



Use of pressurized hot water extraction and high performance liquid chromatography–inductively coupled plasma–mass spectrometry for water soluble halides speciation in atmospheric particulate matter

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ABSTRACT

The feasibility of pressurized hot water extraction (PHWE) has been novelty investigated to speed up water soluble halide species (bromide, Br^- ; bromate, BrO_3^- ; iodide, I^- and iodate, IO_3^-) leaching from atmospheric particulate matter (PM_{10} and $\text{PM}_{2.5}$). Total bromine and iodine and total water soluble bromine and iodine have been assessed by inductively coupled plasma–mass spectrometry (ICP–MS). Water-soluble bromine and iodine species were also measured by ICP–MS after anion exchange high performance liquid chromatography (HPLC). Variables inherent to the pressurized hot water extraction process (temperature, modifier concentration, static time, pressure, number of cycles and dispersing agent mass) were fully studied. Results showed that the pressurized leaching procedure can be performed in 9 min (5 min for pre-heating, 2 min of static time, 1 min of purge time, and 1 min of end relief time). The use of diluted acetic acid as a modifier did not improve the target recoveries. Dispersing agent (diatomaceous earth) was not needed, which reduces the time for filling the cells. Water-soluble halides were reached under the following extraction conditions: extraction temperature of 100 °C, pressure of 1500 psi, static time of 2 min and 1 extraction cycle. Optimized HPLC conditions consisted of an isocratic elution with 175 mM ammonium nitrate plus 15% (v/v) methanol as mobile phase (optimum flow rate of at 1.5 mL min⁻¹). Analytical performances, such as limits of detection and quantification, repeatability and analytical recoveries of the over-all procedure have been established. Results obtained show water soluble halides accounted for approximately 20.9 ± 1.3 and 11.8 ± 0.6% of the total bromine and total iodine, respectively. A 79 and 89% of bromine and iodine was non-water soluble, which may be organic non-water soluble species. Br^- and IO_3^- were found to be the major species, and they accounted for 100% of the total water-soluble bromine and iodine.

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1. Introduction

Bromine and iodine are naturally occurring non-metallic elements of the periodic table's group VIIA. The action of these elements in humans varies greatly. In the atmosphere the concentration of bromine and iodine ranges from 10 to 100 ng m⁻³ and from 10 to 20 ng m⁻³, respectively; depending on the proximity to the sea and the soil type [1,2]. The generation of sea-salt aerosol at the ocean surface is the major tropospheric source of inorganic bromine (bromide, Br^- ; and BrO_3^-) and iodine (iodide, I^- , and iodate, IO_3^-) and organoiodine compounds [3,4]. Macroalgae play an important role in the biosynthesis of volatile halides species and hence their presence in seawater and in the marine atmosphere. Recent studies

have found that molecular iodine (I_2) and methyl bromide (CH_3Br) are the main emitted species by seaweed to atmosphere [5–7]. Fungi [8] and terrestrial plants [9] are other natural sources of CH_3Br . Concerning anthropogenic sources, the combustion of fossil fuels [1,10], and the use of neutral polyfluorinated iodine alkanes (PFIs), lubricants, varnishes and pesticides are the most important [11,12].

The presence of chlorine and bromine in atmosphere may significantly alter ozone concentrations (O_3 -losses) and the lifetime of pollutants (i.e., halogens act as an oxidant for dimethylsulphide, and they are a pathway for nitrogen oxides removal). The cycling of iodine plays therefore an important role for ozone destruction in the marine atmosphere; and despite the low bromine abundance, the role of this latter halogen is not less important than chlorine in causing ozone destruction [13–15].

Most of the published studies are focused on assessing the total bromine and iodine levels in aerosols as well as on their species (mainly, inorganic species) [1]. However, data about the

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water soluble fraction of these species is scarce. The dissolution in water (water soluble fraction) of certain pollutants bound within the aerosol particles is crucial for biogeochemical issues, which affects environmental mobility of pollutants, aquatic contamination, bioavailability, marine biogeochemistry, cloud processes; and finally, it concerns the public health [16].

Iodine species such as I_2 , HI, ICl, HIO [17,18], organic iodine (CH_3I , C_2H_5I , CH_2ClI and PFIs) and organic bromine (CH_3Br) species have been quantified in aerosol samples [7,12,17]. For inorganic species, isotopic dilution–mass spectrometry after anion exchange HPLC was used by Wimschneider and Heumann [19] for assessing I^- and IO_3^- species in size fractionated atmospheric particles after water extraction of the filters (vigorous stirring at 100 °C for 2 h). The quantification of I^- and IO_3^- at the low $ng\ m^{-3}$ level in aerosol samples was also performed by Brüchert et al. [20] using gel electrophoresis coupled to ICP–MS and isotope dilution after water extraction (ultrasounds assisted at room temperature for 30–40 min). In addition elemental iodine, (probably in form of triiodide) was also identified. Finally, Xu et al. [21] quantified Br^- , BO_3^- , I^- and IO_3^- in aerosol samples by HPLC–ICP–MS after water extraction (ultrasounds assisted at temperature < 35 °C for times within the 5–60 min range).

The new European Council Directive (2008/50/CE) [22] frames the inhalable (PM_{10}) and fine particles ($PM_{2.5}$) on priority to chemically characterize these fractions to understand their possible relation with health effects. Considering this, PM_{10} and $PM_{2.5}$ were collected during different seasons to evaluate iodine and bromine species over suburban area of A Coruña, a coastal city in the northwest of Spain. The area is strongly influenced by sea aerosol because the proximity to the sea. The atmospheric aerosol samples were collected during 2009–2010. The objective of the current work has been the evaluation of PHWE for extracting water soluble bromine and iodine species from atmospheric particulate matter. PHWE allows a rapid, simple and safe sample pre-treatment. The extraction procedure is performed in 9 min, a shorter time than those reported times when using conventional ultrasounds-based procedures [20]. In addition, the developed PHWE process offered other advantages over ultrasounds methods such as extract handling avoidance because a filtration stage is not required. Finally, the developed HPLC–ICP–MS method allows the simultaneous bromine and iodine speciation in the atmospheric samples.

2. Experimental

2.1. Apparatus

Total bromine and iodine contents were measured with an ICP–MS Thermo Finnigan X Series. The HPLC–ICP–MS analysis was performed with a Dionex HPLC UltiMateO 3000 LC (Dionex, Sunnyvale, CA, USA), equipped with a GP50 gradient pump (Dionex), an AS50 thermal compartment (Dionex) and an AS50 auto-sampler (Dionex). Halides species separation was performed with an IonPac AS7 (250 × 4 mm i.d.) anion-exchange column (Dionex) and a guard column IonPac AG7 (Dionex). The chromatographic system was coupled to an ICP–MS Thermo Finnigan X Series. Halide leaching was performed with a Dionex ASE-200 system (Sunnyvale, CA, USA) equipped with 11 mL stainless steel extraction cells (Sunnyvale) and cellulose filters (D28, 1.983 cm diameter, Dionex). Finally, an Ethos Plus microwave lab-station (Milestone, Sorisole, Italy) with 100 mL closed Teflon vessels and Teflon covers, HTC adapter plate and HTC safety springs (Milestone) has been used for alkaline digestion of filters.

2.2. Reagents

All chemicals used were of ultrapure grade, and diluted using ultrapure water resistance $18\ M\Omega\ cm^{-1}$ obtained from a Milli-Q purification device (Millipore Co., Bedford, MA, USA). Stock standard solutions, $1000\ mg\ L^{-1}$, were prepared from 99.5% potassium iodide (Merck, Darmstadt, Germany), 99.95% potassium bromide (Sigma Chemicals, St Louis, MO, USA), 99.7–100.4% potassium iodate (Merck) and 99.8% potassium bromate (Merck). Tellurium chloride and yttrium nitrate standard solutions, $1000\ mg\ L^{-1}$, were from SCP Science (Montreal, Canada). Diatomaceous earth, 95% SiO_2 , used as dispersing agent, was from Aldrich Chemical Co. (Milwaukee, WI, USA). Ammonium nitrate salts and methanol (gradient grade) were from Merck. Tetramethyl-ammonium hydroxide (TMAH) 25% (m/m) in water (Merck) was used for the alkaline solubilisation of PM_{10} and $PM_{2.5}$ filters. To avoid metal contamination, all glassware and plastic ware were washed and kept for 48 h in 10% (v/v) nitric acid, then rinsed several times with ultra-pure water before use.

2.3. Atmospheric particulate matter sample collection

Atmospheric particulate matter samples were collected in a suburban area (Oleiros, latitude 43.2°N, longitude 8.17°W) of A Coruña, Spain in 2009–2010. A Graseby-Andersen High volume sampler, which meets the requirements of UNE EN 12341 European Norm [23], was used for PM_{10} particulate matter collection on QF20 quartz fiber filters ($20.3 \times 25.4\ cm^2$) by using an aspiration volume of $68\ m^3\ h^{-1}$ during 24 h. A Digitel Automatic High Volume Dust Sampler DA80, recommended by the Commission of European Communities [24], was used for $PM_{2.5}$ particulate matter collection on 15 cm diameter QF20 quartz fiber filters (Schleicher&Schuell, D-Dassel, Germany). The atmospheric particulate matter was collected by using an aspiration volume of $30\ m^3\ h^{-1}$ during 24 h. Preceding sampling, filters were pre-heated at 400 °C for 12 h, conditioned in a desiccator at constant temperature ($20 \pm 1\ ^\circ C$) and relative humidity conditions ($50 \pm 5\%$) according to EN 12341 European Norm for 48 h, and finally weighed. After sampling, PM_{10} and $PM_{2.5}$ samples were stored in a freezer ($-18\ ^\circ C$) until further analysis.

2.4. Pressurised hot water extraction

Ten circular portions of $3.14\ cm^2$ were cut from the same particulate matter filter using a hollow and sharp-edged steel cylinder (Selecta, Barcelona, Spain). The extraction cells were filled with the ten circular portions and fitted with a cellulose filter, and were situated in the carousel of the ASE 200 system after cells closure. The extracting solution consisted of Milli-Q water without modifier working with a PLE flush volume (the volume of fresh solvent used to clean the extraction cell after static extraction) fixed at 60%. The pressurized conditions (PHWE extraction conditions) are summarized in Table 1. The cells were purged for 60 s with N_2 after the pressurization and the extract was collected in pre-cleaned glass vials. Finally, the extracts were diluted to 25 mL, placed into pre-cleaned plastic bottles and

Table 1
Pressurized liquid extraction conditions.

Extraction temperature (°C)	100
Static time (min)	2
Extraction step	1
Pressure (psi)	1500
Flush volume solvent (%)	60
N_2 purge time (s)	60
Cell size (mL)	5

stored at 4 °C until further analysis. At least 2 different blanks were performed for each set of PHWE conditions.

2.5. Microwave-assisted alkaline digestion

A microwave assisted alkaline digestion (MAAD) was performed to assess total iodine and bromine contents in atmospheric particulate matter samples. Ten circular portions of the same filter ($10 \times 3.14 \text{ cm}^2$) were digested following the method described by Romarís-Hortas et al. [25,26] filter portions were placed into microwave Teflon vessels, and 5 mL of ultrapure water and 5 mL of TMAH were added. After capping the vessels, they were subjected to microwave irradiation at a first step (10 min of ramp time for increasing the temperature from 20 to 200 °C), and at second step at 200 °C for five minutes. After cooling down, sample extracts were filtered, transferring the supernatant to 25 mL volumetric flasks. Finally, extracts were filtered through 0.45 μm cellulose acetate syringe filters (Millipore) before ICP–MS measurements. Each sample was microwave alkaline digested in triplicate and one reagent blank was also prepared for each microwave irradiation set.

2.6. Total bromine and iodine determination by ICP–MS

Total bromine and iodine in the TMAH extracts and total water-soluble bromine and iodine in the PHWE extracts were determined by ICP–MS following the operation conditions listed in Table 2. TMAH and water extracts were conveniently diluted before ICP–MS measurement. Tellurium (^{125}Te) at a concentration of 2.0 mg L^{-1} and yttrium (^{89}Y) at $2 \text{ }\mu\text{g L}^{-1}$ were chosen as internal standards for iodine and bromine determinations, respectively. A flow of 4.5 mL min^{-1} H_2/He in the collision cell was used to minimize the $^{38}\text{Ar}^{40}\text{Ar}^1\text{H}^+$ (m/z 79) bromine polyatomic interference. This gave

Table 2
Operating ICP–MS conditions for total iodine and bromine determination.

General		
	Radiofrequency power (W)	1380
	Peristaltic pump speed (mL min^{-1})	0.45
	Stabilization delay (s)	35
	Number of replicates	3
	Nebulizer type	MicroMist
Gas flows (L min^{-1})		
	Nebulizer	0.98
	Plasma	17.0
	Auxiliary	1.65
	Sheath	0.27
	Skimmer cone	Nickel
	Sampler cone	Nickel
Torch alignment (mm)		
	Sampling death	7.0
Ion optics (V)		
	First extraction lens	–32
	Second extraction lens	–164
	Third extraction lens	–231
	Corner lens	–206
	Mirror lens right	25
	Mirror lens left	24
	Mirror lens bottom	27
	Entrance lens	3
	Fringe Bias	–4.9
	Entrance plate	–3.4
	Pole bias	0
CRI (mL min^{-1})		
	Skimmer gas source	H_2
	Sampler gas source	OFF
	Skimmer flow	80
	Sampler flow	0
Mass-to-charge ratio		
	Br	79
	I	127

Table 3
Analytical recovery \pm SD (for $n=7$) of the microwave alkaline digestion and PHWE procedures.

Analyte	Microwave alkaline digestion			PHWE	
	[] _{added} ($\mu\text{g L}^{-1}$)	[] _{measured} ($\mu\text{g L}^{-1}$)	Analytical recovery (%)	[] _{measured} ($\mu\text{g L}^{-1}$)	Analytical recovery (%)
Br	10	9.6 ± 1	96 ± 3	10 ± 0.3	103 ± 3
	25	25 ± 2	98 ± 6	24 ± 1	97 ± 5
	50	54 ± 2	107 ± 4	47 ± 2	93 ± 4
I	0.25	0.23 ± 0.01	91 ± 4	0.27 ± 0.01	108 ± 4
	2.5	2.6 ± 0.1	102 ± 4	2.6 ± 0.2	104 ± 8
	5.0	4.8 ± 0.2	96 ± 4	5.0 ± 0.3	99 ± 2

the best sensitivity and linear ranges for bromine and also for iodine determinations. Calibrations have covered bromine and iodine concentrations in the range of $0\text{--}250 \text{ }\mu\text{g L}^{-1}$ and $0\text{--}5.0 \text{ }\mu\text{g L}^{-1}$, respectively. ICP–MS determinations gave a limit of detection (LOD) and a limit of quantification (LOQ), based on the 3 SD/10 SD criterion, respectively (SD, standard deviation of 11 measurements of a reagent blank), of 0.08 and 0.25 ng m^{-3} for bromine and 0.02 and 0.07 ng m^{-3} for iodine. Analytical recoveries for total bromine and iodine determination were performed. Ten circular portions of 3.14 cm^2 from the same sampled PM filter were spiked with bromine and iodine at three levels: $10 \text{ }\mu\text{g L}^{-1}$ for Br^- and $0.25 \text{ }\mu\text{g L}^{-1}$ for I^- (low level); $75 \text{ }\mu\text{g L}^{-1}$ Br^- and $2.5 \text{ }\mu\text{g L}^{-1}$ for I^- (intermediate level); and $250 \text{ }\mu\text{g L}^{-1}$ Br^- and $5.0 \text{ }\mu\text{g L}^{-1}$ for I^- (high level). Spiked PM samples were submitted to microwave alkaline digestion ($n=7$) or PHWE extraction ($n=7$). Table 3 lists the concentrations found as well as the analytical recovery values. Analytical recoveries within the 91–108% range were obtained, and good accuracy has been proved for both methods.

2.7. Water-soluble halides determination by HPLC–ICP–MS

Anion exchange HPLC conditions were optimized to separate iodine species (iodide and iodate) and bromine species (bromide and bromate) in a single chromatographic run. An isocratic elution program (175 mM ammonium nitrate plus 15% (v/v) methanol as a mobile phase, flow rate of 1.5 mL min^{-1}) was used (Table 4). The outlet of the separation column was directly connected to the Meinhard nebulizer using a PEEK tubing (50 cm length). Under the ICP–MS conditions (Table 4), problems derived from the use of methanol as a component of the mobile phases were not observed. Collision cell technology (H_2/He at 4.5 mL min^{-1}) was used to reduce the $^{38}\text{Ar}^{40}\text{Ar}^1\text{H}^+$ (m/z 79) bromine polyatomic interference. Tellurium (^{125}Te) at a concentration of 2 mg L^{-1} , and yttrium (^{89}Y) at $2 \text{ }\mu\text{g L}^{-1}$, were used as internal standards by continuously mixing the chromatographic eluate with an external flow of the internal standard mixture (1.25 mL min^{-1}) using a T-junction after the column and just before the nebulizer.

3. Results and discussion

3.1. Optimization of operating anion exchange HPLC conditions

As recently reviewed, anion exchange chromatography (AEC) is commonly used for separating inorganic iodine forms in speciation studies [1]. Several mobile phases such sodium hydroxide [27,28], potassium nitrate/nitric acid [29] and ammonium nitrate [30,31] have been reported in the literature for elution of inorganic bromine (Br^- and BrO_3^-) and iodine (I^- and IO_3^-) forms using different anion exchange columns. Most of the developed methods imply isocratic elution although some gradient programs have been also used [29]. In general, good resolution of iodide and iodate was

Table 4
Operating ICP–MS conditions and anion exchange HPLC–ICP–MS settings for bromine and iodine speciation.

ICP–MS	Radiofrequency power (W)	1400
	Peristaltic pump speed (rpm)	2.5
	Nebulizer type	Beat impact (cooled spray chamber)
Gas flows (L min ⁻¹)	Plasma	14.0
	Auxiliary	0.8
	Nebulizer	0.85
Torch alignment (mm)	Horizontal	117
	Vertical	317
	Sampling depth	210
Ion optics (V)	Extraction	–102
	Lens 1	–1150
	Lens 2	–62
	Focus	–7.8
	D1	–55.7
	D2	–140
	Pole bias	–15
	Hexapole bias	–18
CCT–KED (mL min ⁻¹)	H ₂ /He	4.5
Mass-to-charge ratio	I	127
	Br	79
	¹²⁵ Te (2.0 mg L ⁻¹) and ⁸⁹ Y (5.0 μg L ⁻¹) as internal standards (post-column added at 1.25 mL min ⁻¹)	
AEC–HPLC	Dionex IonPac AS7 (250 mm × 4 mm i.d.) anion-exchange column coupled to a Dionex IonPac AG7 guard column	
	Injection volume	50 μL
	Column temperature (°C)	25
Elution program	Isocratic	
Mobile phase composition	175 mM ammonium nitrate, 15.0% (v/v) methanol	
Mobile phase flow	1.5 mL min ⁻¹	

achieved by using 20 mM ammonium nitrate at a flow rate of 1.0 mL min⁻¹ (retention time of 13.0 min for iodide) [30], while the use of ammonium nitrate at concentrations up to 75 mM allowed a fast elution of iodide [31].

Therefore, anion exchange HPLC conditions were optimized to obtain the separation of inorganic bromine and iodine species (Br⁻, BrO₃⁻, I⁻ and IO₃⁻) in an isocratic elution run using ammonium nitrate solutions at high concentrations. Ammonium nitrate concentrations from 125 to 200 mM were studied (concentration higher than 200 mM were not considered due to the poor resolution achieved for bromate and bromide). Fig. 1 shows different chromatograms when varying the composition of the mobile phase. Good resolution was assessed under all ammonium nitrate concentrations tested, except for BrO₃⁻ and Br⁻ when using a 200 mM ammonium nitrate solution as a mobile phase. However, short chromatographic times, mainly for I⁻, were obtained when working at high ammonium nitrate concentrations. As a compromise condition, an ammonium nitrate concentration of 175 mM was finally chosen.

The use of a small proportion of methanol in the aqueous mobile phase has been reported to improve resolution in the Dionex AS7 anion exchange column [32]. Therefore, experiments involving increased methanol concentrations (up to 30%) were performed. As a result, retention times were not affected but the chromatographic peak schemes were improved in presence of methanol up to 15% (higher methanol concentrations decreased the chromatographic signals). Therefore, the composition of the mobile phase was finally set at 175 mM ammonium nitrate and 15% (v/v) methanol.

The effect of the temperature (15, 25, and 35 °C) on the separation of the inorganic iodine and bromine species was also tested. Iodine elutes faster at temperatures higher than room temperature (Fig. 2), but signal intensities were not increased when working at high temperatures. The influence of the temperature on the elution time appears marginal for other targeted compounds. Room temperature (column oven heated at 25 °C) was therefore selected.

Finally, mobile phase flow rates (within the 0.5–1.5 mL min⁻¹ range) were studied, and a flow rate of 1.5 mL min⁻¹ was finally chosen. Under the chromatographic conditions shown above, good resolution between inorganic bromine species was achieved and separation can be performed in less than 7 min.

3.2. Optimization of PHWE conditions

Different experiments were performed to check the efficiency of PHWE for assessing water soluble bromine and iodine and also water soluble Br⁻, BrO₃⁻, I⁻ and IO₃⁻ species in atmospheric particulate matter. Experiments were performed using a PM₁₀ sample pool. The percentage of water soluble halide was calculated by applying the equation:

$$\text{Percentage water soluble halide} = \left[\frac{[]_{\text{PHWE}}}{[]_{\text{MAAD}}} \right] \times 100.$$

where []_{PHWE} is the water soluble halide concentration (total bromine or total iodine measured by ICP–MS; or Br⁻, BrO₃⁻, I⁻, and IO₃⁻ measured by HPLC–ICP–MS after the PHWE procedure), and []_{MAAD} is the total halide concentration (total bromine or total iodine) after microwave alkaline digestion and ICP–MS detection (27.5 ± 6.4 and 7.23 ± 0.80 ng m⁻³ n=7, for total bromine and iodine, respectively).

Due to BrO₃⁻ and I⁻ concentrations in the PM₁₀ sample pool used for optimization were below LOQs, figures in this section only show percentages of total bromine and iodine, and bromide and iodate.

3.2.1. Extraction temperature

PHWE efficiency depends on temperature because temperature improves diffusion rates, mass transfer and solubility of the analyte (increase of kinetics disruption of analyte–matrix interactions and reduction of solvent viscosity). The minimum and maximum temperature values allowed by the ASE system were room temperature (oven off) and 200 °C, respectively. Thus, PHWE efficiency was evaluated within this range. Other PHWE conditions were fixed

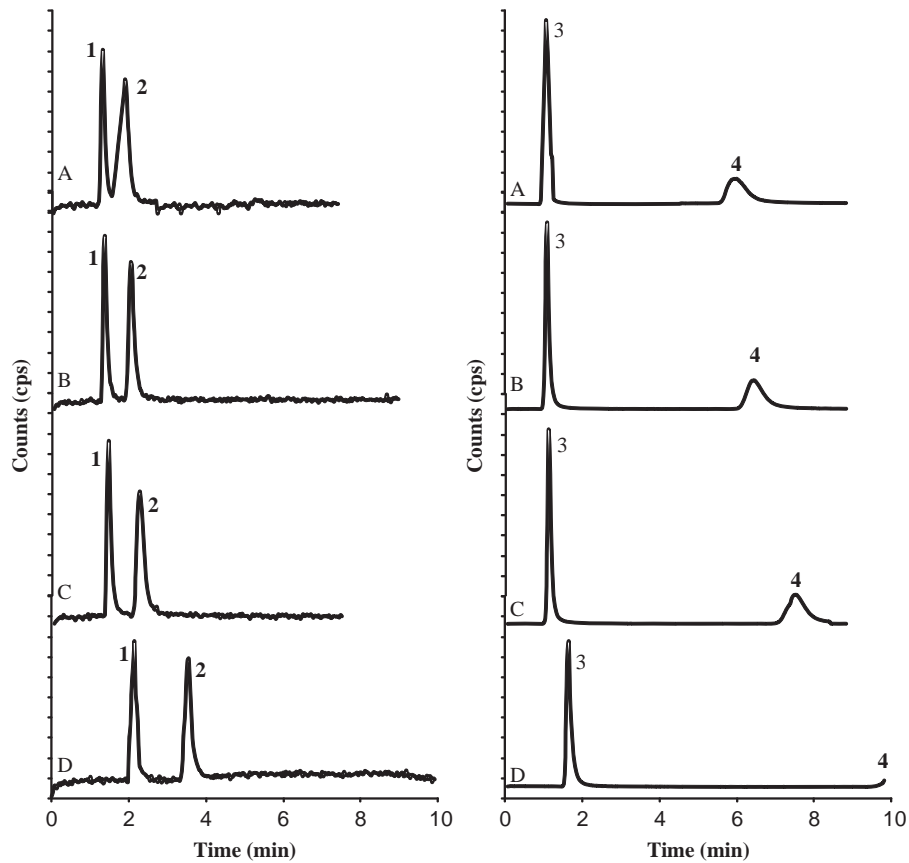


Fig. 1. Chromatograms of inorganic bromine and iodine species standards ($100 \mu\text{g L}^{-1}$ of bromate (1), bromide (2), iodate (3) and iodide (4) for several ammonium nitrate concentration: 200 mM (A), 175 mM (B), 150 mM (C) and 125 mM (D). Other HPLC conditions: injection volume of $50 \mu\text{L}$, column temperature of 25°C , methanol concentration of 5.0% (v/v) and mobile phase flow of 1.5 mL min^{-1} .

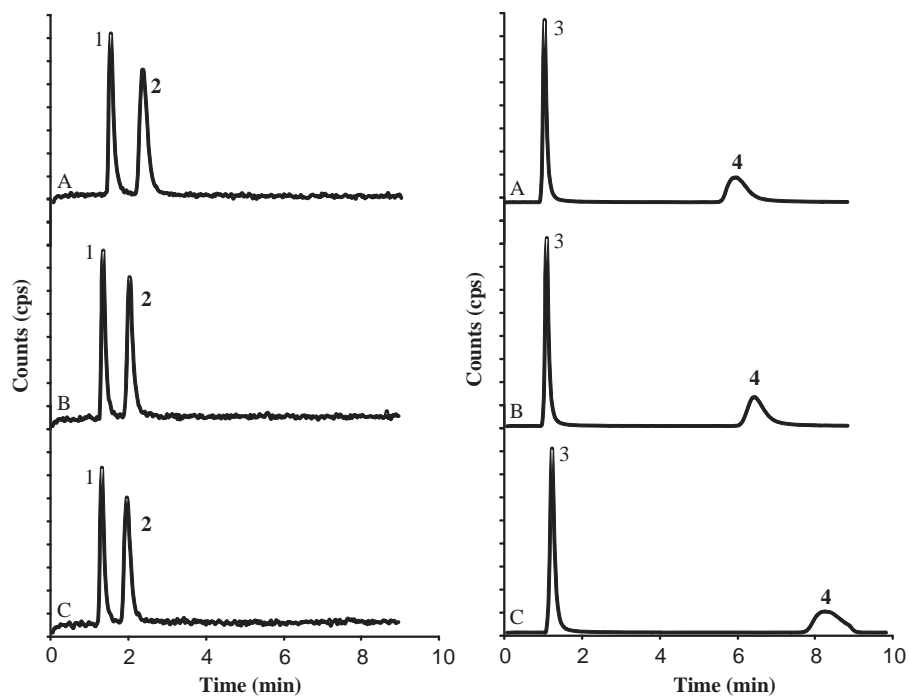


Fig. 2. Chromatograms of inorganic bromine and iodine species standards ($100 \mu\text{g L}^{-1}$ of bromate (1), bromide (2), iodate (3) and iodide (4) for column oven temperature: 35°C (A), 25°C (B) and 15°C (C). Other HPLC conditions: injection volume of $50 \mu\text{L}$, mobile phase composition of 175 mM ammonium nitrate and 15% (v/v) methanol and mobile phase flow of 1.5 mL min^{-1} .

at 1000 psi, and two extraction steps of 5.0 min. Targets releasing is increased when working at temperatures up to 100 °C. This PHWE temperature is therefore chosen as optimum value.

3.2.2. Pressure

Pressure keeps the water in the liquid state at high temperatures and aids solvent penetration of the pores of the matrix. The minimum and the maximum pressure values allowed by the ASE system were 500 and 3000 psi, respectively. Therefore, the pressure was studied from 500 to 3000 psi. Other PHWE conditions were set at 100 °C, and two extraction steps of 5.0 min. Results (concentrations in the ranges of 5.54–5.88, 5.43–5.65, 0.64–0.69 and 0.62–0.72 ng m⁻³ for bromine, Br⁻, iodine and IO₃⁻, respectively) have shown that this variable was not important in the studied pressure range. This parameter was then fixed at 1500 psi.

3.2.3. Extraction time and number of extraction steps

Analyte leaching could not be completed after only one equilibration step (one cycle), so the use of several extraction cycles may be necessary. Regarding the number of extraction steps, the ASE system allows repeating, up five times, the extraction procedure using fresh extracting solvent each time. The number of extraction steps was tested from 1 to 5. Other PHWE conditions were 100 °C, 1500 psi and static time of 5.0 min. Results show that the increase on the number of extraction steps does not enhance bromine and iodide recoveries.

The static time was also studied within the 1–10 min range. Static times greater than 10 min were not considered because a pre-heating time is automatically fixed by the PLE system software when working at temperatures different from room temperature (100 °C was selected as an optimum extraction temperature). Other PHWE conditions were 1500 psi and one extraction step. Results show that the extraction efficiency was increased when using extraction times up to 2.0 min. Therefore, 1 cycle of 2.0 min was selected, which guaranties quantitative recoveries and a fast extraction process.

3.2.4. Other PHWE parameters

Similarly to conventional PLE, PHWE requires the dispersion of the sample in an inert dispersion medium before the extraction. This ensures the uniform sample dispersion and results in good solvent–sample contact within the extraction cell, avoiding the aggregation of sample particles. Amounts of diatomaceous earth within the 0.1–0.5 g range were tested (these amounts were placed between each filter portion and represent diatomaceous earth amount between 1 and 5 g). Target recoveries (data are not given) were similar for all cases. A further experiment was performed without using dispersion material, and the target recoveries were not diminished. This implies that sample dispersion within the cell is not necessary, and the atmospheric particles appear to be conveniently dispersed onto the porous quartz fiber filters. Therefore, addition of any inert dispersion reagent between each circular portion of filters is not needed. This simplifies and reduces the filling of the cells.

The use of organic solvents/acids at low concentration in the extracting solution is a common practice in PLE procedures for enhancing extraction efficiency. Thus, the suitability of different carboxylic acids (formic acid, acetic acid and oxalic acid; added as modifiers at concentrations up to 3.0% m/v) was studied. Result shows similar bromine and iodine recoveries for all modifiers and concentrations tested, and the addition of any modifier was considered.

Finally, the flush volume and the purge time were also studied. Results (data are not given) have shown that these variables were

Table 5
Mean slopes for calibration, and limits of detection and quantification.

Analyte	Mean calibration slope ± SD (L ng ⁻¹) ^a	LOD (ng m ⁻³) ^b	LOQ (ng m ⁻³) ^b
Br ⁻	1124 ± 164	0.10	0.30
BrO ₃ ⁻	615 ± 89	0.12	0.40
I ⁻	19 ± 2	0.01	0.03
IO ₃ ⁻	22 ± 3	0.01	0.03

^a n=5.

^b n=11.

not important within the 60–90% and 60–90 s ranges, and these parameters were finally fixed at 60% and 60 s, respectively.

3.3. Analytical performance

Different calibration curves were obtained by covering total bromine, Br⁻ and BrO₃⁻ concentrations of 0, 10, 20, 30 and 40 µg L⁻¹; while calibrations covered concentrations of 0, 1.0, 2.0, 4.0 and 6.0 µg L⁻¹ for total iodine, I⁻ and IO₃⁻. Table 5 lists the means and standard deviations of the slopes of calibration graphs for each analyte. Since the *P*-values in the ANOVA tables are less than 0.01, there is a statistically significant relationship between each halide signals and halides concentrations at the 99% confidence level. Good repeatability of the calibration curves can be seen over six different days, with RSD lower than 15% for all cases. LODs and LOQs (based on the 3 SD/10 SD criterion (SD is the standard deviation of eleven measurements of a blank)) expressed as ng m⁻³ are also listed in Table 5 for the PHWE–HPLC–ICP–MS method by considering the mean slopes of the calibration graph for each target, and taking into account the extract volume (25 mL) and the air volume aspirated (720 m³). It can be seen that the values are low enough to perform iodine and bromine speciation in atmospheric particulate matter.

Repeatability of the over-all procedure (n=7) has provided RSD values lower than 12% (12% for total bromine; 7% for Br⁻ and BrO₃⁻; 11% for total iodine; and 6% for I⁻ and IO₃⁻). Analytical recoveries for bromine and iodine species determination were performed. Ten circular portions of 3.14 cm² from the same PM filter were spiked with different concentrations of bromine and iodine species at three levels: 10 µg L⁻¹ for Br⁻ and BrO₃⁻, and 0.5 µg L⁻¹ for I⁻ and IO₃⁻ (low level); 20 µg L⁻¹ for Br⁻ and BrO₃⁻, and 2.5 µg L⁻¹ for I⁻ and IO₃⁻ (intermediate level); and 40 µg L⁻¹ for Br⁻ and BrO₃⁻, and 5.0 µg L⁻¹ for I⁻ and IO₃⁻ (high level). Spiked samples were submitted to PHWE (n=3). Table 6 lists the concentrations found as well as the analytical recovery values. Analytical recoveries within the 89–104% range were obtained, and good accuracy has been proved for both methods.

3.4. Application of the method

Several atmospheric particulate matter samples collected at three sampling stations located in a suburban area (A Coruña, Northwestern Spain) in 2009–2010 were extracted by PHWE (for total water soluble bromine and iodine, and water soluble bromide and iodide species). Total bromine and iodine concentration was also assessed after MAAD. Results obtained are showed in Table 7, while Fig. 3 shows typical chromatograms for a PM₁₀ (a) and PM_{2.5} (b) after the proposed PHWE. As can be seen, total halide concentrations were in the <0.6–88.2 and <0.01–24.4 ng m⁻³ ranges, for total bromine and iodine, respectively. Otherwise, total water soluble bromine and iodine concentrations found were low (in the <0.6–17.2 and <0.04–3.12 ng m⁻³ ranges, for bromine and iodine, respectively). Thus, water soluble bromine and iodine accounted approximately 20.9 ± 1.3 and 11.8 ± 0.6% of the total bromine and total iodine,

respectively. About 80 and 88% of bromine and iodine was non-water soluble forms, and it may include non-water soluble organic iodine/bromine species. These non-water soluble organic species have been reported to be as substances bound to mineral dust, and natural organic matter; and/or adsorbed to the black carbon or mineral material such as iron oxides [33].

Br^- and IO_3^- were found in most of the analyzed samples, with concentrations within the <0.3 – 16.6 and <0.03 – 2.84 ng m^{-3} ranges, respectively. I^- was only found in five samples (ranging from <0.03 to 0.20 ng m^{-3}), while BrO_3^- was not detected in any sample. The major water soluble bromine and iodine species found in the analysed samples are therefore Br^- and IO_3^- . Finally, concentrations found in $\text{PM}_{2.5}$ samples (3.7 ± 3.3 and 1.4 ± 1.7 ng m^{-3} for total bromine and total iodine, respectively) are lower than in PM_{10} samples (33.3 ± 29.6 and 5.2 ± 7.9 ng m^{-3} for total bromine and total iodine, respectively).

Target analytes were also extracted from samples listed in Table 7 by using a conventional ultrasound energy procedure according to Brüchert et al. [20]. The extracts were also measured by ICP-MS (for total bromine water soluble and total iodine water soluble) and HPLC-ICP-MS (for Br^- , I^- and IO_3^-). The results from both methods (conventional ultrasound extraction and

PHWE) were compared statistically in terms of analyte concentrations. The analyte concentrations obtained after both extraction procedures were similar. Correlation coefficients (R^2 , $n=15$) of 0.9311, 0.9351, 0.8859, 0.8581 and 0.8681 for total Br water soluble, Br^- water soluble, total I water soluble, I^- water soluble and IO_3^- water soluble, respectively, were obtained. The application of the paired t -test (95% confidence level and 14, 14, 15, 5 and 15 degrees of freedom for total Br water soluble, Br^- water soluble, total I water soluble, I^- water soluble and IO_3^- water soluble, respectively) gave a t_{cal} of 0.30, 0.45, 0.95, 0.16 and 0.002 for total Br water soluble, Br^- water soluble, total I water soluble, I^- water soluble and IO_3^- water soluble, respectively; which are lower than the t_{crit} values (2.16, 2.16, 2.14, 2.77 and 2.14 for total Br water soluble, Br^- water soluble, total I water soluble, I^- water soluble and IO_3^- water soluble, respectively). Therefore, results after PHWE are statistically similar than those obtained after conventional procedure based on ultrasounds energy.

The iodine/bromine concentration ranges shown in Table 7 agree with those reported data from coastal areas. Total iodine and total water-soluble iodine concentrations ranged from 1.3 to 12.7 ng m^{-3} and from 0.74–10 ng m^{-3} over the Southern Ocean and at the tropical Atlantic [34], which accounted high iodine water soluble percentages (from 47 to 80%). The authors concluded that iodine present in the samples is mainly from marine sources [34]. Other reports showed mean annual concentrations of total bromine and iodine in Shanghai, China of 21 and 9 ng m^{-3} for PM_{10} [33], which implied a low water-soluble bromine and iodine ratio (approximately a 32% of the total bromine and iodine in aerosols) [33]. Similar water-soluble iodide ratios were reported by Baker et al. [35], around 25% for iodine in aerosol samples collected at a coastal site in southeast England. Water-soluble iodine levels in the analysed samples (Table 7) show a low marine source contribution (a water-soluble ratio of 11.8%). This finding was confirmed after a statistical study of the water-soluble iodine levels and the water-soluble sodium concentrations in the same samples (regression coefficient between iodine and sodium of 0.1593). Nevertheless, a moderate marine influence is observed when considering bromine data (a mean water-soluble bromine ratio of 20.9%, quite similar than those reported

Table 6
Analytical recovery of PHWE-HPLC-ICP-MS procedure.

Analyte	[] _{added} ($\mu\text{g L}^{-1}$)	[] _{measured} ($\mu\text{g L}^{-1}$) ^a	Analytical recovery (%) ^a
Br^-	10	8.9 ± 1	89 ± 7
	20	19.1 ± 1	95 ± 4
	40	38.4 ± 1	96 ± 3
BrO_3^-	10	10.4 ± 1	104 ± 4
	20	19.7 ± 1	97 ± 3
	40	38.8 ± 1	97 ± 2
I^-	0.5	0.48 ± 0.02	96 ± 4
	2.5	2.6 ± 0.1	102 ± 1
	5.0	5.1 ± 0.1	101 ± 2
IO_3^-	0.5	0.47 ± 0.02	93 ± 4
	2.5	2.4 ± 0.1	96 ± 1
	5.0	4.7 ± 0.1	94 ± 1

^a $n=7$.

Table 7
Concentrations^a (expressed as ng m^{-3}) of total bromine and iodine; total bromine and iodine water soluble; water-soluble bromine and iodide species; and sodium from atmospheric particulate matter (PM_{10} and $\text{PM}_{2.5}$).

Sample	Total Br ^b	Total Br water soluble ^c	Br^- water soluble ^c	Total I ^b	Total I water soluble ^c	I^- water soluble ^c	IO_3^- water soluble ^c	Na ^d
PM₁₀								
1	59 ± 1	11 ± 1	11 ± 1	1.2 ± 0.1	0.12 ± 0.01	< 0.03	0.11 ± 0.01	1804 ± 90
2	4.2 ± 0.2	1.0 ± 0.1	1.1 ± 0.1	0.7 ± 0.03	0.08 ± 0.01	< 0.03	0.06 ± 0.002	409 ± 20
3	8.6 ± 0.3	1.7 ± 0.1	1.5 ± 0.1	0.8 ± 0.03	0.08 ± 0.01	< 0.03	0.08 ± 0.002	603 ± 40
4	< 0.25	< 0.25	< 0.30	< 0.07	< 0.07	< 0.03	< 0.03	593 ± 30
5	26 ± 1	5.5 ± 0.4	5.3 ± 0.1	2.3 ± 0.1	0.30 ± 0.01	0.02 ± 0.001	0.22 ± 0.01	1449 ± 80
6	7.6 ± 0.5	1.7 ± 0.1	1.6 ± 0.1	2.9 ± 0.1	0.32 ± 0.01	< 0.03	0.30 ± 0.01	2589 ± 150
7	47 ± 3	9.8 ± 0.4	10 ± 1	24 ± 2	3.1 ± 0.1	0.20 ± 0.07	2.8 ± 0.1	1634 ± 60
8	58 ± 3	12 ± 1	11 ± 1	14 ± 1	1.7 ± 0.1	0.12 ± 0.08	1.6 ± 0.1	1895 ± 80
9	88 ± 5	17 ± 1	17 ± 1	4.1 ± 0.2	0.52 ± 0.01	0.08 ± 0.004	0.40 ± 0.01	3154 ± 130
10	19 ± 1	4.4 ± 0.2	4.6 ± 0.3	1.3 ± 0.1	0.14 ± 0.01	< 0.03	0.12 ± 0.01	663.4 ± 20
PM_{2.5}								
1	7.2 ± 0.5	1.5 ± 0.1	1.7 ± 0.1	4.9 ± 0.3	0.70 ± 0.02	< 0.03	0.64 ± 0.02	670 ± 20
2	< 0.25	< 0.25	< 0.30	< 0.07	< 0.07	< 0.03	< 0.03	163 ± 5
3	< 0.25	< 0.25	< 0.30	< 0.07	< 0.07	< 0.03	< 0.03	150 ± 4
4	< 0.25	< 0.25	< 0.30	0.8 ± 0.02	0.08 ± 0.002	< 0.03	0.07 ± 0.001	272 ± 10
5	4.3 ± 0.3	0.92 ± 0.08	0.87 ± 0.03	1.0 ± 0.1	0.11 ± 0.01	< 0.03	0.10 ± 0.01	250 ± 20
6	4.2 ± 0.2	0.84 ± 0.03	0.90 ± 0.03	1.6 ± 0.1	0.20 ± 0.01	< 0.03	0.22 ± 0.01	379 ± 20
7	6.6 ± 0.2	1.4 ± 0.1	1.3 ± 0.1	2.7 ± 0.1	0.30 ± 0.01	0.06 ± 0.002	0.22 ± 0.01	205 ± 10
8	7.5 ± 0.3	1.5 ± 0.1	1.5 ± 0.1	0.51 ± 0.01	0.07 ± 0.001	< 0.03	0.07 ± 0.001	315 ± 20

^a $n=7$.

^b After MAAD.

^c After PHWE.

^d After acid digestion.

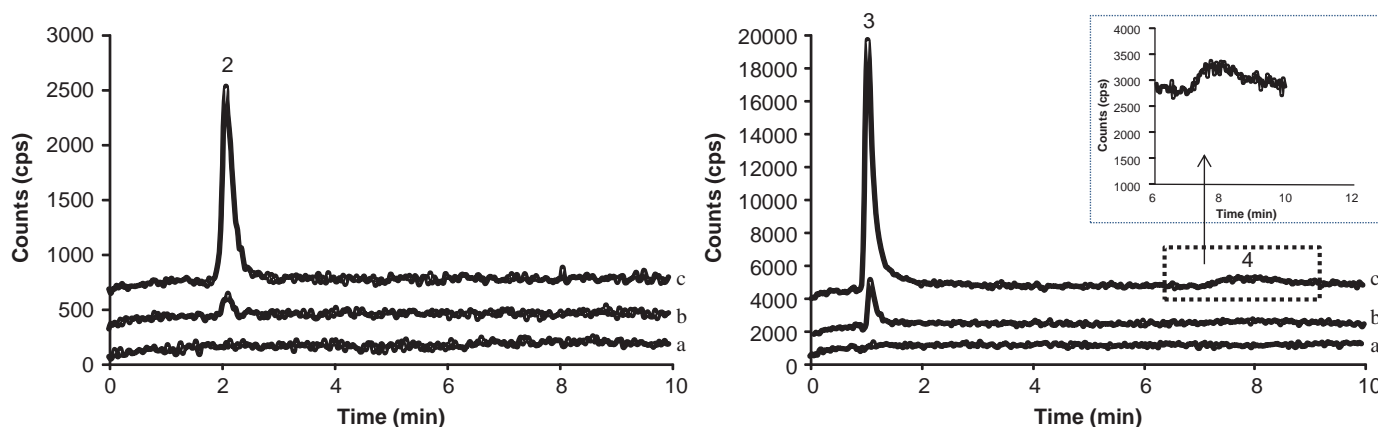


Fig. 3. HPLC-ICP-MS chromatograms for a filter blank (a), a PM_{2.5} (b) and a PM₁₀ (c) after the proposed PHWE using the optimized conditions. Bromide (2), iodate (3) and iodide (4).

in coastal areas [33], and a regression coefficient of 0.6684 after statistical correlation between water-soluble bromine levels and sodium concentrations in the samples).

Concentrations ranging between 0.75 and 1.23 and between 0.18 and 1.08 ng m⁻³ for I⁻ and IO₃⁻, respectively [20] were found at the coastal research station in Mace Head, Ireland. Levels of total bromine and iodine in Hefei (China) aerosols were 70.6 and 29.3 ng m⁻³, respectively; while Br⁻ was found to be the major species and BrO₃⁻ was undetectable [21]. A 70% of total iodine occurred as unidentified forms including soluble organic iodine and insoluble iodine [21]. Otherwise, high levels of I⁻ and IO₃⁻ were reported in continental aerosols from an anthropogenic influence area (0.39–0.91 ng m⁻³ (I⁻) and 1.60–6.88 ng m⁻³ (IO₃⁻) [19].

4. Conclusions

The use of PHWE is a simple and fast extraction procedure for water soluble halides extraction from atmospheric particulate matter (PM₁₀ and PM_{2.5}). The application of this alternative pre-treatment method resulted in an appropriate procedure which provides similar results when comparing with ultrasound assisted methods, but this level of information can be reached in a significantly shorter analysis time. The time required to complete the PHWE sample treatment is around 9 min. The addition of the extracting solution (water) is totally automated. In addition, filtration and centrifugation stages to separate the extract and the solid residues are avoided, and the leachate handling is therefore minimized. The analytical method (anion exchange HPLC-ICP-MS) described here has fairly good precision and accuracy as well as low quantification limits, which meets the requirements for bromine and iodine determination. The analyses of samples collected from A Coruña city suggest that the major water soluble bromine and iodine species found in the analysed samples are Br⁻ and IO₃⁻ and only about the 20% of the total Br and the 11% of the total I in aerosols may readily be soluble at environmental conditions.

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