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Inorganic iodine and bromine speciation in Arctic snow at picogram-per-grams levels by IC-ICP-MS

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Abstract

Iodine and bromine play central roles in polar atmospheric chemistry: iodine influences the atmospheric oxidative capacity and can generate cloud condensation nuclei, while bromine participates in ozone depletion reactions, known as bromine explosions. Here we present a very sensitive analytical method for Br and I speciation by coupling the ion chromatography system (IC) with an inductively coupled plasma sector field mass spectrometer (ICP-SFMS). We achieved sub-picogram-per gram (pg g^{-1}) as limits of detection (LODs) ranging from 0.4 pg g^{-1} for I^- , 0.8 pg g^{-1} for IO_3^- , 4 pg g^{-1} for Br^- , and 1 pg g^{-1} for BrO_3^- , respectively. These values represent a decrease of up to 30 times compared to the LODs reported in other studies. The method was validated using deep snow samples from the Svalbard Islands, collected at the end of the polar night to quantify various oxidized compounds during their seasonal minimum. In the future, this method could prove useful in the paleoclimatic study of ice cores and snow, as well as in ice chemistry research.

Keywords Halogen speciation, Arctic snow, Ion chromatography, ICP-MS

Introduction

The Arctic and Antarctica significantly impact the global atmosphere (Saiz-Lopez et al. 2023), particularly regarding stratospheric ozone depletion (Simpson et al. 2007). Iodine primarily enters the atmosphere from oceanic species through photolysis, linked to biological activity (Frieß et al. 2010; Vogt et al. 1999). In Antarctica, iodine emission is correlated with phytoplankton production, nevertheless, a photochemical remobilization of iodine from the snowpack was found during the summer at

Neumayer station (Frieß et al. 2010) and in Halley Bay (Saiz-Lopez et al. 2008) of IO (Spolaor et al. 2014, 2019). Indeed, these species composed of iodine deposit on the snowpack and subsequently may undergo photo-oxidation leading to the formation of IO_3^- (Frieß et al. 2010; Saiz-Lopez et al. 2008), or photo-reduction with a remobilization of iodine as I_2 (Kim et al. 2016). These reactions have been studied at high concentrations ($100 \mu\text{mol L}^{-1}$), but they can probably occur even at environmental concentrations (Kim et al. 2023). Additionally, iodine oxides form ultrafine particles acting as cloud condensation nuclei in polar and mid-latitude regions (Saiz-Lopez and Plane 2004; O'Dowd et al. 2002; McFiggans 2005). Iodine can also be absorbed by soil and vegetation, adding complexity to the iodine cycle in polar areas (Cuevas et al. 2018).

Bromine mainly sourced from the ocean plays a crucial role in polar regions due its autocatalytic reactions that produce gas species, like $\text{BrO}\cdot$ and other radical

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species responsible for ozone depletion. These reactions are favoured in acidic conditions and cold temperature (Spolaor et al. 2013a, 2014). Since the snowpack is rich in reactive oxygen species (ROS), such as $\cdot\text{OH}$, $\cdot\text{OOH}$, $^1\text{O}_2$ and O_3 (Grannas et al. 2007; Bower and Anastasio 2013; Domine et al. 2013), it can be assumed that there may be production of bromate (BrO_3^-), through reactions similar to those in water treatment plants, where bromide is oxidized to BrO_3^- by O_3 .

Although the concentration of total iodine ($\text{I}^- + \text{IO}_3^-$) in the ocean is 400–500 nmol L⁻¹ (Tian and Nicolas 1995; Chance et al. 2014; Bluhm et al. 2011), during atmospheric transport and deposition (dry or wet) a significant reduction in concentration can occur depending on the distance of the sampling site from the sea. In a previous work by Spolaor et al. (2013b), the concentration of I^- and IO_3^- were measured in an ice core from Talos Dome. The results have shown that for I^- the mean concentration was 11 pg g⁻¹, but IO_3^- was for each analysis under the detection limits (5 pg g⁻¹). A similar behaviour was observed for bromine, in which higher concentrations of Br^- were measured, nevertheless bromate under the detection limits.

The case of iodine and bromine speciation in the Antarctic ice core mentioned above is not the only case where some IO_3^- and BrO_3^- were not determined (Gillfedder et al. 2007a, 2007b, 2008). This might be related to analytical performance. In fact, as reported in previous works (Jones et al. 2023; Cui et al. 2019; Chen et al. 2007; Liu et al. 2011; Wang and Jiang 2008), there are limits above 1 pg g⁻¹ for iodine species, and in the few cases where bromine speciation was performed by analysing iodine at the same time, but LODs above a dozen pg g⁻¹ were obtained.

In this paper, we propose a very sensitive and selective analytical method for the speciation of iodine and bromine using only 1 mL of samples by a high-pressure anion exchange chromatography (HPAEC) coupled with inductively coupled plasma sector field mass spectrometer (ICP-SFMS). Although the speciation of iodine and bromine can be done through other analytical techniques, e.g., IC-conductivity, UV-vis spectroscopy, at present the coupling of ion chromatography and ICP-MS is the one that provides greater sensitivity and selectivity by analysing by performing speciation of the two halogens of interest in the same chromatographic run. This new validated method is applied to four snow samples collected at Ny-Ålesund (Svalbard Archipelago).

Materials and methods

Chemicals

All standards and samples were prepared in polyethylene vials, pre-cleaned with ultrapure water in a sonic

bath for 30 min (UPW, 18.2 MΩ cm, 0.01 TOC, Elga LabWater, HighWycombe, UK). For speciation analysis for Br^- and I^- and their total quantification, standard solutions 1000 mg L⁻¹ (IC standard) were purchased by VWR chemicals (Leuven, Belgium). BrO_3^- and IO_3^- standard solutions were prepared using potassium bromate (Sigma-Aldrich, St. Louis, MO, USA) and iodic acid (99,5%, Acros Organics, Geen, Belgium), respectively.

Instrumentation

Speciation analyses were carried out by ion chromatography system (IC, Dionex-2100, Thermo Scientific) hyphenate to an inductively coupled plasma sector field mass spectrometer (ICP-SFMS, Element XR, Thermo Scientific). Chromatographic separation was carried out using an anion exchange column Dionex Ion AS19 2×250 mm equipped with Dionex Ion Pac AG19 guard column (2×50 mm). The column was thermostated on the oven at 30 °C. The gradient of sodium hydroxide (NaOH), produced by an eluent generator with a 0.25 mL min⁻¹ flow rate was: isocratic elution 0–6 min at 0.5 mM; 6–15 min gradient from 15 to 45 mM; 15–18 min, column cleaning with 45 mM; 18.1–25 min; equilibration at 15 mM. A suppressor (ASRS 600, 2 mm, Thermo Scientific) removed NaOH before entering the ICP-SFMS. 1 mL of sample was manually injected using a peek rheodyne valve, using 5 mL plastic syringes.

The ICP-SFMS instrument was tuned using a solution of 1 ppb of In and the gas flow rate was optimized daily to maximize sensitivity and signal stability. The operating conditions and measurement parameters of the ICP-SFMS are shown in Table 1.

Table 1 ICP-MS instrumental parameters

Plasma power	1250 W
Cool gas	16.03 L min ⁻¹
Auxiliary gas	0.66 L min ⁻¹
Sample gas	0.954 L min ⁻¹
Additional gas	0.251 L min ⁻¹
Accurate mass (I)	126.904
Accurate mass (Br)	78.918
Sample time (mass 129 a.u.)	0.05 s
Spray chamber	Cyclonic Peltier (2 °C)
Nebulizer	Polypro micro-concentric nebulizer, 400 μL min ⁻¹
Scan type	EScan
Sensitivity (direct measurement)*	300,000 cps (1 ng g ⁻¹ of In)

* An indicative value of indium sensitivity is reported since this parameter was being optimized daily

Results and discussion

Instrumental performance

The analytical method was validated considering the linearity, the reproducibility (relative standard deviation), limits of detection and quantification and matrix effect for each species. LOD and LOQ (Table 2) were calculated using the following formulas:

$$\text{LOD} = 3 * \frac{\sigma_b}{m} \quad \text{LOQ} = 10 * \frac{\sigma_b}{m}$$

where σ_b is the standard deviation of the UPW and m is the slope. Subsequently, nine standard solutions in UPW were prepared ranging from 0.1 to 75 pg g^{-1} for I^- , Br^- and IO_3^- , regarding BrO_3^- a calibration curve from 0.1 to 50 pg g^{-1} was used. For each calibration curve, linearity was evaluated by R^2 value, and values greater than 0.9 were obtained for all analytes. However, for Br^- and BrO_3^- the less concentrated standards were discarded because there were lower than the LOD, while for I^- and IO_3^- only the first standard was discarded. The method precision was assessed injecting three times standard at 10 pg g^{-1} . The relative standard deviations (RSD%) were 2% for Br^- , 4% for I^- , 8% for BrO_3^- and 6% for IO_3^- and the LOD calculated for I^- , IO_3^- , Br^- , BrO_3^- , were 0.4 pg g^{-1} , 0.8 pg g^{-1} , 4 pg g^{-1} , and 1.2 pg g^{-1} , respectively.

Since within the plasma the ionization of an element is mainly given by the operating temperature, it can be assumed that the signal is not affected by significant interference when analysing compounds containing the same element. However, it will be necessary to correct the signal for the molar fraction of the compound under analysis. In other words, analysis of a standard at a known concentration of I^- should give a similar signal of a standard at the same concentration of IO_3^- corrected for the mass fraction of iodine contained in IO_3^- (73%). Similarly for bromine, where the mass fraction of bromine in BrO_3^- is 63%. If one corrects the slopes of IO_3^- and BrO_3^- (Table 2) for the relative molar fractions, one obtains values similar to those of I^- and Br^- with an error

of 6% and 1%, respectively. Thus, this assumption allows for a semi-quantitative analysis of unknown compounds in the following section.

Figure 1 shows the triplicate chromatogram of the 10 pg g^{-1} standard. The peaks are chromatographically separated at 9.86 and 12.27 min for BrO_3^- and Br^- , respectively, while 8.83 and 16.81 min for IO_3^- and I^- . The chromatographic performance was also evaluated taking into account possible peak asymmetry effects using the following formula proposed by United States Pharmacopeia (USP) (Song and Wang 2003):

$$\text{TF} = A + B2A$$

where TF is USP tailing factor, A and B refer to bandwidth at 5% height, when the value $\text{TF} > 1$, tailing occurs, while if $\text{TF} < 1$, fronting is defined. In this case, TF was evaluated during the triplicate analysis of the standard at 10 pg g^{-1} values of 1.3 ± 0.1 , 1.6 ± 0.2 , 1.4 ± 0.3 and 1.1 ± 0.2 were obtained for IO_3^- , I^- , BrO_3^- and Br^- , respectively. These effects may be due to the use of a 1-mL loop leading to possible column overload.

Table 3 shows, to the best of our knowledge, the works that use the speciation technique using IC-ICPMS with the lowest possible LODs and the relative aqueous investigation matrices. For all the species analysed, the LOD was lowered by about 10 times, for I^- and IO_3^- , for the first time, it fell below 1 pg g^{-1} . As far as BrO_3^- is concerned, in previous works the value was about 30 pg g^{-1} , but in our case the value of 1.2 pg g^{-1} was reached, almost 30 times lower. Spolaor et al. (2013b) showed the best LODs but they used 0.3 mL of sample, while we improved the method to obtain low LODs but using only 1 mL of sample.

In order to assess potential matrix effects arising from the possible presence of dust and dissolved carbon that can influence ionization within the plasma, the robustness of the method was tested on a sample of Arctic snow. The latter was evaluated by analysing the same sample unfiltered, filtered through a 0.45- μm filter, and through a 0.2- μm filter. The analyses showed that the relative standard deviation (RSD%) among the different analytes were, respectively: 4% for Br^- , 3% for I^- , 6% for BrO_3^- and 2% for IO_3^- , quantified through an external calibration curve. A qualitative evaluation method to determine the effect of particles that could reduce the ionization efficiency was carried out comparing two calibration curves obtained by spiking the analytes into filtered and unfiltered melted snow, and a calibration curve in ultrapure water. The variation in concentration between methods, calculated as the signal response of a standard present in the sample extract compared with the response of a standard prepared in a UPW and expressed as a percentage (Barbaro et al. 2013; Matuszewski et al. 2003), was

Table 2 Parameters of calibration curve for I^- , IO_3^- , Br^- and BrO_3^-

	I^-	IO_3^-	Br^-	BrO_3^-
Slope	17,090	14,726	1294	556
Intercept	55,548	-19,404	5330	2557
R^2	0.97	0.96	0.94	0.98
RSD (%)	4	6	2	8
LOD (pg g^{-1})	0.4	0.8	4	1.2
LOQ (pg g^{-1})	1.3	2.7	13.3	4.0

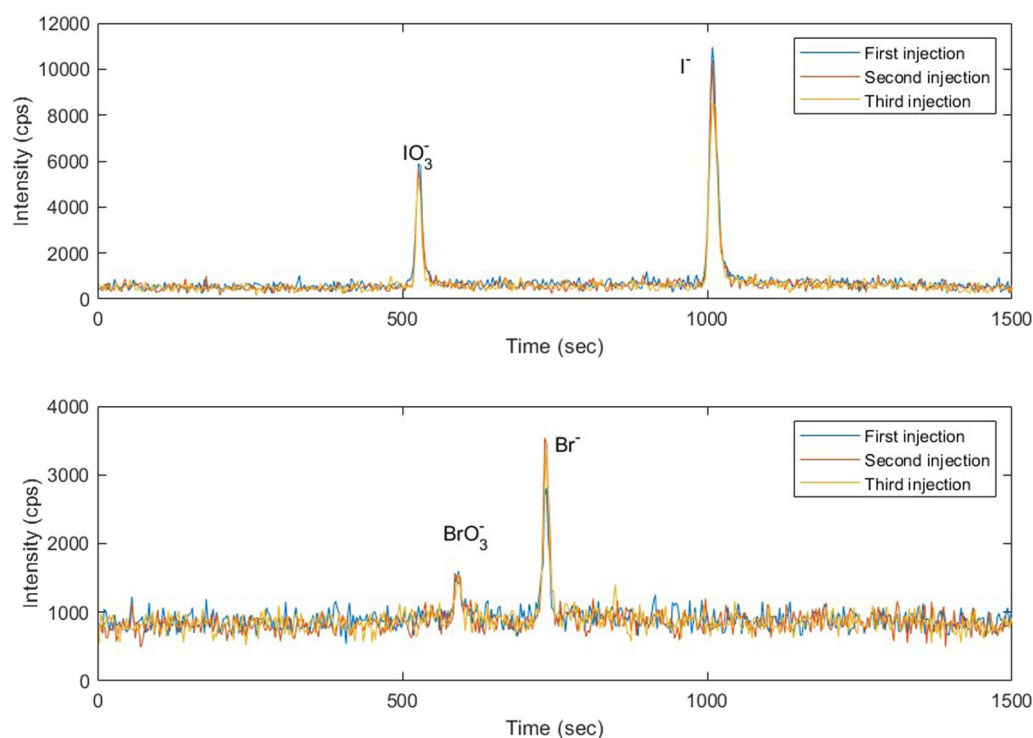


Fig. 1 Triplicate analysis of the standard 10 pg g^{-1} for I^- , Br^- and IO_3^- and 6 pg g^{-1} for BrO_3^- . The chromatogram for iodine is shown in the upper part, while the chromatogram for bromine is shown in the one below

Table 3 Summary of some recent work related to the speciation of iodine and bromine (Gilfedder et al. 2007a, b)

LOD (pg g^{-1})										
Detection	I^-	IO_3^-	Br^-	BrO_3^-	Column	IC flow (mL min^{-1})	Plasma power (W)	mL of sample	Matrices	References
IC-ICP-MS	12	8	63	32	ICS-A23	0.8	1370	1	Tap water	Liu et al. (2011)
IC-ICP-MS	38	52			AS-16	0.9		1	Snow and rain	Gilfedder et al. (2008)
IC-ICP-MS	5	7	8	38	AS-16	0.28	1500	0.3	Ice cores	Spolaor et al. (2013b)
IC-ICP-MS	0.4	0.8	3.7	1.2	AS-19	0.25	1250	1	Snow	This work

5.2% for Br^- , 2.8% for BrO_3^- , 0.87% for I^- and 5.1% for IO_3^- . Consequently, this indicates that the matrix effect (ME) is negligible.

To test the proposed method on environmental matrices, four snow samples from Ny-Ålesund (Svalbard) were analysed. The samples were collected during a snow pit dug on 23 February 2022 (corresponding to the beginning of the day-night cycle at the Svalbard islands) in a delimited sampling area near the Gruvebadet Aerosol Observatory ($78^\circ 55.018' \text{ N}$, $11^\circ 53.698' \text{ E}$, 43 m a.s.l. (Scoto et al. 2023)). Although the total height of the seasonal snowpack was 82 cm, we decided to consider only the deepest snow layers (i.e., the first 40 cm starting from the ground) to exclude

any influence of possible photo-induced reactions that would lead to an increase in the concentrations of iodine-containing species. In fact, the onset of the light period in Arctic areas could bring an increase in marine biological productivity, thus an increase in I_2 in the atmosphere, and trigger photochemical reactions that would lead to the oxidation of I^- to IO_3^- . This assumption then allows these compounds to be identified and quantified in their period of lowest production. A four-point calibration curve was made before each series of analysis, to calculate the concentration in the real samples analysed.

The iodine results, as seen in the chromatogram in Fig. 2, show that the separation of the two analytes of

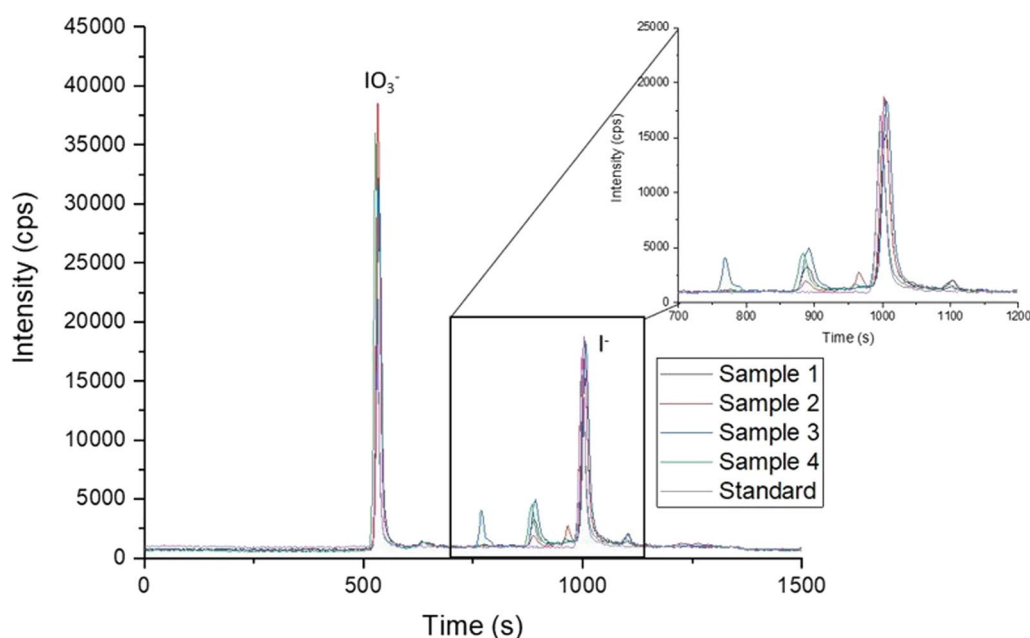


Fig. 2 Overlay of the chromatograms of the iodine-related samples. Moreover, standard (140 pg g^{-1} for IO_3^- and 75 pg g^{-1} for I^-) chromatogram was overlapped to clearly identify the retention times of IO_3^- and I^-

interest was effectively obtained, with concentrations ranging from 146 to 175 pg g^{-1} for IO_3^- and from 67 to 80 pg g^{-1} for I^- .

In addition to I^- and IO_3^- other peaks were found systematically in the real samples, as shown in Fig. 2 snow samples showed other peaks. Since the quantification was done by ICP-MS, it is implicit in the technique that the sample is ionized and then analysed by mass spectrometry, and in the case of iodine, we focused on 127 m/z . However, given the assumptions made in the previous paragraph, it was still possible to perform a semi-quantitative analysis of the results obtained (Table 4). All unknown compounds were quantified using the parameters of the calibration curve for I^- . Although it is implicit in ionization techniques, it is not possible to assign a structure to unknown species that contain iodine. Some works focused on the speciation of iodine by IC-ICPMS in snow and rain suggest that the unknown compounds could be iodine-bound

organic species (Gilfedder et al. 2008, 2007a, 2007b), but it is possible that they are other iodine oxides (e.g., IO^- or IO_2^-) that can be found within the snowpack. Only future studies can confirm the actual structure of these compounds.

Focusing on bromine, concentrations above the detection limit have been obtained for Br^- in the range between 8 and 11 ng g^{-1} , according to other studies on bromine in Svalbard snow (Spolaor et al. 2021), while bromate was under the LOD in any samples. Again, another unknown peak was identified at 637 s retention time. In this case, there are no works, to the best of our knowledge, confirming the structure of this species, so the existence of bromine-related organic species, as well as other bromine oxides, is plausible (Fig. 3). As in the case of iodine, a semi-quantitative analysis was performed on this peak using the bromate calibration curve. In these samples, the average is $56 \pm 4 \text{ pg g}^{-1}$.

Table 4 Iodine-related concentration results expressed as pg g^{-1}

ID	$[\text{IO}_3^-]$	$[\text{I}^-]$	t_R 640 s	t_R 859 s	t_R 965 s	t_R 1113 s
Sample 1	146	67	7	n.d.	15	4
Sample 2	175	75	6	n.d.	7	7
Sample 3	156	80	7	n.d.	24	6
Sample 4	167	67	6	13	21	5

n.d.=not detected

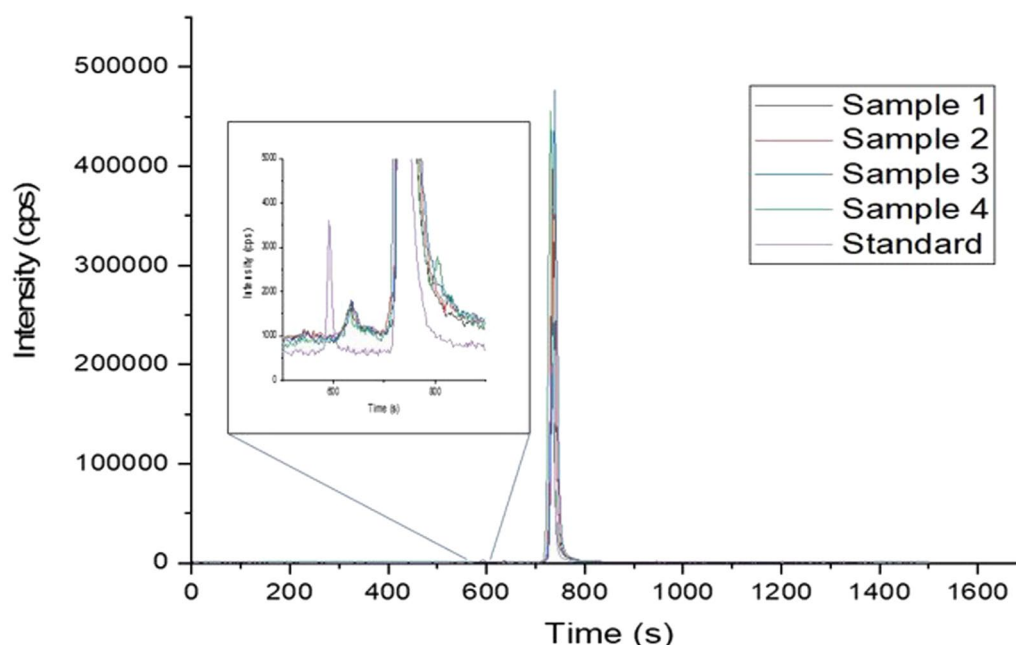


Fig. 3 Overlay of the chromatograms of the samples related to bromine and standard (500 pg g^{-1} for Br^- and 10 pg g^{-1} for BrO_3^-). The inset clearly shows the separation of BrO_3^- of the standard (in purple) from the unknown species present in the samples

Conclusions

This work reported the development of a speciation method using IC-ICPMS that enabled chromatographic separation of iodine and bromine with tenfold lower limits of detection, for I^- , IO_3^- and Br^- , and 30-fold lower for BrO_3^- compared with preexisting work carried out with an analytical method using IC-ICPMS. In particular, LODs were obtained of 0.4 pg g^{-1} for I^- , 0.8 pg g^{-1} for IO_3^- , 4 pg g^{-1} for Br^- , and 1 pg g^{-1} for BrO_3^- , respectively. An additional strength of this work is that we were also able to separate unknown compounds that will need further study to be identified.

This method was developed with the intention of improving the analytical capabilities currently available for halogen speciation. The primary objective of enhancing the detection limits for iodine and bromine species is threefold: i) to provide the scientific community with a powerful analytical tool for two main purposes: ii) the determination of iodine and bromine inorganic species in natural environments that were previously undetectable due to the higher detection limits of existing methods. iii) to investigate the formation of iodine and bromine species and potential changes in speciation under laboratory conditions, even at ultra-trace levels. By achieving lower detection limits for these halogen species, this method opens up new possibilities for studying these elements in both natural and controlled environments, expanding our understanding of their behaviour and impact. Since

these species provide valuable information on various atmospheric chemistry processes and have the potential to be used in paleo and climatic study (e.g., sea ice extent and atmospheric chemistry), it is necessary to improve knowledge of iodine and bromine speciation in polar areas.

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Author contributions

Andrea Spolaor, Elena Barbaro, Stefano Frassati, Giulio Cozzi, Clara Turetta, Kitae Kim contributed to conceptualization; Andrea Spolaor, Elena Barbaro, Stefano Frassati, Giulio Cozzi, Clara Turetta, Kitae Kim, Claudia Rossetti helped in methodology; Andrea Spolaor, Elena Barbaro, Stefano Frassati, Giulio Cozzi, Clara Turetta, Federico Scoto, Matteo Feltracco, Claudia Rossetti helped in formal analysis and investigation; Stefano Frassati, Elena Barbaro, Andrea Spolaor done writing—original draft preparation; Stefano Frassati, Elena Barbaro, Claudia Rossetti, Giulio Cozzi, Clara Turetta, Federico Scoto, Marco Roman, Matteo Feltracco, Kitae Kim, Carlo Barbante, Andrea Gambaro, Andrea Spolaor done writing—review and editing; Andrea Gambaro, Carlo Barbante, Andrea Spolaor helped in supervision.

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Availability of data and materials

Upon reasonable request, the datasets of this study can be available from the corresponding author.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors consent for publication.

Competing interests

The authors declare that there is no conflict of interest regarding the publication of this article.

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