Bromine, Chlorine, and Iodine Determination in Soybean and its Products by ICP-MS After Digestion Using Microwave-Induced Combustion

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Abstract A method for bromine, chlorine, and iodine determination in soybean and related products was developed by inductively coupled plasma mass spectrometry (ICP-MS) after digestion by microwave-induced combustion (MIC). Samples were pressed as pellets and combusted using pressurized oxygen (20 bar) and ammonium nitrate solution (50 μL of 6 mol L^{-1}) as the igniter. Analytes were absorbed in alkaline solution (100 mmol L^{-1} NH_4OH), and a reflux step of 5 min, microwave power of 1,400 W, was applied after combustion in order to improve analyte recoveries. For Cl determination by ICP-MS, a dynamic reaction cell was used with ammonia as the reaction gas. The accuracy was evaluated using certified reference materials (CRMs) and spiked samples. Using MIC, the agreement with CRM values and spike recoveries was higher than 95 % for all analytes for certified reference materials of a similar composition (National Institute of Standards and Technology (NIST), corn bran and NIST, whole milk). Limits of detection were 0.03, 1.2, and 0.002 μg g^{-1} for Br, Cl, and I, respectively. The residual carbon content in the digests obtained after MIC procedure was lower than 0.5 %. Blanks were always negligible and no memory effects were observed. Digestion by MIC allowed processing up to eight samples by each run in 25 min with high efficiency of digestion providing a suitable medium for further bromine, chlorine, and iodine determination by ICP-MS.

Keywords Soybean analysis · Microwave-induced combustion · Food analysis · Halogens · ICP-MS

Introduction

Soybean is the major oilseed produced in Brazil, representing more than 95 % of the total production of oilseeds. (Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA) 2011) Due to increased production of soy-based foods, the determination of trace elements is important in view of toxicity or nutritional assessments. (Kinniburgh et al. 1976; Schnetger and Muramatsu 1996; Kim et al. 2007; Sussulini et al. 2007) The presence of halogens in soybean depends on several factors such as soil, environment, plant genotype, or halogen-containing fertilizers and pesticides. (Biester et al. 2006) Among the halogens, iodine and chlorine in food are essential and required for nutritional purposes and regulation of biological fluids, respectively. However, in excess, they can cause hormonal dysfunction and damage the nervous system. (Sussulini et al. 2007) Already, bromine is considered nonessential to human health and it can be combined with

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hemoglobin causing hematologic diseases. (Edwards 2008) In this sense, halogen determination in low concentration in food requires sensitive analytical techniques as inductively coupled plasma mass spectrometry. (Knapp et al. 1998; Fecher et al. 1998; Sturgeon and Grinberg 2009) However, soybean has a relatively high amount of oil that makes the complete digestion of samples difficult. Thus, there is a need for the development of suitable precise methods for the quantification of the relatively low levels of bromine, chlorine, and iodine usually found in food products (i.e., in milligrams per kilogram and micrograms per kilogram levels). (World Health Organization 2011; Oliveira et al. 2010; Anke et al. 1995; Gélinas et al. 1998)

Microwave-induced combustion (MIC) is a suitable digestion method allowing high efficiency of decomposition of organic samples and a convenient sample throughput. In this method, sample combustion occurs in closed quartz vessels pressurized with oxygen where the ignition step is performed by microwave radiation. (Flores et al. 2008) For this system, the application of a reflux step after combustion also improves analyte recoveries. The feasibility of this sample preparation method has been demonstrated for the digestion of biological matrices, (Duarte et al. 2009) food, (Mesko et al. 2010) humic acids, (Pereira et al. 2011) cigarette tobacco(Muller et al. 2011); industrial products, as elastomers (Moraes et al. 2010) and carbon nanotubes (Pereira et al. 2010a); and fossil fuel samples, as petroleum coke, (Mello et al. 2008) coal, (Antes et al. 2010) heavy crude oil, (Pereira et al. 2010b) and crude oil distillation residues (Mello et al. 2009) for subsequent metals and halogens determinations. Contrary to trace metals, for halogen determination, alkaline solutions could be used as absorbing solutions allowing suitable recoveries. (Moraes et al. 2010; Pereira et al. 2008; Nóbrega et al. 2005) Considering that concentrated solutions are not generally required, it represents a great advantage for further analysis regarding blank values and reagent consumption. (Pereira et al. 2008) It is important to point out that despite the good efficiency of microwave-assisted acid digestion for many matrices using pressurized systems, its use is not suitable for further halogen determination due to analyte losses during the digestion step, even if closed systems are used. (Fecher and Nagengast 1994; Pereira et al. 2009a; Cox and Pickford 1992; Flores et al. 2007; Vtorushina et al. 2009; Shiraishi et al. 1999)

In this work, MIC is proposed for the digestion of soybean samples and its products (textured soy protein pieces, whole soy flour, textured soy protein natural, and textured soy protein natural mean) for further Br, Cl, and I determination by inductively coupled plasma mass spectrometry (ICP-MS). In order to avoid polyatomic interferences over chlorine determination by ICP-MS ((Pereira et al. 2009b)Cl$^+$ isotope), the use of a dynamic reaction cell (DRC) with ammonia as the reaction gas was evaluated. The efficiency

of decomposition procedure was checked by the residual carbon content (RCC) in digests. Accuracy was evaluated using certified reference materials (CRMs) and spiked samples for all analytes.

Materials and Methods

Instrumentation

Soybean and its products were decomposed by MIC using a Multiwave 3000 microwave sample preparation system (Anton Paar, Graz, Austria) with software version v1.27-Synt to run with a maximum pressure rate of 3 bars^{-1}. The system was equipped with high-pressure quartz vessels (maximum pressure and temperature of 80 bar and 280 °C, respectively). A commercial quartz holder (Anton Paar) was used to insert the samples inside the quartz vessels. Digestions were simultaneously performed using up to eight vessels.

An inductively coupled plasma mass spectrometer (PerkinElmer-SCIEX, Model Elan DRC II, Thornhill, Canada) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a baffled cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia), and a quartz torch with a quartz injector tube (2 mm i.d.) was also used for the determination of Br and I. Argon 99.996 % (White Martins-Praxair, São Paulo, Brazil) was used for plasma generation, nebulization, and auxiliary gas. Chlorine was separately determined using the dynamic reaction cell system with ammonia (purity higher than 99.999 %) as the reaction gas. The DRC parameters were adjusted in order to minimize the interferences on (Pereira et al. 2009b)Cl$^+$ isotope according to previous work. (Antes et al. 2008) Operational conditions are described in Table 1.

In order to evaluate the digestion efficiency of MIC, the RCC measurements were performed using an inductively coupled plasma optical emission spectrometer with axial view configuration (Model Spectro Ciros CCD, Spectro Analytical Instruments, Kleve, Germany) equipped with a cross flow nebulizer coupled to a double-pass Scott-type spray chamber. Digests were sonicated with an ultrasonic probe (model VCX 130 PB, 130 W, 20 kHz, Sonics and Materials, Inc., Newtown, CT) for 3 min, prior to carbon determination, in order to avoid volatile carbon compounds in the digests following the procedure reported in a previous work. (Flores et al. 2008) The selected wavelength used for C determination was 193.091 nm, and the operating conditions used by inductively coupled plasma optical emission spectrometry (ICP-OES) were radiofrequency power 1,400 W, 14.0 L min^{-1} plasma gas flow rate, and 1.02 L min^{-1} nebulizer gas flow rate.

Table 1 Operational conditions for halogens determination by ICP-MS

Parameter	ICP-MS
RF power/W	1,400
Plasma gas flow rate/L min^{-1}	15.0
Auxiliary gas flow rate/L min^{-1}	1.2
Nebulizer gas flow rate/L min^{-1}	1.15
Spray chamber	Cyclonic
Nebulizer	Concentric
Sampler and skimmer cones	Pt
Ion lens	Auto lens "on"
Dwell time/ms	50
Isotope (m/z)	^{79}Br
	^{35}Cl
	^{127}I
RPq[a]	0.5
Reaction gas[a]	NH$_3$
Reaction gas flow rate[a]/L min^{-1}	0.5
Parameter	ICP-MS
RF power/W	1400
Plasma gas flow rate/L min^{-1}	15.0
Auxiliary gas flow rate/L min^{-1}	1.2
Nebulizer gas flow rate/L min^{-1}	1.15
Spray chamber	Cyclonic
Nebulizer	Concentric
Sampler and skimmer cones	Pt
Ion lens	Auto lens "on"
Dwell time/ms	50
Isotope (m/z)	^{79}Br
	^{35}Cl
	^{127}I
RPq[a]	0.5
Reaction gas[a]	NH$_3$
Reaction gas flow rate[a]/L min^{-1}	0.5

[a] DRC-ICP-MS mode for detection of Cl

Samples

Samples of commercial soybean and its products were purchased in a local store and were identified as "A" (textured soy protein pieces), "B" (whole soy flour), "C" (textured soy protein natural), "D" (textured soy protein natural mean), and "E" (soybeans). All the samples were ground in a ball mill, model 8000 M (Spex SamplePrep, USA) with a tungsten carbide vial set and tungsten carbide ball and homogenized in nylon sieves of particle size lower than 500 μm.

Samples and CRMs were prepared as pellets (diameter of 13 mm) using a hydraulic press set at 3 tons during 1 min (Specac, Orpington, UK) for digestion by MIC. Certified reference materials from National Institute of Standards and Technology (NIST) of corn bran (NIST 8433) and whole milk (NIST 8435) were used for accuracy evaluation since there is no CRM with similar matrix composition available with halogen certified values. Additionally, spikes were performed by the addition of multielement reference solution in order to obtain analyte concentration correspondent to 4.5 μg g^{-1} Br, 40 μg g^{-1} Cl, and 0.5 μg g^{-1} I. Spike solution was added to the solid sample pellet before the MIC procedure.

The temperature during combustion was determined using an optical pyrometer (Ultimax Infrared Thermometer, Ircon, Niles, IL) equipped with a close-up VX-CL1 lens. All statistical calculations were performed using GraphPad InStat (GraphPad InStat Software, Inc., Version 3.00, 1997) software. A significance level of $P<0.05$ was adopted for all the statistical evaluation.

Reagents and Standards

All the reagents used in this work were of analytical grade (Merck, Darmstadt, Germany). Water obtained from a Milli-Q (18.2 MΩ cm) system was used to prepare all reagents and standard solutions. Working analytical solutions for ICP-MS analysis were prepared before use by serial dilution of stock reference solutions containing 100 mg L^{-1} of chloride and bromine (Multielement solution, Fluka, Buchs, Switzerland) in water. Iodine stock reference solution was prepared by the dissolution of potassium iodine salt (Merck) in water.

Ammonium nitrate solution (6 mol L^{-1}), used as the igniter for the MIC procedure, was prepared by dissolving the salt (Merck) in water. Small discs of paper (15 mm of diameter, about 12 mg) with low ash content (Black Ribbon Ashless, Schleicher and Schuell, Dassel, Germany) were also used as aid for the combustion process. Filter paper was previously cleaned with ethanol (Merck) for 20 min in an ultrasonic bath, rinsed with water, and dried in a class 100 laminar bench (CSLH-12, Veco, Brazil) before use. Ammonium hydroxide solutions were prepared after dilution of commercial reagent (25 %, Merck) in water. Glass or quartz materials were soaked in 1.4 mol L^{-1} HNO$_3$ (Merck) for 24 h and thoroughly washed with water before its use.

Cleaning procedure of vessels and holders was carried out with 6 mL of 14 mol L^{-1} HNO$_3$, in the microwave oven at 1,400 W for 10 min and 0 W for 20 min (cooling step).

The RCC measurements were performed using yttrium as the internal standard (Spex CertiPrep, 1,000 mg L^{-1}, Metuchen, USA) in a final concentration of 1 mg L^{-1} in digests. (Flores et al. 2008) Standard solutions for the calibration curve

of C were prepared in the range of 25 to 500 mg L^{-1} through serial dilution of a carbon stock reference solution (citric acid in water, 10,000 mg L^{-1}).

Digestion of Soybean Samples and their Products by Microwave-Induced Combustion

The microwave-induced combustion method was performed using sample masses of soybean in the range of 100 to 500 mg. Samples and a small disc of filter paper were positioned into the quartz holder, and 50 μL of 6 mol L^{-1} ammonium nitrate solution was added to the paper. The quartz holder was placed inside the quartz vessel, previously loaded with 6 mL of 100 mmol L^{-1} NH$_4$OH. Then, vessels were pressurized with 20 bar of oxygen for 1 min, and the rotor with vessels was placed inside the microwave cavity. The microwave heating program used was 1,400 W for 5 min (with reflux step) and 0 W for 20 min (cooling step). After the end of the heating program, the pressure of each vessel was released and the resultant solutions were transferred to polypropylene vessels and diluted with water to 30 mL for further analysis by ICP-MS.

Results and Discussion

Digestion of Soybean by MIC

It has been reported in literature that the MIC method is suitable for the digestion of many type of organic matrices assuring safety conditions even using high sample masses. In general, up to 500 mg of sample can be completely combusted using 20 bar of oxygen without the maximum pressure exceeding the recommendation of the manufacturer (80 bar). (Pereira et al. 2009b; Pereira et al. 2010c)

In the present work, soybean digestion was performed using an oxygen pressure of 20 bar and sample masses in the range of 100 to 500 mg were combusted. Under these selected conditions, it was observed that the combustion was always complete, with no apparent residues, and the maximum pressure achieved was approximately 40 bar (up to 500 mg of sample), that is about 50 % of the maximum pressure recommended by the manufacturer.

The suitability of the absorbing solution to retain analytes is an important aspect of MIC digestion since it is well known that acid solutions could cause risks of analyte losses by volatilization. (Fecher and Nagengast 1994; Pereira et al. 2009a) In addition, absorbing solution has an important role because the type and concentration of solution are not the same for different analytes as well as the time absorption. (Flores et al. 2007) Although chlorine could be absorbed using water, (Moraes et al. 2010; Pereira et al. 2010a) in general, alkaline solutions are preferred in order to quantitatively

absorb and stabilize halogens in solution. (Flores et al. 2008) Taking into account that NH$_4$OH could be a convenient solution for ICP-MS, this solution was chosen for further studies based on previous works. (Pereira et al. 2011; Muller et al. 2011; Moraes et al. 2010; Pereira et al. 2010a) In this work, tests were carried out using water and NH$_4$OH (5, 10, 25, 50, and 100 mmol L^{-1}) as the absorbing solution. Spike recoveries were evaluated for each concentration of absorbing solution with reflux step for Br, Cl, and I determination by ICP-MS after MIC digestion and are shown in Table 2. It is important to point out that the digestion was performed using an additional reflux step (5 min at 1,400 W) in order to improve the absorption of the analytes and to obtain lower values of relative standard deviation (RSD). It was observed that with the use of water as the absorbing solution, a maximum recovery of 93.6 % was obtained for all halogens (Table 2). On the other hand, using 10 mmol L^{-1} NH$_4$OH, recoveries higher than 95 % were obtained. Using a higher concentration of NH$_4$OH results were even better and RSD was around 5 %. It was observed that RSD was minimized when increasing NH$_4$OH concentration. Using 100 mmol L^{-1} NH$_4$OH, the RSD was below 2.4 % and agreement for bromine, chlorine, and iodine was higher than 99 % in sample E with the addition of corn bran (NIST 8433) with certified values of NIST. In addition, using 100 mmol L^{-1} NH$_4$OH as the absorbing solution, negligible memory effects were observed for all analytes.

Halogen Determination by ICP-MS in Soybean Samples and their Products After MIC Digestion

After selection of combustion parameters of the MIC method, digests were analyzed using ICP-MS. The corresponding results are shown in Table 3. As can be observed, values for Br, Cl, and I were about 3 to 10, 21.8 to 55.7, and 0.002 to 1.23 μg g^{-1}, respectively. However, there were found in the

Table 2 Agreement for bromine, chlorine, and iodine (sample E with the addition of corn bran—NIST 8433) with certified values of NIST 8433 using water or NH$_4$OH as the absorbing solution

Absorbing solution	Agreement (%)		
	Br	Cl	I
H$_2$O	91.3±8.7	93.6±9.2	90.8±8.5
NH$_4$OH-5 mmol L^{-1}	91.5±8.3	94.1±8.8	92.5±8.1
10 mmol L^{-1}	95.7±7.3	97.8±7.5	95.9±7.2
25 mmol L^{-1}	97.2±6.4	98.5±7.2	96.1±5.5
50 mmol L^{-1}	98.4±4.1	98.8±3.1	97.3±4.8
100 mmol L^{-1}	99.5±2.2	100.1±2.4	99.8±2.1

Determination by ICP-MS after MIC digestion with reflux step (mean and standard deviation, $n=3$)

Table 3 Concentration of halogens in soybean and related products

Sample	ICP-MS		
	Br	Cl	I
A	3.04±0.25	47.1±3.3	<0.002
B	3.19±0.12	32.8±1.9	<0.002
C	3.95±0.36	45.2±1.9	1.23±0.02
D	5.04±0.03	55.7±4.4	<0.002
E	9.70±0.28	21.8±0.4	<0.002
NIST 8433	2.25±0.08	28.8±0.5	0.025±0.001
NIST 8435	20.5±0.7	8249±397	2.23±0.06

Determination by ICP-MS after MIC digestion (mean and standard deviation, in micrograms per gram, $n=3$)

Certified values for CRMs (in micrograms per gram) NIST 8433: Br (2.3±0.5), Cl (31±21), and I (0.026±0.006); NIST 8435: Br (20±10), Cl (8240±440), and I (2.3±0.4)

literature, values for halogens in soybean and oilseeds. In order to evaluate the accuracy, MIC was applied for CRMs of corn bran (NIST 8433) and whole milk (NIST 8435) since there is no certified reference material available with the same matrix composition of soybean. The limit of detection (3σ criterion) determined by ICP-MS for Br, Cl, and I was 0.03, 1.2, and 0.002 $\mu g \ g^{-1}$, respectively, and calculated according to IUPAC recommendation. (IUPAC 1997)

It was observed that the results obtained for all halogens for CRMs were in agreement better than 95 % with the certified value, showing the applicability of this sample preparation method for digestion of soybean samples and their products for further halogen determination by ICP-MS in low concentrations with relatively high sample throughput. Spiked samples were performed by the addition of a standard reference solution containing all analytes in the sample pellet prior to the digestion by MIC with recoveries better than 96 % as shown in Table 4.

In this work, as can be seen in Table 5, the figures of merit obtained for Br, Cl, and I were appropriated using MIC with 100 mmol L^{-1} NH$_4$OH as the absorbing solution and reflux step. In addition, using relatively high sample masses (up to

Table 4 Recoveries for Br, Cl, and I in soybean samples and their products using 100 mmol L^{-1} NH$_4$OH and reflux step and determination by ICP-MS (mean and standard deviation, $n=3$)

Sample	Recovery (%)		
	Br	Cl	I
A	97±3	101±4	99±3
B	98±4	96±2	103±5
C	96±3	97±2	99±2
D	101±2	97±4	101±5
E	97±4	102±2	98±4

Table 5 Parameters of merit for Br, Cl, and I determination in soybean and its products by ICP-MS after MIC (100 mmol L^{-1} NH$_4$OH and reflux step)

Parameter	Br	Cl[a]	I
Correlation coefficient (R)	0.9998	0.9996	0.9999
LOD ($\mu g \ g^{-1}$)	0.03	1.25	0.002
LOQ ($\mu g \ g^{-1}$)	0.05	1.61	0.005
RSD (%)	2.2	2.4	2.1

[a] Using DRC-ICP-MS mode

500 mg), it was possible to obtain better limits of detection (LODs) and limits of quantification (LOQs), as well as RSD lower than 2.4 % for all halogens by ICP-MS. The linearity of the standards was satisfactory for all analytes ($R>0.999$).

Residual Carbon Content

The efficiency of a sample decomposition method can be evaluated by means of the residual carbon content in digests. In this work, RCC was evaluated in the samples digested by MIC following the procedure reported in a previous work. (Flores et al. 2008) Digests were sonicated with an ultrasonic probe to remove the volatile carbon compounds before RCC determination by ICP-OES. Yttrium was added to digests as the internal standard with a final concentration of 1 mg L^{-1}. It was observed that the RCC in digests for MIC was always below 0.5 % for all samples. It can be explained by the high temperature achieved during the combustion process (in general, higher than 1,400 °C) that is an important aspect in order to minimize interferences by carbon in the determination by ICP-MS (e.g., iodine).

Conclusions

The microwave-induced combustion method was suitable for the digestion of soybean and its products samples for further halogens determination in a wide range of concentrations by ICP-MS. Up to eight samples could be decomposed in the same digestion step, resulting in a suitable throughput for routine analysis. Using 100 mmol L^{-1} NH$_4$OH as the absorbing solution and a reflux step of 5 min, it was possible to obtain good recoveries and agreement with values very close to 100 %. In addition, RSD values were always lower than 5 %. The results obtained for CRMs by MIC were in agreement with certified values. The proposed MIC method allows the combustion of relatively high sample masses (up to 500 mg) without exceeding 50 % of the maximum operating pressure (80 bar), combining good performance for the digestion of soybean and its products and safety and relatively high sample throughput. Therefore, MIC combined to ICP-MS

determination can be proposed for Br, Cl, and I determination in soybean and its related products making this method suitable for routine analysis.

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