

Determination of Bromine, Fluorine and Iodine in Mineral Supplements using Pyrohydrolysis for Sample Preparation

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Neste trabalho foi utilizada a piroidrólise para a decomposição de suplemento mineral utilizado na nutrição animal, para a posterior determinação de F, Br e I. Flúor foi determinado por potenciometria utilizando eletrodo íon-seletivo para fluoreto, enquanto que Br e I foram determinados por espectrometria de massa com plasma indutivamente acoplado. Os principais parâmetros que influenciam a piroidrólise foram investigados e, após a devida avaliação dos mesmos, foram fixadas as seguintes condições: a temperatura do reator em 1000 °C durante 10 min; a proporção entre a massa de amostra e a massa de acelerador em 1 + 5 e a vazão do gás carreador em 200 mL min⁻¹. A exatidão do método foi avaliada usando teste de recuperação do analito e análise de materiais de referência certificados de rocha fosfática e de solo. O método foi aplicado para análise de suplemento mineral. Os limites de quantificação foram de 16, 0,3 e 0,07 µg g⁻¹ para F, Br e I, respectivamente. Assim, usando-se um método relativamente simples e de baixo custo é possível a decomposição de até 5 amostras por hora. Portanto, a piroidrólise pode ser usada como um método de rotina para o preparo de amostra de suplemento mineral para a determinação de F, Br e I.

Pyrohydrolysis was employed for mineral supplements decomposition prior to F, Br and I determination. Fluoride determination was carried out by potentiometry using a fluoride-ion selective electrode, whereas Br and I were determined by inductively coupled plasma mass spectrometry. The main parameters that influence on pyrohydrolysis were investigated. After evaluation, the following conditions were established: reactor temperature of 1000 °C during 10 min; sample plus accelerator mass ratio of 1 + 5 and carrier gas (air) flow rate of 200 mL min⁻¹. The accuracy of the proposed method was evaluated by analyte recovery tests and analysis of certified reference materials of phosphate rock and soil. Commercial mineral supplement samples were analyzed. The limits of quantification were 16, 0.3 and 0.07 µg g⁻¹ for F, Br and I, respectively. By using a relatively simple and low cost pyrohydrolysis system up to 5 samples can be processed per hour. The developed sample preparation procedure can be routinely employed for F, Br and I determination in mineral supplements.

Keywords: pyrohydrolysis, halogens determination, mineral supplement

Introduction

Several elements are essential for animals growing and breeding. Those elements required in high amounts are called macronutrients (Ca, Cl, K, P, Mg, Na, and S) and those elements required in low concentrations are

called micronutrients (Co, Cu, Fe, I, Mn, Mo, Se, Zn, and eventually Cr and F are included in this group).¹ The main functions of essential elements in the organism are associated to the structural composition of body and enzymatic and hormonal processes.

Although F usually increases the strength of bones and teeth, this element is generally not considered as essential.¹ Fluorine is usually present as a contaminant since it is

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naturally found in phosphate rocks used in animal feed.² Fluorine has an ambiguous effect on the animal health; while at low concentrations it prevents dental caries, at high concentration it can damage bones and even the teeth. Minor morphologic lesions were observed in young cattle receiving 20 mg kg⁻¹ F *per day*. The maximum tolerable F content was set to 40 mg kg⁻¹. Bromine is a non-essential element that is usually toxic to animals. The exposure to relatively high doses of Br may lead to liver and kidney injury within a short period. Low coordination and growth decrease of hepatic function and damages on intestine can be observed if animals are exposed to bromine compounds. Besides, bromine can be converted into bromide, which attacks the central nervous system when concentrations higher than 1 to 2 g day⁻¹ are ingested.³ On the other hand, iodine is an essential element for several animals, mainly for the synthesis of the thyroid hormones (thyroxine and triiodothyronine) that regulate metabolism. Because iodine is naturally found at low concentrations, the element supplementation is recommended (0.4 to 1.3 mg day⁻¹, the maximum is 10 mg day⁻¹).⁴ Deleterious effect caused by iodine has been reported in dairy cows that received 50 mg of iodine *per day*.⁵ Therefore, taking into account the adverse effects caused by Br, F, and I in animals, the concentration of these elements in mineral supplements have to be controlled.

Techniques such as spectrophotometry,⁶ potentiometry using ion-selective electrode (ISE),⁷ ion chromatography,^{8,9} inductively coupled plasma optical emission spectrometry (ICP OES),^{10,11} and inductively coupled plasma mass spectrometry (ICP-MS)¹²⁻¹⁵ can be employed for Br, I and F determination. Fluorine can also be determined by graphite furnace molecular absorption spectrometry,¹⁶ ion chromatography^{10,17} and capillary electrophoresis.¹⁸ It is worth citing that ICP-MS is a powerful technique for halogens determination (except for fluorine) due to the high sensitivity observed.¹⁹ However, the high salt content in mineral supplements used for animal nutrition causes serious interferences and, therefore, matrix separation is necessary.^{20,21}

Sample preparation is usually the bottleneck in halogen determination by ICP-MS, due to memory effects caused by high volatility of halogens in acidic solutions.²²⁻²⁴ Therefore, alkaline fusion,²⁰ dilution or dispersion in alkaline solution, distillation (for fluorine), combustion in bombs,²⁵ microwave-induced combustion (MIC)^{9,26-29} and pyrohydrolysis^{7,17,30-32} are used for sample preparation.

Pyrohydrolysis is a simple alternative for decomposition of organic^{7,19,31,33} and inorganic³⁴⁻³⁶ materials when halogens determination is intended. The main advantages are the possibility of matrix separation and the use of a diluted alkaline solution for analytes absorbing. Application of

pyrohydrolysis for analytical purposes was first investigated by Warf *et al.*³⁷ In their experiment, water steam passed over a heated sample in a platinum assembly furnace was used. Volatile Cl and F species formed during pyrohydrolysis reaction were condensed and further determined by titration. The pyrohydrolysis reaction can be accelerated in presence of U, V, Al, and W oxides. The volatile halogen species evolved can be simply condensed^{33,37} or collected in alkaline solutions such as Na₂CO₃, Na₂CO₃/NaHCO₃ and (NH₄)₂CO₃.^{24,31}

The purpose of the present work was to develop a method for F, Br and I determination in mineral supplements using pyrohydrolysis for sample preparation. Pyrohydrolysis was investigated in view of the difficulties associated with F, Br and I determination in such complex matrix. The main features of the proposed method are the simplicity of sample preparation, low analyte losses and the relatively high sensitivity and sample throughput of ICP-MS for Br and I determination. Fluorine determination was performed by potentiometry because this element cannot be measured by ICP-MS.

Experimental

Pyrohydrolysis apparatus

The pyrohydrolysis apparatus employed is described elsewhere,^{7,33} excepting the collector flask. In the present work two flasks were used and connected by a polytetrafluoroethylene (PTFE) tube. The pyrohydrolysis apparatus employed is shown in Figure 1.

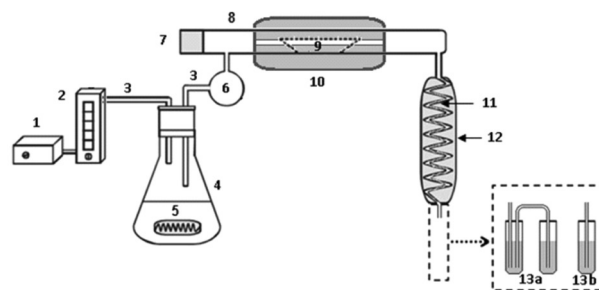


Figure 1. Pyrohydrolysis apparatus used for preparation of mineral supplement samples prior to F, Br and I determination. 1) air pump; 2) flow meter (0.1 to 1.0 L min⁻¹); 3) PTFE tubes (i.d. = 5 mm); 4) 500 mL Erlenmeyer flask containing water; 5) heating element; 6) water trap; 7) silicone rubber; 8) quartz tube (L = 15 cm, i.d. = 2 cm); 9) quartz boat (L = 2 cm, width = 1 cm, depth = 0.5 cm); 10) electrothermal furnace; 11) condenser (PTFE tube, L = 50 cm, i.d. = 0.2 cm); 12) ice bath (1 L flask, filled up with ice and water); 13a) two graduated (15 mL) polypropylene collector vials containing absorbing solution; 13b) graduated (15 mL) polypropylene collector vial.

Briefly, the system (Figure 1) consists of a water vapour generator unit, an electrothermal furnace, a quartz tube used

as reactor where a quartz holder for the sample is placed, a vapour condenser and a collector (one or two flasks) of the products from the pyrohydrolysis reaction. All parts of the system were interconnected with PTFE tubes. An air pump is used in order to force the water vapour through the reactor. The water trap, which is made of glass, avoids the introduction of water drops into the reactor. The condensed solution is collected separately: for F determination the vapour can be simply condensed using one flask, while for Br and I determination the vapour is condensed and trapped in an alkaline medium in two collection flasks connected in series. The determination of Br, F and I was carried out directly in the collected solution, with or without dilution.

Instrumentation

Bromide and I were determined using an inductively coupled plasma mass spectrometer (Perkin-Elmer-SCIEX, model Elan DRC II, Thornhill, Canada) equipped with a concentric nebulizer (Meinhard Associates, Golden, CO), a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia), and a quartz torch with a quartz injector tube (2 mm i.d.). Instrumental performance optimization, including nebulizer gas flow rate and ion lens voltage, was performed following the instructions of the instrument manufacturer. Plasma was operated at 1300 W, while the flow rates of plasma gas, auxiliary gas, and nebulizer gas were 15.0, 1.20, and 1.15 L min⁻¹, respectively. Argon of 99.996% purity (White Martins-Praxair, São Paulo, Brazil) was used. The monitored isotopes were ⁷⁹Br, ⁸¹Br, and ¹²⁹I.

Fluoride was determined using a potentiometer (model 781 pH/ion meter, Metrohm, Herisau, Switzerland) equipped with a fluoride ISE (model 6.0502.150, Metrohm). The method used for F determination is described elsewhere.³³

Reagents

All chemicals used were of analytical grade. Solutions were prepared using distilled/deionised water previously purified in a Milli-Q system (18.2 MΩ cm, Millipore, Billerica, MA, USA). Nitric acid (65% m/m) from Merck (Darmstadt, Germany) was doubly distilled in a quartz still (model duoPUR 2.01E, Milestone, Sorisole, Italy). A 10% (v/v) solution of this acid was used for vessel cleaning.

Vanadium pentoxide (V₂O₅) used as accelerator was obtained by heating ammonium vanadate (NH₄VO₃ from Merck) in a platinum crucible during 4 h at 550 °C.⁷

Total ionic strength adjustment buffer (TISAB) was prepared by mixing 58 g of sodium chloride (Merck), 4 g

of 1,2-cyclohexylenediaminetetraacetic acid (Merck) and 57 mL of acetic acid (Merck) in 500 mL of water. The pH of this solution was adjusted to 5.5 with a 10% (m/v) sodium hydroxide (Merck) solution. Then, the volume of the solution was completed to 1000 mL with water.

A stock solution of sodium carbonate/sodium bicarbonate was prepared by dissolution of 10.6 g of Na₂CO₃ (Merck) and 10.6 g NaHCO₃ (Merck) in water and the volume completed to 1000 mL. Tetramethylammonium hydroxide (25% v/v from Sigma-Aldrich,) and 25% (v/v) ammonium hydroxide (Merck) were also evaluated to be used as absorbing solution for Br and I. All alkaline solutions were diluted as necessary for analyte collection or preparation of calibration solutions.

A 1000 mg L⁻¹ F⁻ solution was prepared in water (by dilution of a Titrisol-Merck solution). Fluoride calibration solutions ranging from 0.25 to 10.0 mg L⁻¹ were prepared in water, by serial dilutions of the 1000 mg L⁻¹ F⁻ stock solution. In order to obtain the F⁻ calibration curve, equal volumes of each calibration solution and TISAB were mixed. Stock solutions containing 1000 mg L⁻¹ of Br⁻ and I⁻ were obtained from KBr (Merck) and KI (Merck), respectively. Calibration solutions of Br⁻ and I⁻ were prepared by serial dilution of the stock solution in (NH₄)₂CO₃/NH₄HCO₃ 50 mmol L⁻¹. The calibration solutions were in the range of 1.0 to 20 mg L⁻¹ for Br and 0.1 to 20 µg L⁻¹ for I.

Samples

Four samples of mineral supplements (named as A, B, C, and D) were obtained in local market. Prior being submitted to pyrohydrolysis, all samples were ground in an agate mortar in order to obtain particle sizes lower than 100 µm. A certified sample of phosphate rock (IPT-18) from Instituto de Pesquisas Tecnológicas (IPT), São Paulo, Brazil, and a certified soil (Montana Soil SRM 2711) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used for accuracy evaluation.

Procedures

Aliquots of sample in the range of 30 to 150 mg and up to 450 mg of V₂O₅ were weighed in quartz holders. Sample A was used for method development. The temperature of the reactor was gradually increased (during 5 min) up to the maximum temperature and hold during 10 min at each selected temperature. The reactor temperature was measured using a thermocouple. Humidified air was passed through the quartz reactor at a flow rate ranging from

100 to 600 mL min⁻¹. For Br and I collection, a solution containing Na₂CO₃ and NaHCO₃ with concentration ranging from 0 to 50 mmol L⁻¹ was used. In this case, it was necessary to use two flasks containing absorbing solution (Figure 1(13a)); one with 5 mL and the other with 3 mL. After pyrohydrolysis reaction, the solutions collected in both flasks were mixed and the volume was completed to 15 mL using ultrapure water. For F determination, about 8 mL of water vapour were collected and the volume was completed to 10 mL using ultrapure water. An aliquot of 10 mL of TISAB was mixed with this solution before F determination. A blank sample was obtained by submitting the sample holder containing V₂O₅ to the same conditions used for the samples. All flasks used were thoroughly washed with 10% (v/v) HNO₃ and water prior use. Recovery tests were carried out by spiking Br⁻, F⁻ and I⁻ to 50 mg of samples A, B, C, and D.

Statistical analysis, including one-way analysis of variance (ANOVA), was performed using GraphPad InStat (GraphPad InStat Software Inc., Version 3.00, 1997) software. A significance level of 95% was used.

Results and Discussion

The influences of alkaline solution concentration used to collect Br and I species, vanadium pentoxide used as accelerator, sample mass, air flow rate through the reactor, temperature and reaction time were firstly studied.

Solution used for analyte collection

According to the literature, the F species (released from samples submitted to pyrohydrolysis) present in the water vapour can be just condensed and then collected.^{7,33,37} However, alkaline solutions are necessary for Br and I collection to avoid analyte losses and circumvent memory effects in their determination by ICP-MS. Therefore, solutions of tetramethylammonium hydroxide, ammonium hydroxide, and sodium carbonate/sodium bicarbonate with concentrations up to 50 mmol L⁻¹ were investigated for collecting the volatile Br and I species obtained from pyrohydrolysis. For comparison, the use of pure water was also evaluated. For these tests, the mass of sample + mass of V₂O₅ (sample A was used for these tests), air flow rate and reaction time were fixed at 1 + 3, 300 mL min⁻¹, and 10 min, respectively. The results obtained showed that the best Br and I recoveries were achieved using Na₂CO₃/NaHCO₃ solution to collect both elements. According to Figure 2, when the concentration of the Na₂CO₃/NaHCO₃ solution was higher than 40 mmol L⁻¹ the relative standard deviation for Br and

I decreased (RSD lower than 8%). For Br, recoveries close to 100% were obtained using Na₂CO₃/NaHCO₃ solutions with concentration higher than 40 mmol L⁻¹. For iodine, no significant difference was found (one-way - ANOVA, P < 0.05) for all absorbing solutions investigated. Thus, a 50 mmol L⁻¹ Na₂CO₃/NaHCO₃ solution was used in subsequent experiments. It is important to point out that in case of F none absorbing solution is necessary. Quantitative recoveries of this element were also obtained using all absorbing solutions evaluated for Br and I. In this sense, it is possible to suggest that if only F should be determined, pyrohydrolysis can be performed without using any absorbing solution. On the other hand, all analytes can be determined by using a 50 mmol L⁻¹ Na₂CO₃/NaHCO₃ solution.

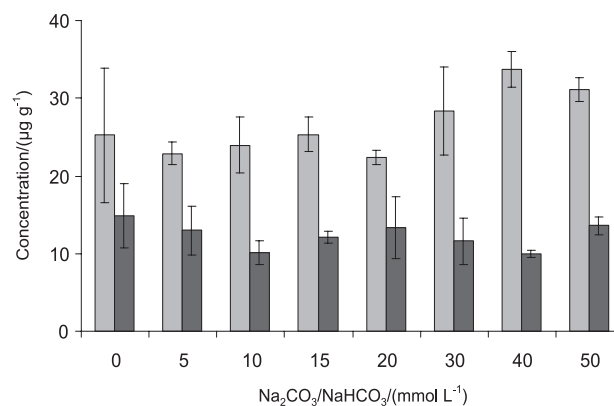


Figure 2. Influence of Na₂CO₃/NaHCO₃ solution concentration used for collection of Br (□) and I (■); error bars are the standard deviations, n = 5.

Influence of accelerator on analyte recoveries

According to early applications of pyrohydrolysis for analytical purposes, the reaction is faster in the presence of certain oxides of U, W, Al and V.³⁷ In the present work, V₂O₅ was used due to its relatively low melting point (about 750 °C) and suitability for different matrices. In order to evaluate the analytes release, 50 mg of the sample A were mixed with aliquots up to 450 mg of V₂O₅ (up to 1 + 9). For these experiments, air flow rate, reaction time and Na₂CO₃/NaHCO₃ concentration were 300 mL min⁻¹, 10 min and 50 mmol L⁻¹, respectively. It was observed that the precision improved with V₂O₅ amount increasing. Therefore, the sample + V₂O₅ mass ratio was kept in 1 + 5 for subsequent experiments. These results are in agreement with results obtained in previous works.^{7,33} According to the literature, usually the use of an accelerator is necessary for halogens release from inorganic sample matrixes.^{7,24,33,36} However, for other samples, like coal and petroleum coke, halogens are released without any auxiliary reagent.^{19,33,38}

Influence of air flow rate

Air saturated with water vapour was employed for analyte transport from the pyrohydrolysis reactor to the condenser. For these experiments, the reaction time, sample mass + V_2O_5 mass proportion and $Na_2CO_3/NaHCO_3$ concentration were set in 10 min, 1 + 5, and 50 mmol L^{-1} , respectively. Air flow rates from 100 to 600 mL^{-1} were evaluated and no significant difference was found for F and I (one-way - ANOVA, $P < 0.05$). In the case of Br, the results obtained for air flow rate higher than 200 $mL\ min^{-1}$ were statistically different (one-way - ANOVA, $P < 0.05$). The volume of water that passes through the pyrohydrolysis unit is dependent on the air flow rate. Thus, the water vapour volume increase with the air flow rate increasing. As a consequence a more diluted solution is produced, worsening the limit of detection (LOD). Therefore, the air flow rate selected was 200 $mL\ min^{-1}$.

Influence of temperature and reaction time

The presence of V_2O_5 , appropriate temperature and time of heating were mandatory for achieving good accuracy and precision. The temperature inside the reactor was varied from 700 to 1100 $^{\circ}C$ and it was verified that both precision and accuracy were better for 1000 $^{\circ}C$. The temperature was gradually increased until the fusion of the mixture sample + accelerator was completed, which occurred at 750 $^{\circ}C$ and after 2 min of heating at this temperature. Then, the temperature was increased up to 1000 $^{\circ}C$. For these experiments, the air flow rate, sample mass + V_2O_5 mass proportion and $Na_2CO_3/NaHCO_3$ concentration were 200 $mL\ min^{-1}$, 1 + 5 and 50 mmol L^{-1} , respectively. The results obtained are shown in Figure 3. In case of Br, no significant differences were found for reaction time up to 10 min (one-way - ANOVA, $P < 0.05$). For iodine, significant difference was found for reaction time up to 7.5 min (one-way - ANOVA, $P < 0.05$). Higher iodine concentration was found for 2.5 min of reaction but the precision was worst. For fluorine, no significant difference was found (one-way - ANOVA, $P < 0.05$) in all tests. Therefore, 10 min was established for further studies. It is important to mention that the pyrohydrolysis time must be enough for complete halogens release from sample matrix and to wash out the system in order to carry the analytes from reactor, capillaries and condenser to the collection flask. Therefore the time necessary for pyrohydrolysis can change according to sample matrix, analyte concentration and also the characteristics of the pyrohydrolysis system employed.^{17,19,32,37,39} In comparison with other sample preparation techniques^{10,20,25} for subsequent halogens

determination, the pyrohydrolysis method proposed in this work can be considered relatively fast because up to 5 samples can be decomposed in 1 h.

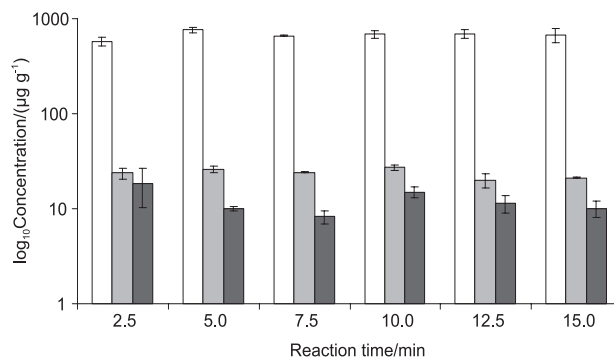


Figure 3. Influence of reaction time on analyte recovery. F (□), Br (▒) and I (■); error bars represents the standard deviation, $n = 5$.

Sample analysis, precision and accuracy

The characteristics of the proposed pyrohydrolysis method, for sample preparation and determination of F, Br and I are shown in Table 1.

Table 1. Characteristics of the developed pyrohydrolysis method for mineral supplement preparation prior to F, Br and I determination

Parameter	Condition
Air flow rate / ($mL\ min^{-1}$)	200
Reactor temperature / $^{\circ}C$	1000
Reaction time / min	10
Sample mass / mg	10-150
Sample mass + V_2O_5 mass proportion	1 + 5
Sample throughput / h^{-1}	5
Absorbing solution $Na_2CO_3/NaHCO_3$ / (mmol L^{-1})	50 (Br and I)
Relative standard deviation (RSD, $n = 6$) / %	F < 4 Br < 4 I < 11
Limit of quantification (LOQ) ^a / ($\mu g\ g^{-1}$)	F: 16 Br: 0.3 I: 0.07

^aLOQ calculated for 50 mg of sample in 10 mL of solution for F (using ISE), and 50 mg of sample in 15 mL of solution for Br and I (measured by ICP-MS).

The limit of quantification (LOQ) of F was calculated considering the lower Nernstian response of the ISE electrode (0.15 $mg\ L^{-1}$ of F^{-}), the sample amount (50 mg) and the final dilution of the sample solution (10 mL). Although the sample mass employed ranged from 10 to 150 mg, it is possible to use higher amount of sample that improves the LOQ. The LOQs of Br and I were calculated according to the 3σ criterion. The use of 50 mg of sample

and a final volume of 15 mL were also taken into account for the LOQs calculation. The LOQs of F, Br and I achieved by using ISE and ICP-MS were sufficiently low for these elements quantification in the analyzed samples.

Memory effects of Br and I in ICP-MS are usually observed when using pneumatic nebulization. However, the accuracy and precision achieved were good. This was mainly due to the use of alkaline solutions for calibration and as absorbing solution in pyrohydrolysis. The precision, expressed as the relative standard deviation (RSD) was better than 11% for all analytes. No certified reference materials with similar matrix of the analyzed samples were available. Therefore, the accuracy was checked by analyte recovery tests and analysis of certified phosphate rock and certified soil. Accuracy was better than 85%, as shown in Table 2. It is important to mention that, although the matrix of certified reference materials used was not the same as the sample matrix, mineral supplements are prepared from phosphate rocks, which enable to suppose that this matrix is similar to sample matrix. The sample throughput is 5 samples *per* hour, which is good if one consider the difficulties related to the determination of F, Br and I in mineral supplement. In addition, pyrohydrolysis is easy to be implemented and no toxic waste is generated.

Table 2. Recoveries of F, Br and I in spiked samples and in reference materials (mean \pm standard deviation, n = 6)

Sample	Recovery / %		
	F ^a	Br ^b	I ^c
A	97 \pm 4	88 \pm 2	100 \pm 8
B	104 \pm 2	90 \pm 3	107 \pm 3
C	100 \pm 4	107 \pm 2	99 \pm 6
D	96 \pm 4	95 \pm 3	85 \pm 9
IPT-18 ^d	104 \pm 5	nd	nd
SRM 2711 ^e	nd	99 \pm 6	90 \pm 7

nd = not determined; ^aaddition of F solution in order to obtain 10 mg L⁻¹ F in the final solution after pyrohydrolysis; ^baddition of Br solution in order to obtain 100 μ g L⁻¹ Br in the final solution after pyrohydrolysis; ^caddition of I solution in order to obtain 50, 100 and 150 μ g L⁻¹ I in the final solution of samples A and D, sample B, and sample C, respectively; ^dcertified value: 1.35 \pm 0.13% of F⁻; ^einformed values: 5.0 μ g g⁻¹ Br and 3.0 μ g g⁻¹ I.

Table 3. Determination of F, Br and I in commercial mineral supplement (mean \pm standard deviation, n = 6)

Samples	Informed values / (μ g g ⁻¹) ^a			Determined values / (μ g g ⁻¹)		
	F	Br	I	F	Br	I
A	757	ni	40	1077 \pm 79	26.7 \pm 0.7	14.7 \pm 1.7
B	900	ni	75	601 \pm 5	26.9 \pm 0.9	44.7 \pm 4.7
C	800	ni	77	900 \pm 51	30.4 \pm 1.2	10.5 \pm 0.8
D	800	ni	75	1049 \pm 102	26.4 \pm 2.2	57.6 \pm 4.3

ni = not informed values; ^avalues informed by the producer of the mineral supplement.

After establishing the most important parameters of the developed method, it was applied to analysis of commercial mineral supplement samples used for animal nutrition. Fluorine determination in all samples was carried out using potentiometry with ISE, while Br and I were determined by ICP-MS. The results are shown in Table 3 where it can be observed that F concentrations in samples A, B, C, and D are relatively high (ranging from 600 to 1100 μ g g⁻¹). This is attributed either to the addition of F to the supplement formula or to the fact that F is naturally present in the phosphate rock used in formulation of the mineral supplements.⁴⁰ Bromide concentrations found were similar for all samples (26 to 31 μ g g⁻¹). The mineral supplement producer did not inform the Br concentration but it was lower than the maximum concentration allowed. Iodide concentrations found in all samples were lower than the concentrations given by the producer (between 14 and 77 μ g g⁻¹), but it was in agreement with the legislation.⁴ In general, the concentrations of F and I determined after decomposition using pyrohydrolysis were different of those informed by the mineral supplements producer. However, it is not possible to suggest the reasons for the differences found. The producer does not inform which method was used to determine the concentrations of the investigated elements.

According to the Brazilian legislation, Br, F and I concentrations found are in agreement and the mineral supplements could be given to animals.

In general, the determination of halogens in mineral supplement is challenging due to matrix complexity mainly the high concentration of salts, contamination and risk of analyte losses by volatilization during sample preparation (even using closed vessels). In this sense, the main drawback related to digestion methods is the high concentration of acid in the final solution. For halogens determination using ISE and ICP-MS techniques the pH of the solution must be 5.5 or higher. Fusion methods would increase matrix complexity due to the presence of additional electrolytes. The relatively high concentration of salts in the final solution can interfere in ICP-MS determinations. Pyrohydrolysis is more feasible because a diluted alkaline solution can be used for analytes collection and the analytes

are separated from the sample matrix. Additionally, the pyrohydrolysis apparatus is of low cost and the method can be easily implemented in laboratories. The LOQ and the accuracy are good.

Conclusions

The results obtained demonstrated that pyrohydrolysis is feasible for preparation of samples of mineral supplements used in animal nutrition prior to F, Br and I determination. The main advantage is that the analytes are separated from sample matrix, avoiding interferences during the determination step, especially when ICP-MS is used. Only water (in case of fluorine) or a diluted alkaline solution is used for absorbing all analytes. The pyrohydrolysis method is fast, its implementation is relatively easy and of low cost. The method is attractive since concentrated acids and toxic reagents are not used. The use of V_2O_5 and $Na_2CO_3/NaHCO_3$ solution is inexpensive and without toxicity. Blank signals are low, which improves the LODs.

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