

This is a repository copy of *Environmental iodine speciation quantification in seawater and snow using ion exchange chromatography and UV spectrophotometric detection*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/195282/>

Version: Published Version

Article:

Jones, Matthew R orcid.org/0000-0001-8077-2331, Chance, Rosie orcid.org/0000-0002-5906-176X, Dadic, Ruzica et al. (4 more authors) (2023) Environmental iodine speciation quantification in seawater and snow using ion exchange chromatography and UV spectrophotometric detection. ANALYTICA CHIMICA ACTA. 340700. ISSN: 0003-2670

<https://doi.org/10.1016/j.aca.2022.340700>

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



Environmental iodine speciation quantification in seawater and snow using ion exchange chromatography and UV spectrophotometric detection

Matthew R. Jones^{a,*}, Rosie Chance^a, Ruzica Dacic^{b,c}, Henna-Reetta Hannula^d, Rebecca May^{e,1}, Martyn Ward^a, Lucy J. Carpenter^a

^a Wolfson Atmospheric Chemistry Laboratory, University of York, York, YO10 5DD, UK

^b Victoria University of Wellington, Antarctic Research Centre, Wellington, 6140, New Zealand

^c WSL Institute for Snow and Avalanche Research SLF, 7260 Davos Dorf, Switzerland

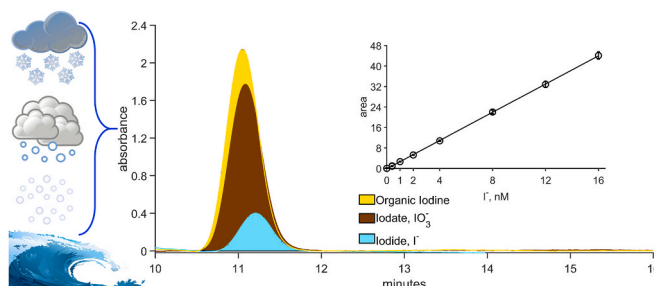
^d Finnish Meteorological Institute, Space and Earth Observation Centre, 00101, Helsinki, Finland

^e Plymouth Marine Laboratory, Prospect Place, Plymouth, PL1 3DH, UK

HIGHLIGHTS

- Simple and rapid iodine speciation analysis.
- Pico-molar detection limit for direct iodide analysis.
- Comprehensive validation of iodine speciation determination.
- The technique is globally applicable to environmental aqueous systems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Iodine speciation
Ion-exchange chromatography (IC)
Seawater
Iodide
Iodate
Dissolved organic iodine

ABSTRACT

The behaviour and distribution of iodine in the environment are of significant interest in a range of scientific disciplines, from health, as iodine is an essential element for humans and animals, to climate and air quality, to geochemistry. Aquatic environments are the reservoir for iodine, where it exists in low concentrations as iodide, iodate and dissolved organic iodine and in which it undergoes redox reactions. The current measurement techniques for iodine species are typically time-consuming, subject to relatively poor precision and require specialist instrumentation including those that require mercury as an electrode. We present a new method for measuring iodine species, that is tailored towards lower dissolved organic carbon waters, such as seawater, rainwater and snow, using ion exchange chromatography (IC) with direct ultra-violet spectrophotometric detection of iodide and without the need for sample pre-concentration. Simple chemical amendments to the sample allow for the quantification of both iodate and dissolved organic iodine in addition to iodide. The developed IC method, which takes 16 min, was applied to contrasting samples that encompass a wide range of aqueous environments, from Arctic sea-ice snow (low concentrations) to coastal seawater (complex sample matrix). Linear calibrations are demonstrated for all matrices, using gravimetrically prepared potassium iodide standards. The detection limit for the iodide ion is 0.12 nM based on the standard deviation of the blank, while

* Corresponding author.

E-mail address: matthew_r_jones@rocketmail.com (M.R. Jones).

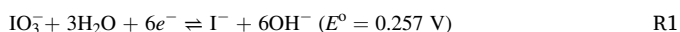
¹ Current address: Bermuda Institute for Ocean Sciences (BIOS), Ferry Road, St. George's, Bermuda.

sample reproducibility is typically <2% at >8 nM and ~4% at <8 nM. Since there is no environmental certified reference material for iodine species, the measurements made on seawater samples using this IC method were compared to those obtained using established analytical techniques; iodide voltammetry and iodate spectrophotometry. We calculated recoveries of $102 \pm 16\%$ ($n = 107$) for iodide and $116 \pm 9\%$ ($n = 103$) for iodate, the latter difference may be due to an underestimation of iodate by the spectrophotometric method. We further compared a chemical oxidation and reduction of the sample to an ultra-violet digestion to establish the total dissolved iodine content, the average recovery following chemical amendments was $98 \pm 4\%$ ($n = 92$). The new method represents a simple, efficient, green, precise and sensitive method for measuring dissolved speciated iodine in complex matrices.

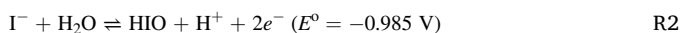
1. Introduction

The environmental biogeochemistry of iodine, directly and indirectly, impacts our lives, because iodine is both an essential mineral [1] and a regulator of climate through cloud formation and reactions with ozone [2,3]. Iodine is present in a range of chemical forms and understanding why and when it changes speciation is essential for an understanding of its biogeochemical functions. Changes can be used to understand atmosphere-hydrosphere interactions [4,5], photochemical processes [6,7], infer paleo-redox circumstances [8,9], assess advanced oxidation process during water treatment [10] and help interpret the redox properties of a medium [11–13]. Analytical sensitivity is a necessity when measuring samples for redox-active species because those species are typically low in concentration relative to the total elemental concentration. Moreover, complex sample matrices, which may contain high amounts of dissolved organic material (rivers and soil water), high total suspended material (estuaries), high ionic strength (seawater and brine) and variable pH (seawater, rainwater, aerosol, snow), can exacerbate analytical issues. Providing the greatest understanding of the biogeochemical cycling of iodine requires opening the ability to measure iodine speciation in a variety of matrices to the widest pool of researchers.

The two primary inorganic iodine species are iodide (I^-) and iodate (IO_3^-). In oxygenated aqueous systems iodate is the thermodynamically stable species in the equilibrium at standard conditions, R1:



Meanwhile, iodide, the more reactive partner, is found in equilibrium with hypiodous acid (HIO, also known as monooxiiodic acid; R2), though iodide is considered in excess of hypiodous acid.



Iodide is recognised as the most influential inorganic iodine species in seawater because it is more reactive than iodate and its equilibrium with hypiodous acid results in a pathway to the formation of iodine and volatile organic iodine complexes that directly impact climate [14,15].

Iodide and iodate can be determined electrochemically. Voltammetry directly measures iodide and quantifies iodate by difference following its reduction. Contrastingly, polarography measures iodate and the iodide is quantified by difference following its oxidation. Electrochemical methods are sensitive, with sub-nanomolar detection for iodide [16,17] and ~20 nM for iodate [18]. However, they are time-consuming, require quantification through standard addition, use mercury and require high analytical expertise to ensure good-quality results [19]. Freshwater samples that are only obtainable in low volumes, such as snow and rain, require the addition of an electrolyte to enable an electrochemical analysis. The minimum volume for our reaction cells is 12 mL and an addition of an electrolyte will dilute, even to a small degree, the already low concentrations. Moreover, additions of inorganic ions for analysis and/or experiment, including sodium chloride, nitrite and nitrate, can contaminate the sample because reagent salts contain significant iodide even with stated concentrations of <0.0001%. For example, using 11 mL of 0.1 M NaCl (5.6 g L⁻¹) as the electrolyte for 1 mL of sample potentially adds >4 μM I⁻. For iodate

analysis, the tri-iodide spectrophotometric method [20] applied by Truesdale [21] has a detection limit of 30–60 nM (1 cm path length) but suffers from background absorbance and chemical interferences. Both the electrochemical and spectrophotometric methods are affected by, *inter alia*, nitrogen compounds and dissolved organic material, with surface-active compounds potentially affecting the signal for iodide voltammetry [17,21].

In seawater, total inorganic iodine is expected to be conserved at ~470 nM [18,22]. When Schwehr and Santschi [23] used microwave-assisted dehydrohalogenation to recover all available iodine, their seawater samples contained 5–30% of the total dissolved iodine as organic iodine (35–150 nM). They concluded that only their method coupled with higher-level analytical techniques, i.e. inductively coupled plasma-mass spectrometry (ICP-MS), was sufficient to recover all iodine in a sample. Conversely, comparisons between ultra-violet (UV) decomposition and ICP-MS analysis of seawater samples found that 100% of the total dissolved iodine was recovered following 90 min of UV decomposition [13,24]. The reason for these conflicting results may well be a reflection of the variability of dissolved, sometimes referred to as soluble, organic iodine in ocean waters. Though dissolved organic iodine is typically considered a minor fraction (<5%) of the total dissolved iodine relative to iodide and iodate in aqueous solutions and especially open ocean seawater, samples containing up to 40% dissolved organic iodine are not uncommon [24–26]. The conserved concentration of total dissolved iodine in seawater can be breached through the lateral migration of low oxygen continental shelf/shelf slope/estuarine and coastal waters across the sediment interface, producing a flux of iodine from sediments into ocean basins resulting in higher than expected concentrations [27,28]. In other aqueous systems, the iodine species composition is more variable and concentrations of dissolved organic iodine can be equal to or greater than iodide in estuarine waters, groundwater, rainwater, snow and atmospheric aerosol [23,26,29–31].

Inorganic and organic iodine species can be separated using chromatography [29] with subsequent quantification using high-level analytical systems such as liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) [32] or ICP-MS [33,34]. However, such systems are expensive and direct analysis of even 10-fold diluted seawater is detrimental to their long-term running. One of the simplest chromatographic detection methods is the direct analysis by ultra-violet/visible (UV/Vis) light absorbance spectroscopy. The molar extinction coefficient of iodide, $2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 226 nm (this article), is higher than iodate and sufficiently high for trace-level detection. Table 1 shows recent techniques for the analysis of iodide in seawater, for more extensive comparisons and other analytical methods, refer to Hernáiz-Izquierdo et al. [32], Frizzarin et al. [35] and Chance et al. [36].

Ion-exchange chromatography (IC) with UV/Vis spectrophotometric detection is a routine analytical method with a central tenet that it is adaptable to a broad range of analytes. Chromatographic separation of iodine in high ionic strength samples is complicated because of matrix ions. In seawater, the chloride ion (0.54 M) is approximately 1×10^6 greater than the concentration of iodide (100 nM) and this causes the sample to self-elute while also impeding the separation of analytes as the cumulative effect of the seawater ions may saturate the stationary

phase's active sites [44]. In 1988, Ito and Sunahara [45] used 0.1 M sodium chloride (NaCl) in their mobile phase to minimise the matrix effects of seawater, this minimisation of interference technique is known as matrix elimination ion chromatography. Sodium chloride amendments during matrix elimination ion chromatography have subsequently been used during the analysis of nitrite, nitrate and iodide (iodide quantified following derivatisation) in seawater samples [23,39,43,46–48]. The self-elution of seawater samples implies that the chloride ion may be used as a cost-effective mobile phase counter ion during ion chromatography because eluent generator modules are not required. The typically <0.001% iodide in NaCl will not affect measurements because it is accounted for during the zeroing of the spectrophotometer before each analysis. Here, we present a novel, simple and universally applicable IC protocol with extensive verification of the results for quantification of iodide, iodate and dissolved organic iodine.

2. Methods

2.1. Samples

Seawater (typically sampled at 3 m depth) and sea surface microlayer seawater samples (~0.65 mm thickness) were collected from the English Channel, ~0.5 km offshore of Rame Head, Cornwall by the crew of the Plymouth Marine Laboratory (UK) research vessel *Plymouth Quest*. Collection of seawater was via a polyurethane Niskin bottle lowered by a winch and the sea surface microlayer by Garrett screen [49]. Following collection, the seawater samples were filtered as soon as possible

through Whatman fine glass fibre membranes (GF/F; nominal pore size 0.7 µm) and then stored at –20 °C in acid-washed centrifuge tubes; freezing is the preferred technique to preserve iodine speciation [16]. Arctic snow laying on sea ice was collected during the 2019–2020 Arctic MOSAiC Expedition and also stored at –20 °C, snow samples were not filtered prior to analysis [50]. Before analysis samples were thawed overnight at 4 °C and in the dark.

2.2. Chemicals

All standards and reagents were made up in 18.1 MΩ deionised water (Di-H₂O). For IC, the isocratic mobile phase was 0.4 M sodium chloride (NaCl, Sigma-Aldrich BioXtra ≥99.5%; 2 M stock solution). Potassium iodide (KI, Fisher ≥99%) standards were produced through serial dilutions of a gravimetrically prepared ~0.1 M solution. The following reagent stock solutions were used; 10% w/v hydroxylamine hydrochloride (NH₂OH·HCl; Sigma-Aldrich Reagent Plus, 99%), 70 mM calcium hypochlorite (Ca(ClO)₂, Sigma-Aldrich Technical Grade) and 500 mM sodium sulphite (Na₂SO₃, Sigma-Aldrich, min. 98%), the Na₂SO₃ was refreshed bi-monthly.

For the comparative methods, KI was used for the standard additions and Triton-X 100 (Sigma-Aldrich) as the signal enhancer in voltammetry [17]. The reagents and standards for iodate spectroscopy were 0.6 M KI, 1.5 M sulfamic acid (H₃NSO₃, Acros Organics, 99%) and 25 mM potassium iodate (KIO₃, Fisher AR grade, ≥99.9%). For UV decomposition, a 9.79 M hydrogen peroxide (H₂O₂, Sigma-Aldrich Puriss, 30%) stock solution was used for small volume additions.

Table 1

Recent and notable, primarily following chromatography, measurements of iodide and iodine species in seawater.

mechanism	stationary phase	detection	species	LOD ^j , nM	v. ^k , µL	verification	Ref.
IC ^a	Acryl-PEG	UV ^b	I [–] IO ₃ [–]	63	0.15	2 spiked seawater	[37]
IC	Cationic surfactant (CTA+)	UV	I [–] IO ₃ [–] DOI	0.2 0.1	100	6 seawater	[38]
LC ^c	Acclaim mixed-mode WAX-1	ESI-MS ^d	I [–] IO ₃ [–]	0.16	5	4 seawater	[32]
IC	IonPac AS14	ICP-MS	I [–] IO ₃ [–]	1.6 0.3		1 seawater	[34]
IC	IonPac AS20	UV	I [–] IO ₃ [–]	9.5	125	3 simulated seawater	[39]
Reverse-phase HPLC ^e	Capcel Pak C8 DD and Capcel Pak C18 MGII	UV and amperometric	I [–] IO ₃ [–] Total I	2.0 3.5	20	4 seawater	[13]
n/a	n/a	FIA-SF ^f	I [–]	2.4	125	5 spiked samples	[35]
IC	dilauryldimethylammonium bromide	UV	I [–]	3.2	100	4 seawater	[40]
IC	G3154A/101	ICP-MS ^h	I [–] IO ₃ [–]	16 9	10	3 spiked samples	[33]
IC	IonPac AS11	UV	I [–] IO ₃ [–] DOI	<3	<140	Milk CRM ⁱ 2 seawater 1 freshwater	[23]
IC	Cetyltrimethyl-ammonium	ampero-metric	I [–]	3.9	500	n/a	[41]
IC	AS9-HC	post-column reaction	IO ₃ [–]	–	–	1 seawater	[42]
IC	Hamilton PRP-X100	UV	I [–] IO ₃ [–]	10	–	10 seawater	[43]
IC	IonPac AS23	UV	I [–] IO ₃ [–] DOI	0.12	400	>100 seawater for both I [–] and IO ₃ [–]	This work

^g octadecyl-bonded silica.

^a Ion exchange chromatography.

^b ultra-violet absorbance.

^c Liquid chromatography.

^d Electro-spray ionization mass spectrometry.

^e High Performance Liquid Chromatography.

^f Flow injection analysis spectrofluorescence.

^h Inductively coupled plasma mass spectrometry.

ⁱ Certified Reference Material.

^j Limit of detection.

^k volume.

2.3. Iodine fractions and speciation measurements

The iodide ion has a molar extinction coefficient of $\sim 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 226 nm (Supporting Information Fig. S11) which allows for its direct quantification following separation from other ions using IC (Section 2.3.1). Iodate and dissolved organic iodine were quantified as iodide following chemical amendments which selectively converted iodine fractions to iodide (Table 2). A chemical reduction of the sample enabled the measurement of the inorganic iodine fraction ($I_{\text{inorg}} = \text{iodide} + \text{iodate}$) allowing for the quantification, by difference, of iodate (Section 2.3.2). A second chemical manipulation enabled measurement of the total dissolved iodine fraction ($dI_T = I_{\text{inorg}} + \text{DOI}$) and hence quantification, by difference, of dissolved organic iodine (DOI; Section 2.3.3). All standards, blanks, samples and chemical amendments were added to acid-washed class 1 hydrolytic glass vials; the caps contained a polytetrafluoroethylene (PTFE) septum.

2.3.1. Iodide

To measure iodide, a chromatographic separation of the sample was performed on a 400 μL analytical replicate using an Agilent 1100 HPLC with a 1260 series detector monitoring absorbance at 226 nm. The flow cell had a 4 μL volume over a 60 mm path length (G4212-60007). The isocratic mobile phase was 0.4 M NaCl (Section 3.1.1) at 0.64 mL min^{-1} . The system utilised two channels, each providing 50% of the flow, but there would likely be no difference using a single pump channel operation. The guard and analytical columns were Dionex IonPac AS-23 $4 \times 50 \text{ mm}$ and $4 \times 250 \text{ mm}$, respectively. Once injected, the chromatogram was collected for 16.1 min; iodide eluted at c.11 min and this was significantly far from the chloride peak to enable quantification (Fig. 1). Seawater samples were diluted, but can be measured directly because the peak area is conserved, whereas snow samples were measured directly (Table 2 and Supporting Information Fig. S12).

For comparison with the IC method, iodide in marine samples was also measured voltammetrically using a VA663 stand (Metrohm) connected to a $\mu\text{autolab III}$ potentiostat (Metrohm) [17]. After adding 90 μL 0.2% v/v Triton X-100 to 12 mL of sample and deoxygenating, the iodide was deposited onto a hanging mercury drop electrode for 30–60 s. Iodide was stripped from the electrode at 200 mV s^{-1} (frequency 75 Hz), and the peak height at -0.29 V was quantified through small volume standard additions of a 27 μM KI standard. The limit of detection is dependent on multiple factors but is usually $<0.2 \text{ nM}$ for a 90 s deposition. A single sample took on the order of 45 min to measure and sample reproducibility was 7.1% (average from 110 samples measured in duplicate or triplicate).

2.3.2. Iodate

The determination of iodate requires enabling the ion exchange chromatography of the inorganic iodine fraction as the iodide ion (Fig. 1 and Section 2.3.1). The difference between this fraction and the sample's iodide provides the iodate. A single offline addition of $\text{NH}_2\text{OH-HCl}$ to a final concentration of 7 mM (Table 2) reduces all iodate to iodide without significantly altering pH (Section 3.2).

For comparison with this method, the iodate in seawater samples, following conversion to tri-iodide, was quantified spectrophotometrically over a 1 cm path length using a Shimadzu UV-1800 spectrophotometer [21,51,52]. Sixty seconds after the addition of 0.05 mL 1.5 M

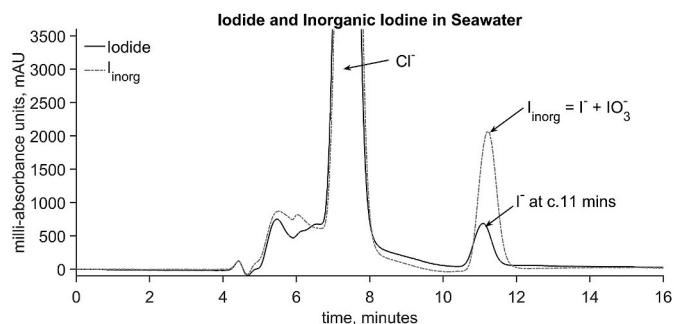


Fig. 1. Overlain chromatograms of the same diluted seawater sample (400 μL) before and after treatment with $\text{NH}_2\text{OH-HCl}$, showing the chloride ion (Cl^-) and the iodide (I^-) and inorganic iodine iodide peaks ($I_{\text{inorg}} = \text{I}^- + \text{IO}_3^-$); IonPac AS-23 $4 \times 250 \text{ mm}$ column, mobile phase 0.4 M NaCl at 0.64 mL min^{-1} , signal measured at 226 nm.

H_3NSO_3 to 2.3 mL of sample a background measurement was taken, thereafter, 0.15 mL of 0.6 M KI was added to reduce all iodate iodine to tri-iodide, which is a two-step reaction in an acidic medium ($5\text{I}^- + \text{IO}_3^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$, and then $3\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$); the H_3NSO_3 both acidifies the sample and limits nitrite interference. The tri-iodide absorbance was measured 150 s later at 350 nm. Iodate standards were used for calibration. For a 1 cm path length, the limit of detection ranged between 30 and 60 nM. Sample reproducibility was 4.5% ($n = 106$).

2.3.3. Dissolved organic iodine

The concentration of dissolved organic iodine is calculated by difference from the total dissolved and inorganic iodine fractions (Section 2.3.2). Recovering the total dissolved iodine requires a three-step offline procedure (Table 2). In step one, $\text{Ca}(\text{ClO})_2$ is added to a final concentration of 189 μM and the sample is left for c.1 h. Step two is a small volume addition of Na_2SO_3 to a final concentration of 380 μM . The SO_3^{2-} neutralises ClO^- ($\text{ClO}^- + \text{SO}_3^{2-} \rightarrow \text{Cl}^- + \text{SO}_4^{2-}$) and this prevents the ClO^- from interfering with the iodate/iodine reduction [53,54]. In step three, $\text{NH}_2\text{OH-HCl}$ is added to a final concentration of 7 mM and this reduces all available iodine to iodide, which is quantified.

Total dissolved iodine was also assayed as iodide using the IC method following oxidation of the sample's organic material by high-intensity UV light in a Metrohm 909 UV digester for 90 min at 90°C [13,24,55]. Prior to digestion, a small volume addition of 30% H_2O_2 was made to a final concentration of 8.2 mM. The H_2O_2 helps initiate hydroxyl radical formation. Once UV irradiation had completed, the samples were left for 24 h to let residual H_2O_2 decompose before the addition of $\text{NH}_2\text{OH-HCl}$ to a final concentration of 7 mM to reduce all available iodine species to iodide.

3. Results and discussion

3.1. Chromatography optimisation

Initial column testing was with Dionex IonPac AS-11 ($2 \times 250 \text{ mm}$), AS-20 ($2 \times 250 \text{ mm}$) and AS-23 ($4 \times 250 \text{ mm}$) columns. For the final analyses, we continued with an AS-23 column ($4 \times 250 \text{ mm}$, column capacity = 320 μeq), which has a higher capacity than the previously

Table 2

Off-line chemical amendments added to the sample to enable the quantification of iodine fractions as iodide (volumes, μL) for Di- H_2O diluted seawater and snow. †There is a 60-min wait between adding the ClO^- and adding the Na_2SO_3 followed directly by the $\text{NH}_2\text{OH-HCl}$.

Fraction	Iodide (I^-)		Inorganic Iodine (I_{inorg})		Total dissolved Iodine (dI_T)			
	sample	Di	sample	$\text{NH}_2\text{OH-HCl}$	sample	$\text{Ca}(\text{ClO})_2^\dagger$	Na_2SO_3	$\text{NH}_2\text{OH-HCl}$
Final conc.	–	–	–	7 mM	–	189 μM	380 μM	7 mM
Seawater	800	850	800	850	800	810	20	20
Snow	1600	50	1600	50	1600	10	20	20

used AS-20 (4×250 mm; column capacity = 310 μeq) and AS-11 (4×250 mm; column capacity = 45 μeq) columns [23,39,46]. Tests were also performed on a Metrosep A Supp 5 (4×250 mm; Metrohm). The relative characteristics of the iodide elution profiles, i.e., peak size and elution timing, example given in Fig. 1, were similar across all four columns indicating how universal the 0.4 M NaCl mobile phase is. Iodide peak areas in the chromatogram were conserved in seawater relative to Di-H₂O indicating that iodide standards prepared in Di-H₂O are sufficient to enable the quantification of complex media samples (Fig. 2A and Supporting Information Fig. SI2).

3.1.1. Optimisation

In seawater, the chloride ion concentration is 0.54 M. A slightly lower strength (0.4 M) NaCl mobile phase was selected because of a decrease in reproducibility (Fig. 2C) and peak area (Fig. 2D) above 0.6 M NaCl. At higher concentrations of NaCl the exchange equilibrium between the analyte ion and the chloride ion shifts towards the side of the mobile phase, thereby reducing the retention times. At 0.4 M NaCl the reduced retention time between elution of the chloride and iodide ions decreased overall analysis time while still retaining adequate peak separation. The NaCl concentration used is similar to the 0.3 M NaCl used by McTaggart et al. [43] with a Hamilton PRP-X100 (150×4.1 mm) column. Peak separation was more than 6.5 min for <0.3 M NaCl (Fig. 2B to D) but at <0.3 M NaCl, the peak form deteriorated as indicated by peak tailing factors exceeding 1.2. Because the method uses a chloride counter ion it is robust against pH changes that occur through the absorption of atmospheric carbon dioxide into the aqueous mobile phase. Though iodide peak splitting was not observed, even at NaCl concentrations <0.05 M, the dilution of seawater improved the peak shape likely by limiting the self-elution of the sample.

3.1.2. Detection limits and calibration range

The detection limit (Table 3) is calculated from the standard deviation of triplicate analysis of either three blanks or a low concentration standard. The calculated value of the detection limit typically increases when the calibration range increases, unless the correlation coefficient is precisely equal to 1. We calculate detection limits each time standards are measured and because these calibration curves and blank measurements differ there is a range of detection limits. Higher concentration standards, which are further away from the origin, have a greater relative control on where the slope intercepts the y-axis resulting in the magnitude of the deviation of the intercept from the origin increasing, compare the large and small range Di-H₂O calibrations in Fig. SI2 (0–772 nM calibration range, $R^2 = 0.9997$, intercept = 16) and Fig. SI3

Table 3

Detection limits were calculated from $3 \times$ the standard deviation of a 400 μL iodide standard or blank following IC separation and as measured through its absorbance at 226 nm with a 0.4 M NaCl isocratic mobile phase running at 0.64 mL min^{-1} . Ultraviolet absorbance detection was across a 6 cm path length.

Sample type	Calibration range	Detection limit	standard
Di-H ₂ O, trace quantification	0.1–4 nM	0.08 nM (n = 1)	0 nM
Snow	0.4–16 nM	0.12 nM (n = 16)	0 and 1 or 2 nM
Diluted seawater	4–240 nM	1.2 nM (n = 13)	0 nM
Diluted seawater	4–240 nM	1.8 nM (n = 13)	4 nM

(0–16 nM calibration range, $R^2 = 0.9995$, intercept = −0.1). Fig. 3 shows a calibration for diluted seawater samples and Supporting Information Fig. SI3, a calibration for snow samples. The system's response to iodide was linear up to the highest standard measured, 4.1 μM .

3.2. Iodine speciation in seawater

To test the applicability of the IC technique, the different fractions of iodine and the species they represent (total dissolved iodine, total inorganic iodine, I^- , IO_3^- and DOI) were compared to established analytical techniques (Table 4, Fig. 4A and B) for the coastal English

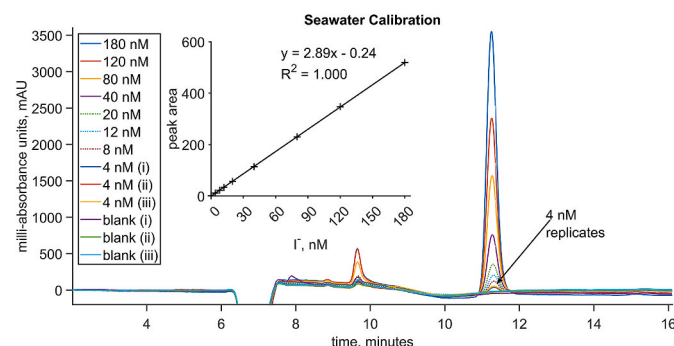


Fig. 3. Overlain chromatograms of potassium iodide (I^-) standards in deionised water (400 μL injection volume) that are used to calibrate diluted seawater samples, each standard was measured in triplicate and the relative standard deviation of these is typically <2%: IonPac AS-23 4×250 mm column, mobile phase 0.4 M NaCl at 0.64 mL min^{-1} , signal monitored at 226 nm.

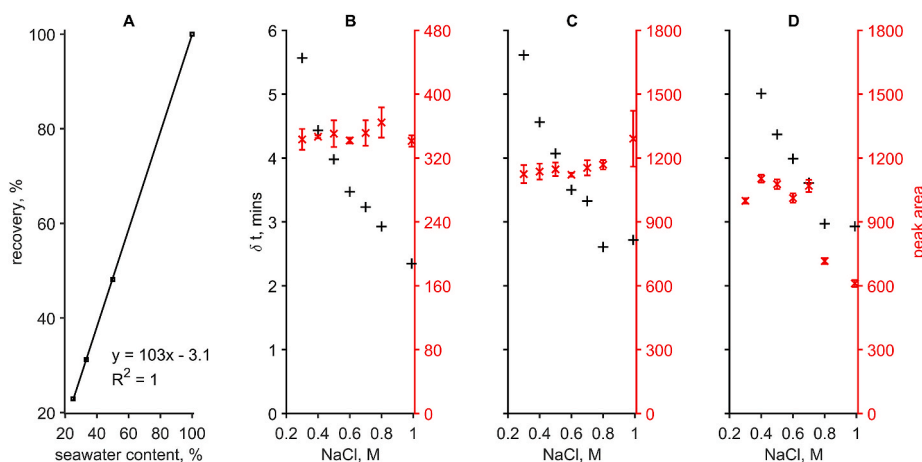


Fig. 2. Panel A, relative conservation of iodide peak area following dilution of a seawater sample with deionised water. Panels B to D, the effect of mobile phase sodium chloride (NaCl) concentration on the retention time difference between iodide and chloride (δt ; black +) and peak area (red x) for iodide (B), inorganic iodine as iodide (C) and total dissolved iodine as iodide (D) in natural seawater. Iodide was measured at 226 nm and the flow rate was 0.64 mL min^{-1} .

Table 4

Comparison of York linear regression (Fig. 4) and relative percentage recoveries of iodine species iodide (I^-) and iodate (IO_3^-) and the total dissolved iodine fraction (dI_T).

	Average recovery	York fit	
		slope	intercept
I^-	$102 \pm 16\%$ ($n = 107$)	0.95 ± 0.03	8.12 ± 2.12
IO_3^-	$116 \pm 9\%$ ($n = 103$)	1.13 ± 0.03	0.34 ± 7.04
dI_T	$98 \pm 4\%$ ($n = 92$)	1.23 ± 0.01	-107 ± 4

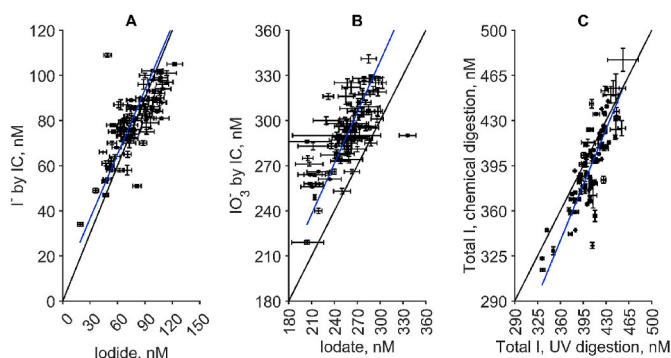


Fig. 4. Comparison of iodine species concentrations in ~100 seawater samples as measured by the IC technique to established analytical methods for iodide (voltammetry – Panel A) and iodate (spectrophotometry – panel B). Panel C compares the concentration of total dissolved iodine measured by IC following chemical oxidation to a UV decomposition of the sample. Error bars represent the measurement error, for IC this is calculated from the standard deviation of triplicate measurements. The thin black line is the one-to-one line and the blue line is the York et al. [56] linear regression fit. Supporting Information Figure S15 shows the distribution of samples broken down by sample type which are either those from 3 m deep or those from the surface layer to a depth of 0.6 mm.

Channel seawater samples (Salinity, $S_p = 34.0 \pm 1.2$). The chemical method to recover the total dissolved iodine was also compared to a UV-decomposition (Table 4 and Fig. 4C). The results were compared using two approaches; average percentage recovery was calculated using Equation 1, and a regression analysis using the York method [56]. Equation (1); Y_i is the measured concentration, X_i is the expected concentration, n is the number of samples with the standard deviation of the recoveries providing the error.

$$\bar{x}_{\text{percentage recovery}} = \frac{\sum \left(\frac{Y_i}{X_i} \times 100 \right)}{n} \quad (1)$$

The York linear regression model accounts for both X and Y measurements and their errors and provides errors on the computed slope and intercept but cannot provide a goodness of fit value for the calculated line such as the regression statistic, r [56–58]. The average percentage recovery, Equation (1), does not include the measurement errors and therefore the slope of the York regression and the average have the potential to be different. Nevertheless, for iodide and iodate, the recoveries and slopes agree within error (Table 4). However, though the recoveries of total dissolved iodine are excellent ($98 \pm 4\%$, $n = 92$) there is disagreement with the York regression. The regression analysis produces a large offset in the intercept indicating that the chemical decomposition method may not be recovering all of the total iodine fraction when the total dissolved iodine concentrations are low (Fig. 4C and Section 3.2.3, *infra vide*). Overall, the average relative contributions of each iodine species in all the seawater samples were: $I^- = 21 \pm 4\%$ (range 11–37%, $n = 179$), $IO_3^- = 74 \pm 6\%$ (range 55–91%, $n = 179$) and $DOI = 6 \pm 4\%$ (range 1–32%, $n = 151$, samples below the detection limit are not included).

3.2.1. Iodide

Voltammetry is an analytical technique that has a very high sensitivity. For the two types of sample measured, surface microlayer and seawater, and relative to voltammetry, low concentrations of iodide were overestimated by IC and high concentrations underestimated (Fig. 4A). Voltammetry does have instrument uncertainties, for example, electrode size, and though these are minimised their effects resulted in a higher relative error compared to IC, ~7% vs <2%. As there is no evidence for either iodide contamination or interferent peaks that could artificially raise the IC iodide signal, it is likely the IC measurements are more accurate, and the voltammetric method has underestimated the low iodide concentrations. The complex nature of sea surface microlayer and near coastal seawaters may not be a suitable sample for voltammetry. Iodide quantification by voltammetry relies on standard additions, and an inaccurate determination may be possible because of a combination of matrix effects and the difficulty of operating the equipment reproducibly [19]. Fig. S15 Panel A (Supporting Information) shows that more of the low-concentration iodide samples were collected from the organic-rich surface microlayer and that sample's matrix may have influenced the voltammetric determination of iodide. The sensitivity of voltammetry is enhanced by surfactants [17,59] and even though the use of standard additions should account for matrix effects this is not the case when there is a proportional instead of absolute change following addition. Low iodide concentrations in our samples were potentially underestimated by voltammetry because the matrix enhanced sensitivity and the slope of the standard addition series was too steep and the intercept of the regression was too low (Supporting Information Fig. S16). While high IC measured concentrations of iodide were overestimated by voltammetry because the sensitivity was lower resulting in the slope of the standard additions being too low and the intercept too far from the origin (Fig. S16). Nevertheless, for the analyses of a large number of complex matrix samples the agreement between two different techniques is still excellent.

3.2.2. Iodate

Reduction of oxidised iodine species, primarily iodate, to iodide is required to facilitate IC UV-vis analysis of the inorganic iodine fraction. The reduction should take place above pH 4 to minimise iodine volatilisation, nitrite interference and precipitation of humic-like organics, which all occur at a lower pH. It was found that a final concentration of 7 mM hydroxylamine hydrochloride ($NH_2OH-HCl$), commonly used in trace metal analysis [60,61], reduced inorganic iodine in both seawater and $Di-H_2O$ (Table 5) while maintaining a suitable sample pH. Following the addition of $NH_2OH-HCl$ to 7 mM, the pH decreased in $Di-H_2O$ from pH 5.71 to 4.12, and in seawater from pH_{NIST} 7.7 to pH_{NIST} 5.7. National Institute of Standards and Technology (NIST) traceable pH buffers have a systematic error when measuring higher ionic strength samples, for example, sea and estuarine waters, because of ionic interference at the electrode and this leads to an underestimation of pH by 0.1–0.3 pH units, nevertheless, measurements are still precise [62,63]. Compared to other established reductants the pH change with $NH_2OH-HCl$ is far lower. Reduction of iodate by ascorbic acid requires < pH 2.7 and reduction of iodate by iodide to form tri-iodide is best at < pH 2 [16,21]. With 7 mM $NH_2OH-HCl$ the recoveries of iodate and iodine fractions were excellent at each stage in the chemical transformation of iodine fractions to iodide; the average recovery in $Di-H_2O$ was $102 \pm 3\%$ ($n = 120$) and in seawater, it was $101 \pm 2\%$ ($n = 120$; Table 5).

The iodate concentrations determined by IC were, on average, 16% higher than those determined spectrophotometrically. Overall, the IC method determined concentrations within the range 219–341 nM ($\bar{x} = 289 \pm 22$ nM, $n = 106$) while the spectrophotometric method determined concentrations of 176–336 nM ($\bar{x} = 252 \pm 29$ nM, $n = 106$). From the measurement of blanks and spiked samples there is no evidence to suggest that the IC method is subject to iodate contamination or interferences. Nevertheless, it could be possible that the addition of $NH_2OH-HCl$ may have released iodine from within the organic fraction

Table 5

Average percentage recoveries of iodine measured as iodide. Recoveries are following additions of either iodide (I^-), iodate (IO_3^-) or an I^-/IO_3^- mix for total iodine addition concentrations of 200, 400 and 800 nM (5 replicates of each) into Di- H_2O and seawater. Recoveries are compared at each phase of the chemical amendment sequence (Section 2.3) inducing the transformation of select iodine fractions to iodide.

Iodine species (total additional concentrations, 200, 400 and 800 nM)	% Recovery	
	Di- H_2O	Seawater
I^-	102 ± 2.8 (n = 15)	102 ± 2.3 (n = 15)
$\text{I}^- + \text{NH}_2\text{OH-HCl}$	102 ± 2.9 (n = 15)	100 ± 1.0 (n = 15)
$\text{I}^- + \text{Ca}(\text{ClO})_2$ then $\text{Na}_2\text{SO}_3 + \text{NH}_2\text{OH-HCl}$	98 ± 2.2 (n = 15)	102 ± 4.0 (n = 15)
IO_3^-	< blank (n = 15) ¹	< blank (n = 15) ¹
$\text{IO}_3^- + \text{NH}_2\text{OH-HCl}$	101 ± 1.4 (n = 15)	97 ± 1.7 (n = 15)
$\text{IO}_3^- + \text{Ca}(\text{ClO})_2$ then $\text{Na}_2\text{SO}_3 + \text{NH}_2\text{OH-HCl}$	101 ± 1.6 (n = 15)	98 ± 2.2 (n = 15)
50% I^- & 50% IO_3^-	51 ± 1.3 (n = 15) ²	52 ± 1.6 (n = 15) ²
50% I^- & 50% $\text{IO}_3^- + \text{NH}_2\text{OH-HCl}$	107 ± 3.6 (n = 15)	102 ± 1.5 (n = 15)
50% I^- & 50% $\text{IO}_3^- + \text{Ca}(\text{ClO})_2$ then $\text{Na}_2\text{SO}_3 + \text{NH}_2\text{OH-HCl}$	104 ± 2.3 (n = 15)	103 ± 3.4 (n = 15)

¹ Not included in the calculation of average recovery.

² Value is doubled in the calculation of average recovery.

that may have been unavailable to the spectrophotometric method. Conversely, it is known that coastal and open ocean seawaters, especially those with high primary productivity (organic material), can result in the spectrophotometric method determining lower iodate concentrations [21,64]. There are four reasons why organic material can affect the determination of iodate by the spectrophotometric method. Firstly, the formation of tri-iodide should follow a stoichiometric two-step process with molecular iodine (I_2) forming as the intermediate. Therefore, reactions reducing molecular iodine, such as its oxidation of organic material or trace metals, will prevent some tri-iodide formation. Secondly, the light absorbance spectrum of organic material encompasses the tri-iodide absorbance spectrum, this is why each sample is blank corrected prior to analysis. At extreme levels, the absorbance of marine organic material can produce a signal equivalent to 200 nM IO_3^- which is very high compared to typical iodate levels ($\bar{x} \text{IO}_3^- = 289 \pm 22$ nM), and combined with a low sensitivity for tri-iodide across a 1 cm path length lowers the measurement accuracy [26]. The third and fourth reasons are related to the addition of the 1.5 M H_3NSO_3 which is added to prevent nitrite interference and lower the pH of the sample to $\sim\text{pH } 2$. As pH decreases humic like organic material becomes more insoluble and this results in lower concentrations of dissolved organic material and a reduction in background absorbance at 350 nm. The background absorbance is read after a period of 1 min, by which time the signal should be stable, and this value is used to correct the second reading that encompasses both the tri-iodide and the background signal. However, if the background absorbance continues to fall after this reading has been taken, this will result in under-estimation of the tri-iodide signal. Finally, iodate ions attached to the humic like organic may also be removed from the solution phase as it becomes insoluble. There is some likelihood that iodate ions can attach to organic material because the iodate ion has a region that acts like a strongly hydrated cation [65], a characteristic which allows organic material to substitute for water molecules, as occurs for solution phase alkali earth and transition metal cations.

3.2.3. Dissolved organic iodine

Hypochlorite (ClO^-) oxidises organic material in aqueous samples, including seawater, breaking up high molecular weight amorphous

organics to lower molecular weight compounds and simultaneously releasing inorganic ions from within that organic framework. The hypochlorite ion was added as 189 μM $\text{Ca}(\text{ClO})_2$ (378 μM ClO^-). This concentration is $\sim 1.8\times$ greater than the 215 μM sodium hypochlorite (NaClO) previously used for this role [54,55]. The 380 μM ClO^- was sufficient to break down the dissolved organic carbon (DOC) and release the iodine in the marine samples (\bar{x} DOC = 1.5 mg L^{-1} ; range 0.5–3.4 mg L^{-1}). However, freshwater samples may contain higher DOC necessitating higher concentrations of ClO^- ; the estimated mean global lake water DOC is 3.9 mg L^{-1} (range 0.0002–27 mg L^{-1}) [66]. The iodine released by the digestion step was subsequently reduced with $\text{NH}_2\text{OH-HCl}$ (as above). The concentrations of hypochlorite and sodium sulfite (chlorite neutralising agent) provided the ability to recover close to 100% of iodide or iodate in both fresh and seawater mediums (Table 5).

The dissolved organic iodine fraction within environmental samples, including seawater and atmospheric aerosol, is generally neglected and little is known about its chemical nature. Organic iodine may include organic molecules in which iodine is covalently bonded to carbon, for example, the very low concentrations of low molecular weight volatile organoiodine compounds (e.g., methyl iodide) or there are higher molecular weight complexes such as iodinated metabolites or complexes in which the denticity and type of ligands are unknown [67–69]. Nevertheless, Wong and Cheng [70] found that the presence of dissolved organic iodine is important in the oceans, and therefore likely in other environments, because it easily converts to iodide. In marine atmospheric aerosol, iodine speciation is poorly understood but dissolved organic iodine has been found to comprise the major component of the soluble iodine content of fine aerosol [30]. Conversion of dissolved organic iodine to iodide could be an important mechanism to recycle particle phase iodine to the gas phase, which is thought to occur via iodide [71].

The chemical oxidation method was sufficient to enable the measurement of total dissolved iodine, from which the dissolved organic iodine fraction is determined. Approximately half of all samples used for verification were from the organic-rich sea surface microlayer of a high primary productivity coastal seawater. The determined total dissolved iodine in the microlayer ($d\text{I}_T = 396 \pm 33$ nM) and the 3 m deep seawater ($d\text{I}_T = 397 \pm 35$ nM) samples are statistically and visually similar (Supporting Information Fig. S15 Panel C). On average, and within the combined seawater and microlayer samples taken over two years, there was a concentration of 23 ± 16 nM (n = 151) dissolved organic iodine equating to $6 \pm 5\%$ of the total dissolved iodine. The highest measured concentration was 125 nM (32% of the total). The fraction composition of dissolved organic iodine is similar to that reported [26,70]. However, when low total dissolved iodine concentrations were determined those samples had low concentrations of dissolved organic iodine (Fig. S17 A). The determination of the total iodine may not have been realised and this is because a sub-fraction of the organic iodine may not be susceptible to chemical and/or UV decomposition and therefore will not be recovered [24,70,72]. To aid in the measurement of the total iodine and the estimation of the dissolved organic iodine fraction a higher level analytical instrument, such as ICP-MS, can be advantageous.

3.3. Interference and secondary ions, nitrite and nitrate

At low pH, nitrite oxidises iodide resulting in nitrogen monoxide and iodine, $2\text{NO}_2^- + 2\text{I}^- + 4\text{H}^+ \rightarrow 2\text{NO} + \text{I}_2 + 2\text{H}_2\text{O}$ [73]. The addition of oxidants and reductants alters the sample's pH and this may influence direct and indirect reactions of iodine species. To test the hypothesis that nitrate and nitrite did not interfere during the chemical amendments, the recoveries of iodide, iodate and iodide + iodate were determined in their presence. The concentrations of nitrate and nitrite amendments were representative of high marine concentrations, 20 μM nitrate and 2 μM nitrite [74,75]. Recoveries (Eqn. (1)) of iodide and iodate in seawater for the three iodine fractions, iodide, inorganic iodine and total

dissolved iodine were excellent for each stage in the analysis, with recoveries ranging between 96 and 102% (Fig. 5 and Table S11). In Fig. 5 (Panel A) recoveries during the iodide only analysis and with an addition of iodate to the experiment show negative recoveries of -1.6% , which are equivalent to a difference of ~ 4 nM. We consider the magnitude of this difference is within an acceptable error and was likely caused by sample-to-sample variability during preparation, dilution and measurement; measurement reproducibility of a standard is $<4\%$. In terms of measuring nitrate and nitrite in seawater, the elevated NaCl mobile phase made it impossible to differentiate these ions from the chloride ion peak when monitoring at 226 nm (Fig. 1). Nevertheless, at 226 nm and in freshwater, nitrite (elution time, 6.9 min) and nitrate (elution time, 7.7 min) can be determined and calibrations produced (Fig. 6 and Supporting Information Fig. S18).

3.4. Low-concentration samples

Though the IC method for quantifying iodine species was extensively verified through comparison to natural marine samples, a requirement was that it worked across a range of samples. To test the sensitivity of the method we measured iodine species in snow samples collected from the high Arctic during the 2019–2020 MOSAiC research cruise [50]. The only difference between freshwater and seawater sample analysis was that the freshwater samples were measured undiluted, except for those additions of $\text{D}_2\text{H}_2\text{O}$ required with the reagents. For the subset of samples shown, the average iodide, iodate and dissolved organic iodine were 0.93 ± 0.91 nM, 3.2 ± 3.7 nM and 0.5 ± 0.7 nM, respectively (Table 6). Even with a sample volume of 400 μL and a detection limit of 0.12 nM, distinct fractions of iodine were unmeasurable in some samples. The quantification of the samples necessitated a calibration curve (Fig. S13) trade-off because it was used for both relatively high and low concentrations. The best practice for a calibration curve that enables the greatest accuracy is to have the samples signal central to those generated by the standards [76]. Nevertheless, as Fig. 3 and Figure S13 show, and also from what we observed, the slopes of uniquely prepared calibrations are similar at ~ 2.85 nM mAU^{-1} . The conservation of signal across sample ranges provides confidence when quantifying low and high-concentration samples even if the initial iodide content is close to the detection limit of 0.12 nM.

As of yet, there are no direct comparisons for iodine species concentrations in pristine maritime snow. However, there are total iodine values and relative composition of iodine species from continental locations including Antarctica and from within maritime rain and aerosol. In general, the median concentration of total iodine was lower than that

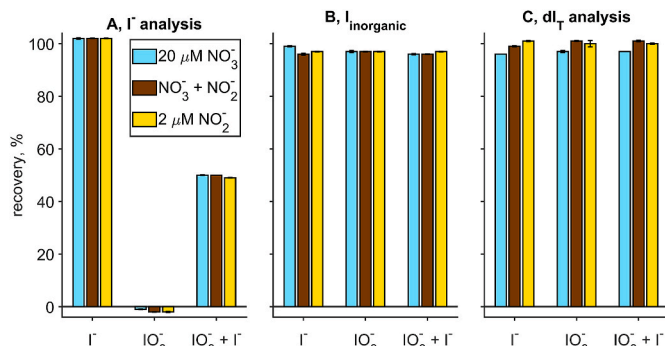


Fig. 5. Average recovery of 200 and 400 nM iodine spikes (5 replicates of each) into seawater amended with nitrite (NO_2^-) or nitrate (NO_3^-) at each phase of the iodine speciation determination sequence. Panel A, iodide analysis, Panel B inorganic iodine fraction and Panel C total dissolved iodine. The recoveries are for iodide (I^-), iodate (IO_3^-) or an I^-/IO_3^- mix and the nitrogen amendments are either an additional 20 μM nitrate (NO_3^- ; blue bars) or 20 μM $\text{NO}_3^- + 2$ μM nitrite (NO_2^- ; brown bars) or 2 μM NO_2^- (yellow bars). Each iodine addition was made in quintuplicate, error bars represent one standard deviation.

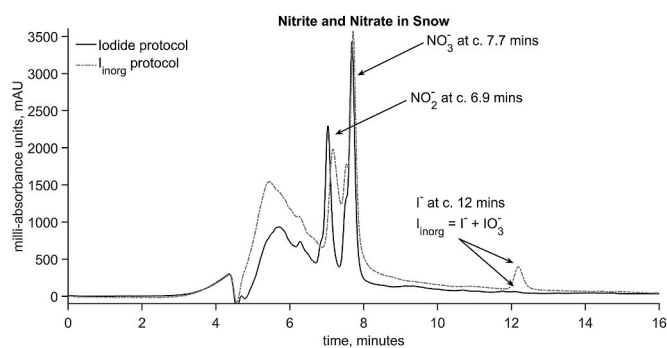


Fig. 6. Overlain chromatograms showing nitrite (NO_2^-) and nitrate (NO_3^-) in a freshwater sample (snow, 400 μL) with and without the addition of hydroxylamine hydrochloride which acts to reduce iodate (IO_3^-) to iodide (I^-); Ionpac AS-23 4 \times 250 mm column, mobile phase 0.4 M NaCl at 0.64 mL min^{-1} , signal monitored at 226 nm.

Table 6

Late summer (22nd August to 18th September 2020) concentrations (nanomolar, nM) of iodide (I^-) and the iodine fractions, inorganic iodine (I_{inorg}) and total iodine (I_T ; snow samples were analysed unfiltered and with the assumption that particulate iodine should be low) and iodine species, iodate (IO_3^-) and dissolved organic iodine (DOI) in Arctic sea-ice snow profiles. The heights are given in centimetres (cm) from the snow sea-ice interface (0 cm). Errors for IO_3^- and DOI are calculated through the propagation of errors method, all other errors are derived from multiple measurements of the sample.

sample	Height	I^- , nM	IO_3^- , nM	DOI, nM	I_{inorg} , nM	I_T , nM
PS122-5_59-204	5	0.28 ± 0.02	nd	0.2 ± 0.04	0.28 ± 0.01	0.45 ± 0.04
PS122-5_59-204	3	0.33 ± 0.14	nd	nd	0.33 ± 0.01	0.16 ± 0.01
PS122-5_59-204	1	nd	nd	0.1 ± 0.01	nd	0.12 ± 0.01
PS122-5_59-313	5	nd	nd	0.2 ± 0.01	nd	0.19 ± 0.01
PS122-5_59-313	3	nd	nd	0.3 ± 0.03	nd	0.31 ± 0.02
PS122-5_60-2	–	nd	nd	0.4 ± 0.06	nd	0.36 ± 0.06
PS122-5_60-2	4	nd	nd	0.2 ± 0.01	nd	0.15 ± 0.01
PS122-5_60-2	4	nd	0.46 ± 0.03	nd	0.46 ± 0.03	0.35 ± 0.24
PS122-5_61-198	7	2.86 ± 0.54	10.1 ± 0.54	2.3 ± 0.10	12.9 ± 0.01	15.2 ± 0.10
PS122-5_61-198	4	0.24 ± 0.04	nd	0.1 ± 0.02	0.19 ± 0.01	0.34 ± 0.01
PS122-5_62-124 ¹	6.5	1.64 ± 0.10	2.1 ± 0.10	0.8 ± 0.03	3.77 ± 0.02	4.53 ± 0.02
PS122-5_62-124 ¹	6.5	0.91 ± 0.12	4.6 ± 0.12	1.9 ± 0.12	5.50 ± 0.01	7.39 ± 0.12
PS122-5_62-124 ¹	6.5	0.49 ± 0.11	1.7 ± 0.12	0.4 ± 0.05	2.23 ± 0.04	2.62 ± 0.02
PS122-5_62-124	4.5	nd	0.28 ± 0.02	0.2 ± 0.01	0.28 ± 0.01	0.44 ± 0.01
PS122-5_62-124	2.5	0.64 ± 0.06	nd	0.2 ± 0.09	0.58 ± 0.08	0.82 ± 0.04
$\bar{x} \pm \sigma$	–	0.93 ± 0.91	3.2 ± 3.7	0.5 ± 0.7	2.65 ± 4.0	2.2 ± 4.1
median $\pm \sigma$	–	0.57 ± 0.91	1.9 ± 3.7	0.2 ± 0.7	0.5 ± 4.0	0.4 ± 4.1

¹ Sampled at different locations. nd = non-detectable.

found in Antarctic snow (~ 3 nM)[77] and European Continental mountain snow (~ 15 nM)[78]. We also found that the higher contributions of iodate and dissolved organic iodine and low contribution of

iodide in the late summer Arctic sea-ice snow samples were similar to those in rain, continental snow and aerosol [29,30,79,78] but significantly different to what occurs in marine surface waters (Section 3.2).

4. Conclusions

The IC method developed in this work provides accurate and precise iodide measurements (>95% recovery, error ~2% based on triplicate analyses), compared to established techniques (Fig. 4A and B). The method is efficient, one week of IC run time will measure all iodine fractions in 100 samples and this requires c.3 h preparation time for the mobile phase, standards and samples. The introduced technique directly quantifies iodide, and through chemical amendments, it enables a quantification of the primary iodine fractions, inorganic iodine and total dissolved iodine. Using the by-difference approach the iodine species iodate and dissolved organic iodine can be determined. We have proved that the technique is successful through the comparison of values for over 100 marine samples to established techniques in enabling the quantification of iodide and iodate and the easy measurement of dissolved organic iodine. The method can measure iodine species in marine and snow samples and therefore will be capable of determining concentrations in a range of aqueous matrices such as aerosol, rain and freshwater. These characteristics make it an excellent tool for understanding the environmental redox cycling of iodine.

CRedit authorship contribution statement

Matthew R. Jones: Formal analysis, Investigation, Methodology, Writing – original draft. **Rosie Chance:** Methodology, Investigation, Writing – review & editing. **Ruzica Dacic:** Resources, Writing – review & editing. **Henna-Reetta Hannula:** Resources, Writing – review & editing. **Rebecca May:** Resources, Writing – review & editing. **Martyn Ward:** Methodology, Investigation, Writing – review & editing. **Lucy J. Carpenter:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was funded by a European Research Council (ERC) (project O3-SML; grant agreement no. 833290) grant under the European Union's Horizon 2020 programme to L.J.C. RD was funded by the Swiss Polar Institute (SPI reference DIRCR-2018-003) and WSL Institute for Snow and Avalanche Research SLF, WSL 201812N1678. Berth fees associated with the participation of RD and HRH in the DEARice project were covered by the European Union's Horizon 2020 research and innovation program projects ARICE (grant 730965). The snow samples used in this work come from the international Multidisciplinary drifting Observatory for the Study of the Arctic Climate (MOSAiC) with the tag MOSAiC20192020 (AWI_PS122_00) [80]. We thank all those who contributed to MOSAiC and made that endeavour possible as listed in Nixdorf et al., 2021 [81]. We are especially grateful to Plymouth Marine Laboratory and the crew of the RV *Plymouth Quest*, for collecting and filtering seawater samples. We thank the three anonymous reviewers for their time, insights and comments that helped improve this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2022.340700>.

References

- [1] A.C. Ross, B.H. Caballero, R.J. Cousins, K.L. Tucker, T.R. Ziegler, *Modern Nutrition in Health and Disease*, eleventh ed., Wolters Kluwer Health Adis (ESP), 2012. <https://jhu.pure.elsevier.com/en/publications/modern-nutrition-in-health-and-disease-eleventh-edition>. (Accessed 13 October 2022).
- [2] C.A. Cuevas, R.P. Fernandez, D.E. Kinnison, Q. Li, J.-F. Lamarque, T. Trabelsi, J. S. Francisco, S. Solomon, A. Saiz-Lopez, The influence of iodine on the Antarctic stratospheric ozone hole, *Proc. Natl. Acad. Sci. USA* 119 (2022), e2110864119, <https://doi.org/10.1073/pnas.2110864119>.
- [3] X.-C. He, Y.-J. Tham, L. Dada, M. Wang, H. Finkenzeller, D. Stolzenburg, S. Iyer, M. Simon, A. Kürten, J. Shen, B. Rörup, M. Rissanen, S. Schobesberger, R. Baalbaki, D.S. Wang, T.K. Koenig, T. Jokinen, N. Sarnela, L.J. Beck, J. Almeida, S. Amanatidis, A. Amorim, F. Ataei, A. Baccarini, B. Bertozzi, F. Bianchi, S. Brilke, L. Caudillo, D. Chen, R. Chiu, B. Chu, A. Dias, A. Ding, J. Dommen, J. Duplissy, I. E. Haddad, L.G. Carracedo, M. Granzin, A. Hansel, M. Heinritzi, V. Hofbauer, H. Junninen, J. Kangasluoma, D. Kemppainen, C. Kim, W. Kong, J.E. Krechmer, A. Kvashin, T. Laitinen, H. Lamkaddam, C.P. Lee, K. Lehtipalo, M. Leiminger, Z. Li, V. Makhmutov, H.E. Manninen, G. Marie, R. Marten, S. Mathot, R.L. Mauldin, B. Mentler, O. Möhler, T. Müller, W. Nie, A. Onnela, T. Petäjä, J. Pfeifer, M. Philipov, A. Ranjithkumar, A. Saiz-Lopez, I. Salma, W. Scholz, S. Schuchmann, B. Schulze, G. Steiner, Y. Stozhkov, C. Tauber, A. Tomé, R.C. Thakur, O. Väisänen, M. Vazquez-Pufeu, A.C. Wagner, Y. Wang, S.K. Weber, P.M. Winkler, Y. Wu, M. Xiao, C. Yan, Q. Ye, A. Ylisirniö, M. Zauner-Wieczorek, Q. Zha, P. Zhou, R. C. Flagan, J. Curtius, U. Baltensperger, M. Kulmala, V.-M. Kerminen, T. Kurtén, N. M. Donahue, R. Volkamer, J. Kirkby, D.R. Worsnop, M. Sipilä, Role of iodine oxoacids in atmospheric aerosol nucleation, *Science* 371 (2021) 589–595, <https://doi.org/10.1126/science.abe0298>.
- [4] L.J. Carpenter, Iodine in the marine boundary layer, *Chem. Rev.* 103 (2003) 4953–4962, <https://doi.org/10.1021/cr0206465>.
- [5] C. Hardacre, O. Wild, L. Emberson, An evaluation of ozone dry deposition in global scale chemistry climate models, *Atmos. Chem. Phys.* 15 (2015) 6419–6436, <https://doi.org/10.5194/acp-15-6419-2015>.
- [6] I. Stemmler, I. Hense, B. Quack, E. Maier-Reimer, Methyl iodide production in the open ocean, *Biogeosciences* 11 (2014) 4459–4476, <https://doi.org/10.5194/bg-11-4459-2014>.
- [7] Y. Yokouchi, Y. Nojiri, D. Toom-Saunty, P. Fraser, Y. Inuzuka, H. Tanimoto, H. Nara, R. Murakami, H. Mukai, Long-term variation of atmospheric methyl iodide and its link to global environmental change, *Geophys. Res. Lett.* 39 (2012), <https://doi.org/10.1029/2012GL053695>.
- [8] Z. Lu, B.A.A. Hoogakker, C.-D. Hillenbrand, X. Zhou, E. Thomas, K.M. Gutchess, W. Lu, L. Jones, R.E.M. Rickaby, Oxygen depletion recorded in upper waters of the glacial Southern Ocean, *Nat. Commun.* 7 (2016), 11146, <https://doi.org/10.1038/ncomms11146>.
- [9] X. Zhou, E. Thomas, A.M.E. Winguth, A. Ridgwell, H. Scher, B.A.A. Hoogakker, R.E. M. Rickaby, Z. Lu, Expanded oxygen minimum zones during the late Paleocene–early Eocene: hints from multiproxy comparison and ocean modeling, *Paleoceanography* 31 (2016) 1532–1546, <https://doi.org/10.1002/2016PA003020>.
- [10] H. MacKeown, U. von Gunten, J. Criquet, Iodide sources in the aquatic environment and its fate during oxidative water treatment – a critical review, *Water Res.* 217 (2022), 118417, <https://doi.org/10.1016/j.watres.2022.118417>.
- [11] R. Chance, A.R. Baker, L. Carpenter, T.D. Jickells, The distribution of iodide at the sea surface, *Environ. Sci.: Process. Impacts* 16 (2014) 1841–1859, <https://doi.org/10.1039/C4EM00139G>.
- [12] R. Moriyasu, N. Evans, K.M. Bolster, D.S. Hardisty, J.W. Moffett, The distribution and redox speciation of iodine in the eastern tropical North Pacific Ocean, *Global Biogeochem. Cycles* 34 (2020), e2019GB006302, <https://doi.org/10.1029/2019GB006302>.
- [13] A. Takeda, H. Tsukada, Y. Takaku, N. Satta, M. Baba, T. Shibata, H. Hasegawa, Y. Unno, S. Hisamatsu, Determination of iodide, iodate and total iodine in natural water samples by HPLC with amperometric and spectrophotometric detection, and off-line uv irradiation, *Anal. Sci.* 32 (2016) 839–845, <https://doi.org/10.2116/analsci.32.839>.
- [14] L.J. Carpenter, S.M. MacDonald, M.D. Shaw, R. Kumar, R.W. Saunders, R. Parthipan, J. Wilson, J.M.C. Plane, Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine, *Nat. Geosci.* 6 (2013) 108–111, <https://doi.org/10.1038/ngeo1687>.
- [15] A. Saiz-Lopez, J.M.C. Plane, A.R. Baker, L.J. Carpenter, R. von Glasow, J.C. Gómez Martín, G. McFiggans, R.W. Saunders, Atmospheric chemistry of iodine, *Chem. Rev.* 112 (2012) 1773–1804, <https://doi.org/10.1021/cr200029u>.
- [16] M.L.A.M. Campos, New approach to evaluating dissolved iodine speciation in natural waters using cathodic stripping voltammetry and a storage study for preserving iodine species, *Mar. Chem.* 57 (1997) 107–117, [https://doi.org/10.1016/S0304-4203\(96\)00093-X](https://doi.org/10.1016/S0304-4203(96)00093-X).
- [17] G.W. Luther, C. Branson Swartz, W.J. Ullman, Direct determination of iodide in seawater by cathodic stripping square wave voltammetry, *Anal. Chem.* 60 (1988) 1721–1724, <https://doi.org/10.1021/ac00168a017>.

- [18] J.R. Herring, P.S. Liss, A new method for the determination of iodine species in seawater, *Deep Sea Res. Oceanogr. Abstr.* 21 (1974) 777–783, [https://doi.org/10.1016/0011-7471\(74\)90085-0](https://doi.org/10.1016/0011-7471(74)90085-0).
- [19] M. Nimmo, Polarography | inorganic applications, in: P. Worsfold, A. Townshend, C. Poole (Eds.), *Encyclopedia of Analytical Science*, second ed., Elsevier, Oxford, 2005, pp. 198–206, <https://doi.org/10.1016/B0-12-369397-7/00470-2>.
- [20] R.A. Barkley, T.G. Thompson, The total iodine and iodate-iodine content of seawater, *Deep-Sea Res.* 7 (1960) (1953) 24–34, [https://doi.org/10.1016/0146-6313\(60\)90004-6](https://doi.org/10.1016/0146-6313(60)90004-6).
- [21] V.W. Truesdale, The automatic determination of iodate- and total-iodine in seawater, *Mar. Chem.* 6 (1978) 253–273, [https://doi.org/10.1016/0304-4203\(78\)90034-8](https://doi.org/10.1016/0304-4203(78)90034-8).
- [22] V.W. Truesdale, A.J. Bale, E.M.S. Woodward, The meridional distribution of dissolved iodine in near-surface waters of the Atlantic Ocean, *Prog. Oceanogr.* 45 (2000) 387–400, [https://doi.org/10.1016/S0079-6611\(00\)00009-4](https://doi.org/10.1016/S0079-6611(00)00009-4).
- [23] K.A. Schwehr, P.H. Santschi, Sensitive determination of iodine species, including organo-iodine, for freshwater and seawater samples using high performance liquid chromatography and spectrophotometric detection, *Anal. Chim. Acta* 482 (2003) 59–71, [https://doi.org/10.1016/S0003-2670\(03\)00197-1](https://doi.org/10.1016/S0003-2670(03)00197-1).
- [24] G.T.F. Wong, X.-H. Cheng, Dissolved organic iodine in marine waters: determination, occurrence and analytical implications, *Mar. Chem.* 59 (1998) 271–281, [https://doi.org/10.1016/S0304-4203\(97\)00078-9](https://doi.org/10.1016/S0304-4203(97)00078-9).
- [25] V.W. Truesdale, 'Reactive' and 'unreactive' iodine in seawater — a possible indication of an organically bound iodine fraction, *Mar. Chem.* 3 (1975) 111–119, [https://doi.org/10.1016/0304-4203\(75\)90018-3](https://doi.org/10.1016/0304-4203(75)90018-3).
- [26] V.W. Truesdale, G. Nausch, A. Baker, The distribution of iodine in the Baltic Sea during summer, *Mar. Chem.* 74 (2001) 87–98, [https://doi.org/10.1016/S0304-4203\(00\)00115-8](https://doi.org/10.1016/S0304-4203(00)00115-8).
- [27] A.M. Farrenkopf, G.W. Luther III, Iodine chemistry reflects productivity and denitrification in the Arabian Sea: evidence for flux of dissolved species from sediments of western India into the OMZ, *Deep Sea Research Part II, Topical Studies in Oceanography* 49 (2002) 2303–2318, [https://doi.org/10.1016/S0967-0645\(02\)00038-3](https://doi.org/10.1016/S0967-0645(02)00038-3).
- [28] S.D. Oktay, P.H. Santschi, J.E. Moran, P. Sharma, 129I and 127I transport in the Mississippi River, *Environ. Sci. Technol.* 35 (2001) 4470–4476, <https://doi.org/10.1021/es0109444>.
- [29] B.S. Gilfedder, M. Petri, H. Biester, Iodine speciation in rain and snow: implications for the atmospheric iodine sink, *J. Geophys. Res. Atmos.* 112 (2007), <https://doi.org/10.1029/2006JD007356>.
- [30] J.C. Gómez Martín, A. Saiz-López, C.A. Cuevas, A.R. Baker, R.P. Fernández, On the speciation of iodine in marine aerosol, *J. Geophys. Res. Atmos.* 127 (2022), e2021JD036081, <https://doi.org/10.1029/2021JD036081>.
- [31] G.T.F. Wong, X.-H. Cheng, Dissolved organic iodine in marine waters: role in the estuarine geochemistry of iodine, *J. Environ. Monit.* 3 (2001) 257–263, <https://doi.org/10.1039/B007229J>.
- [32] M. Hernández-Izquierdo, P. Galindo-Iranzo, M.P. García-Armada, A. Saiz-López, B. Gómara, J.E. Quintanilla-López, R. Lebrón-Aguilar, Direct quantification of inorganic iodine in seawater by mixed-mode liquid chromatography-electrospray ionization-mass spectrometry, *J. Chromatogr. A* 1588 (2019) 99–107, <https://doi.org/10.1016/j.chroma.2018.12.046>.
- [33] Z. Chen, M. Megharaj, R. Naidu, Speciation of iodate and iodide in seawater by non-suppressed ion chromatography with inductively coupled plasma mass spectrometry, *Talanta* 72 (2007) 1842–1846, <https://doi.org/10.1016/j.talanta.2007.02.014>.
- [34] W. Cui, H. Hou, J. Chen, X. Yu, Y. Guo, Z. Tao, T. Deng, Y.-W. Chen, N. Belzile, The speciation analysis of iodate and iodide in high salt brine by high performance liquid chromatography and inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 34 (2019) 1374–1379, <https://doi.org/10.1039/C9JA00121B>.
- [35] R.M. Frizzarin, E. Aguado, L.A. Portugal, D. Moreno, J.M. Estela, F.R.P. Rocha, V. Cerdà, A portable multi-syringe flow system for spectrofluorimetric determination of iodide in seawater, *Talanta* 144 (2015) 1155–1162, <https://doi.org/10.1016/j.talanta.2015.07.069>.
- [36] R.J. Chance, L. Tinel, T. Sherwen, A.R. Baker, T. Bell, J. Brindle, M.L.A.M. Campos, P. Croot, H. Ducklow, H. Peng, F. Hopkins, B. Hoogakker, C. Hughes, T.D. Jickells, D. Loades, D.A.R. Macaya, A.S. Mahajan, G. Malin, D. Phillips, I. Roberts, R. Roy, A. Sarkar, A.K. Sinha, X. Song, H. Winkelbauer, K. Wuttig, M. Yang, Z. Peng, L. J. Carpenter, Global sea-surface iodide observations, 1967–2018, *Sci. Data* 6 (2019) 286, <https://doi.org/10.1038/s41597-019-0288-y>.
- [37] L. Rong, L.W. Lim, T. Takeuchi, Poly(ethylene glycol) methyl ether methacrylate-bonded stationary phase in ion chromatography and its application to seawater samples, *Anal. Sci.* 37 (2021) 1003–1006, <https://doi.org/10.2116/analsci.20P374>.
- [38] K. Ito, K. Takeda, T. Hirokawa, Determination of trace iodine in seawater - use of ion chromatography and capillary zone electrophoresis, *Bunseki Kagaku = Journal of Japanese Society for Analytical Chemistry* 68 (2019) 227–239.
- [39] E.S. Rodríguez, A.N. Setiawan, S. Pope, P.R. Haddad, P.N. Nesterenko, B. Paull, A simple and sensitive method for the determination of iodide and iodate in raw, ultraviolet- and ozone-treated aquacultural seawater samples using ion chromatography coupled to an ultraviolet detector, *Anal. Methods* 8 (2016) 5587–5595, <https://doi.org/10.1039/C6AY01381C>.
- [40] K. Ito, R. Nomura, T. Fujii, M. Tanaka, T. Tsumura, H. Shibata, T. Hirokawa, Determination of nitrite, nitrate, bromide, and iodide in seawater by ion chromatography with UV detection using dilaurildimethylammonium-coated monolithic ODS columns and sodium chloride as an eluent, *Anal. Bioanal. Chem.* 404 (2012) 2513–2517, <https://doi.org/10.1007/s00216-012-6405-9>.
- [41] K. Ito, T. Hirokawa, Enhanced detection of iodide in seawater by ion chromatography using an ODS column coated with cetyltrimethylammonium, *Anal. Sci.* 17 (2001) 579–581, <https://doi.org/10.2116/analsci.17.579>.
- [42] E. Salhi, U. von Gunten, Simultaneous determination of bromide, bromate and nitrite in low $\mu\text{g l}^{-1}$ levels by ion chromatography without sample pretreatment, *Water Res.* 33 (1999) 3239–3244, [https://doi.org/10.1016/S0043-1354\(99\)00053-6](https://doi.org/10.1016/S0043-1354(99)00053-6).
- [43] A.R. McTaggart, E.C.V. Butler, P.R. Haddad, J.H. Middleton, Iodide and iodate concentrations in eastern Australian subtropical waters, with iodide by ion chromatography, *Mar. Chem.* 47 (1994) 159–172, [https://doi.org/10.1016/0304-4203\(94\)90106-6](https://doi.org/10.1016/0304-4203(94)90106-6).
- [44] W. Hu, P.R. Haddad, K. Hasebe, K. Tanaka, P. Tong, C. Khoo, Direct determination of bromide, nitrate, and iodide in saline matrices using electrostatic ion chromatography with an electrolyte as eluent, *Anal. Chem.* 71 (1999) 1617–1620, <https://doi.org/10.1021/ac980860m>.
- [45] K. Ito, H. Sunahara, Ion chromatography of iodide ion in seawater using concentrated sodium chloride solution as eluent, *Bunseki Kagaku* 37 (1988) 292–295, <https://doi.org/10.2116/bunsekikagaku.37.6.292>.
- [46] A.C.M. Brandão, W.W. Buchberger, E.C.V. Butler, P.A. Fagan, P.R. Haddad, Matrix-elimination ion chromatography with post-column reaction detection for the determination of iodide in saline waters, *J. Chromatogr. A* 706 (1995) 271–275, [https://doi.org/10.1016/0021-9673\(94\)01207-U](https://doi.org/10.1016/0021-9673(94)01207-U).
- [47] K. Ito, Semi-micro ion chromatography of iodide in seawater, *J. Chromatogr. A* 830 (1999) 211–217, [https://doi.org/10.1016/S0021-9673\(98\)00910-8](https://doi.org/10.1016/S0021-9673(98)00910-8).
- [48] K. Ito, Determination of iodide in seawater by ion chromatography, *Anal. Chem.* 69 (1997) 3628–3632, <https://doi.org/10.1021/ac9700787>.
- [49] W.D. Garrett, Collection of slick-forming materials from the sea surface, *Limnol. Oceanogr.* 10 (1965) 602–605.
- [50] M. Nicolaus, D.K. Perovich, G. Spreen, M.A. Granskog, L. von Albedyll, M. Angelopoulos, P. Anhaus, S. Arndt, H.J. Belter, V. Bessonov, G. Birnbaum, J. Brauchle, R. Calmer, E. Cardellach, B. Cheng, D. Clemens-Sewall, R. Dadić, E. Damm, G. de Boer, O. Demir, K. Dethloff, D.V. Divine, A.A. Fong, S. Fons, M. M. Frey, N. Fuchs, C. Gabarró, S. Gerland, H.F. Goessling, R. Gradinger, J. Haapala, C. Haas, J. Hamilton, H.-R. Hannula, S. Hendricks, A. Herber, C. Heuzé, M. Hoppmann, K.V. Høyland, M. Huntemann, J.K. Hutchings, B. Hwang, P. Itkin, H.-W. Jacobi, M. Jaggi, A. Jutila, L. Kaleschke, C. Kattlein, N. Kolabutin, D. Krampe, S.S. Kristensen, T. Krumpen, N. Kurtz, A. Lampert, B.A. Lange, R. Lei, B. Light, F. Linhardt, G.E. Liston, B. Loose, A.R. Macfarlane, M. Mahmud, I.O. Matero, S. Maus, A. Morgenstern, R. Naderpour, V. Nandan, A. Niubom, M. Oggier, N. Oppelt, F. Pätzold, C. Perron, T. Petrovsky, R. Pirazzini, C. Polashenski, B. Rabe, I.A. Raphael, J. Regnery, M. Rex, R. Ricker, K. Riemann-Campe, A. Rinke, J. Rohde, E. Salganik, R.K. Scharien, M. Schiller, M. Schneebeli, M. Semmling, E. Shimanchuk, M.D. Shupe, M.M. Smith, V. Smolyanitsky, V. Sokolov, T. Stanton, J. Stroeve, L. Thielke, A. Timofeeva, R.T. Tonboe, A. Tavri, M. Tsimadous, D. N. Wagner, D. Watkins, M. Webster, M. Wendisch, Overview of the MOSAIC expedition: snow and sea ice, *Elementa: Science of the Anthropocene* 10 (2022), 000046, <https://doi.org/10.1525/elementa.2021.000046>.
- [51] M. Campos, R. Sanders, T. Jickells, The dissolved iodate and iodide distribution in the South Atlantic from the Weddell Sea to Brazil, *Mar. Chem.* 65 (1999) 167–175.
- [52] T.D. Jickells, S.S. Boyd, A.H. Knap, Iodine cycling in the Sargasso Sea and the Bermuda inshore waters, *Mar. Chem.* 24 (1988) 61–82, [https://doi.org/10.1016/0304-4203\(88\)90006-0](https://doi.org/10.1016/0304-4203(88)90006-0).
- [53] M.W. Lister, P. Rosenblum, Rates of reaction of hypochlorite ions with sulphite and iodide ions, *Can. J. Chem.* (1963), <https://doi.org/10.1139/v63-442>.
- [54] K. Takayanagi, G.T.F. Wong, The oxidation of iodide to iodate for the polarographic determination of total iodine in natural waters, *Talanta* 33 (1986) 451–454, [https://doi.org/10.1016/0039-9140\(86\)80115-1](https://doi.org/10.1016/0039-9140(86)80115-1).
- [55] M.A.R. Abdel-Moati, Iodine speciation in the Nile river estuary, *Mar. Chem.* 65 (1999) 211–225, [https://doi.org/10.1016/S0304-4203\(99\)00003-1](https://doi.org/10.1016/S0304-4203(99)00003-1).
- [56] D. York, N.M. Evensen, M.L. Martínez, J. De Basabe Delgado, Unified equations for the slope, intercept, and standard errors of the best straight line, *Am. J. Phys.* 72 (2004) 367–375, <https://doi.org/10.1119/1.1632486>.
- [57] C. Wu, J.Z. Yu, Evaluation of linear regression techniques for atmospheric applications: the importance of appropriate weighting, *Atmos. Meas. Tech.* 11 (2018) 1233–1250, <https://doi.org/10.5194/amt-11-1233-2018>.
- [58] D. York, Least squares fitting of a straight line with correlated errors, *Earth Planet. Sci. Lett.* 5 (1968) 320–324, [https://doi.org/10.1016/S0012-821X\(68\)80059-7](https://doi.org/10.1016/S0012-821X(68)80059-7).
- [59] G. Colovos, G.S. Wilson, J.L. Moyers, Exchange reactions involving electrogenerated mercurous halide films, *Anal. Chem.* 46 (1974) 1045–1050, <https://doi.org/10.1021/ac60344a009>.
- [60] K.A. Hofmann, U. Ehrhardt, Innerkomplexe metallsalze der oxalsäure-derivate und des trifluor-oxims, *Ber. Dtsch. Chem. Ges.* 46 (1913) 1457–1466, <https://doi.org/10.1002/cber.19130460230>.
- [61] M.R. Jones, B.M. Tebo, Novel manganese cycling at very low ionic strengths in the Columbia River Estuary, *Water Res.* 207 (2021), 117801, <https://doi.org/10.1016/j.watres.2021.117801>.
- [62] F.F. Perez, F. Fraga, The pH measurements in seawater on the NBS scale, *Mar. Chem.* 21 (1987) 315–327, [https://doi.org/10.1016/0304-4203\(87\)90054-5](https://doi.org/10.1016/0304-4203(87)90054-5).
- [63] G.M. Marion, F.J. Millero, M.F. Camões, P. Spitzer, R. Feistel, C.-T.A. Chen, pH of seawater, *Mar. Chem.* 126 (2011) 89–96, <https://doi.org/10.1016/j.marchem.2011.04.002>.
- [64] V.W. Truesdale, C.P. Spencer, Studies on the determination of inorganic iodine in seawater, *Mar. Chem.* 2 (1974) 33–47, [https://doi.org/10.1016/0304-4203\(74\)90004-8](https://doi.org/10.1016/0304-4203(74)90004-8).

- [65] M.D. Baer, V.-T. Pham, J.L. Fulton, G.K. Schenter, M. Balasubramanian, C. J. Mundy, Is iodate a strongly hydrated cation? *J. Phys. Chem. Lett.* 2 (2011) 2650–2654, <https://doi.org/10.1021/jz2011435>.
- [66] K. Toming, J. Kotta, E. Uuemaa, S. Sobek, T. Kutser, L.J. Tranvik, Predicting lake dissolved organic carbon at a global scale, *Sci. Rep.* 10 (2020) 8471, <https://doi.org/10.1038/s41598-020-65010-3>.
- [67] J.E. Lovelock, Natural halocarbons in the air and in the sea, *Nature* 256 (1975) 193–194, <https://doi.org/10.1038/256193a0>.
- [68] C. Schall, K.G. Heumann, GC determination of volatile organoiodine and organobromine compounds in Arctic seawater and air samples, *Fresenius' J. Anal. Chem.* 346 (1993) 717–722, <https://doi.org/10.1007/BF00321279>.
- [69] V.M. Dembitsky, Biogenic iodine and iodine-containing metabolites, *Nat. Prod. Commun.* 1 (2006), <https://doi.org/10.1177/1934578X0600100210>.
- [70] G.T.F. Wong, X.-H. Cheng, The formation of iodide in inshore waters from the photochemical decomposition of dissolved organic iodine, *Mar. Chem.* 74 (2001) 53–64, [https://doi.org/10.1016/S0304-4203\(00\)00095-5](https://doi.org/10.1016/S0304-4203(00)00095-5).
- [71] R. Vogt, R. Sander, R. von Glasow, P.J. Crutzen, Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: a model study, *J. Atmos. Chem.* 32 (1999) 375–395, <https://doi.org/10.1023/A:1006179901037>.
- [72] G.W. Luther, H. Cole, Iodine speciation in Chesapeake Bay waters, *Mar. Chem.* 24 (1988) 315–325, [https://doi.org/10.1016/0304-4203\(88\)90039-4](https://doi.org/10.1016/0304-4203(88)90039-4).
- [73] C.A. Abeledo, I.M. Kolthoff, The reaction between nitrite and iodide and its application to the iodimetric titration of these anions, *J. Am. Chem. Soc.* 53 (1931) 2893–2897, <https://doi.org/10.1021/ja01359a008>.
- [74] K.S. Johnson, S.C. Riser, D.M. Karl, Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre, *Nature* 465 (2010) 1062–1065, <https://doi.org/10.1038/nature09170>.
- [75] M. Yücel, A.D. Beaton, M. Dengler, M.C. Mowlem, F. Sohl, S. Sommer, Nitrate and nitrite variability at the seafloor of an oxygen minimum zone revealed by a novel microfluidic in-situ chemical sensor, *PLoS One* 10 (2015), e0132785, <https://doi.org/10.1371/journal.pone.0132785>.
- [76] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood PTR Prentice Hall, New York, 1993.
- [77] N. Maffezzoli, A. Spolaor, C. Barbante, M. Bertò, M. Frezzotti, P. Vallelonga, Bromine, iodine and sodium in surface snow along the 2013 Talos Dome–GV7 traverse (northern Victoria Land, East Antarctica), *Cryosphere* 11 (2017) 693–705, <https://doi.org/10.5194/tc-11-693-2017>.
- [78] B.S. Gilfedder, S.C. Lai, M. Petri, H. Biester, T. Hoffmann, Iodine speciation in rain, snow and aerosols, *Atmos. Chem. Phys.* 8 (2008) 6069–6084, <https://doi.org/10.5194/acp-8-6069-2008>.
- [79] A.R. Baker, C. Tunnicliffe, T.D. Jickells, Iodine speciation and deposition fluxes from the marine atmosphere, *J. Geophys. Res. Atmos.* 106 (2001) 28743–28749, <https://doi.org/10.1029/2000JD000004>.
- [80] R. Knust, Polar research and supply vessel POLARSTERN operated by the Alfred-Wegener-Institute, *Journal of Large-Scale Research Facilities JLSRF* 3 (2017), <https://doi.org/10.17815/jlsrf-3-163>. A119–A119.
- [81] N. Uwe, MOSAiC extended acknowledgement | Zenodo, n.d. <https://zenodo.org/record/5179739>. (Accessed 28 October 2022).