added to 500 mL of seawater (Table 1). However, for analysis of seawater with ultralow levels of  $^{129}\text{I}$ , such as deep seawater or seawater from the southern hemisphere and

equator, addition of  $^{127}\text{I}$  carrier is not expected, because it will increase the analytical uncertainty by introducing external  $^{129}\text{I}$  from the  $^{127}\text{I}$  carrier to the sample.

Due to the relatively high  $K_{\text{sp}}$  of  $\text{AgIO}_3$  compared to AgI, AgCl, and AgBr,  $\text{AgIO}_3$  could not be completely coprecipitated with AgCl and AgCl, and so iodate has to be reduced to iodide before precipitation for determination of  $^{129}\text{I}$  in iodate and total inorganic iodine forms.  $\text{NaHSO}_3$  is a commonly used reductant for reducing iodate to iodide in acidic media. Surprisingly, when  $\text{NaHSO}_3$  was added to seawater (to 0.3 mmol/L), the recovery of iodine in the precipitate significantly increased up to 97% after addition of 50 mg of  $\text{Ag}^+$  even without  $^{127}\text{I}$  carrier (Table 1). Although the increase in  $\text{Ag}^+$  amount from 10 to 50 mg added to 500 mL of seawater could increase the recovery of iodide from 19% to 97% (Table 1), it is clear that  $\text{NaHSO}_3$  is the key factor for coprecipitation of AgI, because without addition of  $\text{NaHSO}_3$ , only a maximum of 50% of iodide could be coprecipitated even when 200 mg/L  $\text{Ag}^+$  was added and pH was reduced to 1. In acidic media, both iodide and iodate will be coprecipitated due to reduction of iodate to iodide. It is interesting that when the pH value of seawater is higher than 5, carrier-free iodide can still be coprecipitated, while iodate remains in the water phase without reduction to iodide and coprecipitation with AgI. These results reveal that iodide can be selectively coprecipitated under suitable conditions. Concentration of  $\text{NaHSO}_3$ , pH value of solution, and amount of  $\text{Ag}^+$  are key parameters for separation of carrier-free iodide and iodate in seawater by coprecipitation.

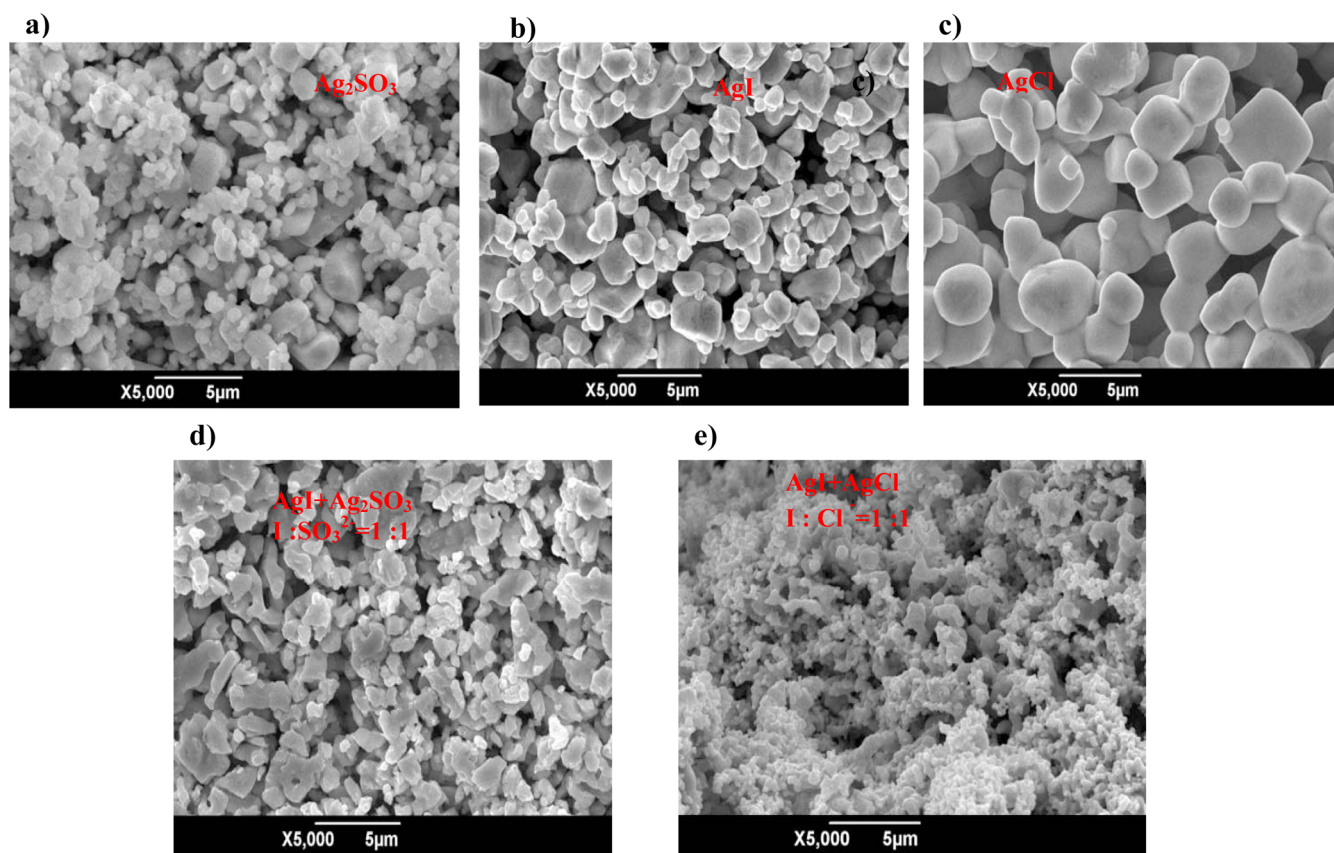
**Influence of  $\text{NaHSO}_3$  on Coprecipitation of Carrier-Free Iodide and Iodate from Seawater.** The results (Figure 1) show that, at pH 4.7 and with addition of 100 mg/L  $\text{Ag}^+$  to



**Figure 1.** Effect of  $\text{NaHSO}_3$  concentration added to the solution on the precipitation of iodide and iodate (solution: 500 mL of seawater no. 7 spiked with 200 Bq of  $^{125}\text{I}^-$  and 200 Bq of  $^{131}\text{IO}_3^-$ , 50 mg  $\text{Ag}^+$ , pH 4.7).

seawater, the recovery of iodide in the precipitate increased from 62% to 97% when the concentration of  $\text{NaHSO}_3$  was increased from 0.10 to 0.30 mmol/L, and to more than 99% when the concentration of  $\text{NaHSO}_3$  was  $\geq 0.60$  mmol/L. However, when the concentration of  $\text{NaHSO}_3$  was increased to  $\geq 0.60$  mmol/L, some iodate was also precipitated, and the iodate in the precipitate increases with increasing concentration of  $\text{NaHSO}_3$ . Fifty-five percent of iodate could be coprecipitated when  $\text{NaHSO}_3$  concentration increased to 2.0 mmol/L. Therefore, the optimal concentrations of  $\text{NaHSO}_3$  for speciation analysis of  $^{129}\text{I}$  in seawater are 0.3–0.60 mmol/L.





**Figure 2.** Images of scanning electron microscope for precipitates of (a)  $\text{Ag}_2\text{SO}_3$ , (b)  $\text{AgI}$ , (c)  $\text{AgCl}$ , (d)  $\text{AgI-Ag}_2\text{SO}_3$  ( $\text{I}^-/\text{SO}_3^{2-}$  mol ratio 1:1), and (e)  $\text{AgI-AgCl}$  ( $\text{I}^-/\text{Cl}^-$  mol ratio 1:1).

Under this condition, more than 97% of iodide can be precipitated from seawater while crossover of iodate to the coprecipitate is less than 3%.

Although chloride and bromide are chemically similar to iodide, sulfite shows a strong influence on coprecipitation of iodide, which might be related to the formation of crystals of  $\text{AgI}$ ,  $\text{Ag}_2\text{SO}_3$ ,  $\text{AgCl}$ , and  $\text{AgBr}$ . From scanning electron microscopic images of the precipitates of  $\text{Ag}_2\text{SO}_3$ ,  $\text{AgI}$ , and  $\text{AgCl}$  (Figure 2) and counting of the size distribution of  $\text{AgCl}$ ,  $\text{AgI}$ , and  $\text{Ag}_2\text{SO}_3$  crystals in individual precipitates (Figure S3, Supporting Information), it was observed that the size of  $\text{Ag}_2\text{SO}_3$  crystals (mainly  $0.5\text{--}1.5\text{ }\mu\text{m}$ ) is similar to that of  $\text{AgI}$  (mainly  $0.5\text{--}2.0\text{ }\mu\text{m}$ ), but much smaller than that of  $\text{AgCl}$  (mainly  $1.5\text{--}4.5\text{ }\mu\text{m}$ ). In addition, the image of a mixture of  $\text{AgI-Ag}_2\text{SO}_3$  (with molecular ratio of 1:1, Figure 2d) shows a much more homogeneous distribution of the crystals compared to  $\text{AgI-AgCl}$  mixture (Figure 2e). In seawater, iodine concentration is normally  $<0.50\text{ }\mu\text{mol/L}$  and the  $\text{AgI}$  could not form a sufficient amount of particles to be precipitated from the solution. It is therefore important to determine if it can form a coprecipitate with other compounds or be adsorbed and carried by other precipitate (formed particles) to be able to separate it from the seawater. The similar size distribution of  $\text{AgI}$  crystal (particles) and  $\text{Ag}_2\text{SO}_3$  might favor the formation of mixed crystals of  $\text{AgI}$  and  $\text{Ag}_2\text{SO}_3$  and coprecipitation of iodide from seawater when a sufficient amount of  $\text{Ag}_2\text{SO}_3$  is formed. The larger size of the crystals of  $\text{AgCl}$  and  $\text{AgBr}$  (not shown) precipitates might prevent them from forming a homogeneous mixture of crystals with  $\text{AgI}$ . This might explain why a low

recovery of  $\text{AgI}$  was obtained in the coprecipitate of  $\text{AgI}$  when  $\text{NaHSO}_3$  was not added.

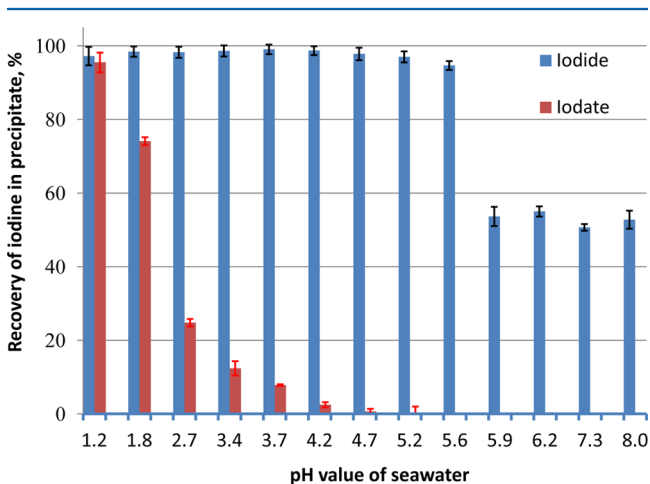
The lower recovery of iodide at lower  $\text{NaHSO}_3$  concentrations might be attributed to insufficient  $\text{Ag}_2\text{SO}_3$  precipitate formed during coprecipitation and to the competition of chloride and bromide with sulfite during the formation of precipitate. When the concentration of  $\text{NaHSO}_3$  is  $<0.20\text{ mmol/L}$ , which is more than 3 orders of magnitude lower than that of chloride and about 5 times lower than that of bromide, the excess amount of chloride and bromide will compete with sulfite to form precipitate with insufficient amount of  $\text{Ag}^+$ , causing insufficient  $\text{Ag}_2\text{SO}_3$  formed in the seawater to carry  $\text{AgI}$  into precipitate.

The  $K_{\text{sp}}$  of  $\text{AgIO}_3$  ( $3.2 \times 10^{-8}$ ) is much higher than that of  $\text{Ag}_2\text{SO}_3$ ,  $\text{AgBr}$ , and  $\text{AgCl}$ , and therefore  $\text{AgIO}_3$  should not be precipitated prior to  $\text{AgCl}$  and  $\text{AgBr}$ . However, it was observed that when the  $\text{NaHSO}_3$  concentration increases, a significant amount of iodate (up to 53%) enters the precipitate. This might be attributed to the reduction of iodate to iodide when  $\text{NaHSO}_3$  concentration was increased. Sulfite is a strong reductant that can reduce iodate to iodide in acidic solution. This reduction reaction is concentration-dependent; the increased  $\text{NaHSO}_3$  concentration can therefore reduce iodate to iodide in slightly acidic solution of pH 4–5. This assumption was confirmed by anion-exchange separation of species of iodine in the treated seawater.  $\text{NaHSO}_3$  was added to a seawater sample spiked with  $^{125}\text{IO}_3^-$  to a concentration of  $2.0\text{ mmol/L}$ , the solution was loaded on an anion-exchange column, and the column was washed with  $0.2\text{ mol/L NaNO}_3$ . Only about 50% of the total  $^{125}\text{I}$  spiked to the seawater was

observed in the effluent and wash, indicating reduction of about 50% of iodate in the seawater.

During reduction of iodate to iodide, sulfite will be oxidized to sulfate ( $\text{SO}_4^{2-}$ ). Although sulfate can also form a precipitate with  $\text{Ag}^+$ , the high solubility product of  $\text{Ag}_2\text{SO}_4$  ( $K_{\text{sp}} = 1.5 \times 10^{-5}$ ) compared to those of  $\text{AgCl}$  and  $\text{Ag}_2\text{SO}_3$  prevents the formation of  $\text{Ag}_2\text{SO}_4$  in the seawater when  $\text{Ag}^+$  and  $\text{SO}_4^{2-}$  concentrations are low. Our experimental results have shown that addition of  $\text{Na}_2\text{SO}_4$  to seawater instead of  $\text{NaHSO}_3$  did not improve the recovery of iodide in the precipitate; this confirmed insignificant influence of sulfate on the coprecipitation of  $\text{AgI}$ .

**Influence of pH Values on Coprecipitate Separation of Carrier-Free Iodide and Iodate.** Figure 3 shows the



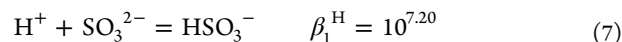
**Figure 3.** Effect of pH value of the solution on the precipitation of iodide and iodate. (solution: 500 mL of seawater no. 7 spiked with 200 Bq of  $^{125}\text{I}$  and 200 Bq of  $^{131}\text{IO}_3^-$ , 50 mg  $\text{Ag}^+$ , 0.30 mmol/L  $\text{NaHSO}_3$ ).

variation of recovery of iodide in the coprecipitate with pH value of the seawater. At  $\text{NaHSO}_3$  concentration of 0.30 mmol/L and addition of 50 mg of  $\text{Ag}^+$  to 500 mL of seawater, more than 95% of iodide was coprecipitated when the pH value of the seawater was lower than 5.6. The recoveries of iodide in the coprecipitate decrease significantly to about 50% when the pH value of seawater increased to more than 5.9. Iodate was also coprecipitated when pH value of the seawater was lower than 4.2, and iodate in the precipitate increases with decreasing pH value. When the seawater was acidified to  $\text{pH} < 1.2$ , more than 95% of iodate in the seawater was coprecipitated. For speciation analysis of  $^{129}\text{I}$ , the pH value of the seawater should be adjusted to 4.2–5.5 with an optimal value of 5.0.

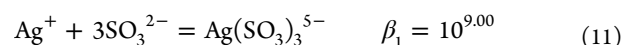
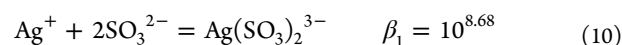
The increased amount of iodate observed in the coprecipitate with decreased pH of seawater can be attributed to the reduction of iodate to iodide in the acidic medium because of addition of sulfite. The reduction capacity of sulfite increased with decreasing pH of solution. It has been found that, in a solution of  $\text{pH} < 2$ , sulfite can rapidly reduce iodate to iodide. This was also confirmed by anion-exchange chromatography. Seawater sample spiked with  $^{125}\text{IO}_3^-$  was adjusted to  $\text{pH} 1.0$  after addition of  $\text{NaHSO}_3$  to 0.4 mmol/L and loaded on a strong anion-exchange column. No  $^{125}\text{I}$  was measured in the effluent, indicating all iodate was reduced to iodide, which was adsorbed on the column.

The significantly reduced recoveries of iodide in the precipitate at higher pH values of seawater might be attributed

to the difficulties in formation of  $\text{Ag}_2\text{SO}_3$  at higher pH. In the solution, sulfite shows a weak acid, which can hydrolyze to  $\text{HSO}_3^-$  and  $\text{H}_2\text{SO}_3$ , and the different species of sulfite and its hydrolysis products will reach equilibrium at a given pH. The sulfite and its hydrolysis product in solution were not measured in this work. Based on the formation constants<sup>36</sup> of these hydrolysis products ( $\beta_1^{\text{H}} = [\text{HSO}_3^-]/[\text{H}^+][\text{SO}_3^{2-}]$ ), the distributions of different species of sulfite with pH were calculated by use of Visual MINTEQ software (Figure S-4, Supporting Information).

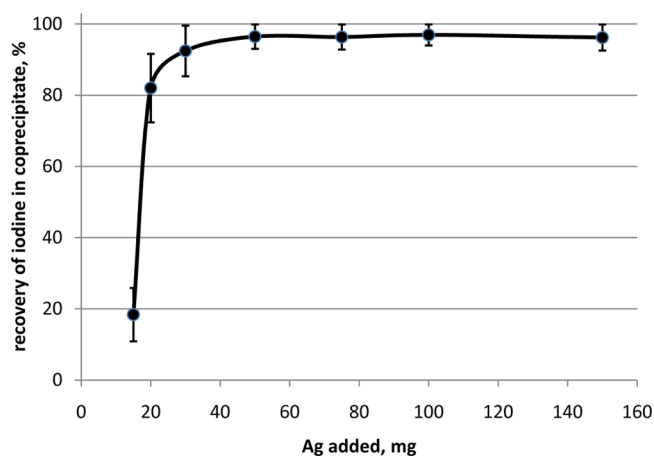


At  $\text{pH} > 4$ , only  $\text{SO}_3^{2-}$  and  $\text{HSO}_3^-$  exist, while at  $\text{pH} < 4$ , only  $\text{H}_2\text{SO}_3$  and  $\text{HSO}_3^-$  exist. Therefore, high pH should favor the formation of  $\text{Ag}_2\text{SO}_3$ . However, with increasing concentration of  $\text{SO}_3^{2-}$ ,  $\text{Ag}^+$  can form soluble complexes with  $\text{SO}_3^{2-}$ , such as  $\text{AgSO}_3^-$ ,  $\text{Ag}(\text{SO}_3)_2^{3-}$ , and  $\text{Ag}(\text{SO}_3)_3^{5-}$ . These formation reactions and their formation constants<sup>37</sup> (e.g.,  $\beta_1 = [\text{AgSO}_3^-]/[\text{Ag}^+][\text{SO}_3^{2-}]$ ) are shown in eqs 9–11.



On the basis of the above theoretical calculation, it can be proposed that the significantly reduced recovery of iodide in precipitate for  $\text{pH} > 5.8$  might be attributed to the increased fraction of soluble complex of  $\text{Ag}^+$  and  $\text{SO}_3^{2-}$ ; consequently  $\text{Ag}_2\text{SO}_3$  precipitate decreased in the seawater, causing less  $\text{AgI}$  to be carried to the precipitate. It should be mentioned that  $\text{NaHSO}_3$  is not stable in acidic solution, and decomposed to sulfate. Therefore the solution should be adjusted to  $\text{pH} 1$ –2 when inorganic iodine (both iodide and iodate) is separated by coprecipitation to prevent the decomposition of most sulfite and formation of less  $\text{Ag}_2\text{SO}_3$  in high acidic solution.

**Influence of Amount of  $\text{Ag}^+$  and Coprecipitation Process.** The recoveries of iodide in the coprecipitate increased with increasing amount of  $\text{Ag}^+$  added to seawater up to 80 mg/L. (Figure 4). To seawater containing 0.30 mmol/L



**Figure 4.** Influence of the amount of  $\text{Ag}^+$  added on the coprecipitation of iodide (solution: 1000 mL of seawater no. 7 spiked with 200 Bq of  $^{125}\text{I}^-$ , 0.30 mmol/L  $\text{NaHSO}_3$ ,  $\text{pH} 5.0$ ).

**Table 2.** Comparison of Analytical Results for  $^{129}\text{I}$  Species in Seawater from Norwegian Sea by Coprecipitation (Method 1) and Ion-Exchange Chromatography (Method 2)<sup>a</sup>

sample	total inorganic $^{129}\text{I}$ , $\times 10^6$ atoms/L		$^{129}\text{I}^-$ , $\times 10^6$ atoms/L		$^{129}\text{IO}_3^-$ , $\times 10^6$ atoms/L		sum of $^{129}\text{I}^-$ and $^{129}\text{IO}_3^-$ , $\times 10^6$ atoms/L	
	method 1	method 2	method 1	method 2	method 1	method 2	method 1	method 2
SW-1	76.2 $\pm$ 2.4	74.1 $\pm$ 2.2	7.7 $\pm$ 1.5	8.2 $\pm$ 1.6	66.5 $\pm$ 2.1	65.2 $\pm$ 2.8	74.2 $\pm$ 2.6	73.4 $\pm$ 2.5
SW-2	102.1 $\pm$ 3.4	99.9 $\pm$ 3.1	23.1 $\pm$ 0.9	24.1 $\pm$ 0.9	78.9 $\pm$ 3.1	78.2 $\pm$ 2.6	102.0 $\pm$ 3.2	102.3 $\pm$ 2.8
SW-3	123.1 $\pm$ 3.7	119.5 $\pm$ 3.4	35.0 $\pm$ 4.4	35.2 $\pm$ 5.5	89.1 $\pm$ 6.9	90.2 $\pm$ 5.3	124.1 $\pm$ 5.3	125.4 $\pm$ 6.2
SW-4	142.3 $\pm$ 4.5	138.5 $\pm$ 3.8	23.1 $\pm$ 3.7	29.5 $\pm$ 4.6	117.2 $\pm$ 8.8	110.2 $\pm$ 4.9	143.3 $\pm$ 5.3	139.7 $\pm$ 5.7
SW-5	251.3 $\pm$ 7.7	248.7 $\pm$ 6.7	66.8 $\pm$ 14.7	73.8 $\pm$ 18.5	184.3 $\pm$ 8.6	174.2 $\pm$ 9.0	251.1 $\pm$ 15.7	248.0 $\pm$ 19.1
SW-6	249.2 $\pm$ 7.6	247.4 $\pm$ 6.7	67.9 $\pm$ 10.1	69.8 $\pm$ 13.5	179.6 $\pm$ 7.9	180.4 $\pm$ 7.1	247.5 $\pm$ 12.8	250.2 $\pm$ 15.1

<sup>a</sup>All data are presented as average  $\pm$  1 SD of six measurements. *t*-Test of the pairs of results by two methods shows no significant difference between two methods at  $p = 0.05$  ( $t < 2$ ).

L  $\text{NaHSO}_3$  and at pH 5.0, about 96% of iodide was coprecipitated when 100 mg/L  $\text{Ag}^+$  was added. Due to the high excess of  $\text{Cl}^-$  and  $\text{Br}^-$  in seawater compared to  $\text{Ag}^+$  added, the amount of precipitate is proportional to the amount of  $\text{Ag}^+$  added to the sample. The small quantity of precipitate in a large volume of seawater (>500 mL) will cause a significant loss of  $\text{AgI}$  during separation of precipitate due to adsorption of precipitate on the wall of the centrifuge tube as well as plastic pipet. Therefore 100 mg/L  $\text{Ag}^+$  is chosen for separation of iodine species from less than 1 L of seawater.

It was observed that the concentration of  $\text{AgNO}_3$  added to seawater has a strong influence on the composition of the coprecipitate and recovery of iodide. When a relatively higher concentration of  $\text{AgNO}_3$  (>0.5 mol/L) was used, the corresponding small volume of  $\text{AgNO}_3$  solution (<2 mL of  $\text{AgNO}_3$  to 500 mL of seawater) added to the seawater will cause formation of a large fraction of  $\text{AgCl}$  in the coprecipitate and a significantly low recovery of iodide, down to less than 30%. This is because  $\text{Ag}^+$  added to the seawater will immediately be consumed by excess  $\text{Cl}^-$  in the local area to form  $\text{AgCl}$  before it is completely mixed in the seawater, and iodide homogeneously distributed in seawater could not contact well with  $\text{Ag}^+$  ion to form  $\text{AgI}$ . Therefore a diluted  $\text{AgNO}_3$  solution of 46 mmol/L (5 mg/mL  $\text{Ag}^+$ ) was applied in this work. In this case, 20 mL of diluted  $\text{AgNO}_3$  should be added to 1.0 L of seawater under stirring, which significantly improved the coprecipitation of  $\text{AgI}$  with  $\text{Ag}_2\text{SO}_3$  and ensured a high recovery of iodide in the coprecipitate.

It was observed that only 60% of iodide was recovered when the precipitate was separated 10 min after addition of  $\text{AgNO}_3$ , and the recovery of iodide increases with extended time of stirring after addition of  $\text{AgNO}_3$ . When the stirring time was extended to 45 min, the recovery of iodide increased to more than 95%. This might be attributed to the slow process of adsorption of a tiny amount of  $\text{AgI}$  (<120  $\mu\text{g}$ ) onto  $\text{Ag}_2\text{SO}_3$  and  $\text{AgCl}$  precipitates. When the seawater was stirred for more than 3 h, a decreased recovery of iodide in precipitate was obtained; this might be attributed to the decomposition of  $\text{AgI}$  and  $\text{Ag}_2\text{SO}_3$  during long time stirring and exposure to light.

Direct centrifuge and settling overnight (10–15 h) were tested for separation of the precipitate from supernatant and the results show that both methods can be used, although a slightly higher recovery of iodide was obtained by direct centrifugation (>95%) compared to the settling method (>93%). In the settling method, after stirring, the solution was kept in the dark overnight, the supernatant was decanted, and the slurry was then centrifuged to separate the precipitate. The slightly higher loss of iodide in the settling method can be

attributed to the decanting step; a small amount of precipitate might be lost during decanting of the supernatant. Settling and decanting followed by centrifugation might be a suitable method for handling large numbers of samples, especially to treat a large volume of seawater (>1 L). However, the direct centrifugation method is suitable for handling samples less than 250 mL with a large centrifuge.

On the basis of the results and discussion presented above, it is therefore recommended that diluted  $\text{AgNO}_3$  (25–75 mmol/L) should be slowly added to seawater that has been spiked with  $^{125}\text{I}^-$  and  $\text{NaHSO}_3$  to 0.2–0.4  $\mu\text{mol/L}$  and adjusted to pH 4.2–5.5 during stirring, and the solution should be stirred for 45–60 min before centrifugation or settling.

#### Preparation of Target for AMS Measurement of $^{129}\text{I}$ .

For AMS measurement of  $^{129}\text{I}$ ,  $\text{AgI}$  or coprecipitate of  $\text{AgI}$ – $\text{AgCl}$ – $\text{AgBr}$  is mixed with niobium or silver powder in a mass ratio of 1:3 and pressed into a target holder.<sup>34</sup> Due to the fact that only 1–2 mg of precipitate is required to be pressed in the target holder for AMS measurement, the  $\text{AgI}$  in the obtained coprecipitate of more than 130 mg has to be separated from other precipitates, especially  $\text{Ag}_2\text{SO}_3$  and  $\text{AgCl}$ . Otherwise only a very small percentage of  $\text{AgI}$  in the coprecipitate can be directly used for AMS measurement, consequently resulting in reduced signal intensity for  $^{127}\text{I}$  current and  $^{129}\text{I}$  counts. Because  $\text{Ag}_2\text{SO}_3$  is not stable in acidic solution, it can be easily decomposed and removed by washing the coprecipitate with  $\text{HNO}_3$ . Our experiment showed that  $\text{Ag}_2\text{SO}_3$  can be completely dissolved in  $\text{HNO}_3$  solution of >1 mol/L, while precipitates of  $\text{AgI}$ ,  $\text{AgCl}$ , and  $\text{AgBr}$  are stable and remained in the precipitate after acid wash. It is well-known that precipitates of  $\text{AgCl}$  and  $\text{AgBr}$  are soluble in ammonium solution, while  $\text{AgI}$  cannot be dissolved, even in concentrated ammonium. However if concentrated ammonium is used,  $\text{AgCl}$  and  $\text{AgBr}$  are rapidly dissolved, which will cause an invisible amount of  $\text{AgI}$  to be obtained. This might be attributed to the very small amount of iodine (<65  $\mu\text{g/L}$ ) in seawater compared to  $\text{Cl}$  and  $\text{Br}$ . To obtain a suitable amount of coprecipitate (1–3 mg) for AMS measurement, sequential washing of the coprecipitate was employed with 7.5%, 2.5%, and 1% ammonium. By this process, the amount of coprecipitate can be reduced to 1–3 mg without significant loss of  $\text{AgI}$ . The overall recovery of 70–85% for iodide has been obtained with  $^{125}\text{I}$  tracer. This indicates  $\text{AgI}$  remained during washing with different concentrations of ammonium, while most  $\text{AgCl}$  and  $\text{AgBr}$  was removed. The composition of the final obtained coprecipitate depends on the amount of the coprecipitate but should be a mixture of  $\text{AgI}$ ,  $\text{AgBr}$ , and  $\text{AgCl}$ .



**Speciation Analysis of  $^{129}\text{I}$  in Seawater by the Developed Method.** Because certified reference material of seawater for chemical species of  $^{129}\text{I}$  is not available, the developed method was validated by analysis of six seawater samples collected from the Norwegian Sea by both the developed method and the conventional anion-exchange chromatography method (see Supporting Information for detailed separation procedure).<sup>20,31</sup>  $^{129}\text{I}$  in the iodide, iodate, and total inorganic forms separated by two methods as  $\text{AgI}$ – $\text{AgCl}$  or  $\text{AgI}$  were measured by AMS.

The concentrations of total inorganic  $^{129}\text{I}$ ,  $^{129}\text{I}^-$ ,  $^{129}\text{IO}_3^-$ , and the sum of  $^{129}\text{I}^-$  and  $^{129}\text{IO}_3^-$  obtained by the two methods are presented in Table 2, which shows excellent agreement between the analytical results for  $^{129}\text{I}$  species obtained by the developed coprecipitation method and those obtained by the conventional anion-exchange chromatographic method ( $p < 0.05$  for  $t$  test). This confirms that the method presented here is reliable and suitable for speciation analysis of carrier-free  $^{129}\text{I}$  in seawater.

In comparison with the previous reported method for  $^{129}\text{I}$  speciation analysis using anion-exchange chromatography, the major advantages of the method presented here are as follows: (1) ability to separate carrier-free  $^{129}\text{I}$  in iodide and iodate forms from seawater, which avoids introduction of external  $^{129}\text{I}$  to samples from  $^{127}\text{I}$  carrier and reduces the analytical uncertainty for analysis of ultralow levels of  $^{129}\text{I}$ ; (2) single-step separation, which makes the separation easy to operate and requires less chemicals; (3) addition of less chemicals, which reduces the possible contamination of external  $^{129}\text{I}$  from chemicals and thus improves the reliability of analytical results for low-level  $^{129}\text{I}$  samples; (4) easy operation and short procedure, which make the method suitable for in situ separation of  $^{129}\text{I}$  species on board sampling vessels during expedition, therefore reducing the risk of iodine species change during storage and transport of samples, as well as the risk of contamination by high  $^{129}\text{I}$  levels, especially in Europe. In the meantime, this also reduced the cost of transportation of large-volume seawater samples.

It should be mentioned that in some seawater, such as estuarine and coastal seawater, organic iodine might be an important species of iodine.<sup>23,33</sup> The method discussed above can only measure iodide, iodate, and total inorganic iodine. To measure organic  $^{129}\text{I}$ , a modified procedure has to be applied. Evaporation/freezing-drying followed by combustion has been applied to convert organic iodine to inorganic form for measurement of total  $^{129}\text{I}$  and organic  $^{129}\text{I}$ . However, this method is only suitable for fresh water with low salt content such as precipitation, lake, river, and groundwater.<sup>33,37</sup> For seawater, an ultrasonic-assisted dehydrohalogenation method using  $\text{NaOH}$  and ethanol under heating has been reported to decompose organic matter and convert organic iodine to inorganic forms. But this procedure is complicated and time-consuming. A simple digestion procedure using  $\text{K}_2\text{S}_2\text{O}_8$  at pH 1–2 has been developed in our laboratory to convert organic iodine in environmental water samples, including seawater, to inorganic forms.<sup>38</sup> By this procedure, organic iodine can be quantitatively converted to inorganic form, which can be then separated from water matrix by the coprecipitation method presented in this article for measurement of organic  $^{129}\text{I}$ .

The presented method also might be useful for preconcentration of iodine from seawater for the measurement of short-lived radioactive iodine (e.g.,  $^{131}\text{I}$ ,  $^{132}\text{I}$ ,  $^{133}\text{I}$ ), which is a very important issue for monitoring radioactive iodine contami-

nation in the seawater, especially during possible nuclear accidents. By this method, iodine can be easily concentrated from a large volume of seawater (e.g., 10 L) to a small size (1–2 g) to be measured by  $\gamma$  spectrometry, therefore improving the detection limit of these radionuclides by a factor of more than 100.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Additional text describing separation of iodine species by anion-exchange chromatography and solvent extraction; one table listing sampling information for seawater; and four figures showing schematic diagram of procedure for speciation analysis of  $^{129}\text{I}$  by coprecipitation; distribution of iodide, chloride, and bromide precipitated as  $\text{AgI}$ ,  $\text{AgCl}$ , and  $\text{AgBr}$  from seawater with  $\text{Ag}^+$  concentration simulated by use of Visual MINTEQ software; size distribution in precipitates of  $\text{Ag}_2\text{SO}_3$ ,  $\text{AgI}$ , and  $\text{AgCl}$ ; and distribution of species of  $\text{SO}_3^{2-}$ ,  $\text{HSO}_3^-$ , and  $\text{H}_2\text{SO}_3$  with pH value in solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail [xiho@dtu.dk](mailto:xiho@dtu.dk); tel +45-46775357; fax +45-46775347.

### Notes

The authors declare no competing financial interest.

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