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PhD thesis

Thesis submitted to the Chemistry Graduate Program of the Federal University of Santa Catarina, Florianópolis - SC, Brazil and the Faculty of Sciences of the Ghent University, Ghent, Belgium in the modality of Joint PhD.

Advisers: Prof. Dr. Daniel L. G. Borges
Prof. Dr. Frank Vanhaecke

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Strategies for halogen determination and isotopic analysis via ICP-MS

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This work presents new approaches for halogen determination in a variety of samples using inductively coupled plasma - mass spectrometry (ICP-MS) and for isotope ratio measurements by multicollector – inductively coupled plasma – mass spectrometry (MC-ICP-MS) and application of the methods developed to real environmental cases

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Resumo expandido

Os halogênios são um grupo de elementos que apresentam diversas particularidades, tornando-os muito importantes para diversos propósitos. No entanto, esses elementos apresentam elevado grau de toxicidade quando ingeridos ou inalados, e são considerados perigosos quando presentes no meio ambiente, devido principalmente ao fato de poderem reagir com moléculas de O_3, promovendo a destruição da camada de ozônio.

Considerando a alta aplicabilidade dos halogênios e seus efeitos adversos ao ambiente e em sistemas biológicos, faz-se necessário o estabelecimento de métodos sensíveis, com exatidão e precisão, para a sua determinação.

Técnicas como eletrodos de íon seletivos, cromatografia de íons, análise por ativação de nêutrons instrumental, espectroscopia de fluorescência por raios-X, entre outros, foram propostos e aplicados com sucesso para analise de halogêneos em diversas matrizes, no entanto, em alguns casos, morosas etapas de preparo de amostras são necessárias, além de algumas das técnicas apresentarem limitações para analise multielementar, baixa sensibilidade, baixa frequência analítica, incidência de interferências e curta faixa linear para quantificação.

Além de problemas para sua quantificação, a medida de razão isotópica de halogênios ainda é um desafio. Algumas técnicas têm sido aplicadas para este propósito como a espectrometria de massas de razão isotópica e espectrometria de massas por ionização química, entretanto, normalmente apresentam baixa precisão além de apresentarem muitos dos problemas apresentados para quantificação.

Desta forma, o objetivo geral deste trabalho é apresentar propostas a fim de solucionar os problemas enfrentados para análise de halogênios por espectrometria de massas por plasma indutivamente acoplado (ICP-MS) e analise de razões isotópicas por multicoletor (MC)-ICP-MS, aplicando os métodos desenvolvidos para o estudo de casos ambientais reais.

Uma breve introdução abordando os conceitos básicos sobre a importância dos halogênios, uma visão geral sobre funcionamento de equipamentos ICP-MS, determinação e análise isotópica de halogênios por ICP-MS é apresentada no Capítulo 1 o qual é seguindo pelos Capítulos 2, 3 e 4 onde se apresentam novas propostas para determinação de halogênios por meio da analise direta de sólidos utilizando vaporização eletrotérmica (SS-ETV)-ICP-MS e aplicação dos métodos propostos a analise de amostras biológicas, minerais e ambientais em diferentes estudos. O Capítulo 5 apresenta o desenvolvimento de um método simples para determinação direta de Br em amostras de polímeros por ablação a laser (LA)-ICP-MS, enquanto que os Capítulos 6, 7 e 8 abordam o desenvolvimento de métodos para medida da razão isotópica de halogênios em água do mar e amostras de gelo marinho por MC-ICP-MS.

No Capítulo 2, uma nova metodologia para a determinação de Cl em amostras biológicas e botânicas usando SS-ETV-ICP-MS é apresentada. As amostras sólidas foram pesadas diretamente em plataformas de grafite (copos de grafite da técnica *cup-in-tube*) e inseridas no forno de grafite. Os parâmetros de potencial de rádio frequência (RF) e a vazão de gás carreador foram otimizados em 1300 W e 0,7 L min^{-1}, respectivamente.

Padrões aquosos foram utilizados para a obtenção da curva de calibração com o auxílio de modificadores pré-secos (Pd + Nd ou Pd + Ca) ou utilizando um material de referencia certificado (CRM) sólido com os mesmos modificadores pré-secos ou sem a utilização de modificadores. O limite de quantificação (LOQ) obtido foi 5 μg g^{-1} sob condições otimizadas.

A concentração de Cl foi determinada em cinco amostras de referência certificadas, com concentrações certificados para Cl, além de três amostras de referência certificados com concentrações certificadas para Cl indisponíveis, neste último caso, os resultados foram comparados àqueles obtidos utilizando espectrometria de absorção molecular de alta resolução com fonte contínua (HR-CS MAS). As concentrações obtidas demonstraram-se em acordo, a um nível de confiança estatística de 95%, com os valores certificados ou de referência.

O Capítulo 3 apresenta um novo método para a determinação direta e simultânea Br e Cl em amostras de carvão utilizando SS-ETV-ICP-MS. O processo não requer pré-tratamento de amostras e necessita de pequenas alíquotas de massa de amostra (cerca de 0,5 mg). Todos os parâmetros operacionais, incluindo vazão de gás carreador e potencial de RF, foram otimizados para o máximo de sensibilidade.

O uso de modificadores/ carreadores de aerossóis (Pd, Pd + Al e Pd + Ca) foi avaliado e a combinação de Pd e Ca foi escolhida, permitindo a adoção das temperaturas de pirólise e vaporização de 700 ^{o}C e 1900 ^{o}C, respectivamente. Cloro foi determinado com o auxilio de calibração utilizando padrões sólidos, enquanto Br foi determinado tanto por calibração aquosa quanto utilizando CRM sólidos. Os LOQs obtidos foram de 0,03 μg g^{-1} para Br e 7 μg g^{-1} para Cl, interferências espectrais não foram observadas.

No Capítulo 4 foi avaliada a viabilidade da análise direta de sólidos por HR-CS MAS para a determinação de F e ETV-ICP-MS para determinação simultânea de Cl, Br e I em material particulado inalável no ar (PM_{10}), coletados na região metropolitana de Aracaju, Sergipe, Brasil.

As análises de F por HR-CS MAS foram realizadas monitorando a molécula de CaF que foi gerada a altas temperaturas na câmara de grafite após a adição de cálcio em uma relação Ca/ F de 35. As análises por ETV-ICP-MS foram realizadas utilizando Ca como modificador químico/ carreador de aerossol com a utilização concomitante de Pd como modificador permanente, a fim de evitar perdas de Cl, Br e I durante a etapa de pirólise.

A abordagem de analise direta de sólidos resultou em LOQs adequados para a determinação de halogêneos em PM_{10}, usando a calibração por adição de analito ou calibração utilizando um CRM solido. O método permitiu a quantificação dos halogênios em 14 PM_{10} coletadas em uma cidade costeira do nordeste do Brasil. Os resultados demonstraram variações de teor de halogênios de acordo com as condições meteorológicas, principalmente relacionados a chuvas, umidade e irradiação solar.

O Capítulo 5 foi destinado à avaliação da utilização da LA-ICP-MS para análise de Br em amostras de polímeros. Os parâmetros operacionais do LA-ICP-MS, incluindo a vazão de gás carreador, potencial de RF, tamanho da cratera de ablação e frequência do laser foram otimizados para o máximo de sensibilidade. Os valores otimizados foram 0,6 L min^{-1} para vazão de gás carreador (He), 950 W de potencial de RF, 120 μm de tamanho da cratera de ablação e 15 Hz de frequência do laser.

Sob condições otimizadas foi possível determinar, com exatidão, Br em 5 amostras certificadas de polímeros e 5 amostras reais de polímeros obtidas em estabelecimentos locais em Ghent, Bélgica por calibração externa utilizando CRMs contendo diferentes concentrações de Br e por calibração externa utilizando apenas um CRM monitorando $^{12}C^{+}$ como padrão interno. O LOQ obtido foi de 110 μg g^{-1} para Br.

O Capítulo 6 apresenta um método simples para medida da razão isotópica de Br em água do mar por MC-ICP-MS, utilizando nebulização pneumática para introdução da amostra. Os sinais dos isótopos de Br^{+} foram medidos livre de interferências utilizando alta resolução. O efeitos de memória para Br foi diminuído utilizando 5 mmol L^{-1} NH_4OH como solução de limpeza entre as medidas. O conteúdo catiônico da água do mar foi removido por cromatografia catiônica utilizando uma resina Dowex 50WX8. Pré-concentração das amostras foi obtida por evaporação a 90°C, sem perda ou fraccionamento isotópico de Br.

Discriminação de massas foi corrigida por correção externa utilizando *bracketing*, embora Sr, Ge e Se foram testados como potenciais padrões internos. Os valores $^{81}Br/^{79}Br$ obtidos para os materiais de referência isotópicos (NaBr) NIST (material de referencia padrão) SRM 977 e (água do mar) IRMM BCR-403 demonstraram estar de acordo com os valores da literatura.

No Capítulo 7, a medida da razão isotópica de Cl em água do mar por MC-ICP-MS através de nebulização pneumática tradicional foi realizada utilizando, i) alta resolução de massa (potencial de resolução de 10.000) para resolver interferências espectrais, ii) 5 mmol L^{-1} NH_4OH como solução de limpeza a fim de diminuir o efeito de memória e iii) uma concentração de Cl de ≥ 70 mg L^{-1}.

A carga catiônica da água do mar e de sais de cloreto (NaCl, KCl) foi eficientemente removida sem afetar a composição isotópica original da Cl através de cromatografia catiônica utilizando resina de troca iônica Dowex 50WX8. O método desenvolvido demonstrou alta exatidão e precisão, atestadas pela medição da razão isotópica $^{37}Cl/^{35}Cl$ na amostra CRM NIST 975a (valor obtido de 0,319765 ± 0,000022, em comparação com um valor de referência de 0,319768 ± 0,000187 a uma precisão de ~ 0,007%, desvio padrão relativo, n = 3).

Além disso, o valor δ^{37}Cl (baseado no padrão de cloro em agua do mar, SMOC) foi determinado para cinco padrões diferentes que variaram de -0,54 a + 0,89 ‰.

O Capítulo 8 apresenta um estudo ambiental de Br e Cl em gelo marinho coletados durante a expedição *Sea Ice Physics and Ecosystem eXperiment 2012*, em diferentes profundidades e locais. Todas as medições de razão isotópicas de Br e Cl foram realizadas de acordo com os métodos apresentados no Capítulo 6 e 7.

A concentração destes elementos variou de 700 para 31000 μg L $^{-1}$ para Br e de 200 para 8000 mg L^{-1} para Cl, sendo que as menores concentrações foram relacionados com o gelo coletado em maiores profundidades, estando a diminuição da concentração de Br e Cl provavelmente relacionadas a processos de dessalinização.

Os valores de δ^{81}Br e δ^{37}Cl apresentaram relação linear com a suas concentrações, sugerindo que o processo de dessalinização desempenha um papel no fraccionamento isotópico no gelo do mar.

Abstract

Dit werk presenteert nieuwe methodes voor de kwantitatieve bepaling van halogenen door middel van inductief gekoppeld plasma massaspectrometrie (ICP-MS) en voor de meting van isotopen verhoudingen gebruikmakend van multicollector (MC) ICP-MS.

Vier methodes voor directe vastestofanalyse (SS) door middel van ICP-MS – drie met behulp van elektrothermische vervluchtiging (ETV) en één middels laser ablatie (LA) – en twee methodes voor de isotopenanalyse van Br en Cl in zeewater met MC-ICP-MS werden ontwikkeld. Deze methodes werden toegepast op stalen afkomstig uit concrete studies en geven als dusdanig relevante resultaten met betrekking tot milieuprocessen. In alle methodes waarin SS-ETV-ICP-MS toegepast werd, werden de vaste stalen direct afgewogen in grafietbuisjes en ingebracht in de grafietoven. De instrumentele parameters werden geoptimaliseerd voor het bekomen van een hoge gevoeligheid en efficiënte verwijdering van de matrix. Chloorbepaling in biologische stalen kon uitgevoerd worden via kalibratie tegenover waterige standaardoplossingen, in de aanwezigheid van vooraf gedroogde modifiers (Pd + Nd of Pd + Ca) of met gecertificeerde vaste referentiematerialen (CRMs), eveneens in de aanwezigheid van vooraf gedroogde modifiers of zonder gebruik te maken van modifiers, wat leidt tot een kwantificatielimiet (LOQ) van 5 μg g^{-1}. Voor de bepaling van Br en Cl in steenkoolstalen werd Cl accuraat gemeten middels kalibratie met vaste standaarden, terwijl Br ook succesvol werd gekwantificeerd via kalibratie met waterige standaardoplossingen, in beide gevallen met vooraf gedroogde modifiers (Pd + Ca). Kwantificatielimieten van 0.03 μg g^{-1} en 7 μg g^{-1} werden bereikt voor respectievelijk Br en Cl. In een derde deel van dit werk werden F, Cl, Br en I bepaald in fijn stof (PM_{10}). Fluor werd bepaald middels hoge resolutie moleculaire absorbtiespectrometrie (HR-CS MAS), waarbij de CaF molecule geobserveerd werd, terwijl Cl, Br en I bepaald werd door middel van SS-ETV-ICP-MS. De methode liet de kwantificatie van halogenen toe in 14 PM_{10}-stalen verzameld in een noordoostelijke kuststad in Brazilië. De resultaten toonden variaties in halogeengehalte naargelang de meteorologische omstandigheden, in het bijzonder gerelateerd aan regenval, relatieve luchtvochtigheid en zonneschijn. In een vierde deel wordt de bepaling van broom in polymeerstalen met LA-ICP-MS behandeld. Onder geoptimaliseerde omstandigheden kon Br accuraat bepaald worden in vijf verschillende polymeerstandaarden (CRM) en vijf ‘echte’ polymeerstalen door externe calibratie tegenover verschillende CRMs en eveneens door externe calibratie tegenover slechts één CRM, mits gebruik van het $^{12}C^{+}$ als interne standaard. De LOQ werd bepaald op 110 μg g^{-1} Br.

Daarnaast werd aangetoond dat de accurate en precieze meting van broom- en chloorisotopen verhoudingen in zeewater via MC-ICP-MS mogelijk is mits het gebruik van hoge massaresolutie, en door toevoeging van 5 mmol L^{-1} NH_4OH aan alle staal-, standaard- en wasoplossingen (voor

analietconcentraties van ≥ 3 mg L^{-1} voor Br en ≥ 70 mg L^{-1} voor Cl). Het overgrote deel van de kationen in zeewater werd voorafgaand aan de analyse verwijderd door kationenuitwisselingschromatografie (Dowex 50WX8 hars). In het geval van Br liet het uitdampen van de stalen bij 90°C toe om de stalen op te concentreren zonder analietverlies of isotopische fractionatie. Voor beide elementen werd gecorrigeerd voor massadiscriminatie door externe correctie in een staal-standaard ‘bracketing’ benadering, en tevens werd ook nagegaan of Sr, Ge of Se kunnen aangewend worden als potentiële interne standaarden voor Br-isotopenanalyse. Vergelijking van de bekomen resultaten bij de analyse van CRMs met de referentiewaarden of waarden uit de literatuur, toonde aan dat beide methodes aanleiding geven tot precieze en accurate resultaten. Tot slot werden deze methodes toegepast als onderdeel van een milieustudie rond de aanwezigheid van Br en Cl in zeeijs verzameld op verschillende dieptes en locaties tijdens de *Sea Ice Physics and Ecosystem eXperiment 2012* expeditie. De concentratie van deze elementen in de stalen bedroeg 700 tot 31000 µg L^{-1} Br en 200 tot 8000 mg L^{-1} Cl en er werd een relatie aangetoond tussen de Br en Cl concentraties in de stalen en de overeenkomstige δ^{81}Br en δ^{37}Cl waarden. De lagere concentraties en δ-waarden werden geobserveerd in diep zeeijs, wat waarschijnlijk verklaard kan worden door de optredende ontzoutingsprocessen.

Abstract

This work presents new approaches for halogen determination in a variety of samples using inductively coupled plasma - mass spectrometry (ICP-MS) and for isotope ratio measurements by multicollector – inductively coupled plasma – mass spectrometry (MC-ICP-MS) and application of the methods developed to real environmental cases. Four methods for solid sampling (SS) analysis by ICP-MS, three using electrothermal vaporization - inductively coupled plasma – mass spectrometry (ETV-ICP-MS) and one using laser ablation - inductively coupled plasma – mass spectrometry (LA-ICP-MS), and two methods for isotopic analysis by MC-ICP-MS, one for Br and another for Cl in sea water, were developed. The methods were applied for studying samples from real study cases, providing significant results with respect to environmental processes. For all three methods using SS-ETV-ICP-MS, the solid samples were directly weighed into graphite 'cups' that were subsequently inserted into the graphite furnace, and the instrumental parameters were optimized for high sensitivity and efficient matrix removal. Chlorine determination in biological samples could be carried out using aqueous standard solutions, when using pre-dried modifiers (Pd + Nd or Pd + Ca) or using solid certified reference material (CRM), accompanied with or without the same pre-dried, achieving a limit of quantification (LOQ) of 5 $\mu g\ g^{-1}$. For Br and Cl determination in coal samples, Cl was accurately determined using calibration against solid standards, whereas Br could also be quantified adequately by using calibration against aqueous standard solutions, both using pre-dried modifiers (Pd + Ca), LOQs of 0.03 $\mu g\ g^{-1}$ for Br and 7 $\mu g\ g^{-1}$ for Cl were achieved. F, Cl, Br and I were determined in particulate matter, F was determined via high resolution – continuum source molecular absorption spectrometry (HR-CS MAS) for monitoring the CaF molecule, while Cl, Br and I were determined via SS-ETV-ICP-MS. This method allowed the quantification of the halogens in 14 PM_{10} samples collected in a Northeastern coastal city in Brazil. The results demonstrated variations of the halogen contents according to meteorological conditions, particularly related to rainfall, humidity and sunlight irradiation. Bromine determination in polymer samples was accomplished via LA-ICP-MS after the optimization of the operational parameters for high sensitivity. Under optimized conditions, it was possible to accurately determine Br in 5 different certified polymer reference materials and 5 real polymer samples by external calibration using different certified materials containing different concentrations of Br and by external calibration against a single certified material monitoring $^{12}C^+$ as internal standard. The LOQ obtained was 110 $\mu g\ g^{-1}$ of Br. Bromine and Cl isotopic analysis in seawater via MC-ICP-MS was proven feasible, operated in high mass resolution and by decreasing the memory effect using 5 mmol L^{-1} of NH_4OH in sample, standard and wash solutions. Optimal analyte concentrations were ≥ 3 mg L^{-1} for Br and ≥ 70 mg L^{-1} for Cl. The major cation load of seawater was removed via cation exchange chromatography (Dowex 50WX8 resin). In the

case of Br, evaporation of the samples at 90°C permitted analyte preconcentration without Br loss or isotope fractionation. Mass discrimination was corrected for by external correction in a sample-standard bracketing approach for both elements. Sr, Ge and Se were also tested as potential internal standards for Br isotopic analysis but provided no advantage. Both methods demonstrated high precision and accuracy based on the comparison of experimental values with certified and literature values. The methods were applied within the context of an environmental study of Br and Cl in sea ice collected during the Sea Ice Physics and Ecosystem eXperiment 2012 voyage at different depths and locations. The concentration of these elements in the samples ranged from 700 to 31000 μg L^{-1} for Br and from 200 mg L^{-1} to 8000 mg L^{-1} for Cl, and a relation between the concentrations and the corresponding δ^{81}Br and δ^{37}Cl values was found. Lower concentrations and δ values were observed for sea ice collected at greater depths and are probably related to desalinization processes.

Acronyms

CRM - Certified Reference Material
ETV - Electrothermal Vaporization
ETV-ICP-MS - Electrothermal Vaporization - Inductively Coupled Plasma - Mass Spectrometry
GF - Graphite Furnace
HR-CS MAS - High-Resolution Continuum Source Molecular Absorption Spectrometry
IC - Ion Chromatography
ICP - Inductively Coupled Plasma
ICP-MS - Inductively Coupled Plasma - Mass Spectrometry
ID - Isotope Dilution
IRMS - Isotope Ratio Mass Spectrometry
LA-ICP-MS - Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry
LOD – Limit of Detection
LOQ – Limit of Quantification
MC-ICP-MS - Multicollector - Inductively Coupled Plasma - Mass Spectrometry
MIC – Microwave - Induced Combustion
NCIMS - Negative Chemical Ionization Mass Spectrometry
NIST - National Institute of Standards and Technology
PC - Principal Component
PFA - Perfluoroalkoxy Alkane
$\mathbf{PM_{10}}$ – Particulate Matter $\leq 10\mu m$
PN - Pneumatic Nebulizer
PN-MC-ICP-MS – Pneumatic Nebulization - Multicollector - Inductively Coupled Plasma - Mass Spectrometry
PTIMS - Positive Thermal Ionization Mass Spectrometry
PVSA - Peak Volume Selected Absorbance
RF – Radio Frequency
RSD – Relative Standard Deviation
SIPEX-2 - Australian-led Sea Ice Physics and Ecosystem eXperiment-2
SMOB - Standard Mean Ocean Bromide
SRM – Standard Reference Material
SSB - Sample-Standard Bracketing Approach
SS-ETV-ICP-MS – Solid Sample - Electrothermal Vaporization - Inductively Coupled Plasma - Mass Spectrometry
TIMS - Thermal Ionization Mass Spectrometry
Tp - Pyrolysis Temperature
Tv - Vaporization Temperature

Contents

Introduction

The halogens are a group of elements that present different applicabilities, properties, toxic effects and behavior in the environment. They are produced and released into the environment either via human activities or via natural processes, such as the burning of fossils fuels or volcanic eruptions, therefore, their monitoring is important in order to evaluate contaminations, impacted areas, environmental reactions and biological mechanisms among others.

The monitoring of halogens is an important task that can be accomplished by the use of different techniques, however most of these techniques present some drawbacks, such as the need for time-consuming sample pretreatment, low sensitivity and mono element character. Specially, the sample pretreatment can be a challenging issue for halogen determination and must be carefully carried out in order not to promote analyte loss or contamination.

In this sense, the use of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) is an attractive alternative for halogen determination, presenting high sensitivity, multielement capabilities, wide linear dynamic range and can be coupled to solid sample techniques. Moreover, it can be used for isotope ratio measurements with high precision.

Thus, the aim of this work was to develop straightforward methods for halogen determination by solid sample – electrothermal vaporization - inductively coupled plasma-Mass Spectrometry (SS-ETV-ICP-MS) and laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS), and for halogen isotope measurements by multicollector - inductively coupled plasma - mass spectrometry (MC-ICP-MS), applying the developed methods for studying samples obtained from real life cases.

This work is divided to eight chapters, consisting of a revision of the literature in Chapter 1; the development of methods for halogen determination by solid sample analysis using ICP-MS and a case study in the Chapters 2, 3 and 4; the development of a straightforward method for Br determination in polymer samples via LA-ICP-MS in Chapter 5; and the development of methods for halogen isotope ratio measurements and a case study in Chapters 6, 7 and 8.

Chapter 1 - Halogens: From a brief look at their importance to their determination by inductively coupled plasma - mass spectrometry

1.1. Introduction

The halogens are a group of elements which present distinct applications, physiological functions, properties and toxicological importance [1-2]. They are released into the environment either by human activities or natural processes, hence their monitoring is important in order to assess, among others, contamination, impacted areas, environmental reactions and biological mechanisms [1-2].

The monitoring of halogens in environmental and biological systems is still a challenging task due to analytical issues, which range from the sample preparation to the instrumental detection by the selected technique [3-4].

In order to avoid analyte loss or contamination, the sample pretreatment must be wisely selected and carefully carried out. A few approaches may be used, such as pyrohydrolysis, combustion bomb, oxygen flask, microwave - induced combustion (MIC) or even extraction procedures. In this sense, direct solid sample analysis is a very attractive alternative since no sample pretreatment is required, thus avoiding the risk of contamination and/or analyte loss [4].

Among the available techniques for halogen analysis, ICP-MS has demonstrated to be attractive due to its multielement capabilities, high sensitivity and wide linear range for calibration, in addition to the possibility to carry out high precision isotope ratios measurements, mainly using MC-ICP-MS [5].

Thus, the aim of this chapter is to introduce the concepts associated to halogen analysis, from sample pretreatment to the instrumental analysis by ICP-MS, addressing part of the discussion on principles and basic concepts of the techniques.

1.2. Halogens

Halogens are reactive elements from group 17 of the periodic table, which present different physical properties among them. These differences lead to distinct reactions and applications [1-6].

In nature, the halogens can be found in several natural reservoirs as halides combined with other elements [1-2, 6]. The distribution of halogens in nature is not entirely known, firstly because, in some cases, they are present at very low concentrations, hindering their monitoring using the available traditional techniques [6,7-9], and secondly, due to their dynamic characteristics regarding environmental processes such as volcanic eruptions, movement of wind and sea, and environmental reactions, as for example bromine explosion events (which is a photocatalytic reaction that converts halides salts into reactive halogens which are released to the environment) [6,10].

Industrially, the halogens are employed for several purposes, including water treatment [11], as polymers additives and in paper manufacturing [12] and oral hygiene products [13]. Despite their wide applicability, a few problems are generally related to their presence in the environment, such as the ability to destroy O_3 [14] molecules. Therefore, the halogens are regarded as powerful disrupting agents of the ozone layer [7, 15-17].

The halogens can be released to the atmosphere by anthropogenic processes as well as by natural processes, such as volcanic eruptions and evaporation from the ocean. The majority of the organic gases containing halogens is man-made and may remain in the atmosphere for up to 100 years [9-10].

In biological systems, the halogens can be found either as halide ions or as part of organic molecules, which include proteins, and present different properties [18-19]. An example is the capture of iodine by the thyroids acting on the hormonal adjustment [20], and the decrease in the incidence of teeth cavities by the use of fluorine. Chlorine helps regulating the osmotic pressure in extracellular fluids and is also present in saliva and digestive fluids in the stomach [10].

The properties of the halogens and halogenated compounds called the attention of the pharmaceutical industry, and several studies have been carried out applying halogens or compounds containing halogens as medicinal drugs to help the treatment of serious diseases, such as cancer [21] or diseases with a lower death incidence, such as those related to the central nervous system [22].

Despite the potential benefits associated to the diverse uses of halogens, several toxic effects are related to their presence which are more intensified at high concentrations, in some cases the toxic effects of the halogens at high concentrations resemble those attributed to elements such as As and Hg [23].

1.3. Halogen determination

1.3.1. Sample pretreatment

The sample pretreatment required for halogen determination by means of ICP-MS is a critical step since most procedures adopted to decompose solid samples are based on the use of inorganic acids, which promote the volatilization of the halogens as hydrogen halides. In addition, contamination and interferences arising from the reagents used for sample preparation are also important issues to be considered [24]. Thus, methods that do not require the use of inorganic acids during the sample pretreatment may be successfully employed; these include pyrohydrolysis [25], microwave-induced combustion (MIC), combustion based procedures and alkaline treatment. [26]. Moreover, the sample handling in order to reduce the particle's size prior the sample pretreatment is an important issue for halogen determination, methods which avoid the heating of the sample by physical processes may be preferred in order to avoid analyte volatilization.

Pyrohydrolysis was first used for industrial processes and it was applied as a sample pretreatment process for analytical purposes for the first time in 1954 [25], and since then it has been successfully used for sample preparation associated to the determination of volatile analytes in several sorts of samples. The basic principle of pyrohydrolysis is the heating of the sample, which leads to volatilization of the analytes that are carried to and retained in a solution that shows affinity for the analytes [4].

Figure 1 presents the simplified scheme of a pyrohydrolysis device, in which the sample is heated in a sample holder (Figure 1D) positioned into a quartz tube (Figure 1C) volatilizing the analyte, while water is inserted through a tube using a peristaltic pump in order to produce water vapor. The water vapor is carried by a gas flow inserted by a tube (Figure 1A) that also carries the analytes to the condenser. The water vapor containing the volatized compounds from the sample is condensed and retained into the absorbing solution [28]. Heating is normally provided by a furnace (Figure 1B), which is normally based on electrothermal heating with a temperature control.

Pyrohydrolysis devices have been successfully applied for sample pretreatment prior to the determination of volatile elements in different matrices such as coal, geological samples [29-30], biological samples [31] and even carbon nanotubes [28].

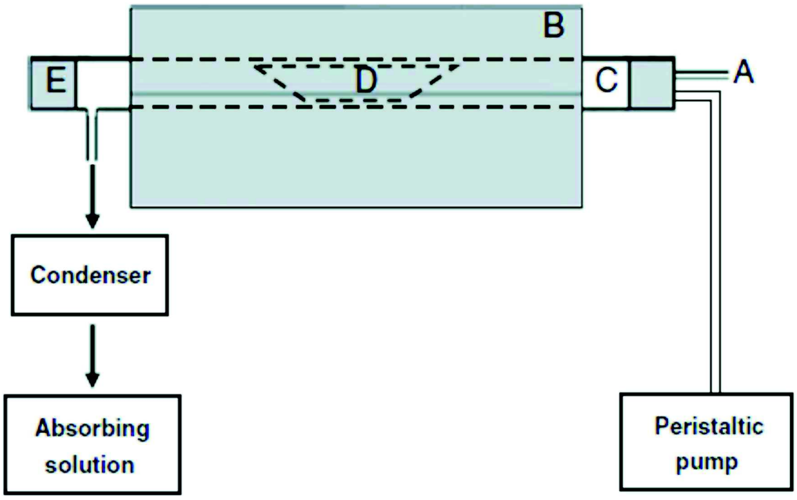

Figure 1. Simplified scheme of a pyrohydrolysis device: A is the gas inlet; B is the furnace; C is the quartz tube, D is the sample holder and E is a silicon stopper [28]. Reprinted from Microchem. J. Vol. 101, Antes, F. G.; Pereira, J. S. F.; Enders, M. S. P.; Moreira, C. M. M.; Muller, E. I.; Flores, E. M. M.; Dressler, V. L., Pyrohydrolysis of carbon nanotubes for Br and I determination by ICP-MS, p. 54-58, 2012.Copyright (2016), with permission from Elsevier.

Combustion techniques have been used for sample pretreatment since the eighteenth century, including combustion of samples for posterior analysis by open, dynamic or closed systems [4, 32]. Closed systems will be focused in this chapter due to the goal of decreasing the possibility of analyte loss by volatilization and therefore, is feasible to be applied for halogen determination.

Closed combustion systems may avoid loss of the analyte due to the retention of the combustion products into the vessels, with subsequent absorption of the analytes in an absorbing solution [32]. These systems comprise the combustion bomb, the oxygen flask and, the more recently developed technique for combustion, the MIC.

The combustion bomb is normally used for organic matrices with the advantage of simplicity and ability to decompose the samples in only a few minutes (normally less than 30 min including cooling step). In the combustion bomb, the sample (at least 0.5 mg) is combusted inside of a vessel made of stainless steel that is pressurized with oxygen. The products generated by the combustion of the sample are absorbed into a suitable solution located into the stainless steel bomb [4].

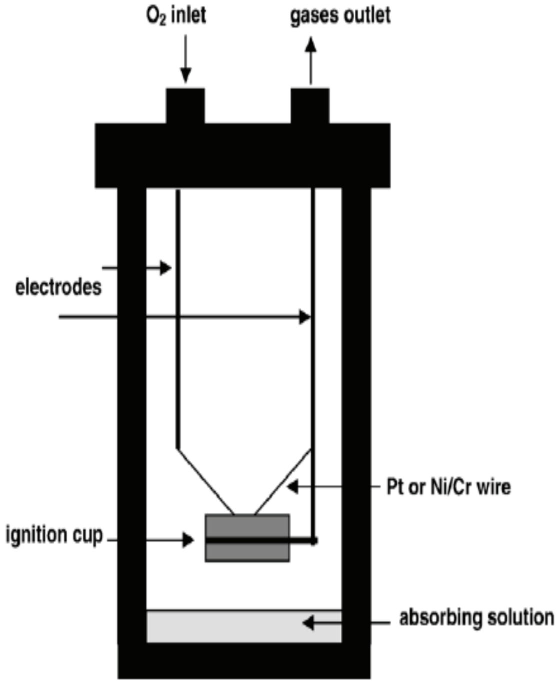

Figure 2. Schematic representation of a combustion bomb [4]. Reprinted from Spectrochim. Acta, Part B. Vol. 62, Flores, É. M. M.; Barin, J. S.; Mesko, M. F.; Knapp, G., Sample preparation techniques based on combustion reactions in closed vessels — A brief overview and recent applications, p. 1051–1064, 2007, Copyright (2016), with permission from Elsevier.

Figure 2 presents a simplified scheme of the combustion bomb in which the sample is inserted as pellets into a metallic cup (ignition cup) and ignited using a Pt or Ni/Cr wire connected to electrodes and positioned in close contact with the pellet. An aliquot of about 5 to 10 mL of the absorbing solution is inserted onto the bottom of the vessel in order to trap the products of the combustion reaction. Oxygen is used to pressurize the system from 20 to 30 atm [4].

Due to the high temperature generated from the combustion, it is necessary to cool down the system before removing the resulting solution, a step that usually requires water or an ice bath can be employed for this purpose [4].

The combustion bomb may be employed for combustible samples, although combusting reagent may be employed in order to extend the use of the combustion bomb for samples which are not easily combusted [4].

The drawbacks associated to combustion bombs include the possibility of contamination with metals from the metallic parts of the device, the processing of one sample per time, reducing the sample throughput, and the need for an adequate absorbing solution, considering the analyte [4].

Another combustion system that can be applied is the oxygen flask (Figure 3), also known as Schöniger flask or Schöniger system. The flask is a simple combustion system composed of a glass vessel containing oxygen at atmospheric pressure and an absorbing solution which is inserted at the bottom of the vessel [4, 33].

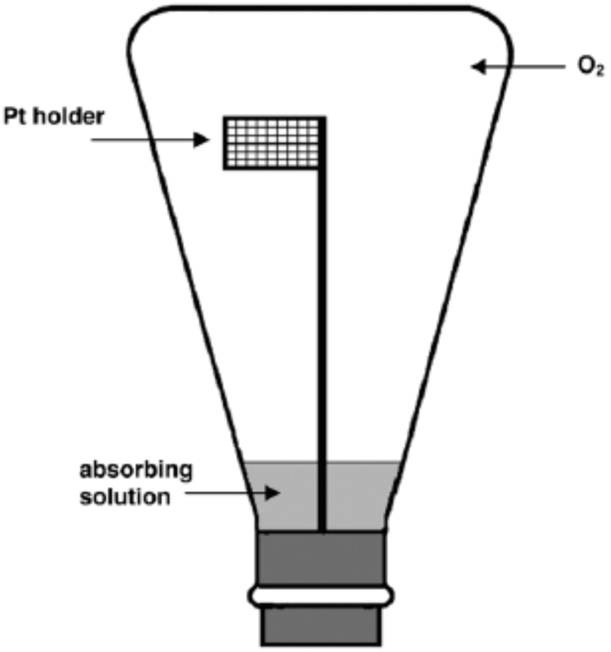

Figure 3. Schematic representation of an Oxygen flask [4]. Reprinted from Spectrochim. Acta, Part B. Vol. 62, Flores, É. M. M.; Barin, J. S.; Mesko, M. F.; Knapp, G., Sample preparation techniques based on combustion reactions in closed vessels — A brief overview and recent applications, p. 1051–1064, 2007, Copyright (2016), with permission from Elsevier.

The sample (usually less than 100 mg) is wrapped with paper and positioned in a platinum holder for subsequent combustion; the system is pressurized with oxygen up to atmospheric pressure and closed for posterior combustion of the sample. The ignition of the sample is initiated by an electrical current applied to the Pt wire or by a focused infrared lamp; another option is the use of a piece of paper which is usually ignited before the introduction of the Pt holder into the vessel [33].

Unlike the combustion bomb, there is a limitation of sample mass that can be used (which is considerably lower than that for the combustion bomb), which means that analysis of samples containing trace levels of the analyte may be compromised. Moreover, the system requires constant monitoring during the sample pretreatment and contamination from the materials used for the combustion may be expected [33]

More recently, MIC has been introduced as a sample pretreatment technique that can be applied for to a wide range of analytes and matrices including, for example, soil and carbon nanotubes (which were successfully combusted by this technique after proper optimization of the operating parameters) [4, 32]. In MIC, an aliquot of the sample is combusted inside of a quartz vessel pressurized with oxygen; the ignition is started by microwave irradiation. Similarly to other combustion techniques, in MIC the gases resulting from the combustion are absorbed in a solution, although in MIC the absorbing solution is subject to reflux [32].

The MIC system (Figure 4) is basically a combination of a commercially available microwave oven for wet sample digestion and the combustion techniques. The samples are prepared as pellets and positioned on top of a small piece of low-ash filter paper in a quartz holder. An ammonium nitrate solution is added as an igniter and the system is then closed, pressurized with oxygen to 15 to 25 atm and then the microwave radiation (maximum power of 1400 W) is applied to start the combustion [4, 32].

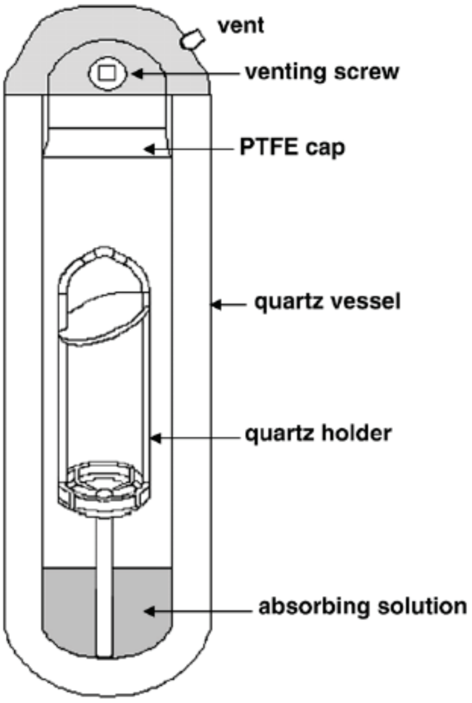

Figure 4. Schematic representation of a MIC vessel [4]. Reprinted from Spectrochim. Acta, Part B. Vol. 62, Flores, É. M. M.; Barin, J. S.; Mesko, M. F.; Knapp, G., Sample preparation techniques based on combustion reactions in closed vessels — A brief overview and recent applications, p. 1051–1064, 2007, Copyright (2016), with permission from Elsevier.

Once the combustion starts, it is not possible to stop the reaction. Thus, rupture disks are used in the cap to release the pressure of the system in case of 'violent' reactions. The quartz vessels are the same as those used for conventional digestion procedures using a microwave oven. Contamination is reduced by the use of quartz instead of stainless steel, which is normally used in the combustion bomb [4, 32].

Temperatures of about 1300 ^{o}C are reached during the combustion of the sample (this temperature is also reached using a combustion bomb), which is suitable for most applications [4].

The absorbing solution is added at the bottom of the vessel in order to absorb the products generated from the combustion. After the system is cooled down the solution can be removed, diluted and analyzed [4,32].

Opposite to the combustion techniques where the total degradation of the sample is aimed at, extraction procedures or even partial degradation of the samples have also demonstrated to be applicable in the context of halogen determination, with the advantage of simplicity and low cost when compared to the combustion techniques [4].

Sample pretreatment in alkaline media employing, for example, tetramethylammonium hydroxide and heating, or even diluted acids concomitantly with ultra-sound energy have gained interest and, in several cases, provided results that were comparable to those obtained using combustion techniques [31, 34].

The use of alkaline media has been successfully applied for sample pretreatment of botanical and biological samples for posterior halogen determination [35-36]. In this method, TMAH and heating were employed, promoting the partial decomposition and partial or complete solubilization of the sample, allowing analysis by ICP-MS after proper selection of the sample introduction system [37].

The employment of alkaline media sample pretreatment for halogen determination presents the advantage of avoiding the formation of volatile halogen compounds, such as HCl, which are easily formed in acidic media [37]. The procedure is also simple and fast, allowing high sample throughput and reducing the risk of contamination.

Analyte extraction may replace sample decomposition in several applications. Ultrasound energy and diluted acids are normally employed in order to extract the analytes from the matrix, resulting in methods that are simple and associated to high sample throughput [38]. However, the use of diluted acids may lead to the formation of volatile forms of halogens.

A very attractive alternative for halogen determination, that does not involve laborious sample pretreatment, is the use of direct solid sample analysis, which will be further described.

1.3.2. Direct solid sample analysis

Although sample pretreatment procedures are considered well-established and accepted, solid and slurry sample analysis present advantages over procedures based on wet sample pretreatment [39]. The associated benefits are summarized below:

1. decreased risk of contamination, since the amount of reagents used is reduced or eliminated and the sample handling is significantly reduced;
2. increased detection capability, since the sample is not diluted;
3. reduced risk of analyte loss;
4. increased sample throughput;
5. reduced need for special apparatus for sample pretreatment;
6. contributes to the environment, since little or no toxic or corrosive reagents are required;
7. allows the study of microhomogeneity.

Solid sample analysis may be accomplished by using the sample as a powder or *in situ*; a few techniques may require some sample pretreatment in order to produce pellets or another form that is suitable for introduction into the instrument [39].

It is clear that direct solid sample analysis presents several advantages over the traditional sample pretreatment procedures by the simple fact that no sample pretreatment is required, although direct solid sample analysis normally requires more from the quantification technique than an analysis carried out after the sample pretreatment, as the matrix of the sample is not destroyed.

In general, interferences are expected to increase when using solid sampling analysis, including those that would not be present while analyzing a digested sample, due to the presence of relatively large quantities of the matrix [39]. Other difficulties that have limited the application of solid sample analysis are based on the fact that only a few instrumental techniques are powerful enough to analyze liquid and solid samples, and normally for those techniques, special apparatus for solid sample analysis are required, and problems with sample homogeneity are intensified at low masses.

Matrix components are responsible for spectral interferences (which will be discussed further) and non-spectral interferences; hence, the analytical technique must be able to avoid or deal with possible interferences. The extent of the effect that may be exerted by the sample matrix is a function of the sample mass introduced in the equipment.

The use of micro amounts of sample is normally preferred; however, a compromise must be considered in order to reduce the effect of heterogeneity of the sample. Typical precision values are expected to be up to 15% of relative standard deviation (RSD), which are considered acceptable for direct solid sample analysis [39-40].

Ideally, the behavior of the analyte in the samples should be the same as the behavior of the analyte in the standards. However, this statement is, sometimes, difficult to achieve using solid sample analysis when aqueous standards are used for calibration, since the chemical form of the analyte in the solid sample normally differs significantly from the chemical form of the analyte in aqueous standards [39]. On occasions, calibration has to be carried out against a solid sample, such as a certified reference material (CRM) [40].

Different approaches can be performed in order to achieve accurate results, such as the use of different calibrations approaches and equipments that allow for the destruction of the matrix of the sample in situ as SS-ETV-ICP-MS.

Other effects that can be expected from the analysis of solid samples are difficulties associated to non-homogeneous distribution of the analyte, since the amount of sample is considerably reduced [40].

1.3.3. Instrumental analysis

The choice of the technique for halogen determination is also considered critical due to the limited number of options that are suitable for this task, particularly when the analytes are expected to be present at trace levels [4, 28].

The quantification of halogens may be carried out by different techniques, including ion chromatography (IC) [41] and ion-selective electrodes [42]. Both techniques require the analyte to be in aqueous medium and in ionic form, which implies the fact that sample pretreatment is required in order to solubilize the analytes properly. In order to avoid the sample pretreatment step, halogens quantification in solid samples may be performed by techniques such as instrumental neutron activation analysis [43], X-ray fluorescence spectrometry [44] and laser-induced breakdown spectroscopy [45].

A few disadvantages are frequently related to these techniques, including low sensitivity, low sample throughput, limitations for multi element analysis, incidence of interferences and short linear range for quantification.

In order to fill the gap associated to alternatives for halogen determination, techniques such as high resolution continuum source molecular absorption spectrometry (HR-CS MAS) [46] and ICP-MS [27, 28] were recently proposed for halogen determination, offering high sensitivity, high sample throughput, and, in the case of ICP-MS, multi element character and a wide linear range for quantification. Nevertheless, there are only a few examples of the application of these techniques for halogen determination in the literature.

Isotope ratio measurements of halogens, which is normally limited to Br and Cl, are even more complex to be performed, and the amount of techniques that can be applied for this purpose is very limited.

These techniques include isotope ratio mass spectrometry (IRMS) [48], negative chemical ionization mass spectrometry (NCIMS) [49], thermal ionization mass spectrometry (TIMS) [50, 51] and one application example using HR-CS MAS [52]. Unfortunately, these techniques are characterized by a number of drawbacks, such as the need for time-consuming sample preparation procedures, the occurrence of memory effect and/or poor precision.

Positive thermal ionization mass spectrometry (PTIMS), relying on the monitoring of the polyatomic Cs_2Cl^+, has been applied to the measurement of Cl isotope ratio in different standards and water samples. However, it was demonstrated that the technique suffers from mass fractionation depending on the Cl concentration [53].

In the case of this work, MC-ICP-MS, which is a powerful technique for high-precision isotopic analysis, was used. However, application of MC-ICP-MS for halogen isotope ratio measurements is limited to a few examples in the literature, typically using sample introduction systems that allow the insertion of a “dry” vapor into the plasma [54, 55].

1.4. Short overview about ICP-MS

ICP-MS is a powerful analytical technique with the ability to perform multi-element analysis at trace levels and in a large variety of sample types [56].

The basic principle of ICP-MS is the detection of analytes which are separated based on their mass charge ratio *(m/z)* following ionization in an inductively coupled plasma (ICP) [5].

A typical analytical routine in ICP-MS begins with aspiration of the sample and aerosol formation that takes place in the sample introduction system. A conventional sample introduction system for ICP-MS is composed of a nebulizer and a spray chamber, which are commercially available with different geometries [5, 56-57].

The nebulizers typically used in ICP-MS are classified as pneumatic (PN) and ultrasonic nebulizers. In PN, the aerosol is formed owing to the interaction between the liquid sample flow and a an Argon gas flow at high speed, while in ultrasonic nebulization the aerosol of the sample is formed as a result of contact of the liquid sample to an ultrasonic transducer, the sample introduction efficiency for these nebulizers can range from about 2 to 20% [5, 56-58].

Immediately after formation, the aerosol droplet diameters are heterogeneously distributed, which often results in the formation of a dense aerosol. In order to reduce the diameter and homogenize the droplets that reach the ICP, the nebulizer is connected to a spray chamber, which allows only small droplets to reach the plasma, hence facilitating the desolvation step that takes place immediately afterwards in the plasma [5, 56]. As a consequence, the steps of dissociation and ionization are also benefited, and the deleterious effects that derive from the addition of water droplets in the plasma are minimized. Typical spray chamber designs include the *Scott* type (or double pass) and cyclonic type and, in some cases, a combination of the Scott type with a cyclonic spray chamber [57].

Once the aerosol has passed the spray chamber, the droplets are carried to the central channel of the plasma, where the processes of desolvation, volatilization, atomization and ionization take place [5, 57]. Argon plasmas are typically used in ICP-MS instruments. The plasma is initially formed by an electrical discharge and is maintained by the energy coupled to it by a radio frequency (RF) generator. The temperature in the plasma may be as high as 10,000 K in the induction zone and from 5,000 to 7,000 K in the central channel of plasma due to the insertion of the cold aerosol of the sample [5].

The ions formed in the ICP are extracted to a region of high vacuum after passing through a region of intermediate vacuum that normally contains two cones, a sampler and a skimmer cone. The ions are extracted from the interface and guided to the mass spectrometer by an ion optic system, which also stops particles, neutral species and photons from entering the mass analyser and the detector [59].

The most common mass analyzer is the quadrupole due to its low cost and simplicity when compared to other commercially available mass analyzer [5, 57]. The main drawback associated to quadrupole mass analyzers is the low mass resolution (about 300u) and its non-simultaneous detection of different isotopes. Mass analyzers based on the combination of magnetic and electric sectors (double focusing) are better suited when a higher mass resolution is required to separate the analyte ions from interfering ions. In these mass analyzers, the ions are spatially separated according to their *m/z* ratio [60] and might be simultaneously detected if more than one detector is available in the equipment.

Once the ions are selected by the mass analyzer, they reach the detector and generate an electrical signal that will be further processed. Electron multipliers are the detectors normally employed in single collector instruments, whereas Faraday cups are preferred for MC-ICP-MS [60-61].

Analysis using ICP-MS may be hindered by interferences. Spectral interferences, such as those originating from the formation of polyatomic ions in the plasma environment, are fairly common and require special instrumentation or operating conditions to be eliminated. These include the use of a collision and/or reaction cell in quadrupole-based instruments, mathematical equations based on the signal measured at alternative *m/z* ratios, changes in the plasma conditions and use of high-resolution mass spectrometers.

Non-spectral interferences, on the other hand, are somehow less predictable than spectral interferences. They lead to a suppression or enhancement of the analyte signal due to the effects in the processes of aspiration and nebulization of the sample, ionization of the analyte and transmission and detection of the ions [5, 62]. In general, non-spectral interferences may be corrected for by the adoption of calibration standards prepared in the same medium as the samples. Alternatives such as the use of standard addition calibration, internal standards or isotope dilution (ID) calibration [5] may be advantageously used.

1.4.1. Isotope ratio measurements by MC-ICP-MS

The ability of obtaining isotopic information makes ICP-MS an attractive technique to perform isotope ratio analysis. In this approach, two or more isotopes of a given element are measured in order to provide information on induced or natural changes in one or more isotopes ratio. Isotope ratio measurements may, e.g. be employed to determine the age of geological materials, to assist in understanding environmental and biological reaction mechanisms and to identify contamination sources. [60, 63].

Unfortunately, the application range of isotope ratio analysis using quadrupole ICP-MS is limited by the relatively low precision, normally higher than 0.1% RSD for "traditional" quadrupole based ICP-MS and about 0.05% RSD for quadrupole based ICP-MS equipped with collision/reaction cell due to the temporal homogenization of the ions before they reach the detector [63]. The main disadvantages of quadrupole based ICP-MS equipment for isotopic analysis are basically the non-simultaneous isotope monitoring and the non-flat peak shape, in addition to other instrumental peculiarities that include low resolution and detector issues.

In this sense, the use of MC-ICP-MS it preferred due to (i) its capability to measure different isotopes of the same element simultaneously, which implies that plasma instabilities will not affect the measured isotope ratio; (ii) the occurrence of flat-shaped peaks, avoiding variations in the measured signal due to small shifts in the position of the signal maximum and (iii) special instrumental peculiarities that increase the stability of the measurements [60].

The simultaneous monitoring of isotopes is of great importance for isotope ratio measurements, since fluctuations in the signals are likely to happen for both isotopes at the same time. This feature is possible due to the use of a double-focusing mass analyzer with Nier–Johnson geometry, which simultaneously separates the isotopes in space within a given mass window, and multiple detectors positioned after the mass analyzer, each one monitoring a different isotope [61, 63].

Another important characteristic of MC-ICP-MS is the flat-shaped peak, obtained by maintaining the width of the exit slit (collector slit) at a higher aperture than the entrance slit (source slit) [63]. A side effect from this approach is the "deterioration" of the equipment's resolution. In this case, peaks that are usually separated using a single collector high resolution ICP-MS instrument are often not completely separated using MC-ICP-MS. Therefore, the instrument is said to operate in “pseudo” medium or high resolution. However, in most cases, a mass window (shoulder) in the signal where the contribution of the signal comes solely from the analyte is observed, which is sufficient to carry out precise isotope ratio measurements [63].

In addition to the basic instrumental requirements for high precision isotope analysis by MC-ICP-MS, other effects, such as mass discrimination, matrix effects and interferences, need to be counteracted in order to allow accurate and precise results. Once the elements have been ionized in the ICP, the ions are extracted into the mass spectrometer and transmitted for posterior detection. Mass discrimination may occur during these steps, resulting in inaccurate results regarding the true isotope ratio. Non-conventional sample introduction systems, such as desolvator systems and vapor generation, certain sample preparation processes and matrix effects may also induce different degrees of mass discrimination [60].

Several approaches have been proposed to correct for mass discrimination, although this is still a challenge and sometimes the correction presents some pitfalls. Common approaches adopted to correct for mass discrimination effect are discussed below.

External correction using a standard with a well-known isotope ratio may be useful. In this case, the standard-sample-standard bracketing approach is used, where the isotope ratio related to the sample is measured, and this measurement is preceded and followed by the measurement of an isotopic standard with a known isotopic composition. In order to apply this method for correction, the concentration of the analyte in the sample and standards must be as similar as possible, ideally not exceeding 30% of difference. However, this theoretical limit may vary depending on the analyte, matrix composition, sample introduction system used and instrumental setup. Since the matrix may influence the magnitude of mass discrimination, it is advisable that both (sample and standards) present the same matrix composition, which can be achieved by the isolation of the analyte from the sample [60, 63].

Correction using an internal standard is also feasible. In this approach, a known concentration of an element (with a known isotopic composition and a similar mass to that of the element for which the isotope ratio will be measured) is added to the sample solution. The bias between the measured and the known isotope ratios of the standard is used to determine the mass discrimination factor per unit of mass, which can be subsequently used to correct the isotope ratio of the analyte in the sample [60, 63].

All elements show isotope fractionation in environmental or biological processes, a few elements show isotope fractionation due to radiogenic decay, as for example, ^{87}Sr which is a result from ^{87}Rb decay. In this case, the ^{88}Sr/^{86}Sr ratio does not suffer variation and may be used in order to correct for mass discrimination [60, 63] – a procedure known as ‘internal correction’.

In a brief look at the current literature, it is possible to find different approaches that have been proposed for mass discrimination correction, demonstrating that there is still some discussion in order to find the most suitable and accurate approach. As the mass fractionation depends on different factors including the analyte and matrix, it is possible that the most suitable approach for correction varies from case to case.

After correction, the isotope ratio is usually represented as the ratio associated to the measured isotopes or relative to a standard or sample, termed as δ values, which is calculated according to Equation 1 [63]:

$$\delta\ (‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \qquad \text{(Equation 1)}$$

In Equation 1, R_{sample} refers to the isotope ratio of the element in the sample and $R_{standard}$ is the isotope ratio of the element in the standard.

1.4.2. Halogen determination by ICP-MS

Quantitative determination of halogens by ICP-MS is usually not a trivial task, mainly due to issues associated with sample pretreatment, memory effect when using conventional sample introduction systems, relatively low sensitivity (when compared to the typical ICP-MS sensitivity for other elements of the periodic table) and the presence of spectral interferences [64].

Memory effect is a critical issue for halogen determination by ICP-MS, especially when acidic solutions are used [65], which is likely due to the formation of volatile species, such as HX (X=Cl, Br and I). In order to reduce the memory effect, a few strategies may be adopted, including the use of alternative sample introduction systems and specific washout solutions that should be employed between successive measurements cycles [36].

The relatively low sensitivity associated to halogen determination by ICP-MS results from their high ionization energy (17.42 eV for F, 12.97 eV for Cl, 11.81 eV for Br and 10.45 eV for I), and hence, low ionization efficiencies (in the order of 30, 5 and 0.9% for I, Br and Cl, respectively). Fluorine is the most critical halogen to be analyzed by ICP-MS, since negligible populations of F^+ are formed in Ar plasma. Quantification of F by ICP-MS may be accomplished using a He plasma [47] or using a non-conventional approach monitoring negative ions by ICP-MS [66], but reports on F analyse by means of ICP-MS are scarce.

Spectral interferences associated to halogens quantification by ICP-MS are due to the formation of polyatomic ions, which include $^{16}O^{18}O^{1}H^+$ and $^{34}S^{1}H^+$ overlapping with the *m/z* of $^{35}Cl^+$; $^{36}Ar^{1}H^+$ and $^{36}S^{1}H^+$, overlapping with the *m/z* of $^{37}Cl^+$; $^{40}Ar^{39}K^+$, $^{31}P^{16}O_3^+$ and $^{38}Ar^{40}Ar^{1}H^+$ overlapping with the *m/z* of $^{79}Br^+$ and $^{32}S^{16}O_3{}^{1}H^+$, $^{40}Ar^{40}Ar^{1}H^+$ and $^{33}S^{16}O_3^+$ overlapping with the *m/z* of $^{81}Br^+$ also jeopardizes the determination of halogens by ICP-MS, mainly in low resolution mode. The impact of these polyatomic ion interferences depend on the sample introduction system and on the sample matrix, since K, P and S are easily found at relatively high concentrations in several matrices, Ar is the plasma gas and O and H come from water and other reagents used for sample preparation.

An alternative to avoid the undesired effects associated to halogen determination by ICP-MS include the use of direct solid sample analysis with devices such as laser ablation (LA-ICP-MS). However, problems regarding calibration strategy for quantification, isotope fractionation for isotopic analysis, and instrumental cost are still significant [60, 69].

Electrothermal vaporization – inductively coupled plasma – mass spectrometry (ETV-ICP-MS) has proved to be an efficient approach for direct solid sample analysis, especially for quantitation of volatile elements and/or for the analysis of samples that are not suitable for conventional sample preparation protocols [69]. The use of electrothermal vaporization (ETV) adds the possibility to remove the major matrix load during the pyrolysis step and the use of aqueous or solid standards for calibration.

The fact that devices especially designed for solid sample analysis by ETV-ICP-MS are not commercially available has limited the number of publications and applications of this technique to only a few examples that are available in the literature, thus, this field of research is believed to be very promising and still holds potential for exploitation.

Antes *et al*. (2013) have developed a system for direct solid analysis by ETV-ICP-MS. The system was applied with success for the determination of Cl in petroleum coke using standard addition calibration in order to correct for differences in the behavior of the analyte in the sample and in the calibration standards [69]. The first application of the ETV for halogen determination was described by Yan *et al*. (1996). In their work, an ETV was developed and successfully employed for the determination of Br, Cl and I in aqueous standards using a He-Ar plasma, resulting in a more energetic plasma, and therefore, better sensitivity for halogen determination using ICP-MS [47].

1.4.3. Solid sample analysis by ICP-MS

Direct analysis of solids by ICP-MS is usually accomplished by using either a laser ablation system (LA-ICP-MS) (Figure 5) or, less common ETV-ICP-MS.

Analysis by LA is based on the focusing of a laser beam on the surface of the sample, which is kept in an inert atmosphere. The pulsed laser converts part of the sample in an aerosol or vapor, which is carried by an inert gas to the ICP [70].

Application of LA extends to several fields of research and is particularly popular in geochemistry, where LA-ICP-MS has become one the main techniques for multielemental determination and isotopic dating, besides being able to map the distribution of chemical elements in the samples.

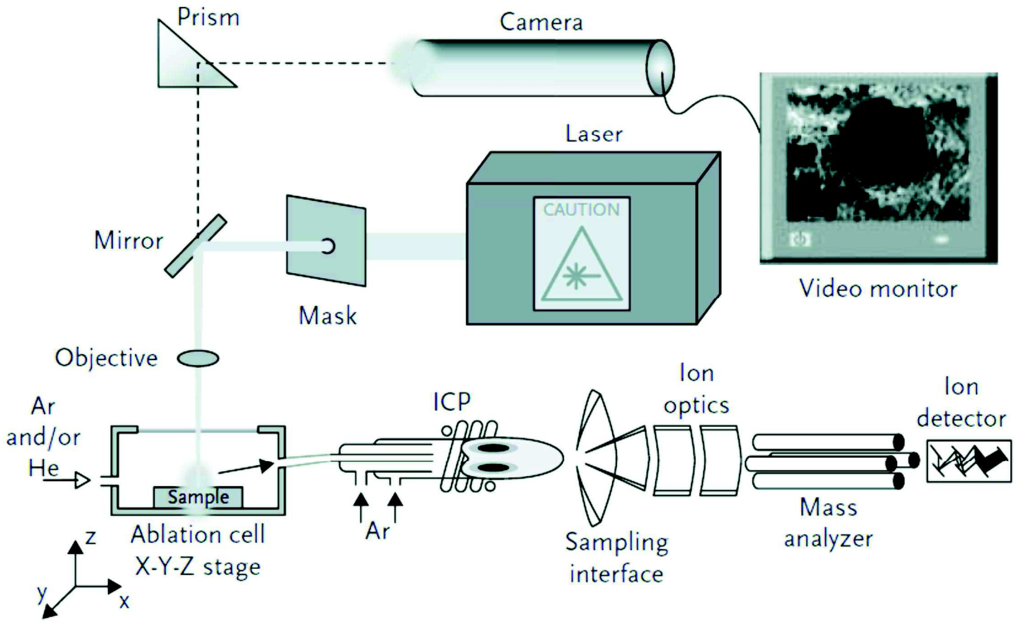

Figure 5. Simplified scheme of LA-ICP-MS [70]. Reprinted from Mass Spectrom. Rev., Vol. 29, Resano, M., Garcia-Ruiz, E., Vanhaecke, F., Laser ablation inductively coupled plasma mass spectrometry in archaeometric research, p. 55–78, 2010, Copyright (2016), with permission from WILEY.

The main disadvantage associated to the use of LA is the difficulty to attain a suitable calibration approach for quantification due to the need for standards with the same characteristics of the samples [70]. Therefore, differences in vapor formation and transportation between sample and standards may lead to errors, requiring special approaches for calibration using this technique [60].

Another drawback of the technique is related to the cost of the equipment when compared to other sample introduction systems, besides that isotope fractionation is more likely to occur in these systems [60].

All in all, LA has been applied successfully for halogen determination by several authors in several matrices presenting the goal of performing spatially resolved analysis. Most of the authors have used isotope dilution ID as a calibration approach to counteract the differences between samples and standards [71, 72].

On the other hand, the use of ETV-ICP-MS may expand the possibilities for direct solid quantification by ICP-MS, enabling the use of aqueous standards for calibration and the sample pretreatment *in situ* [39].

In ETV-ICP-MS (Figure 6), an aliquot of the sample is inserted into a graphite furnace (GF) and a temperature program is applied. The temperature program functions as an *in situ* sample pretreatment step inside of the GF, allowing the elimination of the solvents (in the case of liquid and slurry samples) during a drying step and the elimination of the matrix of the sample during a pyrolysis step. After the solvents and matrix of the sample have been eliminated, the analytes are volatized and carried to the plasma during the vaporization step [73].

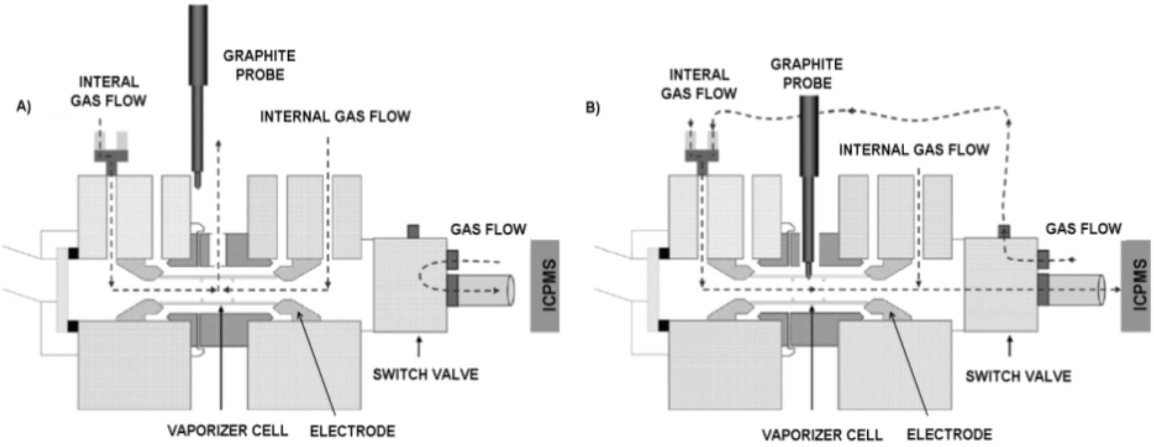

Figure 6. Representation of an HGA 600 MS ETV from Perkin Elmer [73]. Reprinted from Anal. Chim. Acta, Vol. 648, Aramendía, M.; Resano, M.; Vanhaecke, F, Electrothermal vaporization–inductively coupled plasma-mass spectrometry: A versatile tool for tackling challenging samples: A critical review, p. 23– 44, 2009, Copyright (2016), with permission from Elsevier.

The working principle of an ETV is similar to the principle of electrothermal atomizers used in atomic absorption spectrometry. Probably the main difference is that no atomization is required, but only the vaporization of the analytes and their efficient transport to the ICP.

In ETV, an aliquot of the sample, typically 5-50 µL for liquid samples and about 0.5 - 1 mg for solid samples, is inserted into the vaporizer cell which is resistively heated when in contact with graphite electrodes [73]. In order to vaporize the samples, the electrodes connected to the vaporizer cell provide energy capable to produce temperatures as high as 2,800 ^{o}C (for example), which is suitable for the vaporization of most elements of the periodic table. Once vaporized, the analytes and eventually other concomitants from the matrix are carried to the ICP by a carrier gas flow (normally Ar) [73].

Typically, in ETV-ICP-MS a temperature program is applied, which includes drying, pyrolysis and vaporization steps. During the drying step, solvents and products with lower volatilization temperatures from the sample are eliminated, whereas in the pyrolysis step the main objective is to eliminate matrix components, preventing them to be carried to the ICP during the vaporization step [73, 74].

The pyrolysis step must be carefully optimized in order to prevent plasma loading without promoting the concomitant vaporization of the analyte. Chemical modifiers may be used to increase the thermal stability of the analyte, allowing the use of elevated pyrolysis temperatures, and improve the analyte transfer from the ETV to the ICP. Chemical modifiers may be used either as a solution, in which case the modifier is co-injected with each sample aliquot, or it may be deposited onto the graphite tube surface, providing thermal stability to the analytes and /or acting as an aerosol carrier [39, 74].

The vaporization step follows pyrolysis, volatilizing the analytes that are then carried to the ICP. During the pyrolysis step (Figure 6A) the internal gas flow flushes all the vapors out of the vaporizer cell, while during the vaporization step (Figure 6B) the orifice of the vaporizer cell is sealed by a graphite tip and the internal gas flow carries the analytes to the ICP [39, 74].

The use of ETV is suitable for analysis of liquid, slurry and solid samples (using a special apparatus for insertion of the sample into the graphite tube). Völkopf *et al.* have developed the “cup-in-tube” technique, with the purpose of introducing solid samples directly into the graphite tube [74]. In this technique, the sample is weighed inside of glass capillary tubes and transferred into the cup that can be inserted in the graphite tube (Figure 7).

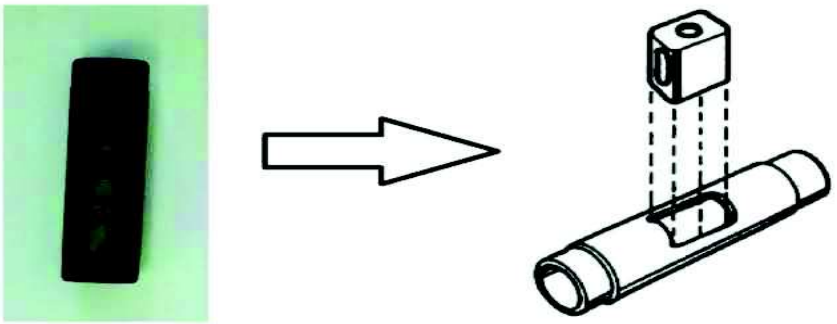

Figure 7. Cup-in-tube technique for ETV-ICP-MS [Adapted from 75, with permission of The Royal Society of Chemistry.

The advantages of the use of ETV-ICP-MS are the possibility of analysis of micro sized samples, high transport efficiency of analytes to the plasma when compared to conventional sample introduction systems, possibility to analyze organic samples and also samples with high solid content, possibility of calibration using aqueous standards, possibility of analysis of solid and slurry samples and separation of the analyte from the matrix of the sample due to the temperature program applied, reducing the risk of interferences [39-40,74].

In quantitative analysis using SS-ETV-ICP-MS, the calibration strategies include external calibration against aqueous standards, solid standards (CRMs), by standards addition, with or without internal standards, and ID [74].

The use of external calibration with aqueous standards, which is widely used for quantification of trace elements in digested samples, is a very attractive alternative for quantification by ICP-MS. However, in SS-ETV-ICP-MS this approach is sometimes not feasible, since the analytes in the sample are normally present in a different form than the analytes in the aqueous standards, resulting in different thermal behavior [39]. Calibration using solid standards, mainly using CRMs with similar composition to that of the samples, may result in better accuracy due to the similarity of the matrices [69].

Under special circumstances, standard addition calibration may be used when solid standards are not available [69]. ID may also be helpful in these cases, although it requires isotopically enriched standards, which are expensive.

Chapter 2 - Application of direct solid sample analysis for the determination of chlorine in biological materials using ETV-ICP-MS

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2.1. Introduction

Chlorine is regularly produced by industries worldwide and has applications that range from purification of drinking water to the production of bleached paper, plastics, solvents and pharmaceuticals [76].

Given the widespread use of Cl, exposition to the element occurs frequently due to manipulation of products, transportation or even due to environmental contamination [76, 77]. According to the Agency for Toxic Substances & Disease Registry, exposure to Cl may affect the respiratory tract and eyes, causing acute irritation and triggering inflammatory processes [78].

Monitoring of Cl in biological and botanical materials is characterized by difficulties that extend from sample pretreatment until the final instrumental determination [79].

Sample preparation must be carefully conducted in order to avoid contamination and analyte loss; acid digestion, which is most frequently used as a sample treatment procedure, is not recommended due to the formation of HCl, which can be lost by volatilization. Moreover the instrumental determination frequently suffers from poor sensitivity, risk of interferences, low analytical throughput and, on occasions, high analytical cost [69, 47, 79 - 81].

Hence, the goal of this work was to develop a method for the direct determination of Cl in biological and botanical samples using SS-ETV-ICP-MS, including a systematic investigation of calibration protocols.

2.2. Experimental

2.2.1. Instrumentation

All experiments were carried out using an Elan ICP-MS, equipped with an HGA-600 MS electrothermal vaporizer and an AS-60 autosampler (Perkin-Elmer SCIEX, Thornhill, Canada). Platinum sampling and skimmer cones were used, the optimized conditions of the ICP-MS were 1300W of RF power, 0.7 L min^{-1} of nebulizer gas flow, 1.2 L min^{-1} of auxiliary gas, 15.0 L min^{-1} of main gas, dwell time for the readings of 50 ms, detector voltages of 1250 V for pulse mode and -2280 V for analogue mode.

All measurements were carried out in *Peak Hopping* scanning mode and autolens mode on. The ‘cup-in-tube’ technique described by Vollkopf *et al.* [75] was used, where the sample introduction opening of the pyrolytically coated graphite tube is enlarged so that the sampling ‘cup’ can be inserted directly into the GF using Teflon tweezers.

The solid sampling cup is made from high-density electrographite and coated with pyrolytic graphite and has approximate dimensions of 7.0 x 4.5 x 6.8 mm, and it supports a maximum of 160 mg of sample [75]. The solid sampling cups, loaded with the sample (using a glass capillary), were inserted into the graphite tube and removed after completion of the analysis using a special apparatus.

The solid samples were weighed using a micro balance model M2P (Sartorius, Göttingen, Germany). Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as plasma, carrier and internal gas of the ETV.

In order to provide comparative results for samples with unknown Cl concentration, a ContrAA 600 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer was used. The SrCl molecule was used for quantitative measurements of Cl at 635.863 nm, using integrated absorbance of three pixels (peak volume selected absorbance (PVSA) $A_{\sum 3,\text{int}}$).

Pyrolytically coated graphite tubes (Analytik Jena) were used in all experiments. The solid samples were weighed directly onto solid sampling platforms (Analytik Jena) using an M2P micro balance. A manual solid sampling system, SSA 6 (Analytik Jena), was used to insert the SS platforms into the graphite tube. The optimized pyrolysis and vaporization temperatures for the HR-CS MAS technique were 600°C and 2300°C, respectively.

2.2.2. Reagents, standards and samples

All reagents used were at least of analytical grade. Deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) with a resistivity of ≥18.2 MΩ cm. Individual stock standard solutions containing 1000 mg L^{-1} of Ca or Cl were obtained from Quimilab (São Paulo, Brazil). A 1000 mg L^{-1} Pd stock standard solution from Sigma-Aldrich (Missouri, US), a 1000 mg L^{-1} Nd (Spex, New Jersey, US), Sr (Vetec, Duque de Caxias, Brazil) and Zr solution (Fluka, Buchs, Switzerland) were used. The liquid samples and modifiers (at a concentration of 1000 mg L^{-1}) were automatically inserted into the GF in 20 µL aliquots using the autosampler.

The following Standard Reference materials (SRM) were used: Corn Bran (SRM 8433), Bovine Muscle Powder (SRM 8414), Whole Egg Powder (SRM 8415), Wheat Flour (SRM 1567a), Bovine Liver (SRM 1577b) and Non-Fat Milk Powder (SRM 1549) all from NIST (Gaithersburg, USA); Pig Kidney (BCR 186) and Mussel Tissue (BCR 278R), both from IRMM (Geel, Belgium) and Beef Liver (NCS-ZC 71001) from NACIS (Beijing, China).

2.2.3. Analytical procedure

Carrier gas flow rate, RF power and pyrolysis and vaporization temperatures (Tp and Tv, respectively) were optimized using the certified sample SRM 8414 for solid sampling studies as the concentration of Cl in this sample is within the concentrations expected in the samples. A 50 mg L^{-1} Cl solution was also used to investigate the experimental parameters.

The use of modifiers was evaluated by pipetting Pd and the mixture of Ca + Pd and Nd + Pd as acidic aqueous solutions directly onto the solid samples. For comparison, the modifiers were also pre-dried into the sampling cup, prior to insertion of the solid samples or aqueous standards. For the studies involving aqueous solutions, 10 µL aliquots of each modifier were added concomitantly to the samples.

Alternatively, the sampling cup was pre-treated with a total of 200 µg Pd as permanent modifier (10 injections of 20 µL of the stock solution). Calcium and Nd were then pre-dried using a Tp of 1000°C [82], before the addition of each sample.

Chlorine determination in SRM was carried out using calibration against aqueous or solid standards using Pd + Nd or Pd + Ca pre-dried as modifiers and also without modifier using a solid standard. The calibration range extended from 0.2 to 3.0 µg Cl. All measurements were carried out monitoring the isotope ^{35}Cl.

The heating temperature of the ETV is based on the 1: solvent and acid removal at 1,000°C for 10s when pre-dried modifiers were used, 2: insertion of the sample at 20°C, 3: Drying step at 100°C for 10s, 4: Pyrolysis step at the optimal temperature for each modifier for 10 s and 5: Vaporization step at the optimal temperature for each modifier for 18 s. The whole process considering the removal and inserting of the cup containing the sample takes about 4 min.

In order to establish a comparison of the results with those from an alternative technique, the biological samples were directly weighed (approximately 0.05 to 0.5 mg) onto SS platforms, previously treated with a total of 400 µg (10 injections of 40 µL containing 40 µg of the modifier) of zirconium as a permanent chemical modifier. Subsequently, 10 µL (2% m/v) of the molecule-forming Sr solution (as $SrCO_3$) was pipetted onto the biological samples and introduced into the GF to be submitted to the temperature program, aiming at the determination using HR-CS MAS.

2.3. Results and discussion

2.3.1. Optimization of ICP-MS operating parameters

Initial experiments involved optimizing the ICP-MS parameters, which include the carrier gas flow rate and the plasma RF power, in addition to the evaluation of the short-term signal stability.

The carrier (internal) gas flow rate exerted significant influence on the analytical signal, as also observed by Antes *et al.* [69]. The analytical signal was found to be maximum at a carrier gas flow rate of 0.7 L min^{-1} (Figure 8a), and symmetrical peaks were observed under this condition. Higher gas flow rates resulted in significant decrease in sensitivity, suggesting that the transport efficiency of Cl from the ETV to the ICP is critically influenced by this parameter. Hence, a carrier gas flow rate of 0.7 L min^{-1} was selected for further experiments.

The RF power (Figure 8b) was also investigated, since the high ionization potential of Cl (12.97 eV) would require a proportionally high plasma power to provide optimum sensitivity. Increasing the RF power from 800 to 1300 W resulted in an increase in sensitivity by a factor of two, as expected. Hence, the RF power was maintained at 1300 W for further experiments.

Considering the organic nature of the samples and the possibility of deposition of carbon on the cones with a direct effect on the analytical signal [69-72], a short-time stability study was conducted by adding mass aliquots of about 500 µg of the solid sample SRM 8414 and monitoring the integrated signal for 40 min. In order to establish a comparison, an aqueous standard was also evaluated, and a relatively low pyrolysis temperature was adopted (200 ^{o}C) in order to simulate an extreme condition.

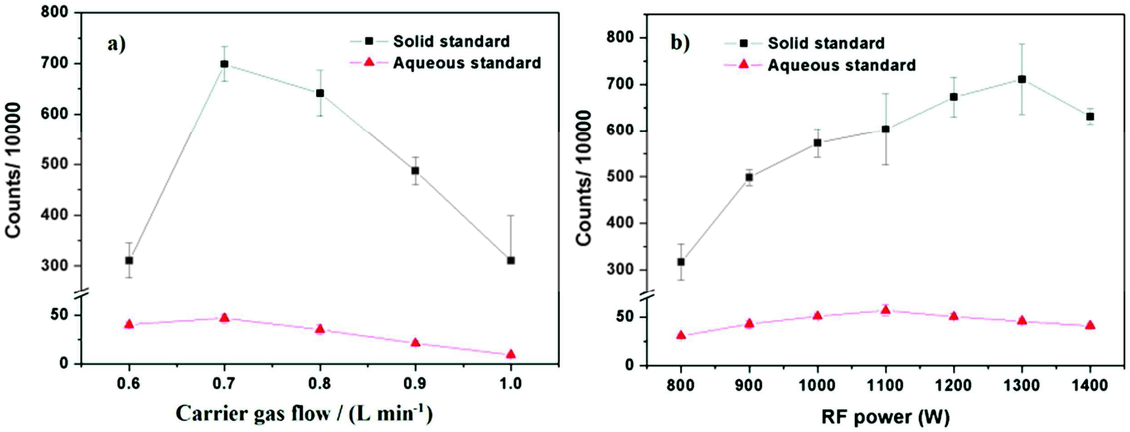

Figure 8. Effect of instrumental operating parameters on the analytical signal for Cl (monitoring the isotope ^{35}Cl) obtained by ETV-ICP-MS: (a) carrier gas flow rate and (b) RF power. Results are shown using the SRM 8414 solid sample and for an aqueous standard without the use of modifiers; in both cases, the absolute Cl mass inserted is approximately 1 µg. Pyrolysis and vaporization temperatures were set at 500 and 2000 ^{o}C, respectively.

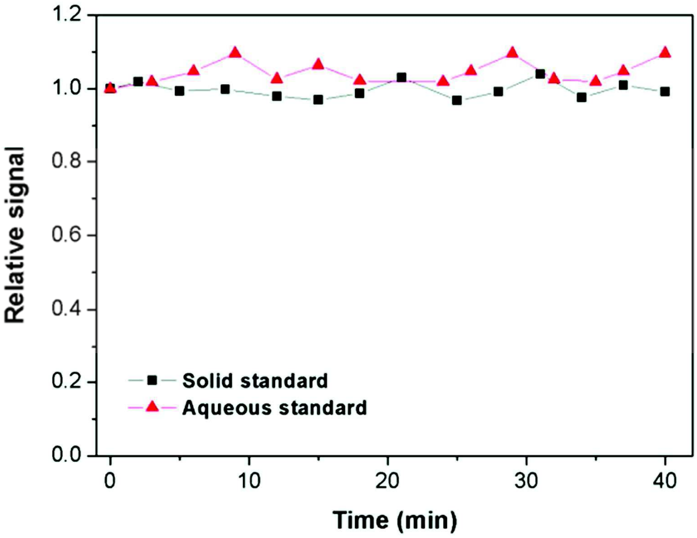

Figure 9. Short-time stability for Cl using about 500 µg of the sample SRM 8414 and an aqueous standard without the use of modifiers, monitoring the isotope ^{35}Cl. Conditions: pyrolysis and vaporization temperatures 200 ^{o}C and 2000 ^{o}C, respectively; 0.7 L min^{-1} carrier gas flow rate and 1300 W RF power. Each individual signal obtained from SS-ETV-ICP-MS was normalized to 1 mg of sample; individual counts were divided by the signal obtained in the first measurement in each series.

The results, shown in Figure 9, demonstrate that the analytical signal did not suffer from significant drift over the evaluated period, suggesting that the sample matrix was efficiently eliminated even at low pyrolysis temperatures and/or the residual matrix that was transported to the ICP could be fully decomposed prior to introduction of the ion stream into the MS. Visual inspection of the sampling and skimmer cones following this experiment has also attested the absence of deposited material, corroborating this assumption.

2.3.2. Pyrolysis and vaporization temperatures

The transient signals obtained by SS-ETV-ICP-MS using either aqueous standards or solid samples were symmetrical (slightly tailed) and relatively short even without the use of modifiers, as shown in Figure 10.

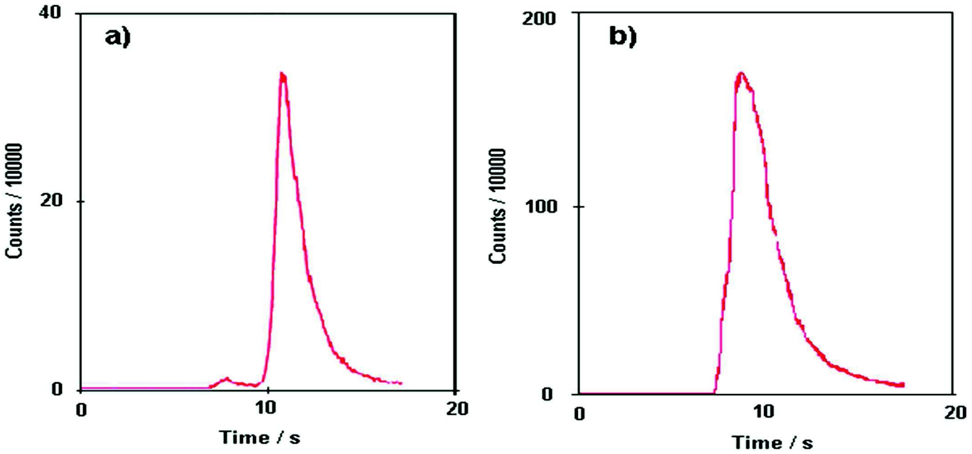

Figure 10. Signal profile obtained by ETV-ICP-MS. Conditions: pyrolysis and vaporization temperatures 500 °C and 2000 °C, respectively; 0.7 L min^{-1} carrier gas flow rate and 1300 W RF power monitoring the isotope ^{35}Cl: a) is aqueous standard signal for 1 µg of Cl and b) is solid standard RM 8414 for 0.2 µg of Cl both without the use of modifiers.

Considering the difference in sensitivity that was detected between aqueous standards and solid samples observed in Figure 10, an evaluation of the effect of chemical modifiers was performed as an attempt to stabilize Cl in aqueous solutions and to equalize the sensitivity for both aqueous and solid standards, which would exert an important influence on the quantification process.

Calcium and Nd were firstly evaluated, since these elements are known to form thermodynamically stable compounds with Cl and the signal profile could be improved with the co-injection of 10 µg of Pd, which coincides with the findings of Resano *et al.* [82], who adopted the use of pre-dried Pd as a modifier to carry out iodine determination by ETV-ICP-MS.

Considering these aspects, pyrolysis and vaporization curves were established in the absence of a modifier and also using Pd alone or its mixtures with Nd or Ca. The results are shown in Figure 11.

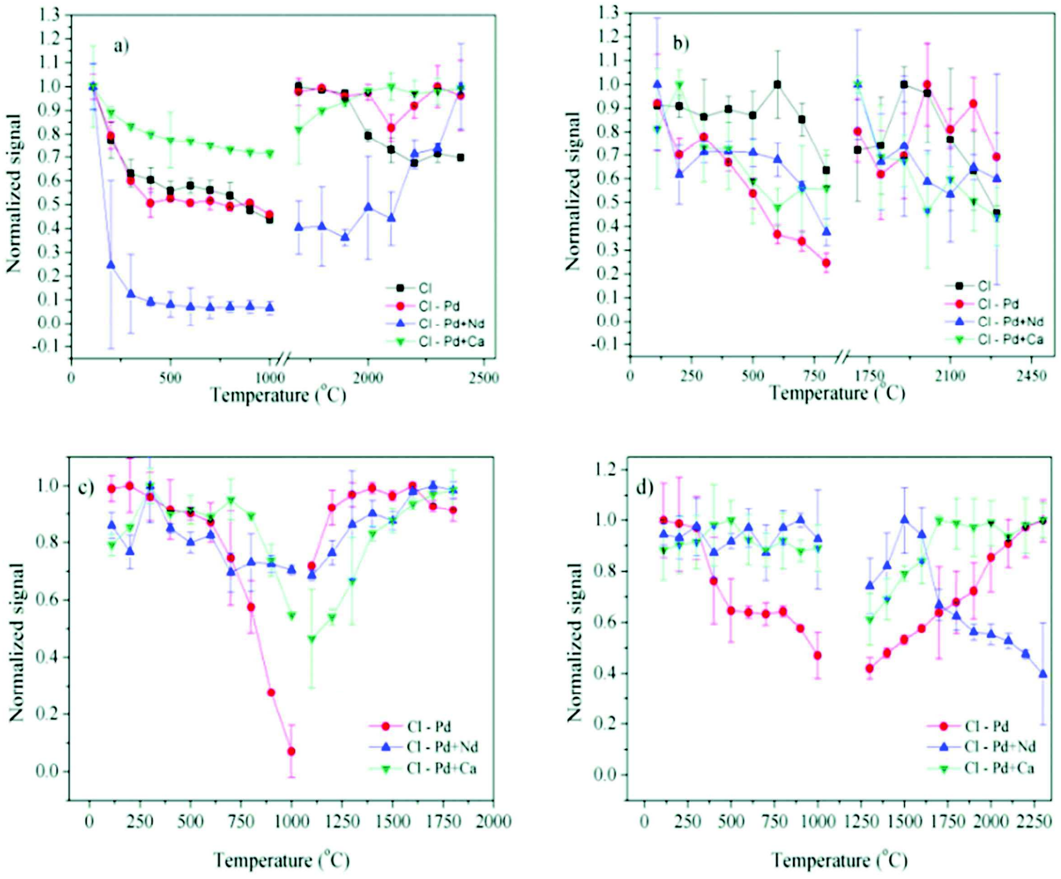

Figure 11. Pyrolysis and vaporization curves obtained by SS-ETV-ICP-MS for Cl in aqueous standards (1 µg) and in the SRM 8414 (bovine muscle) solid sample: (a) aqueous standard using aqueous modifiers; (b) solid SRM using aqueous modifiers; (c) aqueous standard using pre-dried modifiers; (d) solid SRM using pre-dried modifiers. Each individual signal obtained from SS-ETV-ICP-MS was normalized to 1 mg of sample; signals were also normalized to the highest signal achieved in each individual curve. Error bars present the RDS on the y scale.

The use of Pd + Ca as an aqueous chemical modifier for Cl in aqueous solutions (Figure 11a) reduced the analyte loss at temperatures higher than 200 ºC and/or contributed to an improved transport efficiency of the analyte to the ICP.

Curiously, the sensitivity was significantly reduced when a mixture of Pd and Nd was employed, suggesting either a strong interaction of the analyte with the modifiers in the condensed phase, hence reducing the vaporization efficiency, or a reduction in transport efficiency of the analyte to the ICP.

The effect of chemical modifiers pipetted onto solid SRM 8414 is shown in Figure 11b. The curves demonstrate that the analytical signal tends to decrease with increasing pyrolysis temperature, suggesting that premature volatilization of the analyte occurs.

The only condition that allowed the signal to be maintained approximately constant was the absence of a modifier. Overall, the results shown in Figures 11a and 11b demonstrate that the efficiency of chemical modifiers is somewhat limited and the performance is similar or worse than when no modifier is used in the process. A possible conclusion is that somehow the presence of nitric acid from the liquid modifiers medium is leading to the formation of HCl during the stages of thermal pre-treatment and, hence, results in premature loss of the analyte.

In order to avoid any potential effect deriving from the presence of acids in the GF, the modifiers were pre-dried onto the internal surface on the solid sampling cup prior to insertion of the solid samples or aqueous standards. In this sense, Pd was thermally deposited onto the sampling cup by successive injections of the liquid modifier, followed by application of a specific temperature program in order to form a coating containing 200 µg of deposited Pd. The additional modifiers, Nd or Ca, were pre-dried onto the Pd-modified surface immediately before the injection or insertion of the samples [82].

The results, shown in Figures 11c and 11d, demonstrate that the pre-dried modifiers allowed significant thermal stability for Cl to be achieved. Considering the aqueous standard, maximum pyrolysis temperatures of 600 ^{o}C using Pd + Nd and 700 ^{o}C using Pd + Ca (Figure 11c) could be used, whereas Cl in the solid SRM was maintained stable at up to 1000 ºC, using permanently deposited Pd mixed with either Ca or Nd, in their pre-dried forms.

In general, higher stability was observed using the Nd or Ca co-modifiers with Pd, which may be related to the high dissociation energy of the molecules formed between Cl and Nd or Ca [83]. Based on Figure 11, the optimized pyrolysis and vaporization temperatures used for the determination were respectively, 200°C and 2000°C without the use of modifiers, 300°C and 2100°C using Pd as modifier, 600°C and 1500°C using Pd + Nd pre-dried as modifier and 700°C and 1800°C using Pd + Ca pre-dried as modifier

2.3.3. Evaluation of potential interference from sulfur on the analytical signal

Sulfur may promote spectral interference at *m/z* 35 due to the formation of $^{1}H^{34}S^{+}$. Since sulfur may be present at relatively high concentrations in the analyzed samples, a simulation was carried out to evaluate whether any interference would occur under the conditions adopted in this work. Hence, an aqueous solution containing 250 mg L^{-1} S was analyzed using a low Tp (200 °C), in order to prevent volatilization of the element during thermal pre-treatment. The resulting transient signal, measured at *m/z* = 35 and also at *m/z* 34 (for reference), is shown in Figure 12.

The peak area values obtained at *m/z* 35 were similar to those observed from blank solutions, regardless of the chemical modifier adopted, which suggests that interference from polyatomic $^{1}H^{34}S^{+}$ is unlikely to occur.

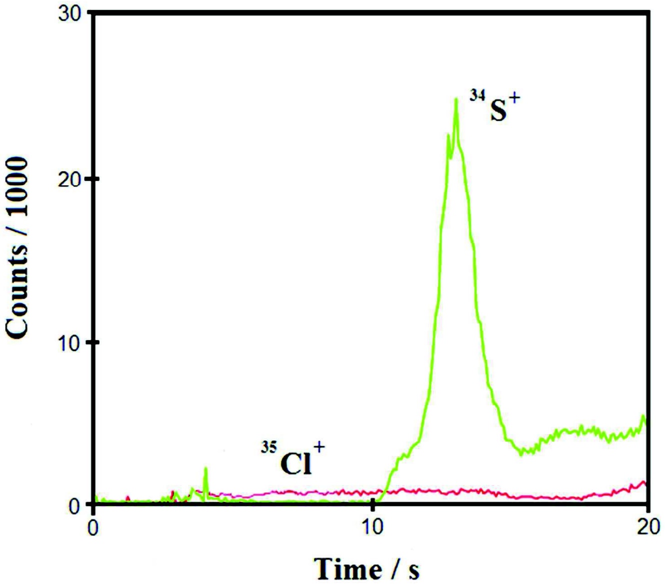

Figure 12. Signal obtained from the vaporization of 5.0 µg of S using SS-ETV-ICP-MS at *m/z* 34 and 35. Conditions: pyrolysis and vaporization temperatures 200 °C and 2000 °C, respectively; 0.7 L min^{-1} carrier gas flow rate and 1300 W RF power; no modifier was used.

2.3.4. Calibration and analytical accuracy

Calibration against aqueous standards is a fast and simple approach, but the fundamental requirement is that the behavior of the analyte (*i.e.* the relative sensitivity) in aqueous standards and in the samples should be similar.

However, analytical procedures employing SS frequently suffer from pronounced matrix effects deriving from the presence of significant amounts of matrix inside the GF [40]. The situation becomes even more complex when transportation between the ETV and the ICP is considered, since the solid particles from the matrix may assist in the process of nucleation and the transport efficiency from solid samples may be significantly better than from aqueous standards.

Hence, in order to establish an adequate calibration procedure, calibration curves were obtained for a sample mass ranging from 0.1 to 1.5 mg of the SRM 8414 (bovine muscle), corresponding the range from 0.188 μg to 2.820 μg of Cl, herewith denominated calibration against a solid sample, and also using aqueous standards resulting in the insertion of Cl masses that varied from 0.2 to 3.0 μg. Both calibration approaches were evaluated with and without the use of pre-dried modifiers, as discussed in the previous session. The resulting figures of merit are shown in Table 1.

Table 1. Figures of merit obtained for different calibration approaches aiming at the determination of Cl by ETV-ICP-MS.

Calibration standards	Modifier	Aqueous modifier		Dried modifier	
		Slope (counts ng^{-1})	R	Slope (counts ng^{-1})	R
Aqueous solutions	No modifier	4386	0.9661	-	-
	Pd	1397	0.9852	3678	0.9864
	Pd-Nd	1883	0.9847	4107	0.9942
	Pd-Ca	1678	0.9844	3358	0.9998
Solid CRM (SRM 8414)	No modifier	3010	0.9995	-	-
	Pd	1007	0.9275	2816	0.9839
	Pd-Nd	1119	0.9287	3923	0.9937
	Pd-Ca	832	0.9824	3160	0.9946

In general, the use of aqueous modifiers resulted in lower linear correlation coefficients for the calibration curves ($R < 0.98$) when compared to the linearity observed with the use of pre-dried modifiers. The sole use of permanently deposited Pd as a chemical modifier also resulted in a low linear correlation coefficient, regardless of the calibration approach adopted. Apparently, the interaction with the modifier and/or the transport efficiency in these cases is concentration-dependent, resulting in polynomial calibration curves.

The use of pre-dried Pd + Ca or Pd + Nd as chemical modifiers resulted in similar sensitivities for calibration against aqueous standards and against a solid SRM, suggesting that calibration against aqueous standards would be a feasible approach. In essence, it can be assumed that analyte interaction with the chemically modified surface is more significant than the analyte interaction with the matrix, an effect that ultimately normalizes the analyte thermal stability and the transport efficiency between aqueous solutions and the solid sample.

As illustrated before (Figure 10), if no modifiers were used, lower signals resulted from the analysis of aqueous standards when compared to a solid SRM, even when the nominal analyte mass introduced into the furnace *via* the aqueous standard exceeded the Cl mass in the solid SRM. This was attributed to the loss of Cl during drying and pyrolysis steps, which were conducted at 100 ^{o}C and 500 ^{o}C, respectively. In contrast, the chemical interaction of chlorine species with the solid matrix appeared to be sufficient to maintain the analyte in the condensed phase under the conditions adopted in this work. Therefore, it is assumed that the used of modifiers is necessary when the use of aqueous standards is aimed.

The limit of quantification (LOQ) was calculated as 10 times the standard deviation of ten measurements of the empty SS cup divided by the slope of the calibration curve obtained, and adjusted to the average sample mass used in the analytical procedure. Using SS-ETV-ICP-MS in this work a LOQ of 5 μg g^{-1} was achieved, which is comparable to that obtained by Antes *et al.* for petroleum coke samples (3.5 μg g^{-1}), although using sample mass aliquots that are ten times higher than those typically used in this work.

This means that the current approach, using pre-dried modifiers and calibration against aqueous standards, is about 10 times more sensitive than the method previously described, with significantly lower sample consumption [28].

Some other techniques which require sample pretreatment as pyrohydrolysis combined with IC can achieve LOQ of 1 µg g^{-1} [80]. However using a considerable mass of sample (1g) and the determination by HR-CS-GF-MAS after acid digestions using 100 mg achieving a LOQ of about 3 µg g^{-1} [84]. However those techniques require extra procedures, equipment, reagents and a relatively high mass of sample.

Five SRMs were analyzed using calibration against a solid SRM and also against aqueous standards in the absence of a modifier and using pre-dried Pd + Nd or Pd + Ca. The results are presented in Table 2. As can be seen, the concentrations obtained using SS-ETV-ICP-MS are in good agreement with the certified values at a 95% statistical confidence level, regardless of the calibration approach adopted.

The fact that calibration against aqueous standards can be applied without compromising the accuracy and regardless of the nature of the sample is remarkable and it is described for the first time for the direct analysis of solid samples using SS-ETV-ICP-MS aiming at halogens determination.

Three SRM without certified Cl concentrations were also analyzed using SS-ETV-ICP-MS. In these cases, the results were compared to those obtained from the analysis using HR-CS-GF-MAS (Table 3). The results from both techniques are in good agreement one another.

Table 2. Chlorine concentration, in weight %, obtained using SS-ETV-ICP-MS for five certified reference materials (mean ± confidence interval at a 95% statistical confidence level; for n = 4).

Sample	Certified	SS ETV ICP-MS				
		Calibration against:				
		Solid standards without modifier	Solid standards using Pd + Nd dried	Aqueous standards using Pd + Nd dried	Solid standards using Pd + Ca dried	Aqueous standards using Pd + Ca dried
SRM 8415	0.508 ± 0.032	0.499 ± 0.020	0.516 ± 0.010	0.493 ± 0.010	0.505 ± 0.015	0.475 ± 0.014
SRM 1549	1.09 ± 0.02	1.04 ± 0.09	1.15 ± 0.11	1.10 ± 0.10	1.07 ± 0.15	1.01 ± 0.14
RM 8433	*31 ± 21	*29 ± 4	*27 ± 2	*25 ± 1	*32 ± 7	*31 ± 6
NIST 1577b	0.278 ± 0.006	0.285 ± 0.021	0.275 ± 0.017	0.263 ± 0.016	0.281 ± 0.030	0.264 ± 0.028
NCS ZC 71001	0.29 ± 0.04	0.280 ± 0.054	0.285 ± 0.092	0.272 ± 0.088	0.301 ± 0.077	0.283 ± 0.073

*Reported as $\mu g\ g^{-1}$.

Table 3. Chlorine concentration, in weight %, obtained using SS-ETV-ICP-MS and HR-CS GF MAS for CRM (mean ± confidence interval at a 95% statistical confidence level; for n = 4).

Sample	HR-CS-GF-MAS	SS ETV ICP-MS				
		Calibration against:				
		Solid standards without modifier	Solid standards using Pd + Nd dried	Aqueous standards using Pd + Nd dried	Solid standards using Pd + Ca dried	Aqueous standards using Pd + Ca dried
SRM 1567a	0.059 ± 0.005	0.051 ± 0.009	0.066 ± 0.012	0.063 ± 0.011	0.062 ± 0.008	0.058 ± 0.007
BCR 186	0.86 ± 0.081	0.718 ± 0.098	0.905 ± 0.064	0.864 ± 0.061	0.872 ± 0.063	0.818 ± 0.059
BCR 278R	1.99 ± 0.4	2.221 ± 0.126	2.103 ± 0.456	2.001 ± 0.435	2.023 ± 0,367	1.90 ± 0.345

2.4. Conclusions

In order to avoid the typical problems related to Cl determination by the commonly employed instrumental and sample preparation techniques, the use of SS-ETV-ICP-MS may be regarded as a sensitive and accurate alternative. The methodology is relatively simple, since it does not require any time-consuming sample pretreatment. Calibration against solid reference materials or against aqueous standards using Pd + Nd or Pd + Ca was proven feasible for the determination of Cl in five certified standard materials and three non-certified samples by SS-ETV-ICP-MS. The procedure may probably be extended to other biological or botanical samples.

Chapter 3 - Simultaneous determination of bromine and chlorine in coal using SS-ETV-ICP-MS

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3.1. Introduction

Chlorine is essential for humans, animals and plants, and is a precious commercial article since ancient times, as it was used, among other things, for the conservation of food. Bromine, in contrast, has no known physiological function. Both elements, however, can also be highly toxic and hazardous to the environment, depending on the compound in which they are present and their concentration [1, 8, 9, 85-87].

Coal is a potential source of halogens due to the release of these elements to the atmosphere during combustion. The release of Br and Cl from coal is a serious concern, mainly because coal is, and probably will remain for quite some time, employed as a major source of energy in many countries [88]. The presence of these elements in coal, considering the increasing consumption of coal in the last decades, may represent a risk to the environment and consequently for living organisms [89-90].

In order to avoid the problems related to sample pretreatment and also to determine trace levels of Br and Cl, solid sample analysis may be carried out using ETV-ICP-MS, which leads to advantages, such as reduced risk of interference, greatly reduced risk of contamination, increased sensitivity and suitability as a simultaneous trace elemental analytical procedure [40].

Given the high importance of Br and Cl determination in coal samples and the feasibility of its determination using SS-ETV-ICP-MS, the aim of this work was to develop an analytical method for Br and Cl determination in coal samples using direct solid sample analysis.

3.2. Experimental

3.2.1. Instrumentation

All experiments were carried out using an Elan 6000 inductively coupled plasma mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer coupled to an autosampler model AS-60 from Perkin-Elmer SCIEX (Thornhill, Canada). The cup-in-tube technique described by Vollkopf *et al.* [75] was used for solid sampling experiments. The samples were directly weighed into a solid sampling glass capillary using a micro-balance model M2P (Sartorius, Göttingen, Germany) and transferred to pyrolytically-coated graphite cups from Perkin-Elmer (Norwalk, USA).

The operating parameters of the ICP-MS instrument are listed in Table 4. Argon with a purity of 99.996% from White Martins (São Paulo, Brazil) was used as plasma, carrier and internal gas of the ETV.

A Model contrAA 600 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer was employed for comparison. Pyrolytically coated graphite tubes (Analytik Jena) were used in all experiments.

Table 4. Operating parameters of ICP-MS.

Sampling/ skimmer cones	Pt	
RF power	1200 W	
Signal measurement	*Peak Hopping*	
Autolens	on	
Detector voltage	Pulse 1500 V	Analog: - 2500 V
Dead Time	55 ns	
Dwell time	12 ms	
Readings/ Replicate	500	
Gas flow rate:		
	Plasma	15.0 L min^{-1}
	Auxiliary	1.2 L min^{-1}
	Nebulizer	1.1 L min^{-1}

The solid samples were weighed directly onto solid sampling platforms (Analytik Jena) using the M2P micro-balance. A manual solid sampling system SSA 6 (Analytik Jena) was used to insert the SS platforms into the graphite tube. For the determination of Br, the optimized pyrolysis and vaporization temperatures were 800 and 2200 °C, respectively, while for Cl determination the pyrolysis and vaporization temperatures were 600 °C and 2300 °C, respectively.

The molecular absorption of CaBr molecule was measured at 625.315 nm and the SrCl molecule was measured at 635.862 nm, both using integrated absorbance over three pixels PVSA, $A_{\Sigma 3,int}$) [91].

3.2.2. Reagents, standards and samples

All reagents used were at least of analytical grade. Deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) with a resistivity of 18.2 MΩ cm. Individual stock solutions containing each 1000 mg L^{-1} Ca, Cl and Br were obtained from Quimilab (São Paulo, Brazil), Pd from Sigma-Aldrich (Missouri, USA) and Al, K, P, S and Sr from Spex (New Jersey, USA).

The coal CRMs used were BCR-180 and BCR-182 from IRMM (Geel, Belgium), NIST 1630a and NIST 1632b from National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA) and Sarm-19 from South Africa Bureau of Standards (Randburg, South Africa).

3.2.3. Analytical procedure

Pyrolysis and vaporization temperatures of the ETV, the carrier gas flow rate and RF power of the ICP-MS were optimized using the CRM BCR-182 for the studies with direct SS analysis, and an aqueous solution containing Br and Cl.

The modifiers studied were Pd and its corresponding mixtures with Ca and Al. In the latter cases, 200 µg Pd was deposited in excess into the sampling cups (10 injections of 20 µL of a solution containing 1 g L^{-1}) whereas Ca and Al were pre-dried using 20 µL of a solution containing 1 g L^{-1} and applying the drying temperature of 100 ^{o}C and a pyrolysis temperature of 1000 ^{o}C before the addition of the samples [82].

The quantification of Br and Cl in the CRM was carried out upon calibration using the CRM BCR-182; Br was also quantified following calibration against aqueous standard solutions. All measurements were carried out monitoring the isotopes ^{79}Br and ^{35}Cl.

For comparison, Br and Cl were also determined by HR-CS GF MAS. For Br determination a Ca^{2+} solution was pipetted directly into the graphite tube as the molecule-forming reagent. The coal samples (≈ 0.2–3 mg) were directly weighed onto the SS platform previously treated with a total of 400 µg Zr (10 injections of 40 µL containing 40 µg Zr each) (i.e., which had not to be renewed throughout the lifetime of the platform) and introduced into the GF to be submitted to the temperature program [91].

Chlorine was determined using Sr^{2+} as the molecule-forming reagent. Coal CRM were directly weighed (≈ 0.05 to 0.5 mg) onto the SS platform, also previously treated with a total of 400 µg of zirconium as a permanent chemical modifier. Afterwards, 10 µL (2% m/v) of the molecule-forming Sr solution (as $SrCO_3$) has been injected over the coal samples on the SS platform and introduced into the GF to be submitted to the temperature program [92].

3.3. Results and discussion

3.3.1. Optimization of ICP-MS operating parameters

RF power and carrier gas flow-rate were optimized aiming at maximum sensitivity for the analytes. The results are shown in Figures 13a and 13b. The RF power was evaluated (Figure 13a) and maximum signal was obtained at 900 W for Br and at 1200 W for Cl, using the BCR-182 coal CRM. This difference is related to the ionization potential of each element; Br an Cl have ionization potentials of 11.81 eV and 12.97 eV, respectively, which means that Cl requires more energy to be ionized. Since the sensitivity associated to Cl determination is lower than for Br, the RF power was chosen to be 1200 W.

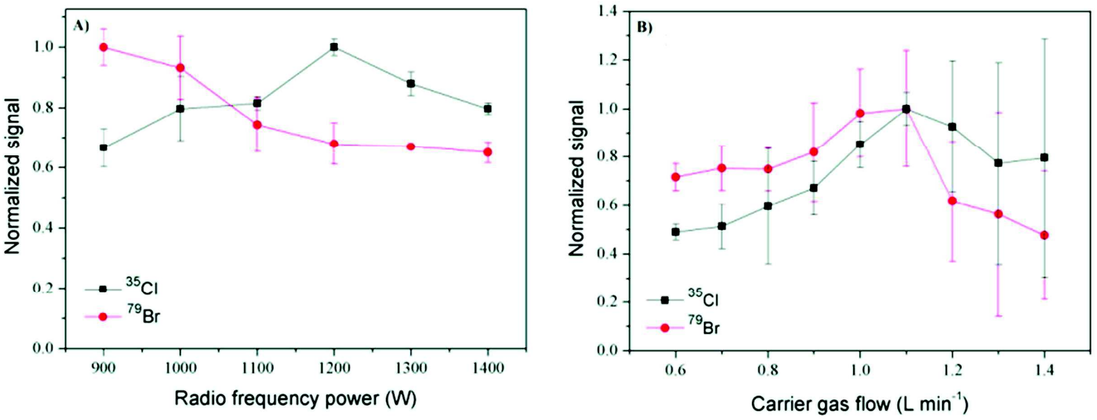

Figure 13. Effect of carrier gas flow-rate (A) and RF power (B) on the analytical signal obtained by SS-ETV-ICP-MS for Br and Cl in BCR-182 coal CRM and in aqueous standard solutions. Pyrolysis and vaporization temperatures were set at 400 °C and 2000 °C, respectively. Normalized signals refer to the ratio between the individual signal and the highest signal in the series.

The carrier gas flow-rate influences the sensitivity and the analytical signal profile, as already observed by Antes *et al.* [69] for Cl determination in coke samples. In our work, the carrier gas flow-rate did not exert significant influence on the analytical signal profile, and a maximum intensity was achieved with a carrier gas flow-rate of 1.1 L min^{-1} (Figure 13b).

3.3.2. Evaluation of pyrolysis and vaporization temperatures

Pyrolysis and vaporization temperatures were evaluated in parallel with a study of modifiers/aerosol carriers. In addition to increased thermal stability, the use of modifiers was evaluated as a means to equalize the sensitivity for both aqueous standard solutions and solid samples, which would allow the subsequent determination of Br and Cl using calibration against aqueous standard solutions.

Calcium and Al were chosen due to their high bonding energies with Br and Cl, which has led to their use as molecule forming reagents in halogen determination by HR-CS MAS [83].

The use of Ca and Al as individual modifiers, however, resulted in distorted transient peaks, and symmetrical signals could only be obtained upon the concomitant use of Pd, a finding that is in agreement with similar studies by Resano et al. [82]. Hence, the combined Pd + Ca and Pd + Al modifiers were evaluated as to their ability to improve the thermal stability for the analytes.

Pyrolysis and vaporization curves are shown in Figure 14 for aqueous standard solutions and a solid CRM. Figure 14 demonstrates that in the absence of modifiers, analyte losses occur already at pyrolysis temperatures as low as 200 °C for aqueous standards, whereas higher stability is observed for the solid sample, which is likely due to the covalent interaction of Cl and Br with matrix components.

In general, the use of chemical modifiers provided a significant increase in thermal stability for both analytes in the aqueous solution, but there is also an improvement in stability for the solid samples. The use of Pd + Ca provided the best thermal stability for aqueous standards compared to Pd alone and Pd + Al in all cases.

Overall, it is likely that the thermal stability provided by the modifiers acts together with improved transport efficiency in the presence of Pd + Ca or Al, which is likely to occur due to the favorable interaction between the halogens and Ca and Al, particularly. The optimum conditions chosen for each modifier are presented in Table 5

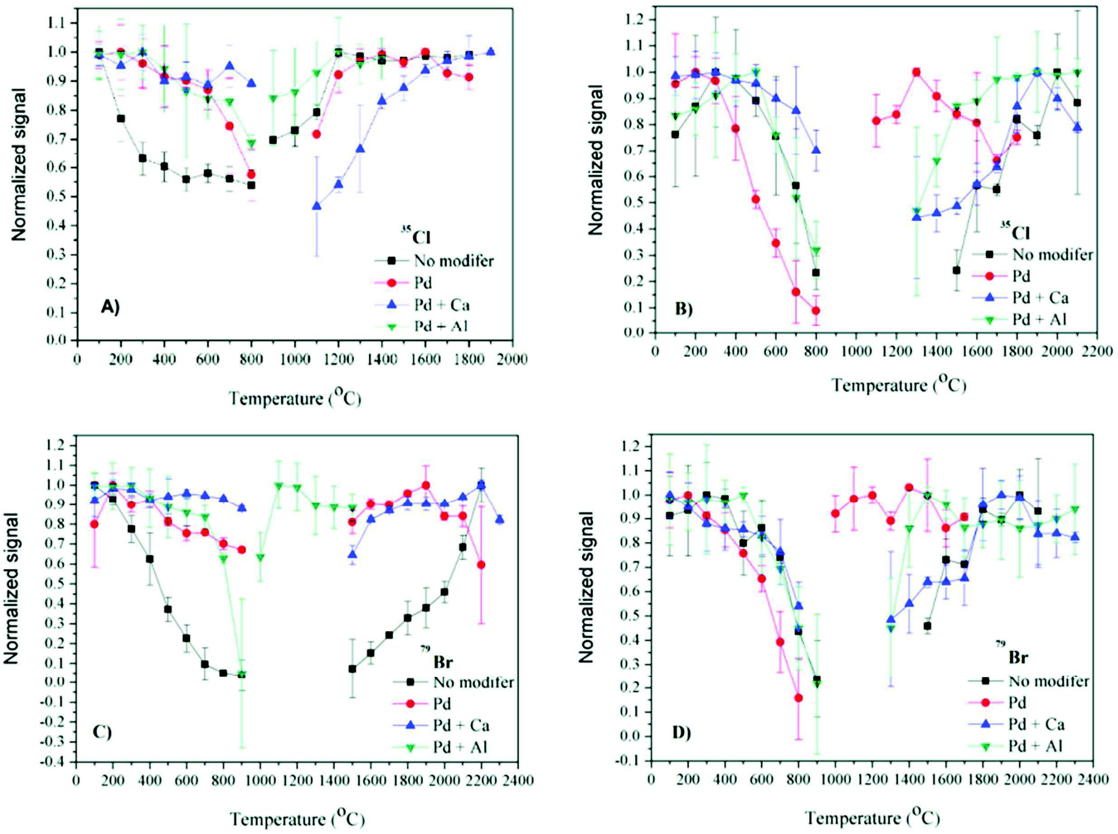

Figure 14. Pyrolysis and vaporization curves obtained by SS-ETV-ICP-MS for 2 µg Cl as an aqueous standard solution (A), Cl in BCR-182 (B), 0.02 µg Br as an aqueous standard solution (C) and Br in BCR-182 (D). Conditions: 1200 W RF power; 1.1 L min^{-1} carrier gas flow-rate. Normalized signals refer to the ratio between the individual signal and the highest signal in the series

Table 5. Optimized conditions of Tp and Tv for Br and Cl determination in coal using SS-ETV-ICP-MS, using RF power of 1200°C and carrier gas flow of 1.1 L min^{-1}.

Modifier	Tp and Tv, respectively
No modifier	100°C, 2000°C
Pd	300°C, 1500°C
Pd + Al	400°C, 1500°C
Pd + Ca	700°C, 1900°C

3.3.3. Evaluation of potential interfering species

Spectral interferences can drastically affect the accuracy of the measurements, particularly considering the formation of polyatomic ions such as $^{16}O^{18}O^{1}H^{+}$ and $^{34}S^{1}H^{+}$, which overlap with $^{35}Cl^{+}$; $^{36}Ar^{1}H^{+}$ and $^{36}S^{1}H^{+}$ which overlap with $^{37}Cl^{+}$; $^{40}Ar^{39}K^{+}$, $^{31}P^{16}O_3^{+}$ and $^{38}Ar^{40}Ar^{1}H^{+}$, which overlap with $^{79}Br^{+}$ and finally $^{32}S^{16}O_3^{1}H^{+}$, $^{40}Ar^{40}Ar^{1}H^{+}$ and $^{33}S^{16}O_3^{+}$,which overlap with $^{81}Br^{+}$. Since coal usually contains substantial amounts of S and K, an interference evaluation was necessary to assure the correctness of the quantification.

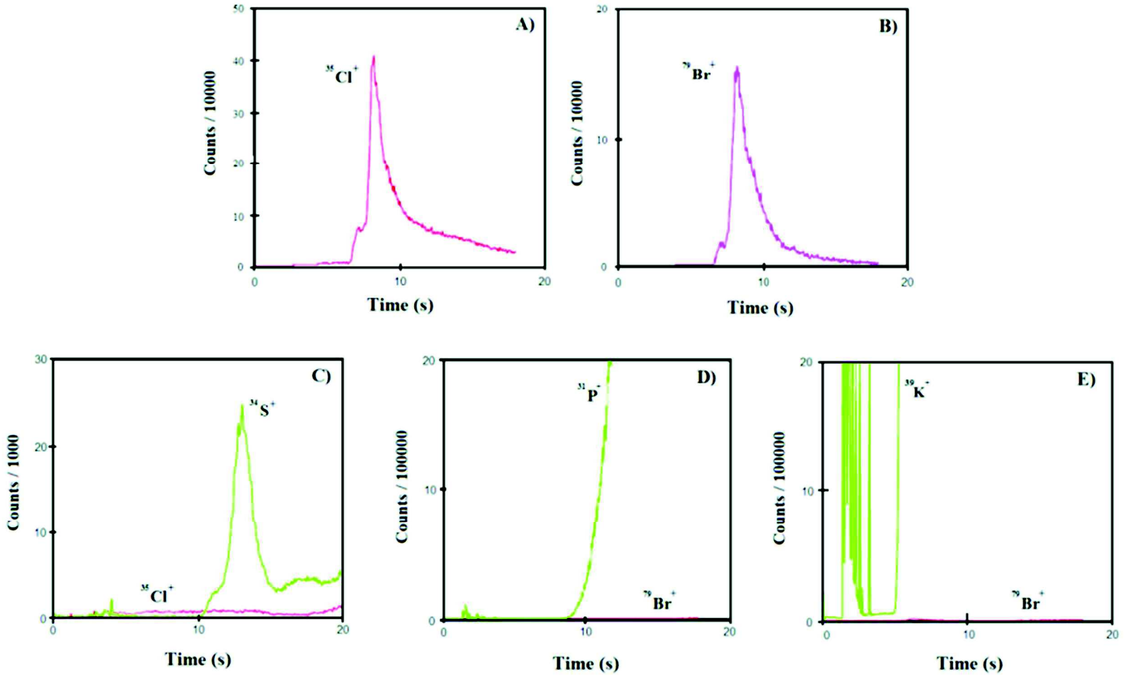

Figure 15. Analytical signal profiles obtained from 20 µL injections of aqueous solutions containing 500 mg L^{-1} of K, P or S, P or K; pyrolysis and vaporization temperatures 100 °C and 2000 °C, respectively. A and B refer to the signal profile obtained for the BCR-182 coal CRM using a sample mass of 100 µg, and C, D and E refer to the signal profiles obtained for aqueous solutions containing S, P and K, respectively.

In order to evaluate if interfering species could be present and affect the accuracy of the measurements, aqueous solutions containing 500 mg L^{-1} of K, P and S were analyzed using the lowest pyrolysis temperature possible (100 °C), in order to avoid volatilization during this step.

As can be seen in Figure 15, although the peaks at the respective *m/z* of K, S and P were pronounced, as shown by the green line, baseline values were obtained for Cl and Br in their respective *m/z*, which leads to the assumption that no interference due to polyatomic ion formation takes place under the conditions adopted. This should be even less significant considering that a higher pyrolysis temperature was chosen for the quantification, with further reduction in the population of concomitant species in the ICP [40].

3.3.4. Figures of merit and analytical application

Although calibration against aqueous standard solutions is regarded as the simplest procedure available for quantification, the behavior of the analyte in aqueous standard solutions must be similar to its behavior in the samples, generating similar responses.

This is particularly critical in SS-ETV-ICP-MS, since the influence of the matrix on analyte vaporization is amplified and the transport efficiency from the ETV to the ICP must be considered. Hence, calibration against aqueous standard solutions is frequently ruled out as a feasible approach in analytical procedures that involve direct sampling analysis and ETV-ICP-MS [40].

Table 6. Calibration parameters obtained by ETV-ICP-MS upon calibration against aqueous standards or using the solid CRM BCR-182 coal.

Modifier	**Calibration approach**	**Cl**		**Br**	
		***Slope**	**R^2**	***Slope**	**R^2**
None	Aqueous	2985	0.8945	37269	0.9603
	Solid	1420	0.9896	40200	0.9987
Pd	Aqueous	5940	0.9442	70556	0.9958
	Solid	1596	0.9901	37493	0.9974
Pd + Ca	Aqueous	8254	0.9918	75730	0.9927
	Solid	3124	0.9958	74641	0.9995
Pd + Al	Aqueous	6952	0.9913	75613	0.9987
	Solid	2133	0.9964	71558	0.9970

*Slope expressed as counts ng^{-1}

In order to establish a comparison, calibration against aqueous standard solutions and using solid CRM were carried out with and without the combined modifiers described in the previous section. Calibration against a solid CRM was carried out using a sample mass ranging from 0.1 to 1.5 mg of BCR-182 coal, whereas calibration against aqueous standard solutions was performed within the range of 0.02 - 0.10 µg Br and 0.1 - 5.0 µg Cl, with and without the use of modifiers and under the optimized pyrolysis and vaporization temperatures presented in Table 6.

Table 6 shows the slope and linear correlation coefficient obtained for each calibration approach for both analytes. As shown, none of the modifiers was able to provide a similar sensitivity for calibration against aqueous and solid standards for Cl, which implies that a solid reference material has to be used for calibration.

The sensitivity deriving from calibration using BCR-182 was significantly lower than the one obtained for Cl using aqueous standard solutions, which suggests that either the transport efficiency is improved in the latter case or analyte vaporization from the solid matrix is hindered by a strong interaction with matrix components. This situation contrasts with the one observed for Br, since for this element the use of Pd + Ca or Pd + Al provided similar sensitivity for both calibration approaches, suggesting that good accuracy could be obtained with calibration against aqueous standard solutions.

Although both Pd + Ca and Pd + Al provided similar sensitivity for calibration against aqueous standard solutions and using a solid CRM for Br determination, the determination of Br and Cl was carried using Pd + Ca due to the higher thermal stability provided by this combination of modifiers, as can be seen in the pyrolysis and vaporization curves shown in Figure 14.

The sensitivity was also improved with the adoption of Pd + Ca, particularly for Cl. Overall, it can be assumed that the chemical interaction between Br and Ca or Al was effective particularly using a solid sample, since the sensitivity improved as a result of higher transport efficiency and thermal stability. The same effect was noticed for Cl, although the interaction of the analyte with the co-modifier (Ca or Al) was not sufficient to equalize the sensitivity for aqueous standard solutions and solid reference material.

The LOQ was calculated as 10 times the standard deviation of ten measurements of the empty cup divided by the slope of the calibration curve, adjusted to the sample mass used for analysis. The LOQs obtained were 0.03 µg g^{-1} for Br and 7 µg g^{-1} for Cl. This is the first time that detection limit for Br is reported using SS-ETV-ICP-MS; a comparison with the LOQ of 5 µg g^{-1} obtained using SS-HR GF MAS [18] shows an improvement of about two orders of magnitude for SS-ETV-ICP-MS, using approximately the same sample mass.

Regarding Cl, Antes *et al.* obtained a similar LOQ for petroleum coke using SS-ETV-ICP-MS (3.5 µg g^{-1}), although using sample mass aliquots of about 5 mg, *i.e.* ten times higher than the typical sample mass required in the current work [69]. Determination of halogens using laser ablation and ICP-MS provide typically higher LOQ, such as 6 µg g^{-1} for Br and 27 µg g^{-1} for Cl in geological and environmental samples, as described by Boulyga and Heumann [64].

Chlorine was determined in five coal CRM using calibration against BCR-181. The results, shown in Table 7, are in agreement with the certified values and with the comparison technique, demonstrating the accuracy of the methodology.

Table 7. Chlorine concentration, in µg g^{-1}, obtained using SS-ETV-ICP-MS for the certified samples, confidence interval of 95% for n = 4.

Sample	Certified	HR-CS GF MAS	SS- ETV-ICP-MS
Sarm 19	32	<LOQ	30 ± 4
BCR-180	593	592 ± 21	575 ± 59
BCR-182	3700	3787 ± 463	*Calibration
Nist 1632b	1260	1281 ± 188	1198 ± 89
Nist 1630a	1144 ± 32	*Calibration	1101 ± 89

Bromine determination could be carried out using both, aqueous and solid standards for calibration. The results for five CRM (Table 8) are in agreement with the certified values and with comparative values.

Table 8. Bromine concentration, in µg g^{-1}, obtained using SS-ETV-ICP-MS for the certified samples, confidence interval of 95% for n = 4.

Sample	Certified	HR-CS GF MAS	SS- ETV-ICP-MS	
			Solid standards	Aqueous standards
Sarm 19	2	<LOQ	2.1 ± 0.2	2.0 ± 0.2
BCR 180	7.2 ± 0.5	<LOQ	6.3 ± 0.6	6.2 ± 0.6
BCR 182	39.7 ± 0.7	40.8 ± 2.4	*Calibration	39.5 ± 2.9
Nist 1632b	17	17.4 ± 3.2	16.9 ± 0.62	16.7 ± 0.6
Nist 1630a	33.0± 2.0	34.2 ± 1.4	38.1 ± 6.2	37.5 ± 6.1

In this sense, if the purpose is to carry out simultaneous determination of Br and Cl, calibration using solid standards is mandatory in order to provide good accuracy for both analytes. Nonetheless, individual determination of Br may be carried out using aqueous standard solutions for calibration.

The method proposed is efficient and fast, taking about 4 min for each analysis and providing RSDs of about 10% (with exception of Br in NIST 1630a for which an RSD of 16% was obtained), which is good since the heterogeneity of the sample must be considered when small amounts of sample are measured.

3.4. Conclusions

Due to the importance of the determination of Br and Cl in coal and aiming at solving the problems related to sample pretreatment for Br and Cl determination, the use of SS-ETV-ICP-MS was proven efficient to determine simultaneously both analytes without any advanced sample pretreatment protocol.

The use of chemical modifiers is recommended in order to provide higher thermal stability, hence avoiding losses during the pyrolysis step. A combination of permanently deposited Pd and pre-dried Ca enabled the determination of Br using aqueous standard solutions for calibration, although simultaneous determination of Br and Cl must be carried out using solid CRM for calibration. LOQ values lower than those found in the literature were achieved for both analytes and the procedure was proven accurate by the analysis of five CRM.

Chapter 4 - Assessment of the halogen content of Brazilian inhalable particulate matter (PM_{10}) using HR-CS MAS and ETV-ICP-MS, with direct solid sample analysis

Note: Portions of the text and data discussed in this chapter are reproduced or adapted from the publication authored by de Gois, J. S., Almeida, T. S., Alves, J. C., Araujo, R. G. O., Borges, D. L. G. available in *Environ. Sci. Technol.* (2016), DOI: 10.1021/acs.est.5b01934. Reprinted with permission from ACS publications.

4.1. Introduction

Halogens and halogenated compounds differ significantly in reactivity, physical properties and toxicity. Although some halogens, such as Cl and I, are regarded as essential elements to several forms of life, it is generally agreed that the presence of halogens in the environment is associated to hazards which include their ability to react with O_3 molecules and the potential to interfere in the balance of atmospheric SO_x and NO_x [14, 93,94].

The majority of the atmospheric halogen content comes from marine aerosols, although the emission of halogens from volcanic eruptions also plays an important role on the dynamics of the halogens in the Earth environment [95-96].

Other sources of halogens include the release of I_2 and CH_3Br from algae and land plants and anthropogenic processes [97], such as the combustion of fossil fuels and the manufacturing of polyfluorinated compounds [98], lubricants, varnishes and pesticides [99-100].

Particulate matter (PM) is normally composed by suspended liquids and solid particles floating in the air which are released in the atmosphere from specific sources or formed by reactions in the atmosphere. The determination of halogens in PM $_{10}$ (droplets from 2.5 to 10 µm in diameter), known as inhalable coarse particle, is an important task due to the high risk to the public health as they can be inhaled and reach the lungs. Moreover this type of analysis can bring important information about pollution [101].

Given the hazardous nature of halogens in the environment and several mechanisms that lead to their release into the atmosphere, the determination of halogens in the air is an important - and complex - analytical task. For this purpose, several techniques have been historically used, and more recently and far less frequently, HR-CS MAS and ICP-MS have been described for this task [91].

The association between direct solid sampling analysis and the above-mentioned spectrometric techniques has been proven effective for trace element determination in a number of applications, which may be particularly useful in the case of the PM_{10} analysis, since the presence of relatively high levels of silicates and oxides turn acid-based digestion into complex routines [102]. In addition, the halogens are prone to react readily under acidic conditions and at high temperatures to form their respective hydrogen halides, which are volatile and may be lost during the digestion procedure.

The use of line source atomic absorption spectrometry is not suitable for fluorine determination due to the fact that its main resonance lines are located below 95 nm, which cannot be achieved.

Recently, the feasibility of adapting a HR-CS atomic absorption spectrometer to carry out analysis based on diatomic molecule formation (which can absorb over a wider spectral range) inside the GF has been demonstrated for F determination by monitoring molecules such as SrF [103], BaF [104], GaF [105], AlF and MgF [106].

More recently, Morés *et al.* [107] demonstrated the feasibility of determining F by monitoring the CaF molecule at 606.440 nm region, which is advantageous because of the reduced risk of spectral interferences in this spectral range and the strong absorption intensity of the molecule at this line. This was a major breakthrough for AAS, since F cannot be directly determined using ICP-MS, due to the high ionization potential of this element, which hinders the formation of positive and singly ionized ions under the typical operating conditions of the instrument.

Given the widespread distribution of halogens in the environment and the importance and challenges associated with their determination, the aim of this work was to assess the application of direct solid sample analysis for the determination of F using HR-CS GF MAS and Br, Cl and I using ETV-ICP-MS in PM_{10}, a procedure which was applied to the analysis of PM_{10} from the city of Aracaju, located in the Northeast of Brazil.

4.2. Experimental

4.2.1. Instrumentation

Fluorine determination was carried out using a high-resolution continuum source atomic absorption spectrometer model ContrAA 700 (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer. The ContrAA 700 is equipped with a high-intensity xenon short-arc lamp operating in “hot-spot” mode, a high resolution monochromator consisting of a pre-dispersing prism and an echelle grating monochromator, and a linear array charge coupled device detector (CCD) with 200 analytically accessible pixels.

Direct insertion of the solid samples was accomplished by means of the SSA 600 automatic solid sampling device (Analytik Jena

AG). The SSA 600 is composed of a set of tweezers, which transport the pyrolytically-coated SS-platforms into the GF.

Solid samples were directly transferred to the SS-platforms using a stainless steel micro spatula. Aqueous standards and reagents were injected manually onto the SS-platform using micropipettes with disposable tips. The CaF diatomic molecule spectrum was used to determine F in the PM_{10} samples. The molecular band head at 606.432 nm was monitored using only one pixel due to the high intensity of this line; the use of less intense lines using more pixels resulted in poor precision compared to this line.

Chlorine, Br and I were determined using an Elan 6000 inductively coupled plasma mass spectrometer equipped with an HGA-600 MS ETV device from Perkin-Elmer (Thornhill, Canada). The 'cup-in-tube' technique described by Vollkopf *et al* [75]. was used for the solid sampling experiments.

The samples were directly weighed using a solid sampling glass capillary and a micro-balance model M2P (Sartorius, Göttingen, Germany) and transferred to pyrolytically-coated graphite cups from Perkin-Elmer (Norwalk, CT, USA). The operating parameters of the ICP-MS instrument are listed in Table 9. Argon with a purity of 99.996% (White Martins São Paulo, Brazil) was used as plasma and carrier gas and as the protective and purge gas of the ETV.

Table 9. Operating parameters adopted for the determination of Br, Cl and I in airborne inhalable particulate matter using SS-ETV-ICP-MS.

Sampling/ skimmer cones	Pt	
RF power	1300 W	
Signal measurement	*Peak Hopping*	
Autolens	On	
Detector voltage	Pulse 1500 V	Analog: - 2500 V
Dwell time	12 ms	
Readings/ Replicate	500	
Gas flow-rate:		
	Plasma	15.0 L min^{-1}
	Auxiliary	1.2 L min^{-1}
	Carrier	0.7 L min^{-1}
Monitored isotopes:	^{35}Cl, ^{79}Br and ^{127}I	

4.2.2. Reagents, Standards and Samples

All reagents used were at least analytical grade. Deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) at a resistivity of 18.2 MΩ cm. Individual stock standard solutions containing each 1000 mg L^{-1} Ca ($Ca(NO_3)_2$), Cl (KCl), Br (KBr) and I (KI) were obtained from Quimilab (São Paulo, SP, Brazil), Pd (Pd(NO3)2) from Sigma-Aldrich (Missouri, USA) and F (NaF) from Spex (New Jersey, NJ, USA).

Two CRMs, NIST 1648 and NIST 1648a Urban Particulate Matter, from NIST (Gaithersburg, USA), were used.

4.2.3. Sampling of Airborne Inhalable Particulate Matter

The PM_{10} samples were collected following the directives of the Brazilian Technical Standards Association (NBR 9547). The collection was carried out using a high volume sampler which was installed in Aracaju, Sergipe, Brazil in a territory administrated by Sergipe's Environment and Water Resources Department (*Secretaria de Estado do Meio Ambiente e dos Recursos Hídricos*, Aracaju, SE, Brasil). The sampling location is adjacent to residential and industrial areas, next to a region with a relatively intense traffic of motorized vehicles.

Sample collection was carried out using glass fiber filters for PM_{10}. Prior to use, the glass fiber filters (Energética, Rio de Janeiro, RJ, Brazil) were maintained on a desiccator for 24 h. Collection of PM_{10} samples was carried out using an air flow of 1677 m^3 for 24 hours. At the end of the sampling procedure, the samples were placed into a desiccator for 24 h before weighing. Sample collection was carried out during dry and rainy seasons in the period ranging from February 06, 2013 to June 09, 2013.

4.2.4. Analytical procedure

The samples were grinded prior analysis. Fluorine determination by SS-HR-CS GF MAS was carried out by monitoring the CaF molecular absorption band at 606.432 nm, which provided adequate sensitivity for the purpose of this work. The absorption spectrum of the CaF molecule is shown in Figure 16 for the real PM_{10} sample from 02/April/2013.

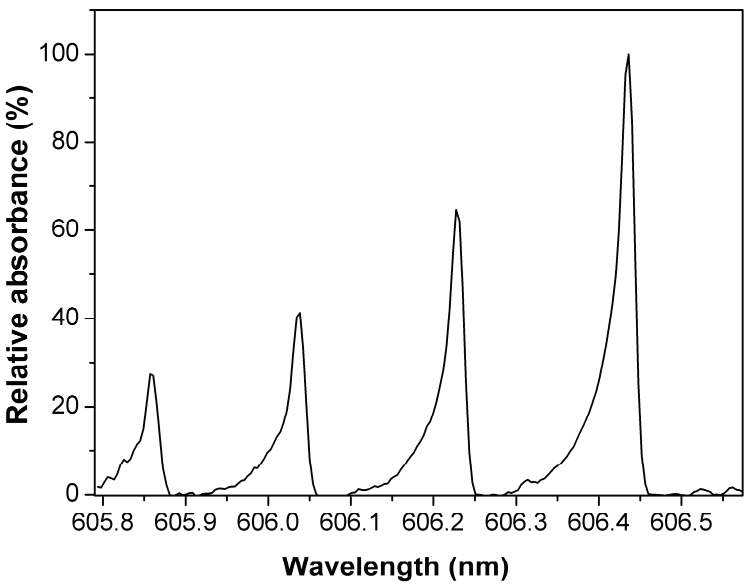

Figure 16. Wavelength resolved absorption spectrum of the CaF diatomic molecule obtained from a PM_{10} sample in the 606.15 ± 0.45 nm spectral region. Absorbance is normalized to the highest absorbance observed in this spectral window.

Pyrolysis and atomization temperatures were optimized using one of the PM_{10} samples and the mass of molecule-forming agent (Ca) was optimized using one of the PM_{10} samples and a standard solution containing F. The PM_{10} samples (or standard solution) were directly weighed (≈ 0.2 - 1 mg) onto the SS platform, previously treated with a total of 400 μg thermally deposited Pd to act as a permanent chemical modifier [108]. Subsequently, 10 μL of the molecule-forming Ca solution at 1.0 g L^{-1} were placed with a micropipette on top of the PM_{10} samples on the SS platform and introduced into the GF, followed by application of the temperature program of the instrument.

Chlorine, Br and I determination were carried out using SS-ETV ICP-MS. Pyrolysis and vaporization temperatures of the ETV, the carrier gas flow rate and RF power of the ICP-MS instrument were optimized. The modifiers studied were Pd and the mixture of Pd + Ca. In these cases, 200 μg Pd was deposited onto the internal surface of the sampling cups (10 injections of 20 μL of a 1.0 g L^{-1} Pd solution), whereas Ca was pre-dried using 20 μL of a 1.0 g L^{-1} Ca solution [9, 105]. The temperature programs of the GF and ETV are presented in Table 10.

The PM_{10} sample from 02/April/2013, collected in the city of Aracaju, was used during all optimization steps, whereas NIST 1648 CRM was used for calibration.

Meteorological data were obtained from the Brazilian Weather Database for Teaching and Research (*Banco de Dados Meterológicos para Ensino e Pesquisa*) [109]. Statistical analysis was performed using STATISTICA v.6.0 (StatSoft Inc., Tulsa, OK, USA). All measurements were carried out at least in triplicate.

Table 10. Temperature program used for halogen determination by SS-HR-CS GF MAS and SS-ETV-ICP-MS.

Steps	F by SS-HR-CS GF MAS	Cl, Br and I by SS-ETV ICP-MS
*Modifier	-	At 20^{o}C (Ca solution)
*Drying	-	100^{o}C (for 10s)
*Solvent/acid removal	-	1000^{o}C (for 10s)
Sample's insertion	At 20^{o}C (Sample + Ca solution)	At 20^{o}C
Drying	110^{o}C (for 10s)	100^{o}C (for 10s)
Pyrolysis	1100^{o}C (for 10s)	500^{o}C (for 10s)
Vaporization	2200^{o}C (8s)	2100^{o}C (for 18s)
Cleaning	2400^{o}C (for 10s)	2200^{o}C (for 10s)

* Steps adopted only to evaluate the effectiveness of pre-dried Ca.

4.3. **Results and discussion**

4.3.1. Optimization of ICP-MS Operating Parameters

In addition to the GF temperature program, the RF power and nebulizer gas flow rate may exert significant influence on sensitivity and signal stability for ETV-ICP-MS analysis.

RF power and carrier gas flow rate of the ICP-MS were optimized and the results showed that the highest sensitivity was achieved upon adoption of an RF power of 1300 W for Cl, 1100 W for Br and 1000 W for I. These differences are likely to be related to the high ionization potential of the elements, which increase in the order Cl > Br > I. Since the most critical element regarding sensitivity is Cl due to its high ionization potential (12.97 eV), the selected RF power was 1300 W.

Similarly, the carrier gas flow rate represents a critical factor for halogen determination by ICP-MS, and aspects such as signal profile and sensitivity are affected by this parameter [28].

The results demonstrated that although the adoption of carrier gas flow rates between 0.5 L min^{-1} and 0.6 L min^{-1} resulted in higher sensitivity, especially for Cl, the RSD were remarkably higher under these conditions, which may be partially attributed to the reduced transfer rate of the analyte containing-vapor through the transfer hose, resulting in condensation losses especially for Cl.

On the other hand, the adoption of carrier gas flow rates higher than 0.7 L min^{-1} resulted in reduced sensitivity, which is believed to be due to the reduced residence time of the analytes in the ICP. Considering these aspects, the carrier gas flow rate was set at 0.7 L min^{-1}.

4.3.2. Fluorine measurements using HR-CS-GF MAS

The molecule forming agent (Ca) must be added favorably in order to promote the formation of CaF, ideally without any measurable residue of F on the platform at the end of each analytical cycle. The required mass of Ca to be added to F-containing samples was evaluated using 100 ng of F in the form of an aqueous standard. Calcium was added as an aqueous solution, prepared from $Ca(NO_3)_2$.

The effect of increasing Ca mass on the measurable signal obtained from the formation of CaF is shown in Figure 17. From this figure, it is clear that at least 6 μg of Ca are required to achieve maximum sensitivity for CaF produced from an aqueous fluorine solution.

The situation is less critical for the solid PM_{10}, since the natural concentration of Ca in these samples was typically sufficient to produce high populations of the CaF molecule even without addition of Ca as an aqueous solution. Nonetheless, in order to assure sufficient excess of Ca in all cases, 10 μg Ca (10 μL of a Ca solution at 1.0 g L^{-1}) was added to all samples to assure uniform molecule formation regardless of the native Ca content of the samples.

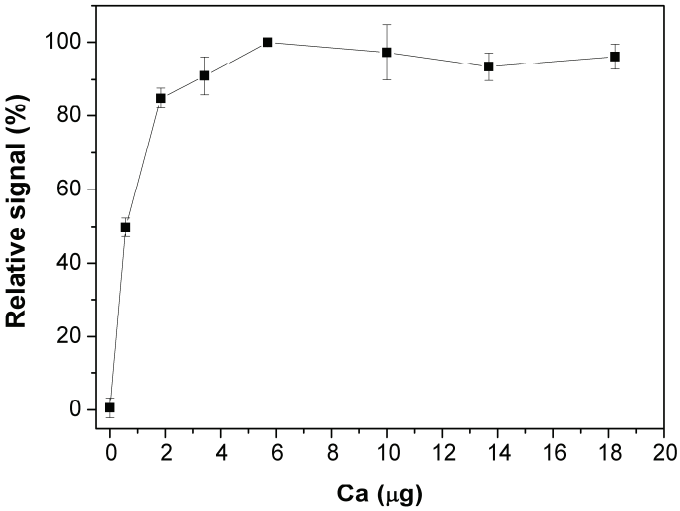

Figure 17. Effect of Ca mass on the signal obtained for the CaF molecule by SS-HR-CS GF MAS at 606.4322 nm using 100 ng of F as aqueous solution. Pyrolysis and vaporization temperatures were set at 1100 °C and 2200 ^{o}C, respectively. Signal was normalized dividing the measurements value by the highest measurement value obtained.

4.3.3. Temperature program optimization

The temperature program should be optimized in order to promote efficient vaporization of the analyte during the vaporization step, and ideally most of the matrix should be removed without analyte loss during the pyrolysis step.

The pyrolysis (Tp) and vaporization temperatures (Tv) for F (as CaF) using SS-HR-CS GF MAS (Figure 18a) and for Cl, Br and I using SS-ETV-ICP-MS (Figures 18b-18d) were optimized using a ‘real’ PM_{10} sample (Sample 02/April/2013).

For F, it is shown in Figure 18a that a Tp of 1200 ^{o}C could be used without analyte loss, which is significantly higher than the previously reported values for the CaF molecule [107]. This additional stability may be attributed to the use of thermally deposited Pd onto the platform surface as a permanent modifier. A pyrolysis temperature of 1100 ^{o}C was chosen for subsequent studies in order not to reduce the lifetime of the graphite tube and SS platform.

The vaporization temperature curve, which is also shown in Figure 18a, demonstrates that diffusional losses and/or molecule dissociation occur to a significant extent at temperatures higher than 2200 °C, which was then selected for subsequent experiments.

Pyrolysis and vaporization temperature curves obtained using SS-ETV-ICP-MS for Cl, Br and I were also evaluated and are shown in Figures 18b-18d. Chemical modifiers, which may also act as aerosol carriers, were evaluated.

The use of chemical modifiers in the form of acidic solutions was proven to promote analyte losses during the pyrolysis step, which is likely due to the formation of volatile hydrogen halides. Hence, as a means to remove the acid from the solution, the chemical modifier solutions were pipetted into the graphite tube and submitted to a drying step prior to insertion of the samples.

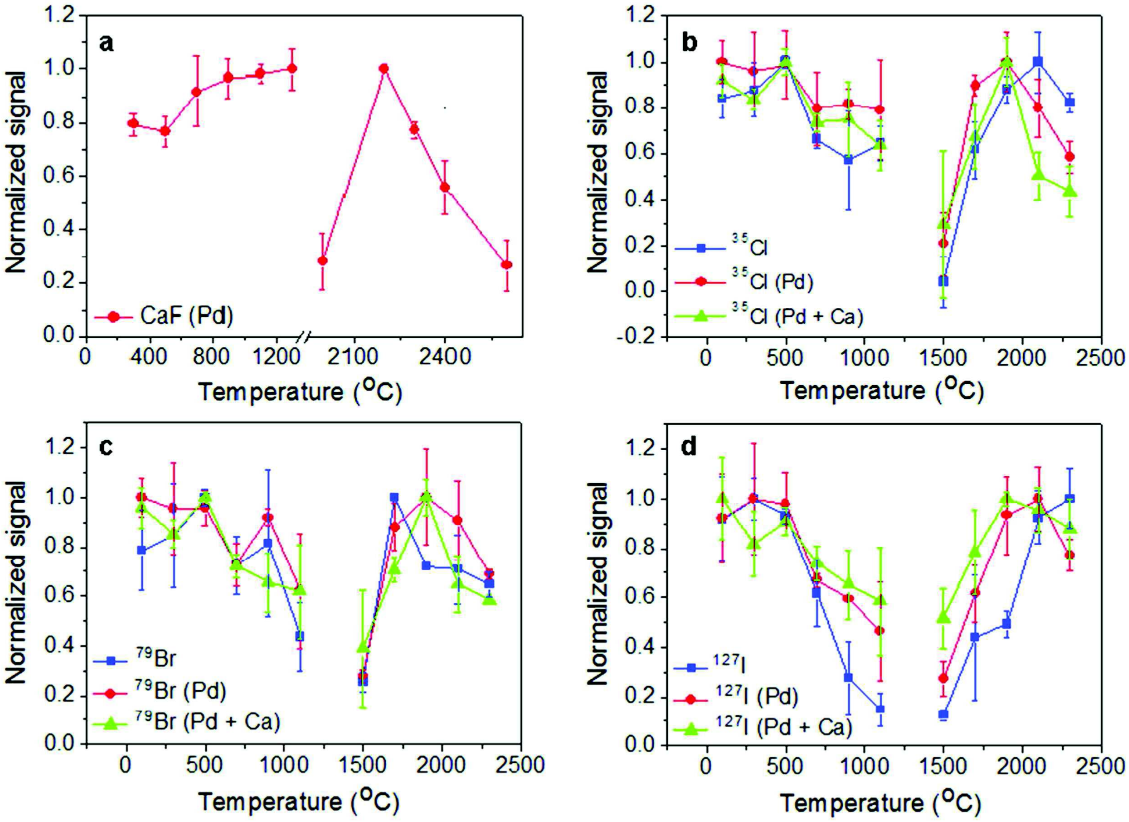

Figure 18. Pyrolysis and vaporization curves obtained for (A) CaF using SS-HR-CS GF MAS and (B) Cl, (C) Br, and (D) I using SS-ETV-ICP-MS. Operating conditions adopted for SS-ETV-ICP-MS measurements: 1300 W RF power; 0.7 L min^{-1} carrier gas flow rate. Normalized signals refer to the ratio between each individual signal and the highest signal in the series. All data were obtained using the 02/April/2013 PM_{10} sample. Palladium was used as permanent chemical modifier for both techniques and Ca in solution form was used as molecule-forming agent for SS-HR-CS GF MAS and modifier/aerosol carrier for SS-ETV-ICP-MS.

Under these conditions, thermal stability was achieved for all elements up to a pyrolysis temperature of 500 °C, and even in the absence of chemical modifiers a similar thermal stability was observed – an effect that may be related to the presence of Ca in the samples, which may itself act as stabilizing agent. Adoption of a Tp of 500 °C allowed the analysis to be carried out without deposition of solid residues on the sampling cone, which suggests efficient matrix elimination.

Optimum vaporization temperatures ranged from 1600 °C for Br to 2300 °C for I, both without the use of chemical modifiers. As a compromise condition, the Tv was maintained at 2100 °C. Despite the apparent usefulness of a modifier-free determination, the concomitant addition of Pd + Ca was considered necessary in order to decrease the interaction of the analytes with the graphite surface [108], and also as a means to reduce the potential influence of Ca concentration on the sensitivity achieved for the analytes vaporized from different samples.

4.3.4. Quantification and analytical figures of merit

One of the challenges of direct solid sample analysis concerns the calibration procedure, since identical analyte behavior in calibration standards and in the solid matrix are, on occasions, hardly achieved. Strategies that include the adoption of specific operating conditions of the instrument and the use of chemical modifiers or aerosol carriers are frequently useful in equalizing the behavior of the analyte in standards and samples [82].

In order to assure maximum similarity between the samples and the calibration standards, the calibration curves were obtained using the NIST 1648 CRM for the determination of Br, Cl and I by SS-ETV ICP-MS. Since there are no APM reference materials with a certified concentration for F, this element was determined by standard addition using SS-HR-CS GF MAS.

In order to check the accuracy of the measurements, the certified reference sample NIST 1648a was analyzed for Br, Cl and I. In addition, three ‘real’ PM_{10} samples were also analyzed using standard addition calibration, in order to further asses the accuracy of the procedure. The results are shown in Table 11.

Due to the high amount of S (5%), K (~1%) and P (~1%) in the certified reference sample NIST 1648, spectral interferences, which are related to the formation of $^{34}S^{1}H^{+}$, which overlaps with $^{35}Cl^{+}$, and $^{40}Ar^{39}K^{+}$ and $^{31}P^{16}O_3^{+}$, which overlap with $^{79}Br^{+}$, could occur. However, as can be seen from the results in Table 11, these interferences do not present a problem with this analytical method.

In the previous studies, it was shown that these interferences are rarely a concern, since the above-mentioned polyatomic ions are not formed quantitatively or are not detected upon vaporization S, K and P using ETV-ICP-MS. Since the determined values were in good statistical agreement (95% confidence level) with the certified values for the analytes in NIST 1648, it is assumed that the procedure is free of interferences.

Since no CRM for F was available, the determination of the referred element was carried out by standard addition in order to check for the presence of matrix effects. Although standard addition calibration using solid samples and aqueous standards may sound as a somewhat odd approach, the results were useful to demonstrate that the added analyte behaves very similarly to the 'native' analyte present in the solid samples, which validates the approach.

The precision was determined as the RSD of three replicate measurements of NIST 1648a CRM. The RSD values ranged between 0.8% (F) and 12.9% (Cl).

The limits of detection were calculated as the ratio between three times the standard deviation of ten blank measurements and the slope of the calibration curves, adjusted to the typical sample masses that were inserted in the graphite tube. The calculated values were 0.3 $\mu g\ g^{-1}$ (0.4 $ng\ m^3$) for F by SS-HR-CS GF MAS, and 0.02 $mg\ g^{-1}$ (30 $ng\ m^3$) for Cl, 0.1 $\mu g\ g^{-1}$ (0.1 $ng\ m^3$) for Br and 2 $ng\ g^{-1}$ (0.003 $ng\ m^3$) for I by SS-ETV-ICP-MS, which are suitable for the analysis of PM_{10} samples.

Table 11. Results obtained for F (determined by SS-HR-CS GF MAS), Cl, Br and I (determined by SS-ETV-ICP-MS) in airborne inhalable particulate matter (mean ± confidence interval; n = 3, RSDs calculated based on the standard deviations) using different calibration strategies.

Sample		F / mg g^{1}	RSD/%	Cl / mg g^{1}	RSD/%	Br / µg g^{1}	RSD/%	I / µg g^{1}	RSD/%
NIST 1648a	Certified value	-		4.543 ± 0.047		502 ± 10		-	
	Obtained value	-		4.73 ± 0.63	5.35	496 ± 8	0.65	19.398 ± 3.479	7.21
06/Feb/13	Standard addition	1.41 ± 0.03	0.76	0. 71 ± 0.01	0.56	2.4 ± 0.4	6.70	1.899 ± 0.052	1.10
	CRM calibration*	-		0.69 ± 0.22	12.82	2.1 ± 0.6	11.49	1.672 ± 0.263	6.32
06/Mar/13	Standard addition	0.74 ± 0.02	1.36	5.56 ± 0.93	6.66	7.6 ± 1.2	6.35	1.902 ± 0.483	10.21
	CRM calibration*	-		5.61 ± 0.48	3.44	7.3 ± 1.5	8.26	2.036 ± 0.055	1.09
10/Apr/13	Standard addition	0.74 ± 0.07	3.64	1.92 ± 0.35	7.33	6.4 ± 1.0	6.28	1.816 ± 0.065	1.44
	CRM calibration*	-		2.33 ± 0.26	4.49	5.8 ± 0.7	4.85	1.901 ± 0.174	3.68

4.3.5. Analysis of PM_{10} samples

The halogen content of 14 PM_{10} samples collected during different periods in the city of Aracaju was assessed using the newly developed methods. Each filter was loaded with PM_{10} masses ranging from 29 mg to 59.3 mg, which corresponds with 17 µg to 36 µg PM_{10} per cubic meter of air. The results are shown in Table 12.

As can be seen, the concentration values ranged from 793.4 to 2642.7 ng m^{-3} for F, 647 to 7573 ng m^{-3} for Cl, 1.4 to 17.6 ng m^{-3} for Br and from 1.167 to 4.285 ng m^{-3} for I. The most significant variation in concentration levels was detected for Cl, which may be related to the fact that the samples originate from a coastal region. As expected, Br was the least abundant element in the analyzed samples.

Precision, reported as RSD, ranged between 0.8 and 9.2% for F, 0.6 and 12.9% for Cl, 0.6 and 12.4% for Br and 0.02 and 9.2% for I, referring to triplicate measurements of the PM_{10} samples. These values reflect an adequate sample homogeneity, which was aided by the grinding process of the glass fiber filters containing PM_{10}.

Table 12. Concentration of airborne inhalable particulate matter (PM_{10}) in air and results obtained for F (determined by SS-HR-CS GF MAS), Cl, Br and I (determined by SS-ETV-ICP-MS (mean ± confidence interval; n = 3, RSDs calculated based on the standard deviations) in PM_{10} samples collected in the coastal city of Aracaju, SE, Brazil.

Date of collection	PM_{10} in air / µg m^{-3}	F / ng m^{-3}	%RSD	Cl / ng m^{-3}	%RSD	Br / ng m^{-3}	%RSD	I / ng m^{-3}	%RSD
06/Feb/2013	36.22	2643 ± 50	0.77	1294 ± 415	12.89	3.9 ± 1.2	12.37	3.1 ± 0.5	6.34
15/Feb/2013	21.25	1859 ± 134	2.91	647 ± 114	7.08	1.4 ± 0.3	8.62	1.4 ± 0.1	1.47
06/Mar/2013	36.22	993 ± 34	1.36	7573 ± 647	3.43	9.8 ± 2.0	8.21	2.7 ± 0.1	1.07
26/Mar/2013	27.76	1403 ± 322	9.24	2097 ± 240	4.60	4.1 ± 0.4	3.92	2.2 ± 0.3	5.80
02/Apr/2013	29.33	1612 ± 191	4.78	4203 ± 446	4.27	6.8 ± 0.9	5.32	1.2 ± 0.1	3.96
10/Apr/2013	25.87	1014 ± 92	3.66	3211 ± 361	4.52	8.0 ± 1.0	5.03	2.6 ± 0.2	3.65
16/Apr/2013	28.10	1291 ± 145	4.50	4661 ± 299	2.58	7.5 ± 0.9	4.82	1.2 ± 0.2	9.20
23/Apr/2013	17.30	1244 ± 66	2.15	3804 ± 375	3.96	11.3 ± 1.9	6.76	1.9 ± 0.1	1.24
30/Apr/2013	21.48	868 ± 82	3.80	5080 ± 562	4.45	8.2 ± 1.1	5.39	1.5 ± 0.2	5.07
07/May/2013	25.76	905 ± 97	4.31	4718 ± 264	2.25	9.3 ± 0.8	3.46	2.9 ± 0.2	2.85
14/May/2013	36.26	793 ± 62	3.15	7068 ± 108	0.61	11.6 ± 0.5	1.73	3.7 ± 0.2	2.06
21/May/2013	24.85	1455 ± 71	1.97	5331 ± 516	3.89	11.4 ± 0.6	2.12	4.3 ± 0.3	3.27
28/May/2013	35.30	1137 ± 77	2.73	6637 ± 365	2.21	17.6 ± 0.7	1.60	3.6 ± 0.1	0.11
09/Jun/2013	29.04	1113 ± 98	3.55	9666 ± 760	3.16	13.3 ± 0.2	0.60	3.8 ± 0.1	0.02

Overall, the increase trend in F concentration levels were found to be opposite to that of the other halogens, whereas variations in Br, Cl and I concentrations showed a similar trend. The similarity regarding variations in the concentrations of Cl, Br and I was already described [110] and it has been suggested that this behavior is related to the fact that these elements originate mainly from the sea, even though a fraction of the Br and I content has also been shown to derive from soil emissions, microbial activity and biomass combustion [111].

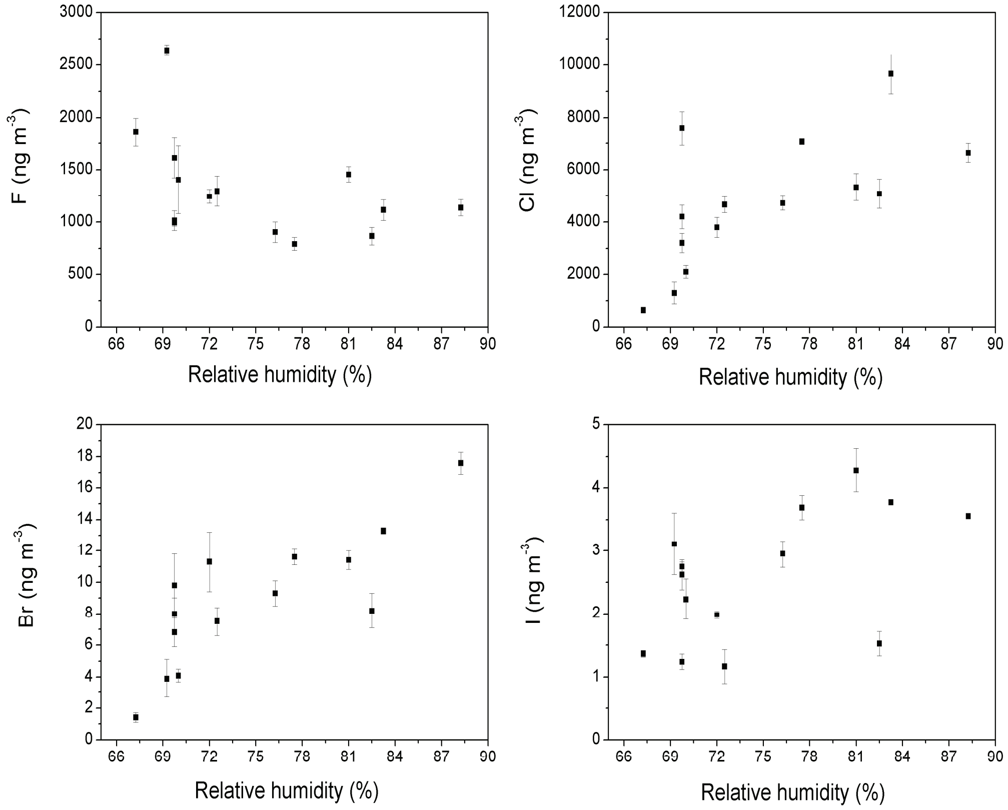

Figure 19. Effect of relative air humidity on the determined concentrations of F (obtained by SS-HR-CS GF MAS), Br, Cl and I (obtained by SS-ETV-ICP-MS) in airborne inhalable particulate matter (PM_{10}) samples. The PM_{10} samples were collected in the coastal city of Aracaju, Sergipe, Brazil, between February and June, 2013.

The concentrations of Cl, Br and I were directly related to the relative air humidity at the time of collection, in the sense that these elements were more abundant in PM_{10} samples collected at higher humidity conditions. The opposite behavior was observed for F, which was determined to be at higher concentrations in samples collected during reduced air humidity conditions (Figure 19). These results suggest that, in fact, the atmospheric Cl, Br and I content originate from sources that differ from those responsible for the presence of F.

The Br/I concentration ratios varied from 1.0 to 6.4, with an average value of 3.7 ± 1.6. These values are comparable to those observed in Hawaii (approximately 3.5) and in the western pacific ocean (approximately 6.4), which is yet another evidence to the fact that these elements originate from marine sources [112].

Fluorine concentrations were also related to the sunlight incidence (Figure 20). Since the main source of F emission is not fully clear, it can be assumed that vaporization of F-containing compounds from urban dust is more efficient at higher irradiation periods, hence increasing the absolute F concentration in PM_{10} samples collected after longer sunlight exposure.

It should be emphasized that the PM_{10} collection site is surrounded by roads with a relatively intense circulation of motorized vehicles, a few industries and a large residential area, which are regarded as potential emission sources of inhalable particles to the atmosphere. Another important factor to be considered is the high reactivity of F with fiberglass, therefore it's concentrations may also to F in vapor form not only to MP_{10}.

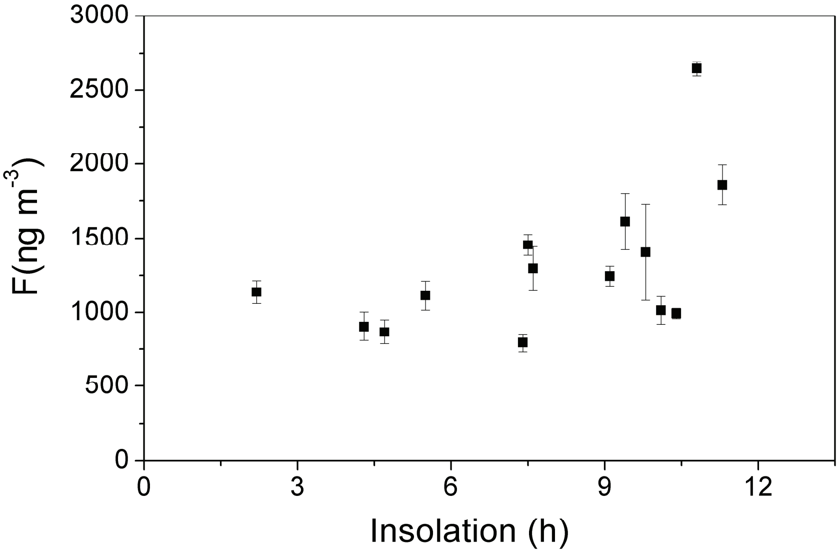

Figure 20. Effect of sunlight irradiation (insolation) on the determined concentration of F obtained by SS-HR-CS GF MAS in airborne inhalable particulate matter (PM_{10}) samples collected in the coastal city of Aracaju, Sergipe, Brazil.

Principal component (PC) analysis of the data related to the halogen concentrations in the PM_{10} samples was carried out in order to investigate statistically the correlation between the halogen content and the weather conditions at the time of sample collection. The score plot of PC1 *versus* PC2 considering the concentrations of F, Cl, Br and I (Figure 21) resulted in the identification of two distinct groups of samples, which are related to the accumulated rainfall during the collection period.

The accumulated rainfall during the months of March and April reached values of 7.8 mm and 10.8 mm, respectively, whereas in May and June these values were raised to 195.8 mm and 115.4 mm, respectively.

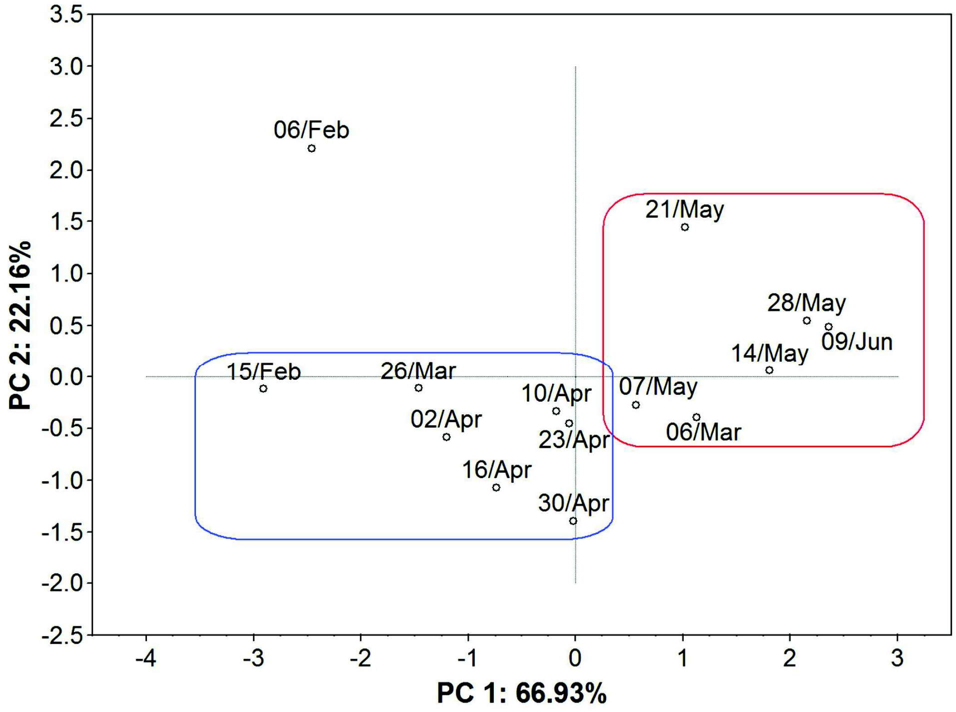

Figure 21. Score plot of PC1 *versus* PC2 considering for halogens in PM_{10} samples. Square on the right side (red) represents samples from rainy periods while the square on the left side (blue) represents the samples from periods without rain.

The sample collected in March 06, 2013 was grouped together with the samples collected during the rainy months, which results from an abnormally high rainfall that occurred the day before the collection. Despite the sample collected in February 06, 2013 has been collected during the dry season it is not grouped together in this group, one possible explanation is based on the relative humidity of the previous days, February 04 and 05 of 2013 (76% and 72 %, respectively), which were higher than the dry days (69% in average) and lower than the rainy days (79% in average) resulting in a different trend for this sample.

In PC1 axis, the right side group shows that the concentrations of Cl, Br and I are predominant parameters. In the left side group, F concentration is the predominant parameters. The concentrations of Cl, Br and I have been directly related to higher humidity conditions, whereas an opposite behavior was observed for F.

4.4. Conclusions

Direct solid sample analysis using HR-CS-GF MAS for F determination and ETV-ICP-MS for Cl, Br and I determination in PM_{10} samples have proven to be efficient and fast approaches and interesting alternatives to avoid the problems related to halogen determination and sample preparation. Monitoring of an analytical line in the visible region for F determination *via* absorption of the CaF molecule provided accurate results with high sensitivity.

The simultaneous determination of Cl, Br and I using SS-ETV-ICP-MS was demonstrated for the first time and it was proven feasible, accurate and sensitive for halogen determination in airborne inhalable particulate matter. Application of both methods to a set of PM_{10} samples collected in a Northeastern coastal city in Brazil revealed that the presence of halogens correlates well to weather conditions, particularly to accumulated rainfall and relative air humidity. Higher relative air humidity resulted in higher concentrations of Cl, Br and I, which are usually originated from marine sources, whereas the F is more abundantly present in periods with higher sunlight incidence.

Chapter 5 - Direct solid sample analysis for Br quantification in polymers by LA-ICP-MS

5.1. Introduction

Plastic materials are widely used in our daily life, requiring different properties for different applications, such as treatment with flame retardants. One technique to achieve flame retardance in polymers is based on scavenging of radicals formed during combustion, which is normally achieved by adding halogenated compounds to the polymer as an additive [113 - 116].

Brominated compounds are preferred over other halogens, which is due to the fact that F presents high electronegativity, generating thermally stable compounds, Cl compounds are not easily degraded in nature and I is large enough to be easily dissociated from the compound it is bounded to. On the other hand, Br compounds are more biodegradable in nature than Cl compounds. Bromine also dissociates readily from organic molecules at high temperatures, forming a radical that acts as scavenger [117].

Although there are advantages associated to the use of Br compounds as flame retardants, its presence in the environment is considered hazardous and its inhalation may produce irritation and tissue damage, in addition to other environmental effects such as the depletion of the ozone layer [23, 116-118].

In this sense, monitoring of Br concentration in products that may release the element to the atmosphere is considered important and the use of ICP-MS is an attractive technique for this task due to the high sensitivity and wide linear calibration range [5]. However, a conventional analysis by ICP-MS normally requires sample pretreatment, which is time consuming, requires additional equipments and promotes dilution of the sample, which leads to increased limit of detection (LOD) and the possibility of contamination.

Halogen determination in polymers requires even more complex sample preparation setups, since extreme conditions of temperature and pressure are required for the destruction of the sample matrix without promoting analyte loss or contamination [114].

In this sense, direct analysis brings the advantages of decreasing the possibility of analyte loss and contamination.

Direct solid sample analysis (SS) by means of laser ablation (LA) or ETV, has shown to be an efficient strategy for Br determination by ICP-MS in different matrices. However, some drawbacks are still present, such as difficulties associated to calibration and low precision of the results due to non-homogenous distribution of the analyte in the samples. Nonetheless, ID calibration has been successfully applied for Br quantification by LA-ICP-MS, whereas external calibration using aqueous and solid standards may be successfully used in SS-ETV-ICP-MS for different matrices [69, 40, 64].

Thus, the aim of this chapter is to evaluate the capability of direct solid sampling analysis by LA-ICP-MS for Br analysis in polymeric samples, exploring simple and straightforward techniques for calibration.

5.2. Experimental

5.2.1. Instrumentation

The LA-ICP-MS experiments were carried out using a GeoLas ArF excimer-based LA system (MicroLas, Germany), coupled to an Element XR single-collector sector field instrument (Thermo Scientific, Germany).

Table 13. Operating parameters adopted for the determination of Br in polymeric samples by LA-ICP-MS using an Element XR ICP-MS and a GeoLas ArF excimer-based LA system.

ICP-MS		
Sampling/ skimmer cones	Ni	
RF power	950 W	
Resolution	Low	
Scan type	E-scan	
Detection mode	Triple	
Gas flow-rate (Ar):		
	Plasma	15.0 L min^{-1}
	Auxiliary	0.8 L min^{-1}
	Carrier gas (after cell)	0.7 L min^{-1}
Monitored isotopes:	^{79}Br and ^{12}C	
Laser Ablation		
Frequency	15 Hz	
Carrier gas (into the cell)	0.6 L min^{-1}	
Spot size	120 μm	

The LA system used is equipped with a 193 nm UV laser beam coming from the Compex102 laser unit (LambdaPhysik, Germany) that undergoes homogenization, enabling flat-bottomed and straight-walled craters to be obtained. The ablation cell was coupled to the ICP-MS torch via a 3-mm-internal-diameter Tygon tubing using Ar-He as the carrier [119]. Helium was driven through the ablation cell to carry the analytes and Ar was added to the gas stream leaving the cell using Teflon connection. The operating parameters of the LA-ICP-MS system are presented in Table 13.

5.2.2. Samples, reagents and standards

All reagents used were at least analytical grade. Deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) at a resistivity of 18.2 MΩ cm. Six CRMs and five 'real' samples obtained from the local markets of the city of Ghent in Belgium were used. The reference materials used were the polyethylene CRMs ERM-EC680, ERM-EC681 and polybrominated diphenyl ether (PBDE) ERM-EC591 obtained from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium). The polyethylene CRMs PE, PE-H-11A and PEL-11A were supplied by Modern Analytical Techniques LLC (Hillsborough, USA). Acrylonitrile butadiene styrene resin CRM BAM was obtained from the Federal Institute for Materials Research and Testing (Berlin, Germany).

5.2.3. Analytical procedure

The samples were placed onto a plastic platform and inserted into the ablation cell. The surfaces of the samples were cleaned prior to the analysis by pre-ablation of the top layer using the optimized conditions and without measuring the signal. Sample ablation was carried out using 300 laser pulses at a frequency of 15 Hz ranging the samples surface. Integrated signals were used.

Quantifications were carried out by external calibration using the CRMs containing different concentrations of the analyte and also by external calibration using only one CRM and monitoring ^{12}C as an internal standard.

5.3. Results and discussion

5.3.1. Optimization of the LA-ICP-MS parameters

Sensitivity is an issue for Br analysis by ICP-MS due to its high ionization energy. Therefore, in order to obtain the maximum sensitivity of the method and to enable its application for trace Br analysis, the operating parameters of carrier gas flow, RF power of the ICP-MS, spot size and pulse frequency of the laser were optimized using a 'real' polyethylene sample.

The use of He as a carrier gas promotes the formation of smaller particles during the ablation of the sample when compared to Ar, increasing the sample transport efficiency and also the process of ionization in the plasma [119,120]. Thus, the He flow rate was optimized maintaining the Ar flow constant at 0.7 L min^{-1}, as can be seen in Figure 22, the selected gas flow was 0.6 L min^{-1}, although little influence on the signal intensity was associated to this parameter. As the Ar flow is connected after the ablation cell, this parameter does not affect the ablation efficiency and vapor flush from the ablation cell thus this parameter was not optimized.

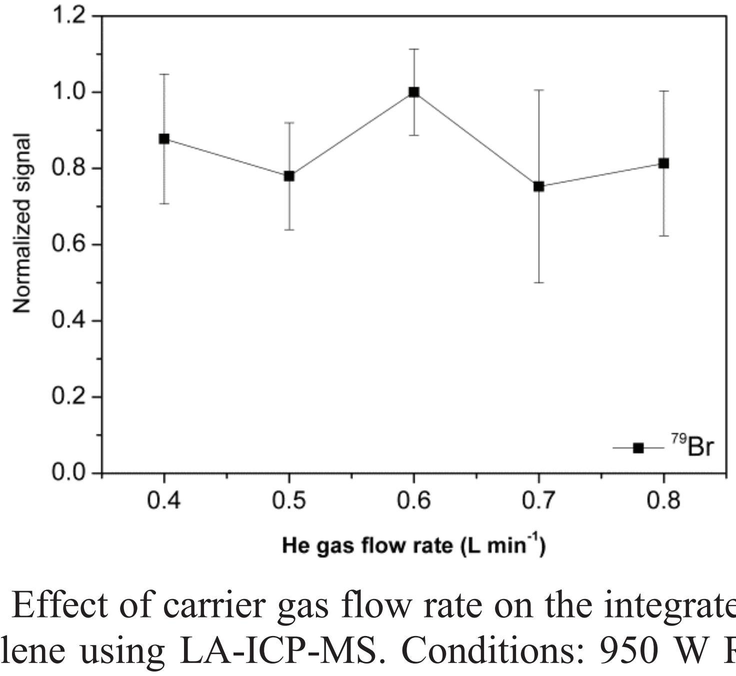

Figure 22. Effect of carrier gas flow rate on the integrated signal for Br in polyethylene using LA-ICP-MS. Conditions: 950 W RF power, spot size of 120 µm and 15 Hz laser pulse frequency. Normalized signal refer to the ratio between each individual signal and the highest signal.

The results in Figure 23 demonstrate that the spot size plays an important role in the achieved sensitivity. The maximum spot size evaluated, 120 µm, provided the highest sensitivity. This is according to expectations, since a smaller amount of sample is ablated with small spot sizes. Smaller spot sizes may also lead to inaccurate results due to variations in the signal, an effect explained by the combination of fluence, mass ablation rate and crater aspect ratio reaching high depth and affecting the ablation efficiency [120, 121].

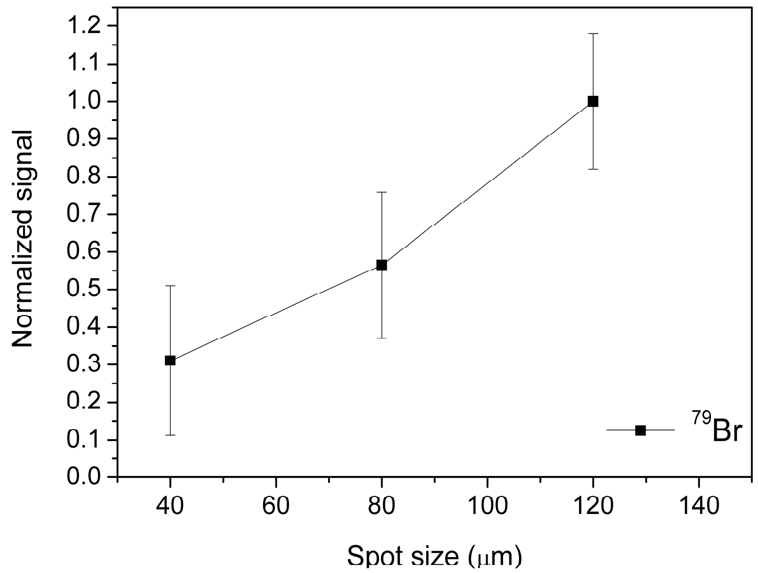

Figure 23. Effect of the spot size on the integrated signal for Br in polyethylene using LA-ICP-MS. Conditions: 950 W RF power, He carrier gas flow of 0.6 L min^{-1} and 15 Hz laser pulse frequency. Normalized signal refer to the ratio between each individual signal and the highest signal.

The repetition rate (Figure 24) and RF power (Figure 25) were optimized for maximum intensities, resulting in maximum signals at 15 Hz and 950 W, respectively. Overlap of craters may be expected when using high repetition rates and large spot sizes, which may promote the heating and melting of plastic samples, modifying the ablation efficiency. However, this effect was not observed in the present work, since the signals were proven sufficiently stable throughout the analysis interval.

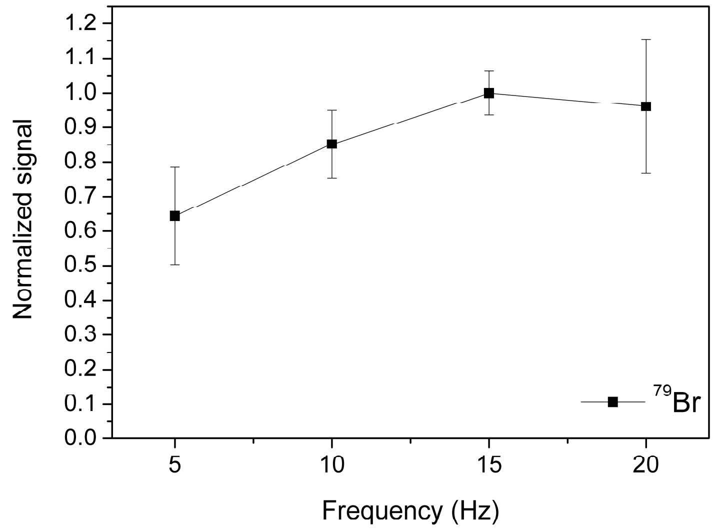

Figure 24. Effect of the frequency on the integrated signal for Br in polyethylene using LA-ICP-MS. Conditions: 950 W RF power, He carrier gas flow of 0.6 L min^{-1} and spot size of 120 µm. Normalized signal refer to the ratio between each individual signal and the highest signal.

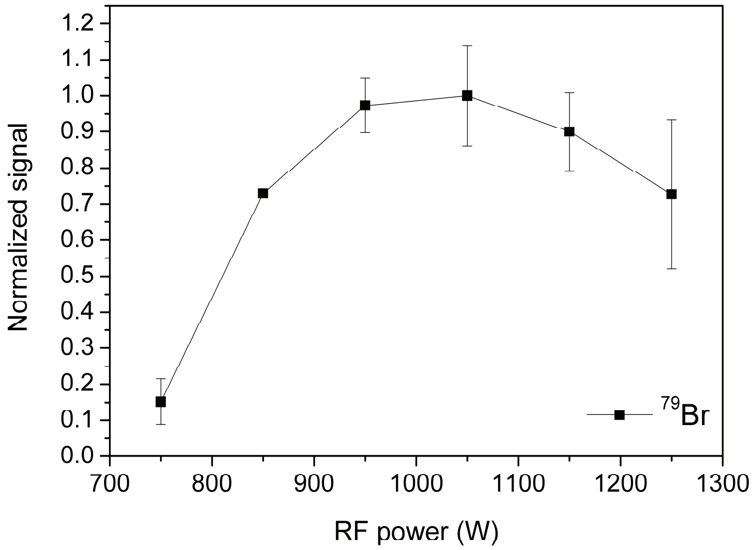

Figure 25. Effect of the RF power on the integrated signal for Br in polyethylene using LA-ICP-MS. Conditions: Laser frequency 15 Hz, He carrier gas flow 0.6 L min^{-1} and spot size 120 µm.

5.3.2. Figures of merit and application

Calibration using solid standards in ICP-MS may be very challenging, mainly in the case of LA-ICP-MS where the interaction of the laser with the sample may change depending on matrix composition. This effect frequently leads to differences in the ablation efficiency of the sample and particle formation, resulting in different sensitivities for different matrices [122].

As previously mentioned, two calibration strategies were evaluated in this work: 1 - External calibration using different CRMs as external standards and 2 - External calibration using a single CRM as external standard, in combination with internal standardization.

Figure 26 presents the calibration curve obtained using different CRMs as external standards. As can be seen, a linear correlation was obtained, despite the differences in sample composition associated to the CRMs. This suggests that the ablation efficiency is not strongly affected by the polymer composition, at least not for the different polymers studied in this work.

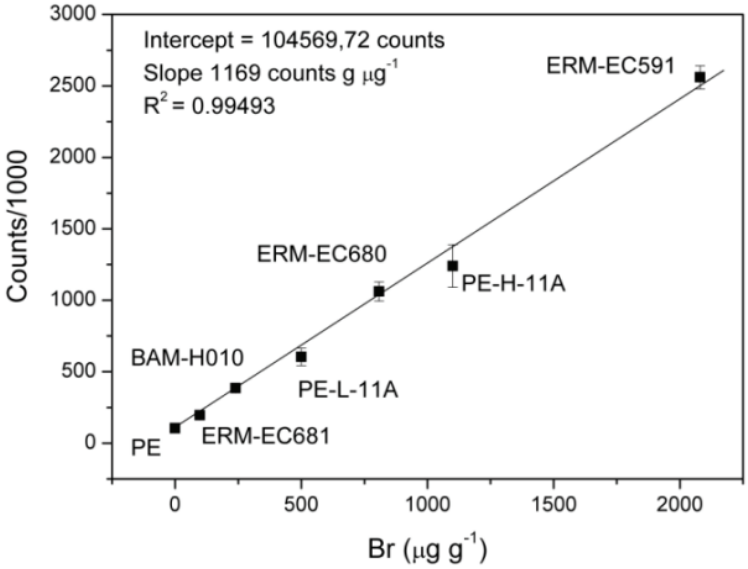

Figure 26. Bromine response in CRMs of polymers containing different concentrations of Br using a LA-ICP-MS composed by a GeoLas ArF system and an Element-XR ICP-MS. RF power of 950 W, He carrier gas flow of 0.6 L min^{-1}, Spot size of 120 µm and frequency of 15 Hz.

The use of external calibration with internal standization using a single CRM as an external standard requires the presence of one element (the internal standard) with known concentration in the samples and standards, which behaves similarly to the analyte during the ablation, transportation and ionization in the plasma [122]. In the case of polymers, it is possible to estimate the carbon concentration based on the polymer composition. This approach prevents additional steps for quantification of the internal standard, thus simplifying the method.

Table 14 presents the results obtained using the polyethylene CRM PE-H-11A as an external standard and monitoring the signal of $^{12}C^{+}$ as an internal standard. It is possible to observe that for all samples, except for one, the determined Br concentrations are in agreement with the certified value. The exception is ERC-EC591, which is a polybrominated diphenyl ether sample. Estimation of the carbon content prior to the quantification of Br is more difficult which hinders the accurate quantitation of the analyte in this sample besides ablation efficiency may be different for this sample.

Table 14. Concentration of Br, in µg g^{-1}, in different polymer CRM samples obtained by LA-ICP-MS using external calibration standard and monitoring $^{12}C^{+}$ as internal standard (mean ± SD, n=3).

Samples	Certified	Obtained
ERM-EC681	98 ± 5	<LOQ
ERM-EC680	808 ± 19	845 ± 30
PE-H11A	1100 ± 44	1127 ± 121
ERM-EC591	2080 ± 77	972 ± 23
BAM-H010	240 ± 21	231 ± 25
PE-L-11A	500 ± 20	Calibration

The LOQ, calculated as ten times the standard deviation of ten measurements of the blank divided by the slope of the calibration curve, was 100 µg g^{-1} Br. The PE sample is namely bromine-free, which allow its use as a matrix blank. However, ten measurements of gas blank did not show significant differences in signal intensity compared to the measurements of this sample; thus, the gas blank may be used as a trustworthy blank.

Bromine was quantified in five commercial samples, 3 polypropylene and 2 polyethylene, by LA-ICP-MS using external calibration using different CRMs as external standards and external calibration using the sample CRM PE-L-11A and monitoring $^{12}C^{+}$ as an internal standard. The results are presented in Table 15, where it is possible to observe that, although accurate results (assuming that the calibration against solid polymer standards is accurate) can be obtained, the precision was deteriorated when $^{12}C^+$ was used as an IS. This may be related to differences between the C and Br behavior during ablation, aerosol transportation and ionization in the plasma. The concentration of Br in the 'real' samples ranged from 117 µg g^{-1} to 225 µg g^{-1}.

Table 15. Concentration of Br, in µg g^{-1}, in different polymer samples, obtained by LA-ICP-MS using 1) external calibration using different CRMs and 2) using the sample PE-L-11A for external calibration, in combination with $^{12}C^+$ as internal standard (mean ± SD, n=3).

Samples	External calibration (7 CRMs)	External + internal calibration (PE-L-11A + $^{12}C^+$ as IS)
Polyethylene 1	225 ± 5	220 ± 24
Polyethylene 2	199 ± 8	197 ± 7
Polypropylene 3	116 ± 1	128 ± 9
Polypropylene 4	117 ± 7	164 ± 52
Polypropylene 5	188 ± 18	192 ± 22

5.4. Conclusions

The quantification of Br in polymers using techniques that require sample dissolution is a challenging task. Therefore, in this work a method has been developed whereby the solid samples can be analysed directly by means of LA-ICP-MS.

The use of external calibration using different polymer reference materials with a variation in Br concentrations between 100 and 2000 µg g^{-1}, provided accurate results, regardless of the polymer composition. The approach whereby a single polymer reference material was used for external calibration, in combination with the use of the $^{12}C^+$ signal as internal standard, demonstrated to provide accurate, but less precise results for most of the samples, with the exception of the CRM ERM-EC591, where a good estimation of the C content was difficult.

Chapter 6 - Bromine isotope ratio measurements in seawater using multi-collector inductively coupled plasma - mass spectrometry with a conventional sample introduction system

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6.1. Introduction

Bromine has two stable isotopes of similar abundance, ^{81}Br (49.31%) and ^{79}Br (50.69%). A common Br isotopic reference material is seawater, which has a fixed Br isotopic composition and is referred to as Standard Mean Ocean Bromide (SMOB). The isotopic composition of SMOB was determined by gas chromatography - mass spectrometry, although the most commonly used reference standard, NIST SRM 977 NaBr salt, was characterized by TIMS [50,51].

The atomic weight of bromine was recently re-evaluated on the basis of previously unknown natural isotope fractionation processes [123]. Bromine isotope fractionation has been reported in brines and saline groundwater, as well as in artificially produced materials [124].

The potential for bromine isotope fractionation induced by other natural processes, such as brine rejection during polar sea ice formation or autocatalytic processes such as “bromine explosions”, are yet to be investigated [125-128]. With the aim of investigating such processes, this chapter presents a simple method for the isotopic analysis of Br in seawater using MC-ICP-MS after minimal sample pre-treatment.

In contrast to the metallic elements normally analyzed for their isotopic composition using MC-ICP-MS, Br is a relatively volatile (when present as Br_2 or as Br^- in acidic medium) non-metal, with a high ionization energy [129]. Isotopic analysis of Br using MC-ICP-MS in its standard configuration (using PN for sample introduction) represents a challenge for a number of reasons.

The use of a nebulizer mounted onto a spray chamber for sample introduction in MC-ICP-MS may result in pronounced memory effects for Br, while the introduction of water and/or other solvents into the central channel of the plasma is known to increase the risk of spectral interference [54, 57, 130].

In order to avoid these problems related to Br isotopic analysis using MC-ICP-MS in its standard configuration, alternative sample introduction strategies have been proposed, including the insertion of Br as a gas into the ICP by oxidation of Br^- into the volatile Br_2 species [54], photochemical vapor generation of Br (as CH_3Br) [131] and the coupling of gas chromatography to MC-ICP-MS [55], as well as the combination of IC and aerosol desolvation (using $NaHCO_3$/Na_2CO_3 buffer in order to avoid Br-losses in the desolvator system) as an online strategy for Br MC-ICP-MS isotopic measurements in natural waters [132].

In addition to the specific problems related to Br isotopic analysis in MC-ICP-MS, the seawater matrix presents an additional challenge as a result of the high concentrations of dissolved salts. Even after dilution, the high salt content may lead to deposits on and damage to the cones, reducing the sensitivity and negatively affecting stability of the measurements [133,134].

The presence of high amounts of easily ionizable elements (such as Na, K and Ca) gives rise to non-spectral interference, while additional polyatomic ions, such as $^{40}Ar^{39}K^+$ and $^{40}Ar^{41}K^+$ overlap with the $^{79}Br^+$ and $^{81}Br^+$ analyte signals, respectively, at low mass resolution [135].

Also correction for mass discrimination is more complicated in the presence of a matrix, unless all samples and the external standard show exactly the same matrix composition Therefore, matrix removal prior to isotopic analysis using MC-ICP-MS is strongly advised to avoid further instrumental and analytical problems. In order to separate the analyte from the seawater matrix, several techniques, such as vapor generation and ion exchange chromatography [55,133,134,136], have been described in the literature. In this work, only column chromatography was considered.

The aim of this work was to develop a simple and accurate methodology for Br isotope ratio measurements in seawater using MC-ICP-MS, with minimal sample pretreatment.

6.2. Experimental

6.2.1. Instrumentation

All isotope ratio measurements were carried out using a Thermo Scientific (Germany) Neptune MC-ICP-MS instrument, with a sample introduction system consisting of a 100 µL min^{-1} PFA (Perfluoroalkoxy Alkane) nebulizer mounted onto a dual spray chamber, consisting of a cyclonic and a Scott-type sub-unit. Three combinations of cones and interface pump were evaluated: (i) a standard interface pump and standard cones, (ii) a jet interface pump and standard cones, and (iii) a jet interface pump, jet sampling cone and X-type skimmer cone.

The measurements were performed using static collection with Faraday cups connected to 10^{11} Ω amplifiers for monitoring the signal intensities for the internal standards and 10^{12} Ω amplifiers for the Br isotopes. Gain calibration and baseline correction were performed before each measurement session. The operating parameters are summarized in Table 16.

Table 16. Instrument settings, cup configurations and data acquisition parameters.

Instrumental parameters	
	RF power: 1350W
	Plasma gas flow rate: 15 L min^{-1}
	Auxiliary gas flow rate: 0.8 L min^{-1}
	Nebulizer gas flow rate: 1.03 L min^{-1}
	Focus Quad: 4.5 V
	Dispersion Quad: 0 V
	Sampling cone: Ni standard cone or Ni jet cone
	Skimmer: Ni standard skimmer or Ni X-type skimmer
Data acquisition parameters	
	Mode: Static
	Resolution: High
	Integration time: 4 s
	Blocks: 6
	Cycles/Block: 6
Cup configuration	
	No IS: C: ^{79}Br and H2: ^{81}Br
	Sr as IS: L1: ^{87}Sr; C: ^{86}Sr; H1: ^{84}Sr; H2: ^{83}Kr; H3: ^{79}Br and H4: ^{81}Br
	Se as IS: L4: ^{74}Se; L2: ^{76}Se; L1: ^{77}Se; C: ^{78}Se; H1: ^{79}Br and H3: ^{81}Br
	Ge as IS: L3: ^{72}Ge; L2: ^{73}Ge; L1: ^{74}Ge; C: ^{76}Ge; H2: ^{79}Br and H3: ^{81}Br

Quantification of Br, Cl and Na was carried out using a quadrupole-based Elan DRC*Plus* ICP-MS unit (Perkin Elmer, CT, USA). The nuclides monitored were ^{79}Br, ^{35}Cl, ^{23}Na and ^{103}Rh (as internal standard).

6.2.2. Reagents, standards and samples

All reagents used were of analytical grade or better. Ultrapure water (resistivity ≥18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France). Pro-analysis purity grade 14 mol L^{-1} HNO_3 (ProLabo, Belgium) was further purified by sub-boiling distillation in PFA equipment. *Trace*SELECT® NH_3 was obtained from Sigma-Aldrich (USA).

Polypropylene chromatographic columns (Eichrom, USA) filled with 1 mL of a cation exchange resin were used for matrix removal. Three cationic resins were evaluated: Dowex® 50WX8 (200-400 mesh) and Dowex® 50WX8 (100-200 mesh) both from Sigma-Aldrich, and Dowex® 50WX4 (200-400 mesh) from Alfa Aesar (USA). These resins differ from one another in particle size and/or degree of cross-linking.

NaBr isotopic standard reference material NIST SRM 977 and Sr isotopic standard reference material NIST SRM 987 $SrCO_3$ were supplied by NIST (MD, USA). Individual 1,000 mg L^{-1} standard solutions of Br, Cl, Ge, Na, Se and Rh were obtained from Inorganic Ventures (the Netherlands)˙ The standard solutions for Br, Cl, Na, Rh were used for quantitative measurements, while Ge and Se were used as internal standards for internal mass bias correction [123]; their isotopic composition was taken from reference [137].

*Suprapu*r NH_4Cl (Merck, Germany) was used as source of Cl for matrix matching. The seawater CRM IRMM BCR-403 was used as an in-house Br isotope ratio standard, while NIST SRM 977 was used as Br isotopic reference material.

6.2.3. Analytical procedure

In-house standards were prepared by dilution of a stock solution of NIST SRM 977 containing 200 mg L^{-1} of Br. The samples were prepared to final concentrations of Br between 1,000 µg L^{-1} and 4,000 µg L^{-1} in 5 mmol L^{-1} of NH_3.

A chlorine matrix was simulated by addition of ultrapure NH_4Cl to obtain final Cl concentrations ranging from 300 to 1000 mg L^{-1}. The concentration of the internal standard was adjusted so as to obtain a minimum signal intensity of 0.5 V for the minor of the two isotopes monitored ($^{86}Sr \cong 0.7$ V, $^{87}Sr \cong 0.5$ V for, $^{77}Se \cong 0.5$ V, $^{78}Se \cong 1.5$ V, $^{72}Ge \cong 0.5$ V and $^{74}Ge \cong 0.7$V).

A number of approaches to correct for instrumental mass discrimination were tested. Internal correction was employed using Sr, Se or Ge as an internal standard with the application of Russell's revised exponential law. External correction was applied using a sample-standard bracketing approach (SSB) [138].

For determination of the concentrations of Br and Cl using quadrupole-based ICP-MS, the calibration standards, blank solutions and samples were prepared in 5 mmol L^{-1} NH_3 with the aim of decreasing memory effects for these elements. For Na determination, all solutions were prepared in 0.07 mol L^{-1} HNO_3. All measurements were carried out using 1 µg L^{-1} Rh as internal standard.

The preparation of the chromatographic columns was preceded by cleaning the polypropylene column with ultrapure water. Subsequently, the column was filled with 1 mL of resin (previously washed with ultrapure water to remove soluble organic compounds). 2 mL of sample solution was loaded onto the column and the Br-fraction was eluted with 2 mL of ultrapure water. The 2 mL of eluent leaving the column during sample loading and the 2 mL of eluent leaving the column during Br elution were collected in the same polytetrafluoroethylene vessel.

An aliquot of NH_3 was added to obtain a final concentration of 5 mmol L^{-1} for water evaporation on a hot plate at 90 °C until a total volume of about 1 mL was reached (about 5 hours of evaporation). No loss of bromine was observed during the evaporation process, as is shown in section 6.3.3.

6.3. Results and discussion

6.3.1. Preliminary studies

The occurrence of spectral interferences is one of the main factors which hinder accurate isotope ratio measurements. In this work, pseudo-high mass resolution (resolving power = 8,000) was used to free the Br^+ signals from spectral overlap, while maintaining a flat peak shoulder, enabling the high precision required for isotopic analysis to be preserved to the largest possible extent [135].

Figure 27 shows the spectral peaks for both Br isotopes after optimization of the instrument settings with the MC-ICP-MS instrument equipped with the standard interface pump and cones (Figure 27a), and with a jet interface pump, jet sampling cone and X-type skimmer

(Figure 27b), respectively. As the signal intensity with the jet interface pump and standard cones was similar to that using the standard interface pump (and standard cones), these results have not been shown in the figure. Optimization of the RF power, nebulizer gas flow rate and torch position were carried out aiming at higher signal intensity for Br^+ and a lower one for the interfering ions. The settings of the focus quad and dispersion quad lenses were optimized daily to achieve the best plateau for $^{81}Br^+$.

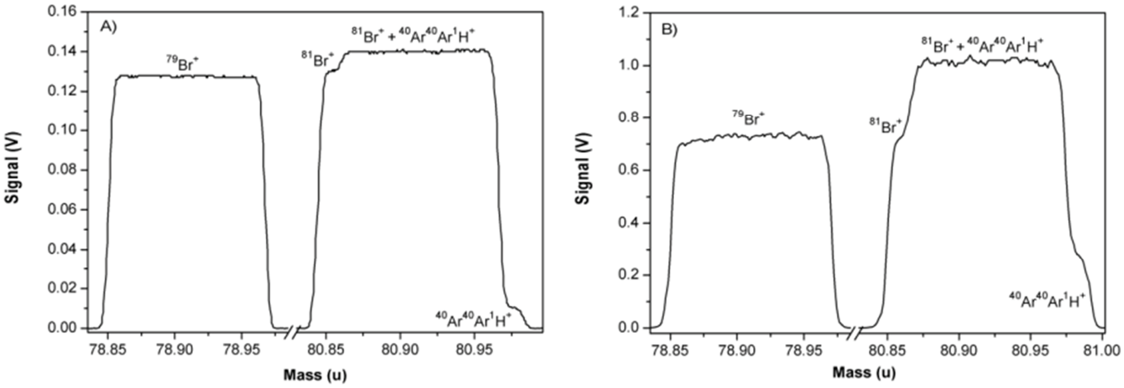

Figure 27. Spectral peaks observed at the m/z ratios of 79 and 81 for a solution containing 2,000 µg L^{-1} of Br in high resolution mode using a Thermo Neptune MC-ICP-MS instrument. (A) Standard interface pump and cones and (B) jet interface pump, jet sampler cone and X-type skimmer cone.

Despite the ca. 5-fold lower signal intensity obtained with the standard cones, a better peak shape (Br^+ plateau) was obtained than when using a jet sampling cone and X-type skimmer. Thus, all further Br isotope ratio measurements were carried out using standard cones. Due to the low sensitivity of ICP-MS for Br, especially at high mass resolution, the concentration of Br may have an important influence on the accuracy and precision attainable. Hence, the use of standard solutions containing from 1,000 µg L^{-1} to 4,000 µg L^{-1} of Br were evaluated (Figure 28).

The signal intensity for these standard solutions ranged from 0.08 V (1,000 µg L^{-1} Br) to 0.32 V (4,000 µg L^{-1} Br) with a standard interface pump and standard cones. According to counting statistics, the precision was slightly worse at 1,000 µg L^{-1} Br, whereas for concentrations ≥2,000 µg L^{-1} an acceptable precision (≤0.003 % RSD for n = 3) was obtained. In addition, after correction for instrumental mass discrimination, the experimentally determined isotope ratios measured were in agreement with the certified value.

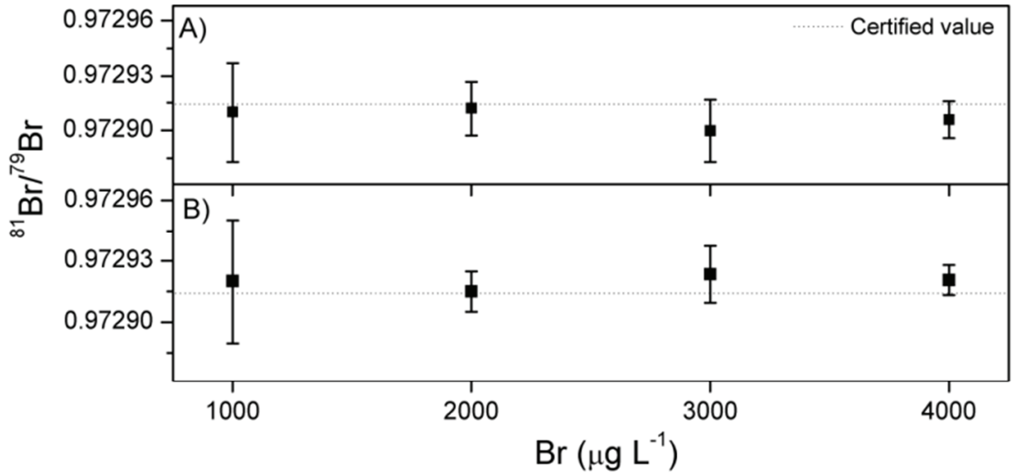

Figure 28. Br isotope ratios measured for NIST SRM 977 using a Thermo Neptune MC-ICP-MS instrument as a function of the target element concentration, mass bias corrected by external calibration. (A) Standard interface pump and standard cones and (B) jet interface pump and standard cones (n = 3, mean ± SD).

Br is one of the elements for which pronounced memory effects may appear. Several wash solutions – milli-Q water, 0.07 mol L^{-1} HNO_3 solution and 5 mmol L^{-1} NH_3 solution – were evaluated for their capability to overcome this drawback and hence, to increase the sample throughput.

The results (Figure 29) demonstrated that the longest washout time was required when using 0.07 mol L^{-1} HNO_3 solution, while also a higher background signal was observed. The best behavior was observed when using 5 mmol L^{-1} NH_3 solution. Considering that among 'real' samples there might be some variation in the pH value, 5 mmol L^{-1} of NH_3 was added to all diluted samples prior to analysis in order to avoid an enhanced memory effect for Br at too low a pH value.

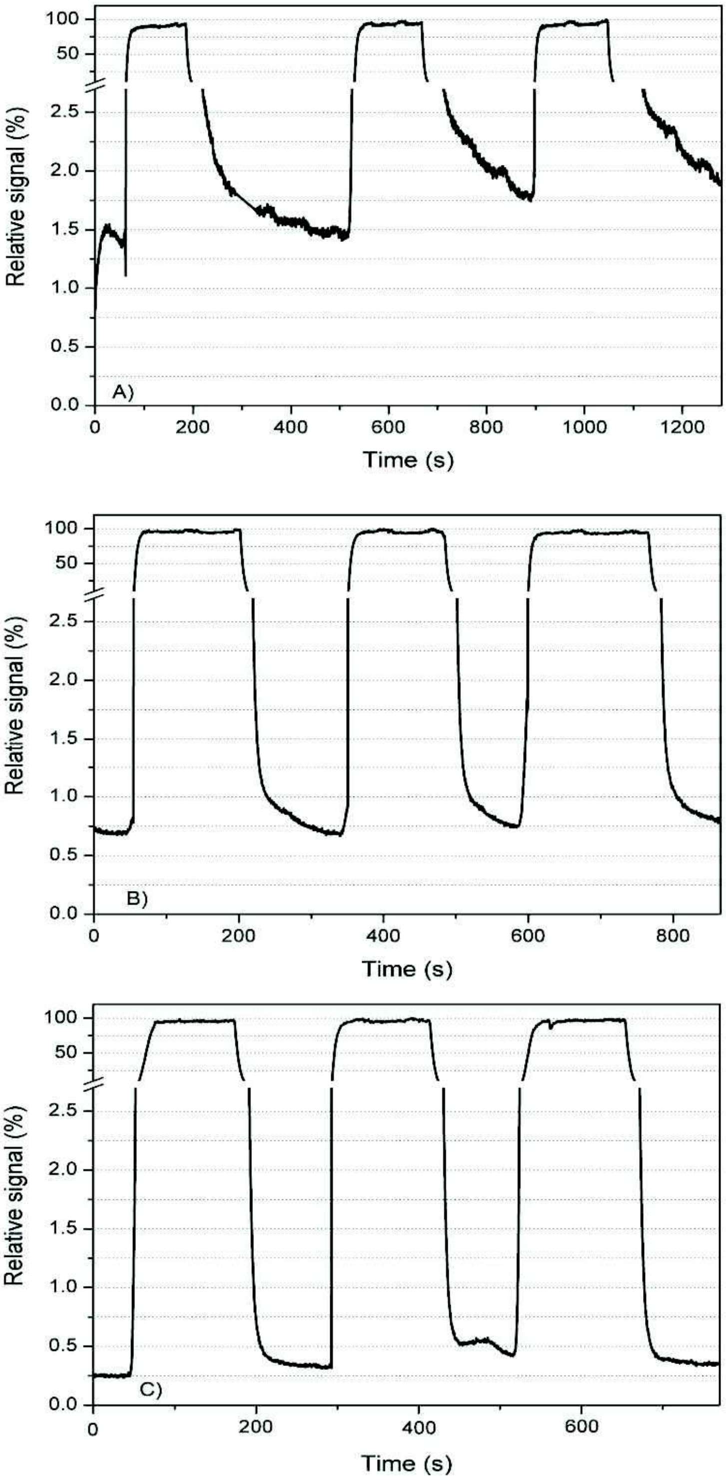

Figure 29. Memory effect (washout behavior) for a solution containing 3,000 µg L^{-1} of Br measured with a Neptune MC-ICP-MS instrument using a sample introduction system consisting of a 100 µL min^{-1} PFA nebulizer mounted onto a dual spray chamber (with a cyclonic and a Scott-type sub-unit). (A) 0.07 mol $L^{-1}HNO_3$; (B) deionized water and (C) 5 mmol $L^{-1}NH_3$.

6.3.2. Correction for instrumental mass discrimination

The internal standards considered for internal correction for instrumental mass discrimination in Br isotopic analysis using MC-ICP-MS were Ge, Se and Sr, for which the isotope ratios $^{74}Ge/^{72}Ge$, $^{78}Se/^{77}Se$ and $^{87}Sr/^{86}Sr$ were considered based on the precision obtained (Table 17).

Table 17. Figures of merit obtained using different internal standards for correction for mass discrimination in $^{81}Br/^{79}Br$ isotope ratio determination using MC-ICP-MS, (relative) standard error calculated based on one single measurement with 6 blocks and 6 cycles (n=36).

IS	Combination	$^{81}Br/^{79}Br$	SD	RSD (%)
Ge	$^{73}Ge/^{72}Ge$	0.97294	0.00020	0.0204
	$^{74}Ge/^{72}Ge$	0.97294	0.00016	0.0162
	$^{74}Ge/^{73}Ge$	0.97294	0.00016	0.0162
	$^{76}Ge/^{73}Ge$	0.97295	0.00022	0.0228
	$^{76}Ge/^{72}Ge$	0.97295	0.00023	0.0234
	$^{76}Ge/^{74}Ge$	0.97295	0.00027	0.0282
Sr	$^{86}Sr/^{84}Sr$	0.97291	0.00060	0.0618
	$^{87}Sr/^{86}Sr$	0.97288	0.00060	0.0618
Se	$^{76}Se/^{74}Se$	0.97292	0.00069	0.0708
	$^{77}Se/^{74}Se$	0.97293	0.00011	0.0108
	$^{77}Se/^{76}Se$	0.97294	0.00103	0.1056
	$^{78}Se/^{74}Se$	0.97293	0.00012	0.0126
	$^{78}Se\ /^{76}Se$	0.97294	0.00055	0.0564
	$^{78}Se\ /^{77}Se$	0.97293	0.00005	0.0048
-	external correction	0.97293	0.00018	0.0186

For some of the m/z ratios involved, spectral interference may still occur after cation removal from seawater due to the occurrence of $^{37}Cl^{35}Cl^+$, $^{36}Ar^{36}Ar^+$, $^{40}Ar^{32}S^+$ and $^{38}Ar^{34}S^+$ at m/z = 72; $^{40}Ar^{34}S^+$, $^{38}Ar^{36}Ar^+$, $^{37}Cl^{37}Cl^+$ and $^{38}Ar^{36}S^+$ at m/z = 74; $^{40}Ar^{37}Cl^+$, $^{40}Ar^{36}Ar^1H^+$, $^{38}Ar^{38}Ar^1H^+$ at m/z = 77, $^{40}Ar^{38}Ar^+$ at m/z = 78 and $^{35}Cl^{35}Cl^{14}N^+$ at m/z = 84. Even though the level of interference is expected to be lower for Sr than for the other candidate internal standards, the results using Sr as an internal standard were accompanied with higher RSDs than the results obtained relying on another internal standard (Figure 30).

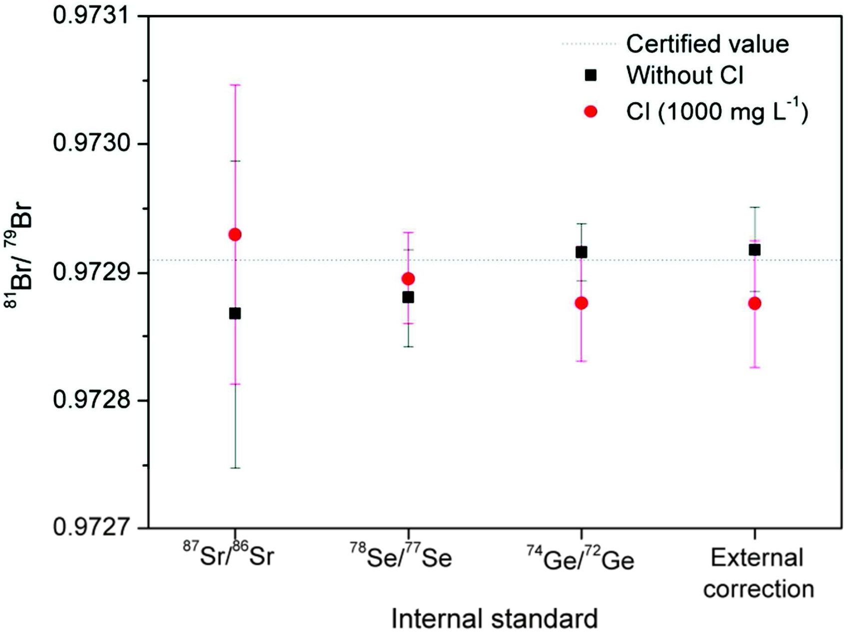

Figure 30. Combination of internal and external correction for instrumental mass discrimination compared to external correction only for a solution containing 2,000 µg L^{-1} of Br without and with 1,000 mg L^{-1} of Cl at high mass resolution using a Thermo Neptune MC-ICP-MS instrument (n = 3, mean ± SD).

This can be attributed to the use of NH_3 as washing solution, which rapidly washes out Br, but causes an extended memory effect for all internal standards tested, most pronounced for Sr. The time required for stabilization of the internal standard signals was also longer in NH_3 medium than in ultrapure water and HNO_3 medium (given this limitation, it was decided to rely on external correction for mass discrimination only). There is no significant deterioration in the precision and accuracy when using external correction in a standard-sample bracketing approach only.

6.3.3. Evaluation of resins

In order to avoid the adverse effects arising from the direct analysis of seawater to the largest possible extent, IC was relied on to remove the bulk of the alkali and earth alkali cations prior to Br isotopic analysis. As shown in Table 18, three variants of a cation exchange resin, differing from one another in particle size and/or degree of cross-linking, were evaluated. Quantitative recovery of Br was easily achieved with all resins as Br^- shows no affinity towards the resin, such that on-column isotope fractionation did not occur.

Table 18. Post-column recovery and measured Br isotope ratio for Br isotopic reference material NIST SRM 977 when using different cationic resins (n=5, mean ± SD).

Resin	Recovery (%)	$^{81}Br/^{79}Br$	RSD (%)
Dowex® 50WX8 (100-200 mesh)	97 ± 4	0.97296 ± 0.00022	0.022
Dowex® 50WX8 (200-400 mesh)	101 ± 2	0.97293 ± 0.00002	0.002
Dowex® 50WX4 (200-400 mesh)	98 ± 3	0.97299 ± 0.00008	0.008

Although quantitative recovery and absence of fractionation was guaranteed given the nature of the approach, the use of Dowex® 50WX8 (100-200 mesh) resulted in a lower precision. Although we have currently no indication as to the reason for the differences in precision observed, Dowex® 50WX8 (200-400 mesh) was selected for further experiments.

The saturation point of the resin was evaluated by monitoring the breakthrough of Na from 500 µL to 3 mL of IRMM BCR 403 seawater samples loaded onto a column filled with 1 mL of Dowex® 50WX8 (200-400 mesh). The maximum tolerable sample volume was determined to be 2 mL.

The Br concentration in seawater is expected to be higher than 4,000 µg L^{-1} [139]. 2 mL of seawater sample was loaded onto the column and a total of 4 mL column eluent was collected. The resulting 2-fold dilution did not negatively affect the precision attainable, but to extend the application range to samples with a lower Br concentration, a pre-concentration step by means of evaporation was included in the sample pre-treatment.

For evaluating this approach, standard solutions containing 1,000 µg L^{-1} of Br were reduced in volume from 4 mL to ≤1 mL; the final volume was subsequently adjusted to 1 mL with Milli-Q water. The Br recovery obtained for standard solutions prepared in HNO_3 was 77 ± 5 % and the $^{81}Br/^{79}Br$ isotope ratio was 0.97284 ± 0.00008; for water-based standards, the recovery was 97 ± 9 % and the $^{81}Br/^{79}Br$ ratio was 0.97293 ± 0.00005, whereas for standards prepared in 5 mmol L^{-1}

NH_3, a recovery of 98 ± 5 % and a $^{81}Br/^{79}Br$ ratio of 0.97293 ± 0.00002 were found. These ratios all compare favorably to the isotope ratio obtained for the standard after dilution only (0.97291 ± 0.00002).

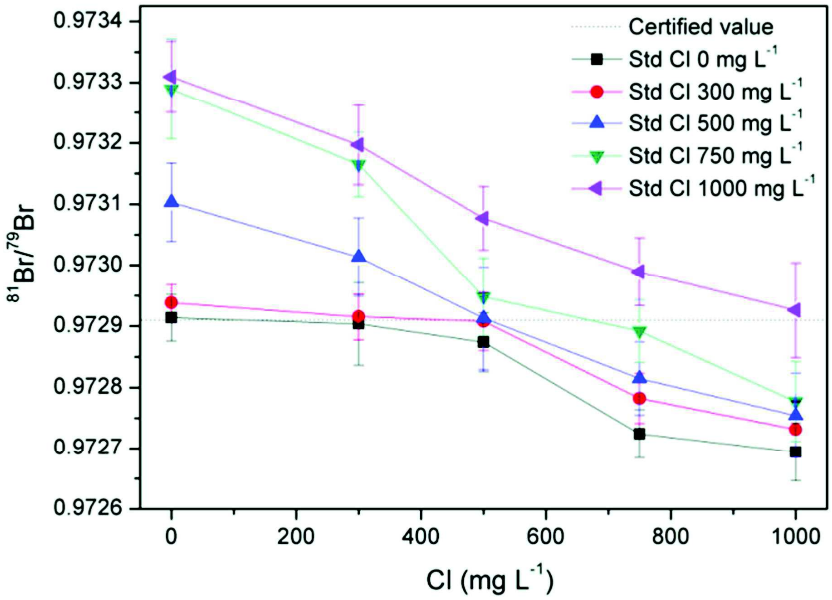

Figure 31. Effect of sample and standard Cl concentration on $^{81}Br/^{79}Br$ measurement results obtained using MC-ICP-MS (external correction in a SSB approach for correction for instrumental mass discrimination, n=3, mean ± SD).

The presence of chlorine in post-column solutions may also lead to non-spectral effects [140]. Figure 31 presents the effect of Cl (added as NH_4Cl) on the $^{81}Br/^{79}Br$ isotope ratio measurement results, corrected for instrumental mass discrimination using external correction in a sample-standard bracketing approach.

It can be concluded from these results that matrix matching for Cl is necessary in order to achieve accurate $^{81}Br/^{79}Br$ ratio measurements, since a lower $^{81}Br/^{79}Br$ ratio than expected was obtained using samples containing higher Cl concentrations than the standards. On the other hand, when using standards containing higher Cl concentrations than the samples, the $^{81}Br/^{79}Br$ ratio was biased high. The same trend was observed using internal correction with an internal standard.

6.3.4. Analytical application

Br standard solutions (with and without admixed Cl) and IRMM BCR-403 seawater reference material were used for method validation. 2 mL aliquots of these samples were passed through 1 mL of Dowex® 50WX8 (200 – 400 mesh) cationic exchange resin, followed by elution with 2 mL of milli-Q water. The total Br and Cl concentrations were measured using a quadrupole-based Elan DRC*Plus* ICP-MS unit. All final sample and standard solutions contained 4,000 μg L^{-1} of Br.

Mass bias correction was performed using Cl-matched standards (concentration of Cl adapted to that of the sample) in a sample-standard bracketing approach. The Br isotope ratio results were expressed as $\delta^{81}Br = [(R_{sample}-R_{standard})/R_{standard}] \times 1000$, in which the standard is SMOB (Standard Mean Ocean Bromine) [5]. Although the precision of the δ^{81}Br (SMOB) values calculated for the samples containing Cl was slightly affected by the Cl concentration, the results obtained for both, Br isotopic reference material NIST SRM 977 and seawater reference material (Table 19), are in accordance with the literature values [55,141].

Table 19. Results obtained using the method developed (n=3, mean ± SD) and literature values.

Sample	81Br(‰)	
	Value obtained	Literature values
Seawater	0.00 ± 0.10	0.0 ± 0.2[a]/0.00 ± 0.03[b]
SRM 977 (Water medium)	-0.62 ± 0.04	-0.7 ± 0.1[a]/- 0.65 ± 0.06[b]
SRM 977 (Cl 1000 mg L^{-1})	-0.65 ± 0.08	-

[a] Values from [55].

[b] Values from [141].

6.4. Conclusions

A method for accurate Br isotope ratio determination in seawater using MC-ICP-MS in its standard configuration (sample introduction via PN after simple removal of the major cation load via cation exchange chromatography) was developed. High mass resolution was used to free the signals from spectral interference (especially the overlap of the signals of $^{81}Br^+$ and $^{40}Ar^{40}Ar^1H^+$). Addition of NH_3 was efficient in reducing the memory effect. The method allowed obtaining accurate and precise results for ^{81}Br/^{79}Br ratio measurements in seawater and standard solutions after external correction for instrumental mass discrimination.

Chapter 7 - A simple method for high-precision isotopic analysis of chlorine via pneumatic nebulization multi-collector inductively coupled plasma-mass spectrometry

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7.1. Introduction

The $^{37}Cl/^{35}Cl$ isotope ratio is considered a useful diagnostic parameter for geochemical processes in seawater, sea ice and the atmosphere [142-143]. However, high-precision isotopic analysis of Cl still is an analytical challenge.

Several techniques have been deployed for the measurement of the Cl isotope ratio, including electron impact ionization mass spectrometry [144], IRMS [145], NCIMS [49] and more recently HR-CS MAS [52]. Unfortunately, these techniques are characterized by a number of drawbacks, such as the need for time-consuming sample preparation procedures, the occurrence of memory effects and/or a poor precision.

PTIMS relying on the monitoring of the polyatomic Cs_2Cl^+ ion, and IRMS are normally employed for Cl isotopic analysis and they have been applied to the measurement of the Cl isotope ratio in different samples, however, mass fractionation which is dependent of the Cl concentration was observed in the case of PTIMS [146-148].

The application of MC-ICP-MS to Cl isotopic analysis is far from trivial, mainly due to i) the low sensitivity, resulting from the high ionization potential of Cl (12.967 V), ii) the occurrence of spectral interference, mainly due to the formation of polyatomic ions containing elements, such as H, O, S and/or Ar – e.g., $^{16}O^{18}O^{1}H^+$ and $^{34}S^{1}H^+$, the signals of which overlap with that of $^{35}Cl^+$, and $^{36}Ar^{1}H^+$, the signal of which overlaps with that of $^{37}Cl^+$, iii) memory effects and iv) potential contamination from samples in HCl medium, routinely analyzed with this instrumentation [148-149].

The introduction of the target element Cl as a dry vapor has shown to be an efficient strategy to avoid or at least strongly reduce the level of spectral interference for Cl determination and isotopic analysis by ICP-MS, as it allows the separation of Cl from the matrix of the sample. In addition, the introduction of a dry aerosol using vapor generation, laser ablation (LA), ET), GC or a dessolvator system may improve the sensitivity due to the enhancement of the sample introduction efficiency [131, 148-150].

Despite the fact that vapor generation has improved the capabilities for Cl determination and isotopic analysis via ICP-MS, the overall procedure is laborious and requires specific equipment and reagents, which on occasions prevents the use of an autosampler. The use of a wet plasma and sample introduction via conventional

PN allows a simpler measurement protocol, use of the standard autosampler and an increased sample throughput with the standard MC-ICP-MS configuration [151].

Most of the current literature on isotopic standards for Cl presents the data as the δ^{37}Cl value, calculated relative to Standard Mean Ocean Chloride (SMOC). However, it was reported that δ^{37}Cl may range from -0.07 (Miyajima, Japan) to +0.08 (Woods Hole, US) ‰ in seawater, depending on the geographical provenance of the sample [142]. In igneous rocks, a variation in δ^{37}Cl (always relative to SMOC) from -0.85 to +0.25 was reported [132], for different commercially available inorganic standards, δ^{37}Cl values from -2.24 ‰ (for KCl) to 0.92 ‰ (for HCl) were reported and for organic solvents from -5.01 ‰ (for 1,1,1-Trichloroethane) to +2.85 ‰ (for 1,1-dichloroethene) [146].

The NaCl isotopic standards SRM 975 and SRM 975a, both from NIST (USA), and ISL-354, from the International Atomic Energy Agency (IAEA, Austria) were used for evaluating the accuracy of the measurements. Those standards were accurately characterized in terms of their Cl isotopic composition by Wei, *et al.* [147], who reported ^{37}Cl/^{35}Cl isotope ratios of 0.319876 ± 0.000067 for NIST SRM 975, of 0.319768 ± 0.000187 for NIST SRM 975a, and of 0.319549 ± 0.000044 for ISL-354. The □^{37}Cl values (expressed relative to SMOC) compiled by Brand *et al.* in an IUPAC Technical Report were +0.43 ‰ for NIST SRM 975, +0.2 ‰ for NIST SRM 975a and +0.05 ‰ for ISL-354 [152].

The aim of the present work was to assess the feasibility of traditional MC-ICP-MS (wet plasma conditions & use of PN for sample introduction) for high-precision isotopic analysis of Cl by adequately addressing the problems of spectral interference, low sensitivity and memory effects. After method optimization δ^{37}Cl was determined for a number of commercially available standards.

7.2. Experimental

7.2.1. Instrumentation

All isotope ratio measurements were carried out using a Thermo Scientific (Germany) Neptune MC-ICP-MS instrument, with a sample introduction system consisting of a 100 μL min^{-1} PFA nebulizer mounted onto a dual spray chamber, consisting of a cyclonic and a Scott-type sub-unit.

The measurements were performed using static collection with Faraday cups connected to 10^{12} Ω amplifiers. Gain calibration and baseline correction were performed before each measurement session. The operating parameters are summarized in Table 20.

Quantification of Cl and Na were carried out using a quadrupole-based Elan DRC*Plus* ICP-MS unit (Perkin Elmer, CT, USA). The nuclides monitored were ^{35}Cl, ^{23}Na and ^{103}Rh (as internal standard).

Table 20. Instrument settings, Faraday cup configuration and data acquisition parameters for Cl isotopic analysis via MC-ICP-MS.

Instrumental parameters	
	RF power: 1350W
	Plasma gas flow rate: 15 L min^{-1}
	Auxiliary gas flow rate: 0.8 L min^{-1}
	Nebulizer gas flow rate: 0.95 L min^{-1}
	Focus Quad: 4.0 V
	Dispersion Quad: 0.2 V
Cones	Standard geometry
	Sampler: Ni (1.1 mm orifice diameter)
	Skimmer: Ni (0.8 mm orifice diameter)
Data acquisition parameters	
	Mode: Static
	Resolution: High (resolving power of approx. 10,000)
	Integration time: 4 s
	Blocks: 6
	Cycles/Block: 6
Cup configuration	
	C: ^{35}Cl and H2: ^{37}Cl

7.2.2. Reagents, standards and samples

All reagents used were of analytical grade or higher purity. Ultrapure water (resistivity ≥ 18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France). Pro-analysis purity grade 14 mol L^{-1} HNO_3 (ProLabo, Belgium) was further purified by sub-boiling distillation in PFA equipment. *TraceSELECT*® NH_3 was obtained from Sigma-Aldrich (USA).

Polypropylene chromatographic columns (Eichrom, USA) filled with 1 mL of Dowex® 50WX8 (200-400 mesh) cation exchange resin were used for matrix removal. Chlorine isotope measurements were carried out for NIST SRM 975a NaCl isotopic reference material (MD, USA), BCR CRM 579 reference material (mercury in coastal sea water) from the Institute for Reference Materials and Measurements of the European Commission (IRMM, Belgium) and in commercially available extra pure NaCl (batch # K04243400), pro analysis KCl (batch # K36308936641) and Suprapur NH_4Cl (batch # B363143), all of which supplied by Merck (Germany). NH_4SO_4 was obtained from Merck (Suprapur purity). Individual 1,000 mg L^{-1} standard solutions of Cl, Na and Rh (Inorganic Ventures, the Netherlands) were used in the context of elemental assay via quadrupole-based ICP-MS.

7.2.3. Analytical procedure

Each sample or standard was prepared by loading a polypropylene chromatographic column filled with 1 mL of Dowex® 50WX8 cation exchange resin (previously washed with ultrapure water to remove soluble organic compounds) with 1 mL of solution containing 1,000 mg L^{-1} of Cl. The Cl-fraction (Cl^- shows no affinity towards the resin) was eluted with 2 mL of milli-Q water and this fraction was diluted to a final volume of 10 mL.

The Cl concentration, as well as the residual (post-column) Na concentration were determined using quadrupole-based ICP-MS after addition of Rh (final concentration of 1 μg L^{-1}) as an internal standard. Chlorine quantification was carried out via external calibration (calibration curve). Standard, blank and sample solutions were prepared in 5 mmol L^{-1} NH_3 in order to decrease memory effects. Sodium determination was carried out using solutions prepared in 0.07 mol L^{-1} HNO_3.

Chlorine isotope ratio measurements were performed in diluted samples with a Cl concentration of 100 mg L^{-1} (samples and standards were all prepared in 5 mmol L^{-1} NH_3). In-between every two solutions, the sample introduction system was rinsed with 5 mmol L^{-1} NH_3 solution during 3 min. The mass bias was corrected for using external correction in a SSB approach.

7.3. Results and discussion

7.3.1. Spectral interferences

Chlorine isotope ratio measurements with MC-ICP-MS may suffer from severe spectral interference, depending on the composition of the sample, the analyte element concentration, the sample introduction system selected and the mass resolution used.

After proper optimization of the instrument settings, a mass resolving power 10,000 (defined as $R = m/\Delta m$, with Δm the difference between the masses where the analyte intensity amounts to 95% and 5% of the maximum signal intensity, respectively) was achieved. A resolving power corresponds to a mass resolution ($R=m/\Delta m$ with Δm the full peak width at 5% of its maximum peak height) of approximately 5,000 [135].

The theoretical resolution required to resolve the analyte signal from that of the polyatomic ion, interfering at low mass resolution, at the *m/z* ratio of $^{35}Cl^+$ is about 1,000 for $^{16}O^{18}O^{1}H^+$ and 5,100 for $^{34}S^{1}H^+$ (assuming equal intensities for analyte and interfering signal). At the *m/z* ratio of $^{37}Cl^+$, a resolution of about 3,900 is required for resolving the analyte signal from that of $^{36}Ar^{1}H^+$ (assuming equal intensities for analyte and interfering signal).

The calculations of the resolutions required were done based on the atomic masses as provided by the Commission on Isotopic Abundances and Atomic Weights from the International Union of Pure and Applied Chemistry [153].

The major cation load of seawater can be removed easily via the use of a cation exchange resin [149]. However, anions containing S (such as $S0_4^{2-}$) are self-evidently not expected to be removed using this approach, leading to the formation of $^{34}S^{1}H^+$ in the plasma. Cl can be isolated from other matrix compounds by alternative or additional approaches, such as precipitation using Ag^+ [6], vapor generation and the use of high performance liquid chromatography or gas chromatography [132]. However, these approaches add complexity to the procedure; therefore, it was decided to rely on the pseudo-high resolution mode to resolve this interference.

Although sulfur is present in seawater, no signal for the $^{34}S^{1}H^{+}$ polyatomic ion was observed for a seawater sample after submitting it to cation exchange chromatography, which is due to the low concentration of S compared to Cl^{-} in seawater, for which the $[SO_4^{2-}]/[Cl^{1-}]$ ratio is, on average, 0.14 [139].

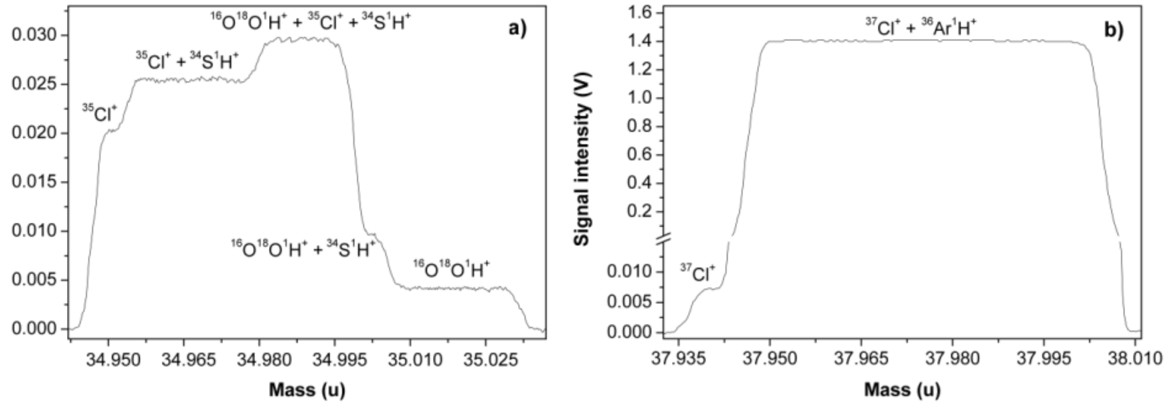

Figure 32. Mass spectra recorded at an *m/z* ratio of 35 (a) and *of* 37 (b) using MC-ICP-MS with sample introduction via conventional PN at pseudo high resolution (resolving power of approximately 10,000) for a standard solution containing 1 mg L^{-1} of Cl and 500 mg L^{-1} of S.

In order to promote the formation of $^{34}S^{1}H^{+}$ and thus, to identify the exact positions of the signals of the analyte and interfering ions, the spectral peaks at *m/z* ratios of 35 and 37 (Figure 32) were recorded for a standard solution containing 1 mg L^{-1} of Cl and 500 mg L^{-1} of S. As can be seen in Figure 32, it is possible to identify a narrow mass window in the lower mass range (left side) of the signal in both figures in which the signal derives solely from Cl. Hence, the final measurements (static mode) were performed in these narrow mass windows with regular monitoring for mass shift. Additionally, due to the use of wet plasma conditions, it is possible to observe a significant contribution of polyatomic ions containing O and H to the signal measured at an *m/z* ratio of 35 and containing Ar and H at an *m/z* ratio of 37.

7.3.2. Memory effect

Cl isotope ratio measurement via pneumatic nebulization (PN)-MC-ICP-MS is hindered by pronounced memory effects, which may also significantly affect isotope ratio measurements. Several wash solutions were studied in terms of washout behavior.

Rapid reduction of the Cl signal intensity back to background levels is desirable when using external correction in a sample-standard bracketing correction for mass bias [132, 151]. Three different wash solutions were evaluated: 0.14 mol L^{-1} HNO_3, ultrapure water (as obtained from a *Milli-Q* system) and 5 mmol L^{-1} NH_3. The standards were also prepared in the corresponding medium.

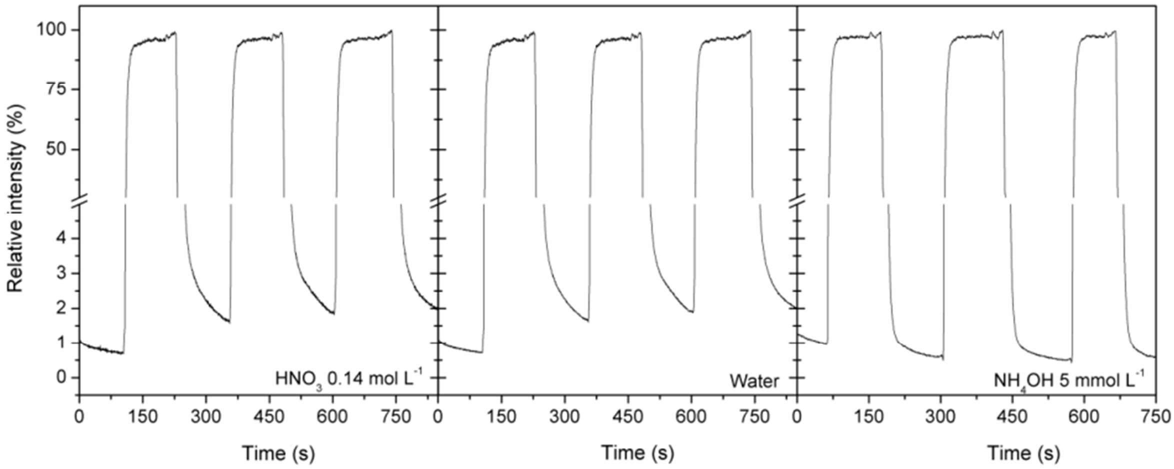

Figure 33. Transient signals recorded for ^{35}Cl using conventional nebulization and MC-ICP-MS with aspiration of different wash solutions between successive injections of a 100 mg L^{-1} Cl standard. The standard solutions were prepared in the same medium.

Figure 33 presents the effect of these three different wash solutions on the remaining signal after measuring a standard containing 100 mg L^{-1} of Cl and made up in the same medium. Under acidic conditions, the formation of HCl is favorable, which is not easily washed out due to vapor formation and retention of the vapor formed inside the spray chamber.

7.3.3. Chlorine concentration and mass bias correction

Due to its high ionization potential, the sensitivity demonstrated by ICP-MS for Cl is low when compared to other elements, an effect that is more pronounced using pneumatic nebulization due its low sample introduction efficiency when compared to vapor generation [131,149]. Therefore, establishing the minimum concentration required for Cl isotope measurement is a critical factor. Figure 34 presents the difference in accuracy and precision observed at different Cl concentrations.

Under the conditions adopted in this work, the Cl isotope ratio could be measured with good accuracy and precision (^{37}Cl/^{35}Cl = 0.319765 ± 0.000022 for NIST SRM 975a, RSD ~ 0.007% for n = 3) at a Cl concentration of $\geq$ 70 mg L^{-1}.

A high concentration of Cl is required due its low ionization efficiency, which is estimated according to the *Saha* equation to be approximately 0.9%, while for the majority of the elements commonly determined by ICP-MS, this value is higher than 90% [67], such that a Cl concentration approximately 100-fold higher than typical for other elements is required.

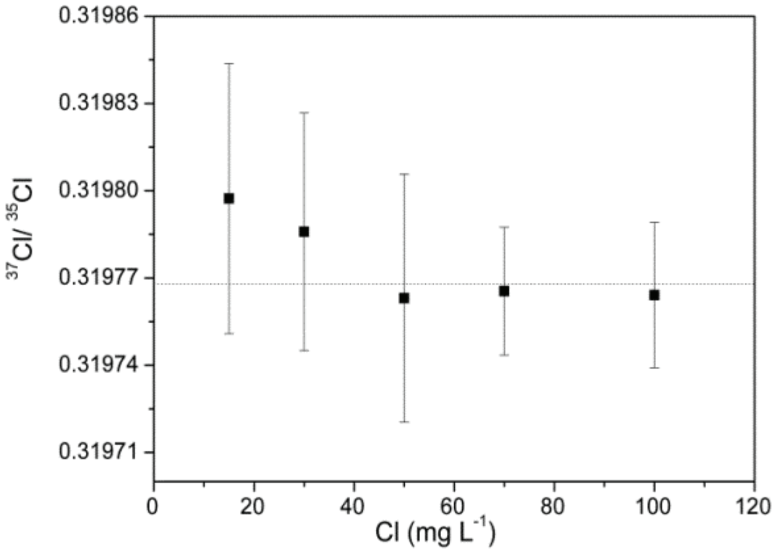

Figure 34. Effect of Cl concentration on the Cl isotope ratio as measured using MC-ICP-MS (wet plasma conditions) in a solution of NIST SRM 975a NaCl (mass bias corrected for by external correction in a sample-standard bracketing approach, n=3).

The relatively high concentration of Cl required for high-quality isotope ratio measurements via PN-MC-ICP-MS, is not problematic as the concentration of Cl in the natural sources of interest, such as seawater, is normally >> 100 mg L^{-1} [151].

Mass bias correction was applied by external correction using an SSB approach. To obtain the best performance using this correction method, it is important that both, standard and sample solutions are matrix- and concentration-matched and the time interval between the measurement of two successive solutions (standard and sample or sample and standard) should not be too long. In this work, the major cation load of the samples was removed via cation exchange chromatography and pronounced Cl memory effects were avoided by using 5 mmol L^{-1} NH_3 as wash solution. Under these conditions, the time interval between the analyses of two solutions was limited to 3 min and external correction was proven feasible.

7.3.4. Sample preparation and method accuracy

Sample preparation was carried out by loading 1 mL of sample solution (e.g., seawater) into a polypropylene chromatographic column filled with 1 mL of Dowex® 50WX8 cation exchange resin and eluting the analyte fraction with 2 mL of milli-Q water. The resulting solution was then diluted to a final concentration of 100 mg L^{-1} of Cl in 5 mmol L^{-1} NH_3. This approach allowed efficient removal of the major cation load – as confirmed by the absence of Na (< LOD = 0.1 μg L^{-1}) in the post-column solution. Absence of Cl isotope fractionation was demonstrated by the results for $\delta^{37}Cl$ in NH_4Cl, analyzed before and after passage through the cation exchange column (Table 21).

Table 21. Experimentally determined $\delta^{37}Cl$ (vs. SMOC) values obtained via PN-MC-ICP-MS (n=10, mean ± standar deviation).

Sample	Obtained value	Reference value
BCR CRM 579	0.00 ± 0.01	0.006 ± 0.038[142,*]
NIST SRM 975a	0.13 ± 0.08	0.2[153]
NH_4Cl (post-column)	0.89 ± 0.12	-
NH_4Cl	0.86 ± 0.10	-
KCl	-0.54 ± 0.08	-
NaCl	0.14 ± 0.07	-

* Average value calculated for several seawater samples, as reported by Godon, *et al*. [142]

This comes as no surprise as Cl^- is not expected to show any affinity towards the chromatographic resin. The results (Table 21) obtained for the seawater sample (BCR CRM 579) and for NIST SRM 975a were in good agreement with the values reported in the literature.

A variation in $\delta^{37}Cl$ from -0.07 to +0.08‰ has been reported for seawater; the reference value reported in Table 21 is the average of the δ^{37}Cl values obtained for seawaters from different geographical locations [142]. δ^{37}Cl values were also reported for NaCl and KCl by Numata, *et al.*[6] However, the values found by these authors, of +0.91 ± 0.15 for NaCl and -2.24 ± 0.07 for KCl, differ significantly from the values determined in the current work (Table 21). These differences may be attributed to differences in the production process of the reagents or in the source of the salts.

7.4. Conclusions

Despite the occurrence of spectral interference, memory effects and the characteristic low sensitivity, isotopic analysis of Cl in seawater can be successfully performed using PN-MC-ICP-MS (wet plasma conditions). High mass resolution, the use of 5 mmol L^{-1} NH_3 as a wash solution and a minimum Cl concentration of 70 mg L^{-1} were required to achieve accurate and precise results. The method is applicable to seawater samples and to saline solutions, after a simple chromatographic cleanup step. The proposed procedure is simpler and faster than other methods typically deployed for Cl isotopic analysis.

Chapter 8 – Quantification of bromine and chlorine and isotope ratio measurements in Antarctic sea ice

8.1. Introduction

The increasing temperature in Earth's atmosphere and oceans has been linked to the so-called global warming, which is considered to be a consequence of several human activities such as land-clearing, fossil-fuel burning, industrial activities and increasing the concentration of greenhouse gases in the atmosphere [154-155].

One of the consequences from the increasing temperature is the decrease of the sea ice extension; this effect has been more notorious in the Arctic Ice and less clear in the Antartic due to its isolation by big amounts of cold water [156-157].

Due to its whiteness, the surface of the sea ice normally reflects the sunlight back to space. When the sea ice surface is reduced, the sunlight focuses on the seawater, increasing the temperature of the oceans. As a consequence, the raise in atmospheric temperature is intensified [158].

Halogens may play an important role in global warming events when present in the environment due to a series of factors, such as destruction of the ozone layer through catalytic reactions, affecting the partitioning of HO_x and NO_x, oxidizing dimethyl sulphide and affecting the oxidation of volatile organic compounds, among others [118,125]. Nevertheless, the halogens have demonstrated great potential as proxies of polar ice extent and are related in concentration to sea water [125-128, 139].

Considering the importance of the sea ice towards a series of environmental phenomena such as influence in the polar albedo, oceanic circulation and the atmosphere-ocean transfer of heat, salts and gases [158], it is of vital importance to understand the mechanisms and timescales by which the sea ice interacts with other components of the Earth's climate system, in order to be able to accurately predict both the nature and rate of future climate change. However, the understanding of Earth's climate system demands accurate and well-resolved records of sea ice extent and rates of change obtained from an independent and reliable sea ice proxy, but existing sea ice proxies suffer from limitations.

Methanesulphonic acid, a product of ocean algae emissions, correlates with satellite observations of sea ice extent off the East Antarctic coast, but is reactive and remobilized in ice cores over centennial time scales [159]. Another example is related to Na in ice cores, that reflects glacial-interglacial sea ice variability, but on shorter timescales is strongly influenced by meteorology as well as competing sea ice and open ocean emission sources. Diatom biomarkers recorded in Southern Ocean sediments are a specific proxy of sea ice extent, but suffer from low temporal and spatial resolution and are not preserved in some regions. Bromine and Cl determined in polar ice cores offer a novel solution to these limitations [158, 125-128].

Given the lack of studies on isotope ratio of halogens in sea ice and the importance associated to well resolved records of sea ice for the better understanding of the environmental phenomena which contributes to the sea ice melting and formation, the aim of this work is to evaluate the halogen isotope ratio in Antartic sea ice from different locations and different collection depths in order to evaluate their behavior in those samples.

8.2. Experimental

8.2.1. Instrumentation

The isotope ratio measurements were carried out using a Thermo Scientific (Germany) Neptune MC-ICP-MS instrument, with a sample introduction system consisting of a 100 µL min^{-1} PFA nebulizer mounted onto a dual spray chamber, consisting of a cyclonic and a Scott-type sub-unit. The measurements were performed using static collection with Faraday cups connected to 10^{12} Ω amplifiers. Gain calibration and baseline correction were performed before each measurement session. The operating parameters are summarized in Table 22.

Quantification of Br, Cl and Na was carried out using a quadrupole-based Elan DRC*Plus* ICP-MS unit (Perkin Elmer, CT, USA). The nuclides monitored were ^{79}Br, ^{35}Cl, ^{23}Na and ^{103}Rh (as internal standard).

Table 22. Instrument settings, cup configurations and data acquisition parameters.

Instrumental eters	Br	Cl
RF power:	1350W	1350W
Plasma gas flow rate:	15 L min^{-1}	15 L min^{-1}
Auxiliary gas flow	0.8 L min^{-1}	0.8 L min^{-1}
Nebulizer gas flow	1.03 L min^{-1}	0.95 L min^{-1}
Focus Quad:	4.5 V	4.0 V
Dispersion Quad:	0 V	0 V
Sampling cone:	Ni	Ni
Skimmer:	Ni	Ni
Data acquisition eters		
Mode:	Static	Static
Resolution:	High	High
Integration time:	4 s	4 s
Blocks:	6	6
Cycles/Block:	6	6
Cup configuration	C: ^{79}Br, H2: ^{81}Br	C: ^{35}Cl, H2: ^{37}Cl

8.2.2. Reagents, standards and samples

All reagents used were of analytical grade or higher purity. Ultrapure water (resistivity $\geq$ 18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France). Pro-analysis purity grade 14 mol L^{-1} HNO_3 (ProLabo, Belgium) was further purified by sub-boiling distillation in PFA equipment. *TraceSELECT*® NH_3 was obtained from Sigma-Aldrich (USA).

Polypropylene chromatographic columns (Eichrom, USA) filled with 1 mL of Dowex® 50WX8 (200-400 mesh) cation exchange resin were used for matrix removal. Chlorine and Br isotope measurements were carried out using a NIST SRM 975a NaCl and a NIST SRM 977 NaBr isotopic reference materials (MD, USA), respectively. These materials were used for mass bias correction and to check the method accuracy.

Individual 1,000 mg L^{-1} standard solutions of Br, Cl, Na, and Rh were obtained from Inorganic Ventures (the Netherlands). Suprapur® NH_4SO_4 was obtained from Merck.

The certified seawater reference material BCR CRM 579 (mercury in coastal sea water), from the Institute for Reference Materials and Measurements of the European Commission (IRMM, Belgium), was used.

8.2.3. Analytical procedure

Each sample or standard was prepared by loading up to 2 mL of sample into a polypropylene chromatographic column filled with 1 mL of Dowex® 50WX8 cation exchange resin (previously washed with ultrapure water to remove soluble organic compounds), eluting with 2 mL of deionized water and diluting to a final volume of 10 mL.

The Br and Cl concentration, as well as the residual (post-column) Na concentration were determined using quadrupole-based ICP-MS after addition of Rh (final concentration of 1 μg L^{-1}) as an internal standard. Quantification was carried out via external calibration (calibration curve). Standard, blank and sample solutions were prepared in 5 mmol L^{-1} NH_3 in order to decrease memory effects. Sodium determination was carried out using solutions prepared in 0.07 mol L^{-1} HNO_3.

Bromine isotope ratio measurements were performed in diluted samples with a Br concentration of 3,000 μg L^{-1}, whereas Cl isotope ratio measurements were performed in diluted samples with a Cl concentration of 100 mg L^{-1} (samples and standards were all prepared in 5 mmol L^{-1} NH_3). A preconcentration step consisting of an evaporation on a hot plate at 90 °C for about 5 hours was carried out for the samples that presented Br concentration lower than 3,000 μg L^{-1}. No preconcentration step was required for Cl isotope ratio measurements.

In-between every two solutions, the sample introduction system was rinsed with a 5 mmol L^{-1} NH_3 solution for 3 min. The mass bias was corrected for using external correction in a SSB approach, matching the Cl concentration in the standards with the samples for Br isotope ratio measurements.

All measurements were performed using high resolution mode, measuring in the narrow mass window where the signal contribution is solely from Br or Cl isotopes. In order to promote the formation of $^{34}S^{1}H^{+}$ and then, to identify the narrow mass window for Cl isotopes, the optimization of this parameter was performed using a solution containing 1 mg L^{-1} of Cl and 500 mg L^{-1} of S.

The values were calculated as $\delta X = [(R_{sample}-R_{standard})/R_{standard}] \times 1000$, where X= ^{81}Br or ^{37}Cl, using as a standard the certified reference sea water BCR CRM 579.

8.2.4. Collection of samples

The samples were carefully collected in order to prevent contamination. The involved personnel was equipped with clean room garments (Tyvek overall, overshoes and polyethylene gloves) over their warm clothes, and items dedicated to sample collection and storage were cleaned and sealed in plastic bags.

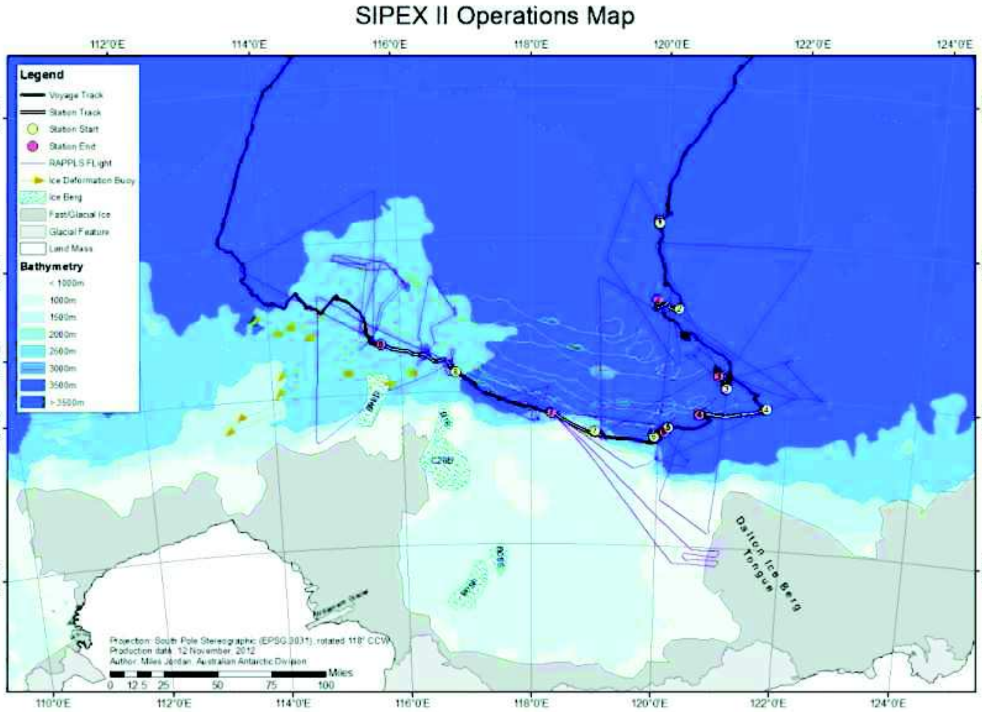

Figure 35. Locations of the ice stations visited during the SIPEX-2 expedition and sample collection.

Contamination-free samples were collected using the equipment designed by Lannuzel, *et al* (2006) [160] in different depths codified from si1 (top of the sea ice) to si6 (bottom of the sea ice). After sample collection, the ice cores were triple bagged and stored at -18^{o}C until processing in the laboratory for analysis.

The collection of the samples was performed during the Australian-led Sea Ice Physics and Ecosystem eXperiment-2 (SIPEX-2) marine expedition in 2012 (26 Sep–10 Nov), geographical location is 64–65^{o}S/116–121^{o}E, presented in Figure 35. Three local sea water and ice samples were collected for comparison proposes.

8.3. Results and discussion

8.3.1. Concentration of Br and Cl in sea ice

The total concentration of Br and Cl was measured in the sea ice samples after the cation load removal through a cationic column.

Chlorine and Br concentrations in the sea ice presented a linear correlation, with a slope of 0.0037 and a correlation coefficient of 0.9896 (Figure 36). The determined slope is similar to the slope obtained by Morris, *et al.* (0.0035), which is considered as a signature of seawater and thus no bromine explosion effect could be observed from the sea ice measurements in this work. The concentration of Br in sea ice ranged from 700 to 31000 μg L^{-1} and for Cl from 200 mg L^{-1} to 8000 mg L^{-1}. The variation in concentration was related to the depth of the sea ice collected; the more deep the sea ice was collected the lower the Cl and Br concentrations were. This finding might be related to desalination effect.

The desalination process in sea ice (which is responsible for decreasing the concentration of elements in the sea ice when compared to seawater) is linked to gravity drainage and flushing [162]. The gravity drainage is explained as equilibrium of the salinity gradient in the interstitial brine that follows the temperature gradient in sea ice. With the cooling of ice from above during the winter, the brine density of the sea ice becomes unstable, maintaining the highest densities at the top of the ice, which may explain the results obtained in terms of concentration, as presented in Figure 36. However, depending on the permeability of the sea ice, a convective overturning of brine within the mushy ice may occur. The flushing effect is, however, explained as a sort of “wash out” of salty brine with fresh meltwater during summer, with the pressure over the meltwater working as the force to move downwards and to elute brine out [161-162].

In Figure 36 it is possible to observe a wide and linear range of concentrations of Br and Cl in the sea ice collected, suggesting that the desalination process acts similarly for both elements.

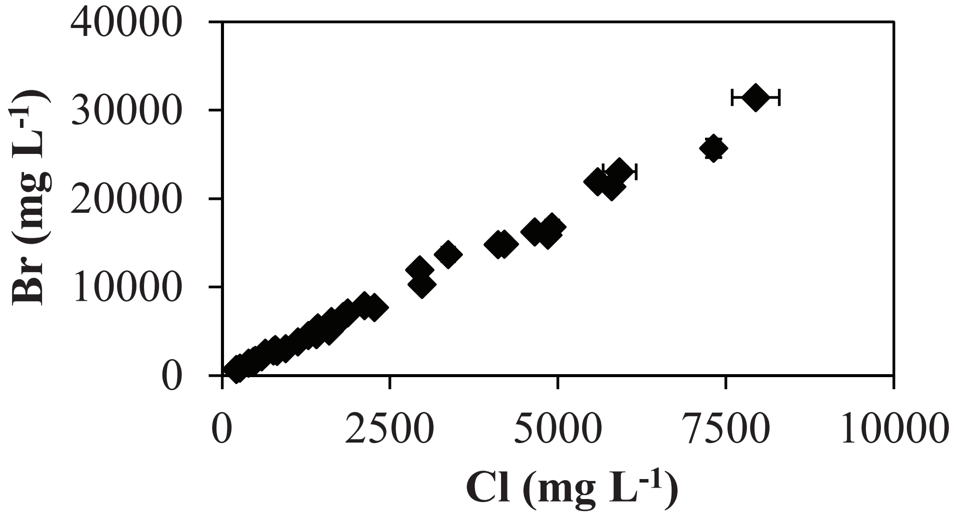

Figure 36. Relation between Br and Cl concentrations, measured by ICP-MS, in the collected sea ice during the SIPEX-2 expedition.

Most of the sea ice collected, specifically stations 2, 6, 7 and 8 is composed of granular sea ice (Figure 37) and columnar sea ice formed by sea water, supporting the idea that the decrease in the concentration is due to desalination from frozen sea water since only a small amount of sea ice is composed of snow.

The condition under which the sea ice was formed plays an important role to determine its structure. Frazil-ice crystals with granular texture are normally linked to the rapid freezing of the ocean surface while ice pancakes are usually formed under turbulent conditions. After the cover is formed, the ice starts to grow from the base to the surface, leading to the formation of crystals with elongated columnar texture.

The formation of the sea ice in this work probably occurred by freezing seawater onto the underside of existing sea ice, tending to form columnar and granular ice. Only a small fraction of the sea ice studied here was composed by compacted snow as can be seen in Figure 37.

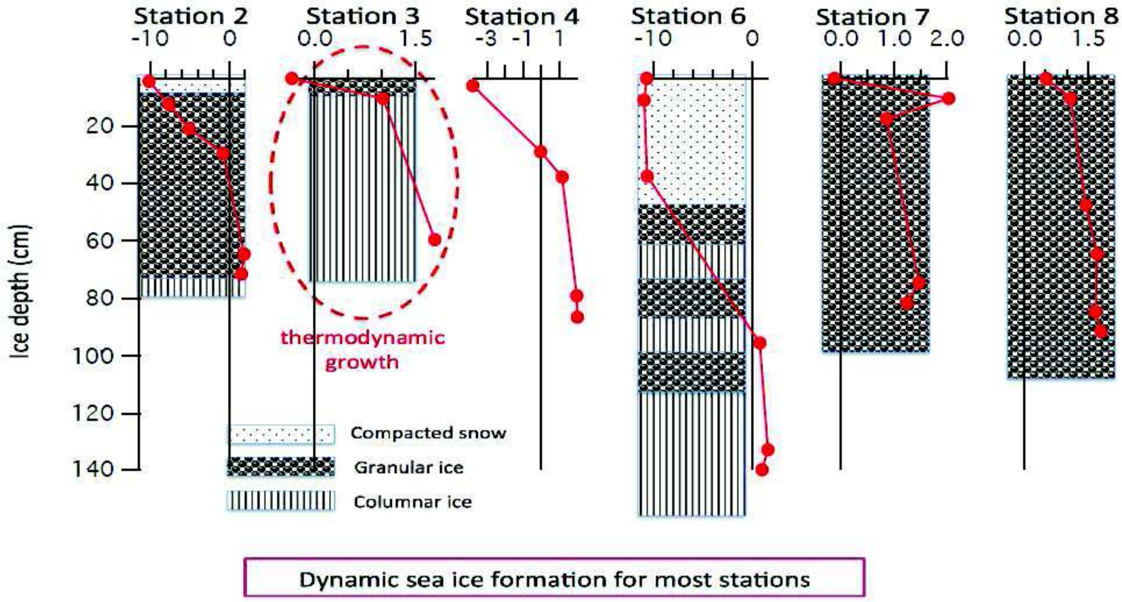

Figure 37. Observed texture of the sea ice collected during the SIPEX-2 expedition.

8.3.2. Isotopic composition of Br and Cl in sea ice

All samples were analyzed regarding their Br and Cl isotope ratios. Figure 38 presents the results of the measurements. A trend is visible for both Br and Cl in the sea ice collected. It is possible to observe that fractionation is more pronounced in deepest samples, which may be explained by the fact that the deep sea ice is older than the top sea ice, being exposed to desalination more severely than the top sea ice. In this case, there is the possibility that during the sea ice formation and desalination the processes of gravity drainage and flushing promoted the fractionation of Br and Cl with approximately the same intensity for both elements, since their concentrations are also related.

It is also possible to notice in Figure 38 that the stations 4 and 7 do not present such a strong fractionation in the bottom of the sea ice as other stations. It is possible that, for these stations, there is a mixing of the composition of the sea ice (top and bottom sea ice) and therefore the homogenization of its composition.

Moreover, the δ values determined in seawater samples were in agreement with the δ values reported in the literature for seawater (about 0), demonstrating that no fractionation takes place in seawater. The determined δ values in the standards were in agreement with the certified values (approximately -0.7 for δ^{81}Br and 0.2 for δ^{37}Cl), attesting the accuracy of the method.

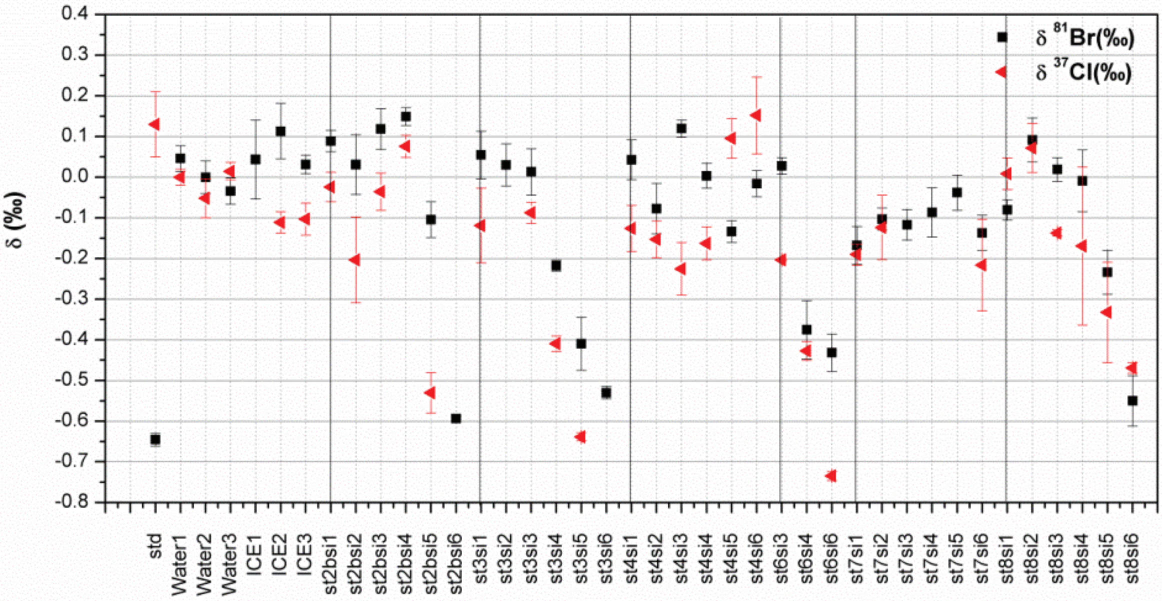

Figure 38. δ^{81}Br and δ^{37}Cl values from the sea ice collected during the SIPEX-2 voyage, measurements were carried out by MC-ICP-MS. std= Standards SRM 975a NaCl and a NIST SRM 977 NaBr, st means stations from 2 to 8, si means depth from 1 to 6. Water 1 to 3 and ICE 1 to 3 are local water and ICE collected for comparison. All the δ values were calculates based on the sea water BCR CRM 579.

Due to the processes that the sea ice undergoes for its formation, including desalination, it is possible that (linked to the decrease of the Br and Cl concentration) some fractionation effects occur, mainly due to the low temperature of the medium and the relative low mass of these elements [161].

Apparently, the process of desalination also plays a role in the isotope ratio of halogens due to differences in isotope migrations in the sea ice. Figure 39 presents the Br and Cl isotopic composition of the collected sea ice regarding the concentrations measured.

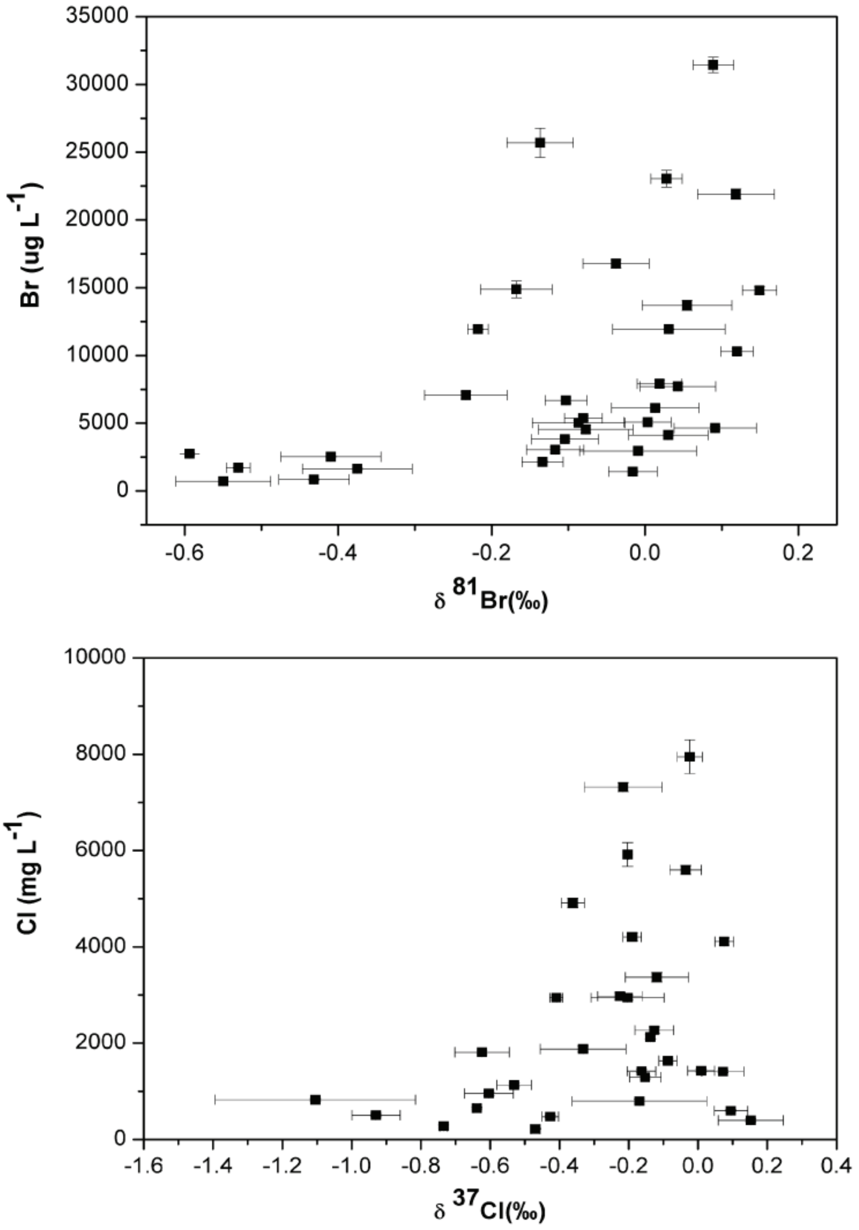

Figure 39. Relation between the Cl and Br concentrations and their isotope ratio in the sea ice collected during the SIPEX-2 expedition**.**

Figure 40 presents the relationship between the determined Br and Cl isotope ratio values. This may support the idea that both elements respond to the environmental processes at the same rate, and also that bromine explosion effects do not seem to play a role in their isotope composition, since variations in isotope composition are observed as a trend for both elements.

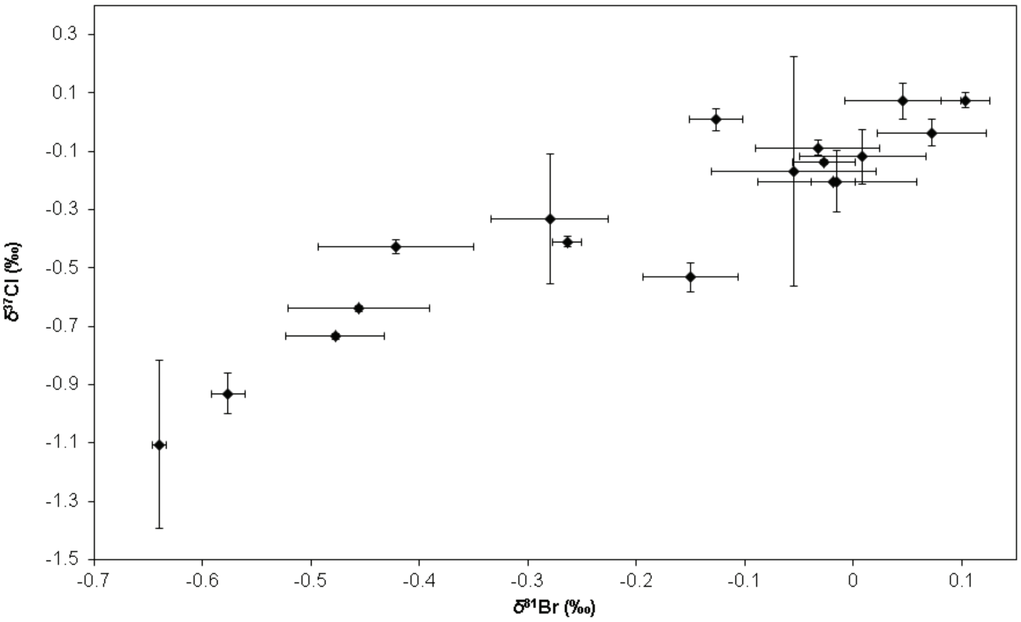

Figure 40. Relation between δ^{81}Br and δ^{37}Cl values from the sea ice collected during the SIPEX-2.

8.4. Conclusions

Differences in Br and Cl concentration in sea ice were observed. There is a general descending trend in the concentration of the halogens at greater depths for sea ice samples. The decrease in the concentrations of Br and Cl is probably related to the desalination process associated to sea ice formation, which also promoted the fractionation of their isotopes with a similar trend. The behavior of both elements is, somehow, linked.

9. Final considerations

Despite challenging, the use of SS-ETV-ICP-MS has proven to be a feasible approach for halogen determination in different matrices, with the potential of decreasing the amount of interferences and allowing calibration using aqueous standards to be carried out.

The LOQs obtained by SS-ETV-ICP-MS were in general improved over those obtained by other approaches for halogen determination by ICP-MS, mainly due to the fact that no sample dilution is needed and to the high sample introduction efficiency of the ETV-ICP-MS. The results demonstrate the feasibility of this technique for halogen analysis in different samples thus the methods can applied for real cases ranging from biological to environmental studies unrevealing the chemistry of halogens which has not been studied due to the limitation of measuring its concentration at low levels.

Moreover, the use of slurry and liquid samples may be studied applying ETV-ICP-MS, which may improve the sample throughput and dispense the use of special apparatus for sample introduction into the ETV.

LA-ICP-MS for direct solid sampling analysis, which is currently commercially available, has demonstrated to be a feasible technique for Br analysis in polymers, allowing its quantification by different straightforward approaches as the use of a single certified standard monitoring $^{12}C^{+}$

Halogen isotope analysis by MC-ICP-MS using conventional sample introduction systems also demonstrated to be a feasible and simple approach, eliminating the need for coupling with other techniques, such as gas chromatography or vapor generation, increasing the sample throughput and simplifying the procedure for analysis. The developed methods allowed accurate and precise isotope ratio measurements of Br and Cl and high sample throughput.

The developed methods were applied for real environmental cases, helping to understand environmental phenomena as well as the investigation of possible contamination sources.

10. References

[1] Greenwood, N.N.; Earnshaw, A. *Chemistry of the Elements*, Pergamon, Oxford, 1984. 2542 p.

[2] Railsback, L.B. An Earth scientist's periodic table of the elements and their ions. Geology, 31, p.737–741, 2003.

[3] Landsberge, S.; Vermette, V. G.; Wolfe, M.; Powell, M. A. Determination of halogens in coal using thermal and epithermal neutron activation analysis. *J. Coal Qual.*, v. 8, p.95–97, 1989.

[4] Flores, É. M. M.; Barin, J. S.; Mesko, M. F.; Knapp, G. Sample preparation techniques based on combustion reactions in closed vessels — A brief overview and recent applications. *Spectrochim. Acta, Part B*, v. 62, p.1051–1064, 2007.

[5] Jarvis; K. E.; Gray, A. L.; Houk, R. S. *Handbook of Inductively Coupled Plasma Mass Spectrometric*, London: Blackie Academic & Professional. 1992. 379 p.

[6] Pyle, D. M., Mather, T. A. Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: A review. *Chem. Geol.;* v. 263, p. 110–121, 2009.

[7] Wasson, J. T. *Meteorites*: Their Record of Early Solar-System History. WH Freeman and Co, New York. 1985. 267 p.

[8] Delmelle, P.; Delfosse, T.; Delvaux, B. Sulfate, chloride and fluoride retention in Andosols exposed to volcanic acid emissions. *Environ. Pollut., v.* 126, p. 445–457, 2003.

[9] Aiuppa, A.; Baker, D. R.; Webster, J. D. Halogens in volcanic systems. *Chem. Geol.*; v. 263, p.1–18, 2009.

[10] *Gutmann, V. Halogen Chemistry. v.3, Academic press: London and New York, 1967.*

[11] Winwarda, G. P.; Avery, L. M.; Stephenson T.; Jefferson, B. Chlorine disinfection of grey water for reuse: Effect of organics and particles. Research, v. 42 p. 483– 491, 2008.

[12] Korshak, V. V.; Vasnev, V. A. Seventh anniversary of the great October socialist revolution, Advances in polymer science. *Polym. Sci. U.S.S.R.*, v. 29, p. 2457-2505, 1987.

[13] Fordyce, F. M. *Fluorine*: Human Health Risks, Reference Module in Earth Systems and Environmental Sciences. Encyclopedia of Environmental Health. 2011, p. 776–785.

[14] Stirces, W.T.; Barrie, L. A. Chlorine, bromine and iodine in arctic aerosols. *Atmos. Environ*. v. 22, p. 1179-1794, 1988.

[15] Vainikka, P.; Hupa, M. Review on bromine in solid fuels – Part 2: Anthropogenic occurrence. Fuel, v. 94, p.34–51, 2012.

[16] Sturges, W. T. Halogens in aerosols in central Alaska. *Atmos. Environ*., v. 27A, p. 2969 2977, 1993.

[17] Snyder, G.T.; Fehn, U. Origin of iodine in volcanic fluids: 129I results from the Central American Volcanic Arc. *Geochim. Cosmochim. Acta*, v. 66, p. 3827–3838, 2002.

[18] Poznański, S. Halogen bonding at the ATP binding site of protein kinases: Preferred geometry and topology of ligand binding. *Biochim. Biophys. Acta,* v. 1834, p. 1381–1386, 2013.

[19] Saraogi, I.; Vijay, V.G.; Das, S.; Sekar, K.; Guru Row, T. N. C–halogen…π interactions in proteins: a database study. *Cryst. Eng.*, v.6, p. 69–77 2003.

[20] Chopra, I. J.; Solomon, D. H. Thyroid function tests and their alterations by drugs. *Pharmac. Therap. C*, v. 1, p. 367-399, 1976.

[21] ClarkI, J. I.; Weiner, L. M. Biologic treatment of human cancer. *Curr Probl Cancer.*, v. 19, p.185-262, 1995.

[22] Gentry, C.L.; Egleton, R. D.; Gillespie, T.; Abbruscato, T.J.; Bechowski, H. B.; Hruby V. J.; Davis, T.P. The effect of halogenation on blood–brain barrier permeability of a novel peptide drug. *Peptides*, v. 20, p.1229–1238, 1999.

[23] Acute toxicity, Available at http://www.fluoridealert.org/issues/health/poisoning/, Accessed in 10/02/2013.

[24] Picoloto, R. S.; Wiltsche, H.; Knapp, G.; Mello, P. A.; Barin, J. S.; Flores, E. M. M. Determination of inorganic pollutants in soil after volatilization using microwave-induced combustion. *Spectrochim. Acta, Part B*, v. 86, p.123–130, 2013.

[25] Warf, J. C.; Cline, W. D.; Tevebaugh, R. D. Pyrohidrolysis in the determination of fluorine and other halides. *Anal. Chem.,* v. 26, p. 342-345,1954.

[26] Knapp, G.; Maichin, B.; Fecher, P.; Hasse, S.; Schramel, P. Iodine determination in biological materials, Options for sample preparation and final determination. *Fresenius J. Anal. Chem.;* v.362, p.508–513, 1998.

[27] Schramel, P.; Hasse, S. Iodine determination in biological materials by ICP-MS. *Mikrochim. Acta,* v. 116, p.205–209, 1994.

[28] Antes, F. G.; Pereira, J. S. F.; Enders, M. S. P.; Moreira, C. M. M.; Muller, E. I.; Flores, E. M. M.; Dressler, V. L. Pyrohydrolysis of carbon nanotubes for Br and I determination by ICP-MS. *Microchem. J.* v. 101, p. 54-58, 2012.

[29] Rice, T. D. Determination of fluorine and chlorine in geological materials by induction furnace pyrohydrolysis and standard-addition ion-selective electrode measurement. *Talanta,* v. 35, p.173-178, 1988.

[30] Hall, G. E. M.; MacLaurin, A. I.; Vaive, J. The analysis of geological materials for fluorine, chlorine and sulphur using pyrohydrolysis and ion chromatography. *J. Geochem. Explor.,* v. 26, p.177-186, 1986.

[31] Langenauer, M.; Krähenbühl, U.; Wyttenbach, A. Determination of fluorine and iodine in biological materials. *Anal. Chim. Acta,* v. 274, p. 253-256, 1993.

[32] Barin, J. S.; Flores, É. M. M.; Mesko. M. F.; Mello, P. A.; Pereira, J. S. F. Chapter 5 – *Microwave-Induced Combustion*, Microwave-Assisted Sample Preparation for Trace Element Analysis, Elsevier, 2014, p. 143–177.

[33] Souza, G. B.; Neide, E.; Carrilho, V. M.; Oliveira, C. V.; Nogueira, A. R. A.; Nóbrega, J. A. Oxygen bomb combustion of biological samples for inductively coupled plasma optical emission spectrometry.*Spectrochim. Acta Part B*, v. 57, p. 2195-2201, 2012.

[34] Barbosa Jr. F.; Palmer, C. D.; Krug, F.J.; Parsons, P.J. Determination of total mercury in whole blood by flow injection cold vapor atomic absorption spectrometry with room temperature digestion

using tetramethylammonium hydroxide. *J. Anal. At. Spectrom.,* v. 19, p.1000–1005, 2004.

[35] Geng, W.; Nakajima, T.; Takanashi, H.; Ohki, A. Determination of total fluorine in coal by use of oxygen flask combustion method with catalyst. *Fuel*, v.86 p.715–721, 2007.

[36] Fecher, P. A.; Goldmann, I.; Nagengast, A. Determination of iodine in food samples by inductively coupled plasma mass spectrometry after alkaline extraction. *J. Anal. At. Spectrom., v.*13, p.977–982, 1998.

[37] Nóbrega, J. A.; Santos, M. C.; de Sousa R. A.; Cadore, S.; Barnes, R. M.; Tatro, M. Sample preparation in alkaline media. *Spectrochim. Acta, Part B*, v. 61 p.465–495, 2006.

[38] Mello, P. A.; Pereira, J. S. F.; Mesko, M. F.; Barin, J. S.; Flores, E. M. M. Sample preparation methods for subsequent determination of metals and non-metals in crude oil—A review. *Anal. Chim. Acta*, v. 746, p.15-36, 2012.

[39] Kurfuerst, U. *Solid sampling analysis: Direct and slurry sampling using GF AAS and ETV-ICP.* Springer, Berlin, Heidelberg, New York, 1998.

[40] Voellkopf, U.; Paul, M.; Denoyer, E. R. Analysis of solid samples by ICP-mass spectrometry. *Fresenius J. Anal. Chem.,* v. 342, p. 917-923, 1992.

[41] Pereira, J. S. F.; Moreira, C. M.; Albers, C. N.; Jacobsen O. S.; Flores, E. M. M. Determination of total organic halogen (TOX) in humic acids after microwave-induced combustion. *Chemosphere*, v. 83, p. 281–286, 2011.

[42] Rakiás, F.; Tóth, K.; Pungor, E. Determination of pharmaceutical compounds containing covalently-bound halogen by means of ion-selective electrodes**.** *Anal. Chem.,* v.121, p.93-99, 1980.

[43] Landsberge, S.; Vermette, V. G.; Wolfe M.; Powell. M. A. Determination of halogens in coal using thermal and epithermal neutron activation analysis. *J. Coal Qual,* v.8, p.95–97, 1989.

[44] An, J.; Jung, H.; Bae, J. R.; Yoon, H. O.; Seo, J. Feasibility of wavelength dispersive X-ray fluorescence spectrometry for a

simplified analysis of bromine in water samples with the aid of a strong anion exchange disk. *Spectrochim. Acta Part B*, v. 91, p. 1-4, 2014.

[45] Gaft, M.; Nagli, L.; Eliezer, N.; Groisman, Y.; Forni, O. Elemental analysis of halogens using molecular emission by laser-induced breakdown spectroscopy in air. *Spectrochimi. Acta Part B*, v.98, p.39-47, 2014.

[46] Bu, X.; Wang, T.; Hall, G. Determination of halogens in organic compounds by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). *J. Anal. At. Spectrom.,* v. 18, p.1443–1451. 2003.

[47] Yan, X.; Tanaka, T.; Kawaguchi, H. Electrothermal vaporization for the determination of halogens by reduced pressure inductively coupled plasma mass spectrometry. *Spectrochim. Acta, Part B,* v. 49, p. 1345-1353, 1996.

[48] Gentile, N.; Siegwolf, R. T. W.; Esseiva, P.; Doyle, S.; Zollinger, K.; Delémont, O. Isotope ratio mass spectrometry as a tool for source inference in forensic science: A critical review. *Forensic Sci. Int.*, v.251, p.139-158, 2015.

[49] Gui, J.; Chen, Z.; Zhang, Y.; Zhang L.; Liu, F. Novel Approach to Stable Chlorine Isotope Analysis using Gas Chromatography-Negative Chemical Ionization Mass Spectrometry. *Anal. Lett.,* v. 48, p.605 – 616, 2015.

[50] Eggenkamp, H. G. M.; Coleman, M. L. Rediscovery of classical methods and their application to the measurement of stable bromine isotopes in natural samples. *Chem. Geol.*, v.167, p.393-402, 2000.

[51] Catanzaro, E. J.; Murphy T. J.; Garner, E. L.; Shields, W. R. Absolute isotopic abundance ratio and the atomic weight of bromine. *J. Res. Natl. Bur. Stand. Sect A*, v.68A, p. 593-599, 1964.

[52] Nakadi, F. V.; da Veiga, M. A. M. S.; Aramendía, M.; Garcia-Ruiz E.; Resano, M. Chlorine isotope determination via the monitoring of the AlCl molecule by high-resolution continuum source graphite furnace molecular absorption spectrometry – a case study. *J. Anal. At. Spectrom.* v. 30, p.1531-1540, 2015.

[53] Xiao, Y.-K.; Zhang, C.-G. High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the

Cs_2Cl^+ ion. *Int. J. Mass Spectrom. Ion Processes*, v.116, p.183-192, 1992.

[54] Gelman, F.; Halicz, L. High precision determination of bromine isotope ratio by GC-MC-ICPMS. *Int. J. Mass Spectrom.* 289 (2010) 167-169.

[55] Gelman, F.; Halicz, L. High-precision isotope ratio analysis of inorganic bromide by continuous flow MC-ICPMS. *Int. J. Mass Spectrom.* v.307, p. 211-213, 2011.

[56] Hill, S.J. *Inductively Coupled Plasma Spectrometry and its Applications*. 2a ed. Blackwell Publishing Ltd: Carlton, 2007. 423p.

[57] Todolí, J. L.; Mermet, J. M. Sample introduction systems for the analysis of liquid microsamples by ICP-AES and ICP-MS. *Spectrochim. Acta Part B,* v. 61, p. 239–283, 2006.

[58] U6000AT+, Available at http://www.cetac.com/__documents/Brochure_U6000AT.pdf. Accessed in 03/11/2015.

[59] Perkin Elmer Sciex, *ICP-MS Training* : Introduction to ICP-MS & the Elan 6000, Seção 1. 17p.

[60] Vanhaecke, F.; Degryse, P. *Isotopic Analysis*: Fundamentals and Applications Using ICP-MS, Wiley-VCH Verlag GmbH, Weinheim, 2012.

[61] Turner, P. J.; Mills, D.J.; Schroder, E.; Lapitajs, G.; Lacone, L. A.; Haydar, D. A.; Montaser, A. *Instrumentation for low- and highresolution ICP-MS, in Inductively Coupled Plasma Mass Spectrometry*. Wiley-VCH Verlag GmbH, Weinheim, 1998, p. 421–501.

[62] Gillson, G. R.; Douglas, D. J.; Fulford J. E.; Halligan, K. W.; Tanner, S. D. Nonspectroscopic interelement interferences in inductively coupled plasma mass spectrometry. *Anal. Chem.*, v. 60, p.1472–1474, 1988.

[63] Vanhaecke, F.; Balcaen, L.; Malinovsky, D. Use of single-collector and multi-collector ICP-mass spectrometry for isotopic Analysis. *J. Anal. At. Spectrom.*, v. 24, p.863–886, 2009.

[64] Boulyga, S. F.; Heumann, K. G. Direct determination of halogens in powdered geological and environmental samples using

isotope dilution laser ablation ICP-MS. *Int. J. Mass Spectrom.,* v. 242, p. 291-296, 2005.

[65] Vanhoe, H.; Allemeersch, F. V.; Versieck, J.; Dams, R. Effect of Solvent Type on the Determination of Total Iodine in Milk Powder and Human Serum by Inductively Coupled Plasma Mass Spectrometry. *Analyst,* v. 118, p. 1015-1019, 1993.

[66] Vickers, G. H.; Wilson, D. A.; Hieftje, G. M. Detection of Negative Ions by Inductively Coupled Plasma Mass Spectrometry. *Anal. Chem., v.* 60, p.1808-1812, 1988.

[67] Houk, R. S. Mass spectrometry of inductively coupled plasmas. *Anal. Chem*., v. 58,p.97 – 105, 1986.

[68] Seo, J. H.; Guillong, M.; Aerts, M.; Zajacz, Z.; Heinrich C. A. Microanalysis of S, Cl, and Br in fluid inclusions by LA–ICP-MS. *Chem. Geol.,* v. 284, p. 35-44, 2011.

[69] Antes, F.G.; Dullius, E.; da Costa, A. B.; Molz. R. F.; Paniz, J. N. G.; Flores, E. M. M.; Dressler, V. L. Development of a vaporization system for direct determination of chlorine in petroleum coke by ICP-MS. *Microchem. J.,* v.109, p. 117–121, 2013.

[70] Resano, M., Garcia-Ruiz, E., Vanhaecke, F. Laser ablation inductively coupled plasma mass spectrometry in archaeometric research. *Mass Spectrom. Rev.*, v. 29, p. 55–78, 2010.

[71]Yang, C. K.; Chi, P.H.; Lin, Y.C.; Sun, Y.C.; Yang, M.H. Development of an on-line isotope dilution laser ablation inductively coupled plasma mass spectrometry (LA–ICP-MS) method for determination of boron in silicon wafers. *Talanta,* v. 80, p.1222-1227, 2010.

[72] Seefield, E.W.; Robinson, J.W. Determination of halogens in polymers and other petroleum products by a two-furnace combustion method. *Anal. Chim. Acta, v.23, p. 301-305, 1960.*

[73] Aramendía, M.; Resano, M.; Vanhaecke, F. Electrothermal vaporization–inductively coupled plasma-mass spectrometry: A versatile tool for tackling challenging samples: A critical review. *Anal. Chim. Acta,* v. 648, p.23– 44, 2009.

[74] Esteban, A. M. Electrothermal Vaporization — Inductively Coupled Plasma–Mass Spectrometry (ETV-ICP-MS): A

Valuable Tool for Direct Multielement Determination in Solid Samples. *Crit. Rev. Anal. Chem*., v. 33, p. 43–55, 2003.

[75] Vollkopf, U.; Grobenski, Z.; Tamm, R.; Welz, B. Solid sampling in graphite furnace atomic-absorption spectrometry using the cup-in-tube technique. *Analyst,* v. 110, p. 573-577, 1985.

[76] Evans, R. B. *Chlorine*: State of the Art. Lung, 2004, p. 151–167.

[77] Buckleya, R. L.; Hunter, C. H.; Wertha, D. W.; Whitesidea, M. T.; Chena, K. F.; Mazzola, C. A. A case study of chlorine transport and fate following a large accidental release. *Atmos. Environ., v.* 62,p. 84-198, 2012.

[78] Available on http://www.atsdr.cdc.gov, accessed in 22 July of 2014.

[79] Mello, P. A.; Barin, J. S.; Duarte, F. A.; Bizzi, C. A.; Diehl, L. O.; Muller, E. I.; Flores, E. M. M. Analytical methods for the determination of halogens in bioanalytical sciences: a review. *Anal. Bioanal. Chem.*, v. 405, p. 7615-7642, 2013.

[80] Peng, B.; Hu, D.; Lai, J.; Xiao, H.; Li, P. Simultaneous determination of halogens (F, Cl, Br, and I) in coal using pyrohydrolysis combined with ion chromatography. *Fuel*, v. 94, p. 629-63, 2012.

[81] Motomlzu, S.; Yoden, T. Porous membrane permeation of halogens and its application to the determination of halide ions and residual chlorine by flow-injection analysis. *Anal. Chim. Acta*, v. 261, p. 461-469, 1992.

[82] Resano, M.; Garcia-Ruiz, E.;, Moens, L.; Vanhaecke, F. Solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry for the direct determination of traces of iodine. *J. Anal. At. Spectrom.,* v. 20, p.81-87, 2005.

[83] Welz, B.; Lepri, F. G.; Araujo, R. G. O.; Ferreira, S. L.C.; Huang, M. D.; Okruss, M.; Becker-Ross, H. Determination of phosphorus, sulfur and the halogens using high-temperature molecular absorption spectrometry in flames and furnaces - A review. *Anal. Chim. Acta*, v. 647, p.137–148, 2009.

[84] Fechetia, M.; Tognon, A. L.; da Veiga, M. A. M. S. Determination of chlorine in food samples via the AlCl molecule using

high-resolution continuum source molecular absorption spectrometry in a graphite furnace. *Spectrochim. Acta Part B*, v. 71-72, p. 98 – 101, 2012.

[85] Sun, J. L.; Zeng, H.; Ni, H. G. Halogenated polycyclic aromatic hydrocarbons in the environment. *Chemosphere, v.* 90, p. 1751-1759, 2013.

[86] Suominen, K. P.; Wittmann, C.; Kähkönen, M. A.; Salkinoja-Salonen, M. S. Organic halogen, heavy metals and biological activities in pristine and pulp mill recipient lake sediments. *Water Sci. Technol.,* v. 37, p. 79–86, 1998.

[87] Herrmann, H.; Majdik, Z.; Ervens, B.; Weise, D. Halogen production from aqueous tropospheric particles. *Chemosphere*, v. 52, p. 485–502, 2003.

[88] Xu, M.; Yan, R.; Zheng, C.; Qiao, Y.; Han, J.; Sheng, C. Status of trace element emission in a coal combustion process: a review. *Fuel Process. Technol., v.* 85, p. 215-237, 2004.

[89] Zhang, J.; Zhao, Y.; Ding, F.; Zeng, H.; Zheng, C. Preliminary study of trace element emissions and control during coal combustion. *Fron. Energy Power Eng. Chin.*, v.1, p. 273-279, 2007.

[90] Yung, Y.L.; Pinto, J. P.; Watson, R.T.; Sander, S.P. Atmospheric bromine and ozone perturbations in the lower stratosphere. *Am. Meteorol. Soc., v.* 37, p. 339-353, 1979.

[91] Pereira, E. R.; Castilho, I. N. B.; Welz, B.; Gois, J.S.; Borges, D.L.G.; Carasek, E.; de Andrade, J.B. Method development for the determination of bromine in coal using high-resolution graphite furnace molecular absorption spectrometry and direct solid sample analysis. *Spectrochim. Acta Part B,* v. 96, p. 33-39, 2014.

[92] Doyle, A.; Saavedra, A.; Tristão, M. L. B.; Mendes, L. A. N.; Aucélio, R. Q. Spectrometric methods for the determination of chlorine in crude oil and petroleum derivatives — A review. *Spectrochim. Acta Part B*, v. 86, p. 102–107, 2013.

[93] Kim, K. H.; Shon, Z. H.; Nguyen, H. T.; Jeon, E. C. A review of major chlorofluorcarbons and their halocarbon alternatives in the air. *Atmos. Environ., v.* 45 (6), p. 1369-1382, 2011.

[94] von Glasow, R.; Crutzen, P. J. Tropospheric Halogen Chemistry. In *Treatise on Geochemistry*; Holland, H. D., Turekian, K. K., Eds.; Elsevier Science: p 1-67, 2007.

[95] Mather, T. A.; Witt, M. L. I.; Pyle, D. M.; Quayle, B. M.; Aiuppa, A.; Bagnato, E.; Martin, R. S.; Sims, K. W. W.; Edmonds, M.; Sutton, A. J.; Ilyinskaya, E. Halogens and trace metal emissions from the ongoing 2008 summit eruption of Kilauea volcano, Hawaii. *Geochim. Cosmochim. Acta*, v. 83 (15), p. 292-323, 2012.

[96] Sawyer, G. M.; Salerno, G. G.; Le Blond, J. S.; Martin, R. S.; Spampinato, L.; Roberts, T. J.; Mather, T. A.; Witt, M. L. I.; Tsanev, V. I.; Oppenheimer, C. Gas and aerosol emissions from Villarrica volcano, Chile. *J. Volcanol. Geotherm. Res.,* v. 203 (1-2), p. 62-75, 2011.

[97] Ball, S. M.; Hollingsworth, A. M.; Humbles, J.; Leblanc, C.; Potin, P.; Mc Figgans, G. Spectroscopic studies of molecular iodine emitted into the gas phase by seaweed. *Atmos. Chem. Phys*., v.10, p. 6237–6254, 2010.

[98] Enami, S.; Vecitis, C. D.; Cheng, J.; Hoffmann, M. R.; Colussi, A. J. Global inorganic source of atmospheric bromine. *J. Phys. Chem. A* **2007,** 111 (36), 8749 - 8752.

[99] Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol*., v. 40 (1), p. 32–44, 2006.

[100] Ruan, T.; Wang, Y.; Zhang, Q.; Ding, L.; Wang, P.; Qu, G.; Wang, C.; Wang, T.; Jiang, G. Trace determination of airborne polyfluorinated iodine alkanes using multisorbent thermal desorption/gas chromatography/high resolution mass spectrometry. *J. Chromatogr. A*, v. 1217 (26), p. 4439–4447, 2010.

[101] Russell, A. G.; Brunekreef, B. A Focus on Particulate Matter and Health. *Environ. Sci. Technol.***, v.** 43 (13), p. 4620–4625, 2009.

[102] Kurfürst, U. Solid Sample Analysis: Direct and Slurry Sampling using GF-AAS and ETV-ICP; Springer Berlin Heidelberg: New York, 1998.

[103] Ozbek, N.; Akman, S. Method development for the determination of fluorine in water samples via the molecular absorption

of strontium monofluoride formed in an electrothermal atomizer. *Spectrochim. Acta Part B***,** v. 69, p. 32-37, 2012.

[104] Ozbek, N.; Akman, S. Determination of fluorine in milk and water via molecular absorption of barium monofluoride by high-resolution continuum source atomic absorption spectrometer. *Microchem. J., v.* 117, p. 111-115, 2014.

[105] Dittrich, K. Molekülabsorptionsspektrometrie bei elektrothermischer verdampfung in einer graphitrohrküvette: II. Bestimmung von fluoridspuren in mikrovolumina durch die molekülabsorption von GaF-molekülen. *Anal. Chim. Acta*, v. 97 (1), p. 69-80, 1978.

[106] Dittrich, K.; Vorberg, B. Molecular absorption spectrometry with electrothermal volatilization in a graphite tube.: Part 7. A study of molecular absorption of alkaline earth halides and determination of traces of fluoride and chloride based on molecular absorption of MgF and MgCl molecules. *Anal. Chim. Acta*, v. 140 (1), p. 237–248, 1982.

[107] Morés, S.; Monteiro, G. C.; Santos, F. S.; Carasek, E.; Welz, B. Determination of fluorine in tea using high-resolution molecular absorption spectrometry with electrothermal vaporization of the calcium mono-fluoride CaF. *Talanta*, v. 85 (5), p. 2681-2685, 2011.

[108] Machado, P. M.; Morés; S.; Pereira, É. R., Welz, B.; Carasek, E.; de Andrade, J. B. Fluorine determination in coal using high-resolution graphite furnace molecular absorption spectrometry and direct solid sample analysis. *Spectrochim. Acta Part B,* v. 105, p. 18 - 24, 2015.

[109] Bank of Weather Data for Teaching and Research (BDMEP-Brazil) Website: http://www.inmet.gov.br/projetos/rede/pesquisa/, Acessed in 05 /11/2015.

[110] Tagami, K.; Uchida, S. Concentrations of chlorine, bromine and iodine in Japanese rivers. *Chemosphere*, v. 65 (11), p. 2358-2365, 2011.

[111] Picoloto, R. S. ; Cruz, S. M. ; Mello, P. A. ; Muller, E. I. ; Smichowski, P.; Flores, E. M. M. Combining pyrohydrolysis and

ICP-MS for bromine and iodine determination in airborne particulate matter. *Microchem. J.*, v. 116, p. 225–229, 2014.

[112] Gao, Y.; Sun, M.; Wu, X.; Liu, Y.; Guo, Y.; Wu, J. Concentration characteristics of bromine and iodine in aerossols in Shanghai, China. *Atmos. Environ.*, v. 44 (34), p. 4298–4302, 2010.

[113] da Silva, S. V.; Picoloto, R. S.; Flores, E. M. M.; Wagner, R.; Richards, N. S. P. S.; Barin, J. S. Evaluation of bromine and iodine content of milk whey proteins combining digestion by microwave-induced combustion and ICP-MS determination. *Food Chem.,* v. 190, p. 364-367, 2016.

[114] Vázquez, A. S.; Costa-Fernandez, J. M.; Encinar, J. R.; Pereiro, R.; Sanz-Medel A. Bromine determination in polymers by inductively coupled plasma-mass spectrometry and its potential for fast first screening of brominated flame retardants in polymers and paintings, *Anal. Chim. Acta,* v. 623, p.140-145, 2008.

[115] Gunduz, G.; Kisakurek, D.; Kayadan, S. Flame retardant alkyd paint. *Polym. Degrad. Stab.*, v. 64, p. 501- 504, 1999.

[116] Fromme, H.; Becher, G.; Hilger, B.; Volkel, W. Brominated flame Retardants – Exposure and risk assessment for the general population, *Int. J. Hyg. Environ. Health.* DOI: 10.1016/j.ijheh.2015.08.004.

[117] Kaspersma, J.; Doumen, C.; Munro, S.; Prins, A. M. Fire retardant mechanism of aliphatic bromine compounds in polystyrene and polypropylene, *Polym. Degrad. Stab.*, v. 77, p. 325-331, 2002.

[118] Saiz-Lopez, A.; von Glasow, R. Reactive halogen chemistry in the troposphere: Critical Review. *Chem.Soc.Rev.*, v. 41, p. 6448-6472, 2012.

[119] Horn, I.; Gunther, D. The influence of ablation carrier gasses Ar, He and Ne on the particle size distribution and transport efficiencies of laser ablation-induced aerosols: implications for LA–ICP–MS. *Appl. Surf. Sci.* , v. 207, p. 144–157, 2003.

[120] Wang, Z.; Hattendorf, B.; Günther, D. Analyte Response in Laser Ablation Inductively Coupled Plasma Mass Spectrometry. *J. Am. Soc. Mass Spectrom.*, v. 17 p. 641–651, 2006.

[121] Diwakar, P. K.; Gonzalez, J. J. ; Harilal, S. S. ; Russo, R. E. ; Hassanein, A. Ultrafast laser ablation ICP-MS: role of spot size, laser fluence, and repetition rate in signal intensity and elemental fractionation. *J. Anal. At. Spectrom.,* v. 29, p.339 –346, 2014.

[122] Russo, R.E.; Mao, X.; Liu, H. ; Gonzalez, J.; Mao, S. S. Laser ablation in analytical chemistry—a review. *Talanta,* v. 57, p. 425–451, 2002.

[123] Wieser, M .E.; Holden, N.; Coplen, T. B.; Böhlke, J. K.; Berglund, M.; Brand, W. A.; De Bièvre, P.; Gröning, M.; Loss, R. D.; Meija, J.; Hirata, T.; Prohaska, T.; Schoenberg, R.; O'Connor, G.; Walczyk, T.; Yoneda, S.; Zhu, X. K. Atomic weights of the elements 2011 (IUPAC Technical Report). *Pure Appl. Chem.*, v. 85, p.1047–1078, 2013.

[124] Carrizo, D.; Unger, M.; Holmstrand, H.; Andersson, P.; Gustafsson, O.; Sylva, S. P.; Reddy, C. M. Compound-specific bromine isotope compositions of one natural and six industrially synthesized organobromine substances. *Environ. Chem*., v. 8, p.127–132, 2011.

[125] Spolaor, A,; Vallelonga, P.; Gabrieli, J.; Kehrwald, N.; Turetta, C.; Cozzi, G.; Poto, L.; Plane, J. M.; Boutron, C.; Barbante, C. Speciation analysis of iodine and bromine at picogram-per-gram levels in polar ice. *Anal. Bioanal. Chem.,* v. 405, p.647-654, 2013.

[126] Spolaor, A.; Vallelonga, P.; Plane, J. M. C.; Kehrwald, N.; Gabrieli, J.; Varin, C.; Turetta, C.; Cozzi, G.; Kumar, R.; Boutron, C.; Barbante, C. Halogen species record Antarctic sea ice extent over glacial-interglacial periods. *Atmos. Chem. Phys*., v. 13, p. 6623-6635, 2013.

[127] Spolaor, A.; Gabrieli, J.; Martma, T.; Kohler, J.; Björkman, M. B.; Isaksson, E.; Varin, C.; Vallelonga, P.; Plane, J. M. C.; Barbante, C.; Sea ice dynamics as a control for halogen deposition to Svalbard. *The Cryosphere, v.* 7, p. 1645-1658, 2013.

[128] Spolaor, A.; Vallelonga, P.; Gabrieli, J.; Martma, T.; Björkman, M. P.; Isaksson, E.; Cozzi, G.; Turetta, C.; Kjær, H. A.; Curran, M. A. J, Moy, A. D.; Schönhardt, A.; Blechschmidt, A. M.; Burrows, J. P.; Plane, J. M. C.; Barbante, C. (2014) Seasonality of halogen deposition in polar snow and ice. *Atmos. Chem. Phys. Discuss.,* v. 14, p. 9613-9622, 2014.

[129] Tagami, K.; Uchida, S.; Hirai, I.; Tsukada, H.; Takeda, H.; Determination of chlorine, bromine and iodine in plant samples by inductively coupled plasma-mass spectrometry after leaching with tetramethyl ammonium hydroxide under a mild temperature condition. *Anal. Chim. Acta*, v. 570, p.88–92, 2006.

[130] Bings, N. H.; von Niessen, J. O. O.; Schaper, J. N. Liquid sample introduction in inductively coupled plasma atomic emission and mass spectrometry — Critical review. *Spectrochim. Acta Part B*, v. 100, p. 14-37, 2014.

[131] Sturgeon, R. E. Detection of bromine by ICP-oa-ToF-MS following photochemical vapor generation. *Anal. Chem.,* v. 87, p. 3072-3079, 2015.

[132] Zakon, Y.; Halicz, L.; Gelman, F. Isotope Analysis of Sulfur, Bromine, and Chlorine in Individual Anionic Species by Ion Chromatography/Multicollector-ICPMS. *Anal. Chem.,* v. 86, p. 6495−6500, 2014.

[133] Nicolaï, M.; Rosin, C.; Tousset, N.; Nicolai, Y. Trace metals analysis in estuarine and seawater by ICP-MS using on line preconcentration and matrix elimination with chelating resin. *Talanta*, v. 50, p. 433-444, 1999.

[134] Willie, S. N.; Lam, J. W. H.; Yang, L.; Tao, G. On-line removal of Ca, Na and Mg from iminodiacetate resin for the determination of trace elements in seawater and fish otoliths by flow injection ICP-MS. *Anal. Chim. Acta,* v. 447, p. 143-152, 2001.

[135] Vanhaecke, F.; Moens, L. Overcoming spectral overlap in isotopic analysis via single- and multi-collector ICP – mass spectrometry. *Anal. Bioanal. Chem., v.* 378, p. 232-240, 2004.

[136] Veguería, S. F. J.; Godoy, J. M.; de Campos, R. C.; Gonçalves, R. A. Trace element determination in seawater by ICP-MS using online, offline and bath procedures of preconcentration and matrix elimination. *Microchem. J.,* v. 106, p. 121-128, 2013.

[137] Berglund, M.; Wieser, M. E. Isotopic compositions of the elements 2009 (IUPAC Technical Report). *Pure Appl. Chem.,* v. 83, p. 397–410, 2011.

[138] Baxter, D. C.; Rodushkin, I.; Engstrom, E.; Malinovsky, D. Revised exponential model for mass bias correction using an internal

standard for isotope abundance ratio measurements by multi-collector inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.,* v. 21, p. 427-430, 2006.

[139] Morris, A. W.; Riley, J. P. The bromide/chlorinity and sulphate/chlorinity ratio in seawater. *Deep-Sea Res.,* v. 13, p. 699-705, 1966.

[140] Lin, A. J.; Yang, T.; Jiang, S. Y. A rapid and high-precision method for sulfur isotope $\delta^{34}S$ determination with a multiple-collector inductively coupled plasma mass spectrometer: matrix effect correction and applications for water samples without chemical purification. *Rapid. Commun. Mass. Spectrom.,* v. 28, p. 750–756, 2014.

[141] Du, Y.; Ma, T.; Yang, J.; Liu, L.; Shan, H.; Cai, H.; Liu, C.; Chen, L. A precise analytical method for bromine stable isotopes in natural waters by GasBench II-IRMS. *Int. J. Mass. Spectrom., v.* 338, p.50-56, 2013.

[142] Godon, A.; Jendrzejewskia, N.; Eggenkamp, H. G. M.; Banks, D. A.; Ader, M.; Coleman, M. L.; Pineau, F. A cross-calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. *Chem. Geol*., v. 207, p. 1–12, 2004.

[143] Hoefs, J. *Stable Isotope Geochemistry*, Springer-Verlag, Berlin, 1997.

[144] Long, A.; Eastoe, C. J.; Kaufmann, R. S.; Martin, J. G.; Wirt, L.; Finley, J. B. High-precision measurement of chlorine stable isotope ratios. *Geochim. Cosmochim. Acta*, v. 57, p. 2907–2912, 1993.

[145] Vengosh, A.; Chivas, A. R.; McCulloch, M. T. Direct determination of boron and chlorine isotopic compositions in geological materials by negative thermal-ionization mass spectrometry. *Chem. Geol*., v. 79, p. 333–343, 1989.

[146] Numata, M.; Nakamura N.; Gamo, T. Precise measurement of chlorine stable isotopic ratios by thermal ionization mass spectrometry. *Geochem. J.*, v.35,p.89 – 100, 2001.

[147] H. Z. Wei,S. Y. Jiang, Y. K. Xiao, J. Wang, H. Lu, B. Wu, H. P. Wu, Q. Li and C. G. Luo, Precise Determination of the Absolute Isotopic Abundance Ratio and the Atomic Weight of Chlorine in Three International Reference Materials by the Positive Thermal

Ionization Mass Spectrometer-Cs_2Cl^+-Graphite Method. *Anal. Chem.*, V. 84, p. 10350-10358, 2012.

[148] Shirodkar, P. V.; Xiao Y. K.; Hai, L. Boron and chlorine isotopic signatures of seawater in the Central Indian Ridge. *Curr. Sci.*, v. 85, p. 313 – 320, 2003.

[149] Toyama, C.; Kimura, J. I.; Chang, Q.; Vaglarov, B. S.; Kuroda, J. A new high-precision method for determining stable chlorine isotopes in halite and igneous rock samples using UV-femtosecond laser ablation multiple Faraday collector inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom*, v. 30, p. 2194-2207, 2015.

[150] Grinberg, P.; Sturgeon, R. E. Photochemical vapor generation of iodine for detection by ICP-MS. *J. Anal. At. Spectrom.*, v.24, p. 508–514, 2009.

[151] Van Acker, M. R. M. D.; Shahar, A.; Young, E. D.; Coleman, M. L. GC/Multiple Collector-ICPMS Method for Chlorine Stable Isotope Analysis of Chlorinated Aliphatic Hydrocarbons. *Anal. Chem.,* v. 78, p. 4663 – 4667, 2006.

[152] Wei, H. Z..; Jiang, S. Y.; Zhu, Z. Y.; Yang, T.; Yang, J. H.; Yan, X.; Wu, H. P.; Yang, T. L. Improvements on high-precision measurement of bromine isotope ratios by multicollector inductively coupled plasma mass spectrometry. *Talanta*, v.143, p. 302-306, 2015.

[153] Brand, W. A.; Coplen, T. B.; Vogl, J.; Rosner M.; Prohaska, T. Assessment of International Reference Materials for Stable Isotope Ratio Analysis 2013 (IUPAC Technical Report). *Pure Appl. Chem.*, v. 86, p. 425–467, 2014.

[154] Wallington, T. J.; Sulbaek Andersen, M. P.; Nielsen, O. J. Atmospheric chemistry of short-chain haloolefins: Photochemical ozone creation potentials (POCPs), global warming potentials (GWPs), and ozone depletion potentials (ODPs), *Chemosphere,* v. 129, p.135-141, 2015.

[155] Naidu, C. V.; Dharma Raju, A.; Satyanarayana, G.C.; Vinay Kumar, P.; Chiranjeevi, G.; Suchitra, P. An observational evidence of decrease in Indian summer monsoon rainfall in the recent three decades of global warming era, *Glob. and Plan. Chan.*, v. 127, p. 91-102, 2015.

[156] Goosse, H.; Renssen, H. A two-phase response of the Southern Ocean to an increase in greenhouse gas concentrations. *Geophys. Res. Lett.,* v. 28, p. 3469-3472, 2001.

[157] Francis, J. A.; Chan, W.; Leathers, D.J.; Miller, J. R.; Veron, D.E. Winter Northern Hemisphere weather patterns remember summer Arctic sea-ice extent. *Geophys. Res. Lett*., v. 36, p. 1-5, 2009.

[158] Dieckmann, G. S.; Hellmer, H. The Importance of Sea Ice: An Overview , in Sea ice: an introduction to its physics, chemistry, biology and geology, *Blackwell Sci. Oxford*. p. 1-21, 2003.

[159] Röthlisberger, R.; Crosta, X.; Abram, N. J.; Armand, L.; Wolff, E. W. Potential and limitations of marine and ice core sea ice proxies: an example from the Indian Ocean sector, *Quaternary Sci. Rev*., v. 29, p. 296-302, 2010.

[160] Lannuzel, D.; de Jong J.; Schoemann, V.; Trevena, A.; Tison, J. L.; Chou L. Development of a sampling and flow injection analysis technique for iron determination in the sea ice environment, Anal. Chim. Acta, v.556, p. 476 – 483, 2006.

[161] Notz, D.; Worster, M. G. Desalination processes of sea ice revisited, *J. Geophys. Res.,* v. 114, p.1-10, 2009.

[162] Guo, K.; Liu, X. Dynamics of meltwater quality and quantity during saline ice melting and its effects on the infiltration and desalinization of coastal saline soils, Agric. Water Manage., v. 139, p.1-6, 2014.