Combining pyrohydrolysis and ICP-MS for bromine and iodine determination in airborne particulate matter ☆

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ABSTRACT

In this work, a method based on pyrohydrolysis of airborne particulate matter (APM) collected on glass fiber filter and subsequent determination of bromine and iodine by inductively coupled plasma mass spectrometry (ICP-MS) was developed. Samples of APM collected on glass fiber filter were ground using an agate mortar, homogenized and placed on an alumina platform. Samples were mixed with solid V_2O_5 and introduced into the pyrohydrolysis system. The main operational conditions of pyrohydrolysis (absorbing solution, heating time, sample mass and use of an auxiliary reagent — V_2O_5) were evaluated. Using selected conditions, samples of APM collected on glass fiber filter (300 mg, including the glass fiber filter) were mixed with 900 mg of V_2O_5 and heated at 950 °C during 15 min in a quartz tube under water vapor and air flow. The accuracy of the proposed method was evaluated by analyte recovery tests and also by analysis of certified reference material (CRM) with a similar matrix composition (NIST 2709 and NIST 1633b). Results were in agreement better than 104 and 95% for bromine and iodine, respectively, with CRM values. The limits of quantification (LOQs) of bromine (0.05 μg g^{-1}) and iodine (0.006 μg g^{-1}) were considered appropriate for APM analysis. The pyrohydrolysis sample preparation method was considered as relatively suitable to be performed in routine analysis and provides a clean solution for analysis by ICP-MS, which is very attractive for bromine and iodine determination in APM samples.

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1. Introduction

Nowadays, the chemical characterization of airborne particulate matter (APM) has been useful for the evaluation of environmental pollution, especially in high populated areas. In general, several studies have been done in order to determine metals and metalloids collected on glass fiber filter [1–5]. On the other hand, even considering the relevance of determining halogens, the studies related to APM samples and halogen determination are relatively scarce [6–9]. This aspect is important because information about some halogens, especially bromine and iodine concentrations, is strongly required once these elements generally are present as trace contaminants in the atmosphere, participating in chemical reactions with many environmental pollutants [10]. The main source of atmospheric iodine and bromine is marine environment, in addition to soil emissions from microbiological activity and

biomass burning [11–14]. Inorganic bromine and iodine present in the atmosphere can be considered as major contributors to the chemical degradation of atmospheric O_3 in open ocean waters and thus to its oceanic dry deposition [15,16]. Furthermore, the inhalation of APM containing bromine and iodine species can cause a significant hazard to health including various respiratory symptoms, decreased lung function and cardiovascular diseases [17].

Many analytical techniques including ion selective electrode (ISE) [18–20], X-ray fluorescence spectrometry [21,22], ion chromatography (IC) [23–26], inductively coupled plasma mass spectrometry (ICP-MS) [27–31], inductively coupled plasma optical emission spectrometry (ICP OES) [32,33], and molecular absorption spectrometry [34] or atomic emission spectrometry [35] have been currently used for bromine and iodine determination in many matrices. However, the sample preparation step is critical to achieve suitable results.

In spite of the high efficiency of methods based on closed-vessels microwave-assisted acid digestion for a number of analytes, it can be considered not suitable for further halogen determination due to analyte losses [36]. These losses can be attributed to the volatility of some species (e.g. HI and HBr) that can be produced during sample digestion using concentrated nitric acid [37–39]. Additionally, the residual carbon

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content (RCC) [40,41] and high acidity can also interfere during IC, ISE and ICP-MS determination. Moreover, another well-known drawback is the iodine memory effect caused by the adsorption of iodine vapors on the walls of a nebulization chamber [42,43]. On the other hand, combustion methods using alkaline absorbing solutions have been used as an appropriate sample preparation strategy for further halogen determination. Combustion methods present the advantage to convert organic materials to the respective combustion products (e.g., CO_2 and H_2O) using only oxygen, which minimizes the risk of contamination and reduce the generation of laboratory residues [44–46]. However, these methods present some limitations related to inorganic or non-combustible matrices [47].

Pyrohydrolysis is a suitable sample preparation method for the decomposition of organic [48–52] and mainly inorganic materials [53–56], for subsequent halogen determination. Pyrohydrolysis consists in pyrolysis of samples in the presence of water vapor, followed by hydrolysis of halogens in their respective volatile halogen acids [48]. The generated volatile species can be simply condensed or collected in diluted alkaline solutions (such as NH_4OH, Na_2CO_3, $Na_2CO_3/NaHCO_3$) for subsequent determination. On this aspect, halogen absorption in diluted solutions is advantageous because these solutions can be directly introduced in IC, ISE, ICP-MS and ICP OES equipments. For inorganic matrices, especially, pyrohydrolysis method provides a convenient separation of analyte from a solid sample that reduces eventual interferences during measurement. In addition, the whole pyrohydrolysis system can be constructed with relatively simple and inexpensive materials resulting in a low cost sample preparation system and attractive to routine analysis.

In this sense, the main purpose of the present work was to develop a method for bromine and iodine determination by ICP-MS in APM collected on glass fiber filters using pyrohydrolysis for sample preparation. Pyrohydrolysis was investigated in view of the difficulties associated with bromine and iodine determination in such a complex matrix, as glass fiber filter containing APM (inorganic solid content generally >85%). In this study, maximum sample mass, use of auxiliary reagent, concentration of absorbing solution and time of pyrohydrolysis reaction were investigated. Accuracy was evaluated using certified reference materials (CRMs) with similar matrix composition and also analyte recovery tests.

2. Experimental

2.1. Instrumentation

The pyrohydrolysis system used in this work was home-made using an electrothermal furnace (Sanchis, Porto Alegre, Brazil) with an automatic temperature control (maximum temperature of 1200 °C), a quartz tube (45 cm length and 1.2 cm i.d.), an alumina platform (8 cm length and 1 cm i.d.), a water vapor generation unit, a condenser and a vessel for gaseous product retention. The reaction tube was constructed using high purity quartz and it was positioned inside the electrothermal furnace. A peristaltic pump (Minipuls, Gilson, Middleton, USA) equipped with a Tygon tube (0.76 mm i.d.) was used to carry water to a ceramic capillary (0.5 mm i.d.) that was connected to the inlet of the quartz tube using a silicone stopper. The outlet of the ceramic capillary was positioned in the entrance of the furnace for in situ water vapor generation. Air was used to transport the water vapor through the quartz tube and the gaseous products to the condenser. Air flow rate was set at 200 mL min^{-1} [50]. The outlet of the quartz tube was connected to a glass serpentine immersed into an ice bath in order to condense the gaseous products from pyrohydrolysis reaction. The condensed solution was collected in a polypropylene vessel containing 10 mL of absorbing solution. A small portion of quartz wool was inserted in the outlet of quartz tube to avoid that solid particles eventually released from samples could be transported to the condenser.

In the present work, the determination of bromine and iodine in absorbing solution obtained after pyrohydrolysis was performed using an inductively coupled plasma mass spectrometer (Perkin-Elmer Sciex, Model Elan DRC II, Thornhill, Canada), equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Merbourne, Australia) and a quartz torch with a quartz injector tube (2 mm i.d.). Argon 99.996% (White Martins, São Paulo, Brazil) was used for plasma generation, nebulization and as auxiliary gas. The following operational conditions were used: a RF power of 1400 W, a plasma gas flow rate of 15 L min^{-1}, an auxiliary gas flow rate of 1.2 L min^{-1} and a nebulizer gas flow rate of 1.08 L min^{-1}. The isotopes monitored were 79 and 127 for bromine and iodine, respectively. Platinum sampler and skimmer cones were used throughout.

2.2. Samples, reagent and standards

Airborne particulate matter samples were collected in different places of Buenos Aires city, Argentina, on ash-free glass-fiber filters using a high-volume air sampler (SIBATA, HV 1000F, Japan) with a PM-10 sampling head. The sampling flow rate was 1000 L min^{-1} and the average total sampling time was 24 h, resulting in an average air volume filtered during 24 h of 1440 m^3. Filter containing the APM samples were ground in an agate mortar and further dried in an oven at 60 °C. Filter "A" was used for the evaluation of absorbing solution, sample mass, V_2O_5 mass and time for pyrohydrolysis method development.

In view of the lack of certified reference materials of APM the accuracy was evaluated using the following CRMs with a similar composition: NIST 2709 (San Joaquin soil, I = 5 µg g^{-1}) and NIST 1633b (constituent elements in coal fly ash, Br = 2.9 µg g^{-1}). Moreover, recovery tests of Br and I were also performed. In this test, solid sample "D" (300 mg) was spiked with 10 µL of solution containing 60 mg L^{-1} of Br and 30 mg L^{-1} of I.

All the reagents used in this work were of analytical grade (Merck, Darmstadt, Germany). Solutions were prepared using distilled and deionized water that was further purified using a Milli-Q system (18.2 MΩ cm, Millipore, Billerica, MA). Vanadium pentoxide (V_2O_5) was used as auxiliary for pyrohydrolysis and it was obtained (and simultaneously purified) by heating ammonium vanadate (NH_4VO_3) in a platinum crucible during 4 h at 550 °C. Absorbing solutions were prepared from concentrated ammonium hydroxide (28–30%). Working analytical solutions for ICP-MS analysis were prepared before use by serial dilution of solutions containing 1000 mg L^{-1} bromine and iodine. Iodine and bromine stock reference solutions were prepared by the dissolution of potassium iodide and potassium bromide in water. Calibration curve for bromine was checked by serial dilution of solution containing 10 mg kg^{-1} of multielement anion standard solution (Fluka, Buchs, Switzerland) in water. A solution of 10% (v/v) nitric acid (65%) from Merck (Darmstadt, Germany) was used for material cleaning.

2.3. Pyrohydrolysis proposed method

Sample mass ranging from 50 to 300 mg was directly weighed in alumina platform and mixed with V_2O_5 (300 to 1200 mg). The platform containing the sample or sample mixed with V_2O_5 was introduced into the quartz reactor tube and the furnace was heated up to 950 °C. Pyrohydrolysis heating time between 5 and 20 min was evaluated. Water was pumped through the heated ceramic capillary (at a flow rate of 0.5 mL min^{-1}) for water vapor generation. The air flow-rate (used as carrier gas) was set at 200 mL min^{-1} [50]. The gaseous products of pyrohydrolysis were collected in a vessel containing 10 mL of absorption solution. The absorbing solutions investigated in this work were diluted with water up to 25 mL before bromine and iodine determination by ICP-MS. After each run, the alumina platform was soaked in a solution of 10% HNO_3 for 2 h.

3. Results and discussion

Initial studies, using filter sample "A", were performed in order to establish the pyrohydrolysis conditions used to digest glass fiber filter samples containing APM. Sample mass, the mass of V_2O_5, pyrohydrolysis reaction time and concentration of absorption solution were evaluated.

3.1. Effect of V_2O_5 and sample mass

Auxiliary reagents are commonly used in pyrohydrolysis to help halogen release from refractory matrices and one of the most used is V_2O_5. This reagent has been used due to the relatively low melting point, about 750 °C, and suitability for different matrices. Moreover, this reagent can be produced in high purity from ammonium metavanadate. It results in lower blank values that are important to achieve low detection limits [57,58].

Initial studies for the digestion of APM collected on glass fiber filter were performed using sample "A" (50 to 300 mg) without the use of an auxiliary reagent. In this condition, even when only 50 mg of samples were used the recoveries obtained for bromine and iodine were not quantitative. The results obtained for bromine and iodine in this study without using V_2O_5 were about 35% lower when compared with the results obtained using this reagent.

In order to evaluate the effect of V_2O_5 in pyrohydrolysis of APM samples for bromine and iodine determination, subsequent tests were performed using 300 mg of sample "A" and increasing the amount of V_2O_5 up to 1200 mg. For these experiments, temperature, air flow rate, water flow rate, reaction time and NH_4OH concentration were selected as 950 °C, 200 mL min^{-1}, 0.5 mL min^{-1}, 30 min and 100 mmol L^{-1}, respectively according to a previous work [50]. The respective results are shown in Fig. 1.

A mixture of 300 mg of sample + 300 or 600 mg of V_2O_5, presented recoveries lower than those obtained when 300 mg of sample was mixed with 900 or 1200 mg (Fig. 1). It is important to mention that the results obtained using 900 or 1200 mg V_2O_5 presented no statistical difference (t-test, 95% of confidence level). Moreover, it was observed that the RSDs were improved (<5%) with the increase of V_2O_5 amount. Furthermore, 900 mg of V_2O_5 was mixed with 50, 100 or 200 mg of APM (sample "A") sample and no statistical difference was observed. Therefore, a mixture of 300 mg of sample + 900 mg of V_2O_5 was used for subsequent experiments. It is important to mention that the use of V_2O_5 did not increase blank values for bromine and iodine, which is important to assure low LODs. In addition, all blank tests were performed using the same glass fiber filter used to collect APM samples and blank values obtained for bromine and iodine were negligible. Another important fact is that even using V_2O_5, after pyrohydrolysis APM digestion, a residue of
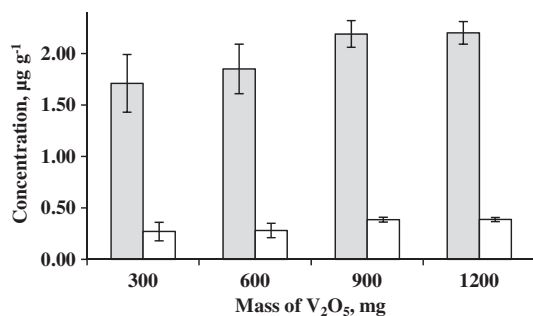
inorganic matrix was observed on the alumina platform and it was removed during the cleaning step of the pyrohydrolysis system.

3.2. Evaluation of absorbing solution

It has been widely discussed in the literature that the choice of absorbing solution in pyrohydrolysis is important to achieve suitable recoveries [23,59]. It is dependent on the nature of analytes and should be compatible with the selected determination technique. Particularly, in the case of halogen determination, absorbing solution should be carefully optimized due to the risk of analyte losses. In this sense, NH_4OH solution (10 to 100 mmol L^{-1}) was evaluated.

In the present work, a systematic study using 10 mL of ammonium, hydroxide (10, 25, 50 or 100 mol L^{-1}) was carried out in order to evaluate the suitability of absorbing solution for bromine and iodine after pyrohydrolysis digestion. Ammonium hydroxide was evaluated in view of its relatively high purity and suitability for bromine and iodine determination by ICP-MS. Spike recoveries in the APM samples were evaluated for each absorbing solution. The results obtained in this study are shown in Fig. 2.

With use of 10 mmol L^{-1} NH_4OH solution, recoveries better than 93 and 71% were obtained for bromine and iodine, respectively. However, the RSDs were of 20 and 25% for bromine and iodine, respectively. On the other hand, when 25 mmol L^{-1} NH_4OH solution was used the recoveries were better than 99% for both analytes and RSDs were between 8 and 10% for bromine and iodine, respectively. Better results were obtained when 50 or 100 mmol L^{-1} NH_4OH solution was used (recoveries close to 100% and RSD lower than 10% for both analytes). In this sense, a solution of 50 mmol L^{-1} NH_4OH was chosen as absorbing solution for subsequent tests using pyrohydrolysis for the digestion of APM collected on the glass fiber filter. It is important to point out that the use of diluted alkaline solution (50 mmol L^{-1} NH_4OH) reduces the memory effect on ICP-MS determination step [60,61].

3.3. Evaluation of pyrohydrolysis time

Pyrohydrolysis reaction time must be enough for complete bromine and iodine release from the sample matrix and to decrease memory effects. Therefore, the time necessary for pyrohydrolysis can change according to the sample matrix, chemical forms of analytes, analyte concentration and also due to the characteristics of the pyrohydrolysis system employed [54,55,62]. The time of pyrohydrolysis reaction was evaluated in the range of 5 to 20 min using sample "B" (300 mg of sample + 1200 mg of V_2O_5; 950 °C; 50 mmol L^{-1} NH_4OH as absorbing solution). The results are shown in Fig. 3.

In this study, it was observed that with 5 min of heating, only 62 and 69% of bromine and iodine, respectively were released from the sample
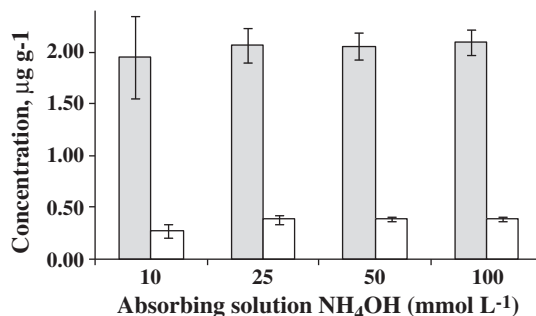

Fig. 1. Effect of V_2O_5 on bromine (□) and iodine (□) release from APM collected on glass fiber filter using 300 mg of sample (filter "A") + V_2O_5. Pyrohydrolysis conditions: temperature of 950 °C, 100 mmol L^{-1} NH_4OH as absorbing solution, reaction time: 30 min, air flow rate: 200 mL min^{-1}, and water flow rate: 0.5 mL min^{-1}. Determination by ICP-MS (error bars are the standard deviation; n = 3).

Fig. 2. Influence of absorbing solutions for bromine (□) and iodine (□) determination in APM collected on glass fiber filter (sample "A"). Pyrohydrolysis temperature: 950 °C, reaction time: 30 min, air flow rate: 200 mL min^{-1}, water flow rate: 0.5 mL min^{-1}, determination by ICP-MS (error bars are the standard deviation; n = 3).
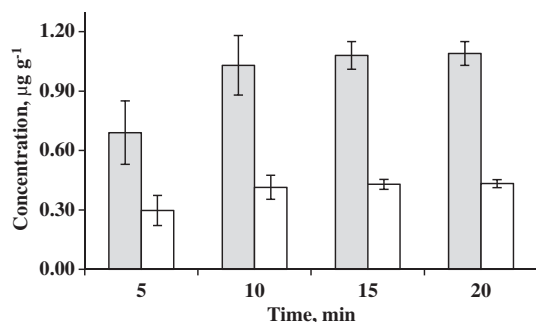
Fig. 3. Effect of time of pyrohydrolysis on bromine (▨) and iodine (☐) release from APM collected on glass fiber filter. Pyrohydrolysis conditions: using 300 mg of sample (filter "B") + 900 mg of V_2O_5, temperature of 950 °C, 50 mmol L^{-1} NH_4OH as absorbing solution, reaction time: 15 min, air flow rate: 200 mL min^{-1}, and water flow rate: 0.5 mL min^{-1}. Determination by ICP-MS (error bars are the standard deviation; n = 3).

(Fig. 3). Relative standard deviation was higher than 23 and 26% for bromine and iodine, respectively. For 10 min of heating the recovery was better than 95% but the RSD was higher than 15% for both analytes. On the other hand, 15 or 20 min of heating time allowed the quantitative release of bromine and iodine from APMs collected on the glass fiber filter. The results presented no statistical difference (t-test, 95% of confidence level). Moreover, the RSD for 15 min of reaction was around 8% for both analytes, and for 20 min of reaction, a RSD lower than 7% was obtained for both elements. Therefore, 15 min was selected for further studies. This time could be considered suitable for routine analysis of APM collected on the glass fiber filter, considering that four samples can be prepared in 1 h. It is important to mention that no memory effects were observed using 15 min of pyrohydrolysis, showing that the analytes were completely released from the sample and carried to the collection flask.

3.4. Bromine and iodine determination by ICP-MS in APM collected on glass fiber filter after pyrohydrolysis digestion

The proposed pyrohydrolysis method was applied to the digestion of four samples of APM collected on a glass fiber filter. Bromine and iodine were determined by ICP-MS. Pyrohydrolysis conditions were 300 mg of sample + 900 mg of V_2O_5, 10 mL of 50 mmol L^{-1} NH_4OH, 15 min at 950 °C. The results are shown in Table 1.

According to the results showed in Table 1, the concentrations of bromine and iodine in APM collected on glass fiber filter samples digested by pyrohydrolysis were in the range of 2.17 to 3.51 µg g^{-1} of bromine and 0.384 to 0.687 µg g^{-1} of iodine (determination by ICP-MS).

Accuracy of the proposed method also was evaluated by recovery tests using the spike of bromine and iodine in sample "D" and subsequent analyte determination by ICP-MS.

Recovery tests for Br and I in APM samples were performed by the addition of the equivalent of 2 µg g^{-1} for Br and 1 µg g^{-1} for I. Recoveries obtained for both analytes using pyrohydrolysis were better than 97%.

Table 1
Concentration of bromine and iodine in APM collected on glass fiber filter. Determination by ICP-MS after pyrohydrolysis method (µg g^{-1}, n = 3).

Sample	Concentration, µg g^{-1}	
	Br	I
A	2.03 ± 0.15	0.398 ± 0.028
B	1.08 ± 0.08	0.433 ± 0.035
C	1.60 ± 0.14	0.407 ± 0.027
D*	3.51 ± 0.28	0.687 ± 0.051
NIST 2709	–	4.75 ± 0.26
NIST 1633b	3.02 ± 0.18	–

Informed values for CRMs: NIST 2709 (I: 5 µg g^{-1}) and NIST 1633b (Br: 2.9 µg g^{-1}).
* Addition equivalent of 2 µg g^{-1} for Br and 1 µg g^{-1} for I.

Furthermore, the RSD was lower than 6% for bromine and lower than 5% for iodine.

In addition, the accuracy of the pyrohydrolysis method was evaluated by performing the digestion of CRMs NIST 2709 and NIST 1633b and further bromine and iodine determination by ICP-MS. The results for bromine and iodine by ICP-MS were in agreement with informed values of CRMs (agreement was better than 104 and 95% for bromine and iodine, respectively), as shown in Table 1.

The limit of detection (LOD, 3σ, n = 10) by the proposed method was 0.05 and 0.006 µg g^{-1} respectively for bromine and iodine. Low blank levels, good precision, high sensitivity of ICP-MS and low dilution factor were the key parameters to achieve low LODs for bromine and iodine.

4. Conclusions

Pyrohydrolysis was used for the first time for sample preparation of APM collected on glass fiber filter for bromine and iodine determination by ICP-MS. The pyrohydrolysis system is relatively easy to be built in laboratories and is feasible for routine analysis. Using the optimized pyrohydrolysis conditions, quantitative recoveries of bromine and iodine were obtained after 15 min of pyrohydrolysis at 950 °C and using a diluted solution (50 mmol L^{-1} NH_4OH) for analyte absorption. Digests could be analyzed by techniques including ICP-MS, ICP-OES or IC. The proposed pyrohydrolysis system allows the decomposition of up to 300 mg of sample, combining safety, relatively high sample throughput, matrix separation and low cost sample preparation step. A suitable LOD was obtained for both analytes: 0.05 and 0.006 µg g^{-1} for Br and I, respectively. Therefore, pyrohydrolysis can be recommended for bromine and iodine determination by ICP-MS in APMs collected on a glass fiber filter.

Acknowledgments

References

[1] S. Atilgan, S. Akman, A. Baysal, Y. Bakircioglu, T. Szigeti, M. Óvári, G. Záray, Monitoring of Pd in airborne particulates by solid sampling high-resolution continuum source electrothermal atomic absorption spectrometry, Spectrochim. Acta B 70 (2012) 33–38.

[2] R.G.O. Araujo, F. Vignola, I.N.B. Castilho, D.L.G. Borges, B. Welz, M.G.R. Vale, P. Smichowski, S.L.C. Ferreira, H. Becker-Ross, Determination of mercury in airborne particulate matter collected on glass fiber filters using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sampling, Spectrochim. Acta B 66 (2011) 378–382.

[3] M. Savio, R.A. Olsina, L.D. Martinez, P. Smichowski, R.A. Gil, Determination of Pb in airborne particulate matter with a heavy matrix of silicon by SR-ETAAS, Microchem. J. 96 (2010) 243–246.

[4] B. Bocca, S. Caimi, P. Smichowski, D. Gomez, S. Caroli, Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina, Sci. Total Environ. 358 (2006) 255–264.

[5] I.N.B. Castilho, B. Welz, M.G.R. Vale, J.B. Andrade, P. Smichowskid, A.A. Shaltout, L. Colares, E. Carasek, Comparison of three different sample preparation procedures for the determination of traffic-related elements in airborne particulate matter collected on glass fiber filters, Talanta 88 (2012) 689–695.

[6] Y. Gao, M. Sun, X. Wu, Y. Liu, Y. Guo, J. Wu, Concentration characteristics of bromine and iodine in aerosols in Shanghai, China, Atmos. Environ. 44 (2010) 4298–4302.

[7] X. Si-Qi, X. Zhou-Qing, L. Wei, Y. Hong-Xia, L. Bing, Extraction and determination of total bromine, iodine, and their species in atmospheric aerosol, Chin. J. Anal. Chem. 38 (2010) 219–224.

[8] A.R. Baker, D. Thompson, M.L.A.M. Campos, S.J. Parry, T.D. Jickells, Iodine concentration and availability in atmospheric aerosol, Atmos. Environ. 34 (2000) 4331–4336.

[9] M. Sun, Y. Gao, B. Wei, X. Wu, Determination of iodine and bromine in coal and atmospheric particles by inductively coupled plasma mass spectrometry, Talanta 81 (2010) 473–476.

[10] L.J. Carpenter, S.M. MacDonald, M.D. Shaw, R. Kumar, R.W. Saunders, R. Parthipan, J. Wilson, J.M.C. Plane, Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine, Nature Geoscience, DOI: http://dx.doi.org/10.1038/NGEO1687 .

[11] L.J. Carpenter, Iodine in the marine boundary layer, Chem. Rev. 103 (2003) 4953–4962.

[12] A. Saiz-Lopez, J.M.C. Plane, G. McFiggans, P.I. Williams, S. Ball, M. Bitter, R.L. Jones, C. Hongwei, T. Hoffmann, Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation, Atmos. Chem. Phys. 6 (2006) 883–895.

[13] R. Sander, W.C. Keene, A.A.P. Pszenny, R. Arimoto, G.P. Ayers, E. Baboukas, J.M. Cainey, P.J. Crutzen, R.A. Duce, G. Honninger, B.J. Huebert, W. Maenhaut, N. Mihalopoulos, V.C. Turekian, R.V. Dingenen, Inorganic bromine in the marine boundary layer: a critical review, Atmos. Chem. Phys. 3 (2003) 1301–1336.

[14] F. Laturnus, B. Giese, C. Wiencke, F. Adams, Low molecular-weight organoiodine and organobromine compounds released by polar macroalgae the influence of abiotic factors, Fresenius J. Anal. Chem. 368 (2000) 297–302.

[15] T.X. Wang, M.D. Kelley, J.N. Cooper, R.C. Beckwith, D.W. Margerum, Equilibrium, kinetic, and UV-spectral characteristics of chloride, bromine and chloride species, Inorg. Chem. 33 (1994) 5872–5878.

[16] R.J. Salawitch, Biogenic bromine, Nature 439 (2006) 275–277.

[17] Morawska, Salthammer, Indoor Environment: Airborne Particles and Settled Dust, Wiley-VCH, 2004.

[18] S.S.M. Hassan, Microdetermination of chlorine and bromine in some organic compounds by ion-selective electrodes, Z. Anal. Chem. 266 (1973) 272–274.

[19] W. Potman, E.A.M.F. Dahmen, Application of ion-selective electrodes for the licrodetermination of chlorine and bromine in volatile organic compounds, Mikrochim. Acta [Wien] (1972) 303–312.

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

[21] I. Varga, Iodine determination in dietary supplement products by TXRF and ICP-AES spectrometry, Microchem. J. 85 (2007) 127–131.

[22] J. An, H. Jung, Jo-Ri Bae, Hye-On Yoon, J. Seo, 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 B 91 (2014) 1–4.

[23] E.M.M. Flores, M.F. Mesko, D.P. Moraes, J.S.F. Pereira, P.A. Mello, J.S. Barin, G. Knapp, Determination of halogens in coal after digestion using the microwave-induced combustion technique, Anal. Chem. 80 (2008) 1865–1870.

[24] D.P. Moraes, J.S.F. Pereira, L.O. Diehl, M.F. Mesko, V.L. Dressler, J.N.G. Paniz, G. Knapp, E.M.M. Flores, Evaluation of sample preparation methods for elastomer digestion for further halogens determination, Anal. Bioanal. Chem. 397 (2010) 563–570.

[25] Y. Noguchia, L. Zhang, T. Marutaa, T. Yamanec, N. Kibad, Simultaneous determination of fluorine, chlorine and bromine in cement with ion chromatography after pyrolysis, Anal. Chim. Acta. 640 (2009) 106–109.

[26] P.A. Blackwell, M.R. Cave, A.E. Davis, S.A. Malik, Determination of chlorine and bromine in rocks by alkaline fusion with ion chromatography detection, J. Chromatogr. A 770 (1997) 93–98.

[27] B. Meermann, A. Hulstaert, A. Laenen, C.V. Looveren, M. Vliegen, F. Cuyckens, F. Vanhaecke, HPLC/ICP-MS in combination with "reverse" online isotope dilution in drug metabolism studies, Anal. Chem. 84 (2012) 2395–2401.

[28] M.F. Mesko, C.A. Hartwig, C.A. Bizzi, J.S.F. Pereira, P.A. Mello, E.M.M. Flores, Sample preparation strategies for bioinorganic analysis by inductively coupled plasma mass spectrometry, Int. J. Mass Spectrom. 307 (2011) 123–136.

[29] M.F. Mesko, P.A. Mello, C.A. Bizzi, V.L. Dressler, G. Knapp, E.M.M. Flores, Iodine determination in food by inductively coupled plasma mass spectrometry after digestion by microwave-induced combustion, Anal. Bioanal. Chem. 398 (2010) 1125–1131.

[30] Kai-en Wang, Shiuh-Jen Jiang, Determination of iodine and bromine compounds by ion chromatography/dynamic reaction cell inductively coupled plasma mass spectrometry, Anal. Sci. 24 (2008) 509–514.

[31] V.L. Dressler, F.G. Antes, C.M. Moreira, D. Pozebon, F.A. Duarte, As, Hg, I, Sb, Se and Sn speciation in body fluids and biological tissues using hyphenated-ICP-MS techniques: a review, Int. J. Mass Spectrom. 307 (2011) 149–162.

[32] A.L.H. Müller, C.A. Bizzi, J.S.F. Pereira, M.F. Mesko, D.P. Moraes, E.M.M. Flores, E.I. Muller, Bromine and chlorine determination in cigarette tobacco using microwave-induced combustion and inductively coupled plasma optical emission spectrometry, J. Braz. Chem. Soc. 22 (2011) 1649–1655.

[33] J. Naozuka, M.A.M.S. Veiga, P.V. Oliveira, E. Oliveira, Determination of chlorine, bromine and iodine in milk samples by ICP-OES, J. Anal. At. Spectrom. 18 (2003) 917–921.

[34] B. Welz, F.G. Lepri, R.G.O. Araujo, S.L.C. Ferreira, Mao-Dong Huang, M. Okruss, H. Becker-Ross, Determination of phosphorus, sulfur and the halogens using high-temperature molecular absorption spectrometry in flames and furnaces — a review, Anal. Chim. Acta. 647 (2009) 137–148.

[35] G.L. Donati, J.A. Nóbrega, C.C. Nascentes, B.T. Jones, Indirect determination of iodide by tungsten coil atomic emission spectrometry, Microchem. J. 93 (2009) 242–246.

[36] E.C. Figueiredo, J.C. Dias, L.T. Kubota, M. Korn, P.V. Oliveira, M.A.Z. Arruda, Influence of microwave heating on fluoride, chloride, nitrate and sulfate concentrations in water, Talanta 85 (2011) 2707–2710.

[37] Y. Gélinas, A. Krushevska, R.M. Barnes, Determination of total iodine in nutritional and biological samples by ICP-MS following their combustion within an oxygen stream, Anal. Chem. 70 (1998) 1021–1025.

[38] G. Knapp, B. Maichin, P. Fecher, S. Hasse, P. Schramel, Iodine determination in biological materials — options for sample preparation and final determination, Fresenius J. Anal. Chem. 362 (1998) 508–513.

[39] E.A. Vtorushina, A.I. Saprykin, G. Knapp, Use of oxidation and reduction vapor generation for lowering the detection limits of iodine in biological samples by inductively coupled plasma atomic emission spectrometry, J. Anal. Chem. 64 (2009) 129–135.

[40] G. Grindlay, J. Mora, M. Loos-Vollebregt, F. Vanhaecke, A systematic study on the influence of carbon on the behavior of hard-to-ionize elements in inductively coupled plasma-mass spectrometry, Spectrochim. Acta B 86 (2013) 42–49.

[41] S.T. Gouveia, F.V. Silva, L.M. Costa, A.R.A. Nogueira, Determination of residual carbon by inductively-coupled plasma optical emission spectrometry with axial and radial view configurations, Anal. Chim. Acta. 445 (2001) 269–275.

[42] P. Grinberg, R.E. Sturgeon, Ultra-trace determination of iodine in sediments and biological material using UV photochemical generation-inductively coupled plasma mass spectrometry, Spectrochim. Acta B 64 (2009) 235–241.

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

[44] Z. Mester, R. Sturgeon, Sample Preparation for Trace Element Analysis, vol. XLI, Elsevier, Amsterdam, The Netherlands, 2003.

[45] M. Stoeppler, Sampling and Sample Preparation, Springer-Verlag, Berlin, Germany, 1997.

[46] Z. Sulcek, P. Povondra, Methods of Decomposition In Inorganic Analysis, CRC Press, Boca Raton, Florida, 1989.

[47] E.M.M. Flores, J.S. Barin, M.F. Mesko, G. Knapp, Sample reparation techniques based on combustion reactions in closed vessels — a brief overview and recent applications, Spectrochim. Acta B 62 (2007) 1051–1064.

[48] V.L. Dressler, D. Pozebon, E.L.M. Flores, J.N.G. Paniz, E.M.M. Flores, Determination of fluoride in coal using pyrohydrolysis for analyte separation, J. Braz. Chem. Soc. 14 (2003) 334–338.

[49] F.G. Antes, M.F.P. Santos, R.C.L. Guimarães, J.N.G. Paniz, E.M.M. Flores, V.L. Dressler, Heavy crude oil sample preparation by pyrohydrolysis for further chlorine determination, Anal. Methods 3 (2011) 288–293.

[50] F.G. Antes, J.S.F. Pereira, M.S.P. Enders, C.M.M. Moreira, E.I. Müller, E.M.M. Flores, V.L. Dressler, Pyrohydrolysis of carbon nanotubes for Br and I determination by ICP-MS, Microchem. J. 101 (2012) 54–58.

[51] T. Shinoda, N. Miyamoto, T. Kuromoto, K. Ito, H. Morikawa, Y. Okamoto, T. Fujiwara, T. Hirokawa, Pyrohydrolysis coupled to ion chromatography for sensitive determination of iodine in food-related materials, Anal. Lett. 45 (2012) 862–871.

[52] B. Peng, D. Wu, J. Lai, H. Xiao, P. Li, Simultaneous determination of halogens (F, Cl, Br, and I) in coal using pyrohydrolysis combined with ion chromatography, Fuel 94 (2012) 629–631.

[53] Q. Wang, A. Makishima, E. Nakamura, Determination of fluorine and chlorine by pyrohydrolysis and ion chromatography: comparison with alkaline fusion digestion and ion chromatography, Geostand. Geoanal. Res. 34 (2010) 175–183.

[54] Y. Noguchi, L. Zhang, T. Maruta, T. Yamane, N. Kiba, Simultaneous determination of fluorine, chlorine and bromine in cement with ion chromatography after pyrolysis, Anal. Chim. Acta. 640 (2009) 106–109.

[55] T. Taflik, F.A. Duarte, E.L.M. Flores, F.G. Antes, J.N.G. Paniz, E.M.M. Flores, V.L. Dressler, Determination of bromine, fluorine and iodine in mineral supplements using pyrohydrolysis for sample preparation, J. Braz. Chem. Soc. 23 (2012) 488–495.

[56] H. Balcone-Boissard, A. Michel, B. Villemant, Simultaneous determination of fluorine, chlorine, bromine and iodine in six geochemical reference materials using pyrohydrolysis, ion chromatography and inductively coupled plasma-mass spectrometry, Geostand. Geoanal. Res. 33 (2009) 477–485.

[57] B. Nebesar, The high-temperature analytical uses of vanadium (V) oxide, Talanta 25 (1978) 185–194.

[58] J.E. Rae, S.A. Malik, The determination of iodine in geochemical samples: the use of pyrohydrolytic decomposition, Chemosphere 33 (1996) 2121–2128.

[59] J.S.F. Pereira, D.P. Moraes, F.G. Antes, L.O. Diehl, M.F.P. Santos, R.C.L. Guimarães, T.C.O. Fonseca, V.L. Dressler, E.M.M. Flores, Determination of metals and metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion, Microchem. J. 96 (2010) 4–11.

[60] D.L. Rocha, A.D. Batista, F.R.P. Rocha, G.L. Donati, J.A. Nóbrega, Greening sample preparation in inorganic analysis, Trends Anal. Chem. 45 (2013) 79–92.

[61] R.E. Santelli, M.A. Bezerra, J.C. Afonso, M.F.B. Carvalho, E.P. Oliveira, A.S. Freire, Environmental analysis, in: Miguel De la Guardia, S. Garrigues (Eds.), Handbook of Green Analytical Chemistry, vol. 22, Wiley Blackwell, Oxford, 2011, pp. 475–503.

[62] F.A. Duarte, E.R. Pereira, E.L.M. Flores, E.I. Muller, E.M.M. Flores, V.L. Dressler, Determinação espectrofotométrica de cloreto em cimento após preparo de amostra por piroidrólise, Quim. Nova 36 (2013) 716–719.