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Analytical Methods

The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples

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ABSTRACT

This paper describes a simple method for the determination of sixteen elements in food samples by using inductively coupled plasma spectrometry (ICP-MS). Prior to analysis, 100–250 mg of powdered food samples were accurately weighed into a Teflon digestion vessel. Then, 4 ml of 20% v/v concentrated nitric acid and 2 ml of hydrogen peroxide were added. Decomposition of samples was carried out in a microwave digestion system. In order to verify the accuracy and precision of the proposed method, five Standard Reference Materials from the National Institute of Standards and Technology (NIST) (Whole Egg Powder RM 8415, Rice Flour SRM 1568a, Typical Diet SRM 1548a, Wheat Flour SRM 1567a and Bovine Muscle Powder RM 8414) were analyzed. Additional validation data are provided based on the analysis of 18 different types of food samples by the proposed method and using comparative methods with AAS as the detector.

1. Introduction

Essential trace elements such as Se, Cu and Zn play an important role in human biology, because they are inadequately or not synthesized in the body. On the other hand, toxic elements, such as Pb, Cd and Hg are not required for normal functioning of living processes and no beneficial health effects have been known by their presence in the human body (Foster & Sumar, 1997; Salgueiro et al., 2000).

Food is the primary source of essential elements for humans and it is an important source of exposure to toxic elements. In this context, levels of essential and toxic elements must be determined routinely in consumed food products. For this purpose, different atomic spectrometry techniques such as flame (FAAS) (Doner & Ege, 2004; Saracoglu, Saygi, Uluozlu, Tuzen, & Soylak, 2007; Tuzen & Soylak, 2007) or graphite furnace atomic absorption spectrometry (GF AAS) (Lima, Barbosa, & Krug, 2001; Lima, Barbosa, Krug, Silva, & Vale, 2000; Lima, Barbosa, Krug, & Tavares, 2002; Santos et al., 2002), inductively coupled plasma atomic emission (ICP-AES) (Kira & Maihara, 2007) and inductively coupled plasma mass spectrometry (ICP-MS) (Chan, Yip, & Chu, 2006; Sahan, Basoglu, & Gucer, 2007) have been used.

Nowadays, the use of ICP-MS is becoming more common in food laboratory analysis (Leblanc et al., 2005). Compared to GF AAS or ICP-OES, this technique has some distinct advantages, including simultaneous multielement measurement capability coupled with very low detection limits (Ammann, 2007; Parsons & Barbosa, 2007). Moreover, it offers a wider linear dynamic range which allows the determination of major and trace elements at same sample injection (Ammann, 2007; Parsons & Barbosa, 2007). Additionally, compared to ICP-OES, ICP-MS provides simpler spectral interpretation and isotopic information.

However, ICP-MS has some limitations. For food sample analysis, the high concentration of organic matrix often results in matrix interferences and/or spectral interferences from polyatomic ions. These effects may be eliminated or minimized by the use of alternative isotopes and/or interference correction equations. Moreover, prior to analysis by ICP-MS, food samples must be decomposed with appropriate methods with the digestates containing reduced amounts of carbon residues. However, sample digestion is a critical step in most analytical methods for routine determination of chemical elements in food samples. For instance, dry ashing methods (Doner & Ege, 2004) require the sample to spend long times in a crucible furnace at elevated temperatures, in most cases following evaporation of the water in the sample and/or carbonizing on a hot-plate. On the other hand, wet digestion procedures in open vessels (Alkanani, Friel, Jackson, & Longerich, 1994) require the use of concentrated acids and careful monitoring of digestion for varying periods. Both methods are time-consuming and losses of analytes by volatilization are common. Alternatively, closed-vessel acid decomposition in

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microwave oven systems may provide faster and more efficient sample digestion. Moreover, the risk of sample contamination and losses of analytes by volatilization are practically eliminated (Delafuente & Juarez, 1995; Lima et al., 2000).

The aim of this study was to develop a suitable method for major and trace elements determination (essential and toxic elements) in different types of food samples (rice, bean, egg, meat, fish, bread, sugar, vegetables, cheese, powder milk, butter, wheat, pear, brazil nuts, coffee, chocolate, biscuits and pasta) by using inductively coupled plasma mass spectrometry (ICP-MS).

2. Materials and methods

2.2. Insruments and apparatus

A microwave oven equipped with PTFE vessels, model Ethos 1600 (Milestone, Monroe, CT) was used for sample digestion. For the elemental determination an ICP-MS (Elan DRC II, PerkinElmer, Norwalk, CT). The ICP-MS operating conditions are shown in Table 1. For comparison purposes a Perkin–Elmer 4100 ZL graphite furnace atomic absorption spectrometry was used. Operating conditions for the GF AAS method is given by Lima et al. (2000) and by Saracoglu et al. (2007). For mercury determination cold vapor atomic absorption spectrometry (CV AAS) was used according to the method proposed by Perring and Andrey (2001).

2.3. Reagents

All reagents used were of analytical-reagent grade, except HNO_3 and HCl which were previously purified in a quartz sub-boiling stills (Kürner) before use. A clean laboratory and laminar-flow hood capable of producing class 100 were used for preparing solutions. High purity de-ionized water (resistivity 18.2 mΩ cm) obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout. All solutions were stored in high-density polyethylene bottles. Plastic materials was cleaned by soaking in 10% (v/v) HNO_3 for 24 h, rinsing five times with Milli-Q water and dried in a class 100 laminar flow hood before use. All operations were performed in a clean bench. Multielement Stock solutions containing 1000 mg/L of each element were obtained from Perkin–Elmer (PerkinElmer, Norwalk, CT). Analytical calibration standards were prepared daily over the range of 0–20 μg/L for all elements by suitable serial dilutions of multielement stock solution in 2% (v/v) HNO_3. Rhodium was used as internal standard at the concentration of 10 μg/L Rh. To avoid memory effects for mercury in the spray chamber samples and standards were prepared also containing 1 mg/L Au (Palmer, Lewis, Geraghty, Barbosa, & Parsons, 2006). Rhodium and gold stock solutions, 1000 mg/L, were obtained by Perkin–Elmer (PerkinElmer, Norwalk, CT, USA).

Table 1
ICP-MS operating conditions

Perkin Elmer Elan DRC II	
Spray chamber	Cyclonic
Nebulizer	Meinhard®
RF power (W)	1100
Ar nebulizer gas flow (L min^{-1})	0.6–0.9 (optimized daily)
Measures	
Scan mode	Peak hopping
Resolution (amu)	0.7
Replicate time (s)	1
Dwell time (s)	50
Sweeps/reading	20
Integration time (ms)	1000
Replicates	3
Isotopes	^{82}Se, ^{66}Zn, ^{63}Cu, ^{111}Cd, ^{208}Pb,^{24}Mg, ^{59}Co, ^{60}Ni, ^{55}Mn, ^{88}Sr, ^{98}Mo, ^{51}V, ^{202}Hg, ^{27}Al, ^{75}As, ^{53}Cr
Correction equations	
Arsenic = ^{75}As–(0.0002 × ^{35}Cl)	
Cadmium = ^{114}Cd–(0.027250 × ^{118}Sn)	
Cobalt = ^{59}Co–(0.001 × ^{43}Ca)	
Chromium = ^{53}Cr–(0.0005 × ^{35}Cl)	
Nickel = ^{60}Ni–(0.003 × ^{43}Ca)	
Vanadium = ^{51}V–(0.001 × ^{35}Cl)	
Selenium = ^{82}Se–(1.0087 × ^{83}Kr)	

Table 2
Microwave oven heating program for the decomposition of food samples

Step	Temperature (°C)	Power (W)	Time (min)
1	160	1000	4.5
2	160	0	0.5
3	230	1000	5.0
4	230	1000	15.0
5	0	0	20.0

2.4. Ordinary food samples and certified reference materials

In order to verify the accuracy and precision of the proposed method, five Standard Reference Materials from the National Institute of Standards and Technology (NIST) (Whole Egg Powder RM 8415, Rice Flour SRM 1568a, Typical Diet SRM 1548a, Wheat Flour SRM 1567a and Bovine Muscle Powder RM 8414). For additional validation purposes 18 different types of food samples (rice, bean, egg, meat, fish, bread, sugar, vegetables, cheese, powder milk, butter, wheat, pear, brazil nuts, coffee, chocolate, biscuits and pasta) were purchased at a local supermarket and analyzed by the proposed method and using comparative methods with AAS as the detector.

2.5. Sample preparatiion

For the proposed method samples were digested in closed-vessels with a microwave oven decomposition system (Milestone ETHOS 1600) according to the following procedure.

Samples (0.10–0.25 g) were accurately weight in a PFA digestion vessel, and then 4 ml of nitric acid 14 mol/L + 2 mL of 30% (v/v) H_2O_2 were added. The bomb was placed inside the microwave oven, and the decomposition was carried out according to the program shown in Table 2. After that, the digestate were left to cool and then the volume made up to 50 mL with Milli-Q water. Then, Rhodium was added as internal standard to a final concentration of 10 μg/L. For the comparative methods (AAS detector), samples were digested according to the method proposed by Lima et al. (2002) for all analytes except mercury. For mercury analysis by CV AAS, samples were digested according to the procedure proposed by Perring and Andrey (2001).

3. Results and discussion

3.1. Evaluation of the microwave sample decomposition method

Sample digestion is a critical step in most analytical methods for routine determination of chemical elements in food samples. In this context, different mixtures of acids for the de-mineralization of food samples were evaluated, such as 4 mL of HNO_3 14 mol/L alone (procedure A), 4 mL of HNO_3 14 mol/L + 2 mL of 30% m/v H_2O_2 (procedure B), 4 mL of HNO_3 2.8 mol/L + 2 mL of 30% m/v H_2O_2 (procedure C) 1 mL of 14 mol/L HNO_3 + 3 mL of 12 mol/L HCl (procedure D). After each different procedure, the digestate were left to cool and then the volume made up to 50 mL with Milli-Q water. The microwave oven heating program showed in Table 2 was used for all procedures.

Table 3
Analysis of certified reference materials for essential elements determination

Sample	Certified value	Found value	Certified value	Found value	Certified value	Found value	Certified value			Found value
	Se (μg/g)	Se (μg/g)	Cu (μg/g)	Cu (μg/g)	Zn (μg/g)	Zn (μg/g)	Co (ng/g)	Co (ng/g)	Mn (μg/g)	Mn (μg/g)
Wheat flour SRM 1567a	1.1 ± 0.2	1.03 ± 0.01	2.1 ± 0.2	1.9 ± 0.1	11.6 ± 0.4	11.0 ± 0.5	6.0[a]	4.0 ± 0.1	9.4 ± 0.9	8.9 ± 0.1
Whole egg powder 8415	1.39 ± 0.17	1.50 ± 0.09	2.70 ± 0.35	2.9 ± 0.2	67.5 ± 7.6	73 ± 4	12 ± 5.0	15.1 ± 0.4	1.78 ± 0.38	1.85 ± 0.03
Rice flour 1568a	0.38 ± 0.04	0.36 ± 0.03	2.4 ± 0.3	2.2 ± 0.1	19.4 ± 0.5	20.1 ± 0.6	18.0[a]	10.1 ± 1.2	20.0 ± 1.6	21.1 ± 0.2
Bovine muscle powder 8414	0.076 ± 0.010	0.08 ± 0.01	2.84 ± 0.45	3.0 ± 0.1	142 ± 14	155 ± 6	7.0 ± 3.0	9.2 ± 0.5	0.37 ± 0.09	0.32 ± 0.02
Typical diet 1548a	0.245 ± 0.028	0.22 ± 0.01	2.32 ± 0.16	2.4 ± 0.2	24.6 ± 1.79	22.9 ± 0.2	28.0[a]	22.4 ± 0.5	5.75 ± 0.17	6.0 ± 0.1
	Mo (μg/g)	Mo (μg/g)	Mg (μg/g)	Mg (μg/g)	Sr (μg/g)	Sr (μg/g)	Cr (ng/g)	Cr (ng/g)	V (ng/g)	V (ng/g)
Wheat flour SRM 1567a	0.48 ± 0.03	0.50 ± 0.02	400 ± 20	383 ± 10	–	–	–	–	11[a]	9.0 ± 1.0
Whole egg powder 8415	0.247 ± 0.023	0.231 ± 0.03	305 ± 27	313 ± 12	5.63 ± 0.46	5.91 ± 0.02	370 ± 180	420 ± 20	459 ± 81	450 ± 21
Rice flour 1568a	1.46 ± 0.08	1.42 ± 0.06	560 ± 20	536 ± 24	–	–	–	–	7.0[a]	8.0 ± 1.0
Bovine muscle powder 8414	0.08 ± 0.06	0.11 ± 0.01	960 ± 95	998 ± 29	0.052 ± 0.015	0.062 ± 0.005	71 ± 38	83 ± 4	5.0[a]	<4.0
Typical diet 1548a	0.260[a]	0.23 ± 0.01	580 ± 26.7	567 ± 28	2.93[a]	2.61 ± 0.12	–	–	–	–

The value given is the mean ± standard deviation (n = 5).
[a] Reference values.

Table 4
Analysis of certified reference materials for toxic elements determination

Sample SRM	Certified value	Found value	Certified value	Found value	Certified value	Found value	Certified value			Found value	Certified value	Found value
	Cd (ng/g)	Cd (ng/g)	Pb (ng/g)	Pb (ng/g)	Al (μg/g)	Al (μg/g)	Ni (ng/g)	Ni (ng/g)	As (ng/g)	As (ng/g)	Hg (ng/g)	Hg (ng/g)
Wheat flour 1567a	26 ± 2	28 ± 1	<20.0[a]	<4.0	5.7 ± 1.3	6.3 ± 0.3	–	–	6.0[a]	<5.0	5.0[a]	<4.0
Whole egg powder 8415	5[a]	7 ± 1	61.0 ± 12.0	70.0 ± 3.0	540 ± 86	585 ± 39	–	–	10.0[a]	8.9 ± 0.2	4.0 ± 3.0	<4.0
Rice flour 1568a	22 ± 2	19 ± 4	<10.0[a]	6.0 ± 0.1	4.4 ± 1.0	3.7 ± 0.3	–	–	290 ± 30	262 ± 14	5.8 ± 0.5	6.0 ± 0.8
Bovine muscle powder 8414	13 ± 11	20 ± 2	380 ± 240	390 ± 23	1.7 ± 1.4	2.6 ± 0.4	50 ± 40	71 ± 3	9.0 ± 3.0	10.0 ± 1.0	5.0 ± 3.0	<4.0
Typical diet 1548a	35.0 ± 1.5	41 ± 5	44 ± 9	39 ± 4	72.4 ± 1.5	71.2 ± 0.8	–	–	200 ± 10	195 ± 10	5.0[a]	7.0 ± 1.0

The value given is the mean ± standard deviation (n = 5).
[a] Reference values.

To check the final carbon residues after sample decomposition procedures, measurements of the intensity of ^{12}C by ICP-MS in the digestate of the Reference Material Whole Egg Powder 8415 were performed. We observed that digestion with procedure A was less effective in breaking down organics than procedures B, C and D. ^{12}C intensity was almost 2 times higher in procedure A, 1.5 times higher in procedure D and almost the same in procedure C compared to procedure B. It demonstrates that the mixture of nitric acid with hydrogen peroxide are more efficient to decompose food samples than other acid mixtures in close-vessel systems, even using low concentrations of HNO_3. Same results have been observed by other groups. (Araújo, Gonzalez, Ferreira, Nogueira, & Nóbrega, 2002; DeBratter et al., 1995; Souza, Santos, Krug, & Barbosa, 2007). Then, for the following experiments samples were decomposed by using the procedure C with the microwave heating program showed in Table 2.

3.2. Evaluation of internal standards

The use of internal standards is recommended in routine analysis by ICP-MS to compensate the possible drift during long term runs. Based on this, three internal standards, namely Rh, Ir and Y, were evaluated in this study. With rhodium as internal standard better results were obtained for the sixteen analytes. Then, for the following experiments, all samples and standards were prepared containing 10 μg/L Rh.

3.3. Spectral interference correction

The major constituents of food matrices (C, Ca, Cl, P, K, Na and S) are also the main sources of spectral interferences in ICP-MS analysis. For instance, C, Ca and Cl can cause interferences for the determination of ^{51}V ($^{35}Cl^{16}O$), ^{52}Cr ($^{40}Ar^{12}C$), ^{60}Ni ($^{44}Ca^{16}O$). This isobaric interference may be eliminated by selecting a suitable isotope, or may be corrected or reduced by applying correction equations.

Then, we have analyzed all Reference Materials digestates (see Section 2.3) to check for the possible isobaric interferences. The primary isotope for each element was used for this study. Good recoveries were obtained for most of the elements. However, for As, Cd, Co, Cr, Se, Ni and V in typical diet reference material and for As, Cr, Ni and V in the whole egg powder reference material, non-satisfactory recoveries was observed (<90% or >110%). These references materials are rich in calcium and chloride. For instance, the level of calcium and chloride in typical diet Reference Material is 0.197% and 1.21%, respectively. In this context, interference correction equations must be applied to correct for isobaric interferences from the matrix. Then, equations showed in Table 1 were used. Moreover, for chromium we have observed better results using the isotope 53 instead of 52.

3.4. Analytical characteristics

The method detection limits (LODs) obtained for Se, Pb, Cd, Mn, Co, Zn, Cu, Sr, Mo, V, Mg, Hg, Al, As, Cr and Ni were 20, 4.0, 0.2, 5.0,

Table 5
Analytical performance for the determination of essential elements in different types of food samples: comparison between AAS and ICP-MS (proposed method)

Sample	GF AAS Se (μg/g)	This method Se (μg/g)	GF AAS Cu (μg/g)	This method Cu (μg/g)	GF AAS Zn (μg/g)	This method Zn (μg/g)	GF AAS Co (ng/g)	This method Co (ng/g)	GF AAS Mn (μg/g)	This method Mn (μg/g)
Rice	0.036 ± 0.002	0.032 ± 0.004	1.2 ± 0.1	1.1 ± 0.1	6.0 ± 0.4	5.3 ± 0.4	nd	6.5 ± 0.2	5.9 ± 0.3	6.3 ± 0.4
Bean	0.028 ± 0.002	0.026 ± 0.002	0.94 ± 0.03	1.1 ± 0.1	2.9 ± 0.5	3.2 ± 0.4	nd	12.1 ± 0.4	9.4 ± 0.5	8.9 ± 0.4
Egg	1.45 ± 0.28	1.60 ± 0.10	0.89 ± 0.03	1.0 ± 0.1	14.2 ± 1.0	12.4 ± 0.9	nd	7.3 ± 0.3	0.23 ± 0.02	0.21 ± 0.01
Meat	nd	0.018 ± 0.002	1.4 ± 0.2	1.5 ± 0.4	47.3 ± 3.1	42.3 ± 2.8	nd	8.9 ± 0.2	0.26 ± 0.02	0.23 ± 0.02
Fish	0.21 ± 0.01	0.23 ± 0.01	0.32 ± 0.02	0.27 ± 0.02	5.2 ± 0.3	4.8 ± 0.5	nd	8.4 ± 0.2	0.39 ± 0.02	0.43 ± 0.02
Bread	0.027 ± 0.001	0.022 ± 0.001	1.82 ± 0.05	1.9 ± 0.1	7.6 ± 0.6	8.3 ± 0.6	nd	3.2 ± 0.1	11.2 ± 0.9	10.1 ± 0.7
Sugar	nd	nd	0.95 ± 0.03	1.1 ± 0.1	0.87 ± 0.03	0.93 ± 0.07	nd	1.2 ± 0.1	2.1 ± 0.2	1.81 ± 0.08
Vegetables	nd	nd	0.76 ± 0.03	0.68 ± 0.03	2.8 ± 0.2	3.2 ± 0.2	nd	4.9 ± 0.2	2.0 ± 0.3	2.3 ± 0.3
Cheese	nd	0.010 ± 0.001	0.65 ± 0.04	0.60 ± 0.02	30.1 ± 1.4	26.4 ± 1.2	nd	8.4 ± 0.4	0.28 ± 0.03	0.25 ± 0.02
Milk (powder)	0.048 ± 0.003	0.043 ± 0.002	0.23 ± 0.01	0.19 ± 0.01	5.8 ± 0.7	4.8 ± 0.6	nd	10.1 ± 0.4	0.14 ± 0.02	0.10 ± 0.01
Butter	nd	nd	0.13 ± 0.01	0.11 ± 0.01	0.79 ± 0.02	0.84 ± 0.01	nd	1.9 ± 0.2	0.10 ± 0.01	0.09 ± 0.01
Wheat	0.028 ± 0.002	0.025 ± 0.001	0.88 ± 0.03	0.92 ± 0.04	2.9 ± 0.3	3.2 ± 0.5	nd	2.8 ± 0.1	2.5 ± 0.2	2.2 ± 0.2
Pear	nd	nd	0.65 ± 0.04	0.60 ± 0.03	0.38 ± 0.02	0.43 ± 0.03	nd	9.4 ± 0.2	1.9 ± 0.1	2.2 ± 0.3
Brazil nut	37.4 ± 2.9	39.5 ± 1.5	17.4 ± 0.6	20.1 ± 1.4	41.1 ± 2.2	39.4 ± 1.8	132 ± 9	122 ± 12	3.7 ± 0.4	3.1 ± 0.2
Coffee	0.027 ± 0.002	0.024 ± 0.001	0.10 ± 0.01	0.12 ± 0.01	0.28 ± 0.03	0.31 ± 0.02	nd	1.1 ± 0.1	0.50 ± 0.04	0.43 ± 0.02
Chocolate	nd	0.018 ± 0.001	0.73 ± 0.03	0.68 ± 0.03	10.9 ± 0.5	12.1 ± 0.5	nd	8.3 ± 1.2	1.7 ± 0.1	1.4 ± 0.1
Biscuit	nd	0.020 ± 0.001	2.24 ± 0.12	2.5 ± 0.2	6.8 ± 0.4	7.4 ± 0.9	nd	5.6 ± 0.2	5.1 ± 0.4	4.5 ± 0.4
Pasta	nd	0.020 ± 0.001	0.75 ± 0.03	0.83 ± 0.03	2.5 ± 0.3	2.1 ± 0.1	nd	1.8 ± 0.1	2.3 ± 0.2	1.8 ± 0.1
	Mo (μg/g)	Mo (μg/g)	Mg (μg/g)	Mg (μg/g)	Sr (μg/g)	Sr (μg/g)	Cr (μg/g)	Cr (μg/g)	V (ng/g)	V (ng/g)
Rice	0.13 ± 0.01	0.11 ± 0.01	243 ± 32	226 ± 17	0.24 ± 0.03	0.30 ± 0.02	4.2 ± 0.4	3.8 ± 0.2	nd	9.60 ± 0.09
Bean	0.046 ± 0.003	0.051 ± 0.003	450 ± 28	432 ± 9	1.1 ± 0.1	1.4 ± 0.1	0.9 ± 0.1	1.2 ± 0.1	nd	nd
Egg	0.059 ± 0.001	0.067 ± 0.001	811 ± 21	780 ± 38	2.8 ± 0.3	3.2 ± 0.2	0.092 ± 0.003	0.081 ± 0.004	32.1 ± 0.3	35.3 ± 0.2
Meat	0.17 ± 0.01	0.15 ± 0.02	212 ± 5	224 ± 9	0.76 ± 0.04	0.83 ± 0.05	0.063 ± 0.003	0.054 ± 0.003	nd	nd
Fish	0.070 ± 0.003	0.065 ± 0.003	296 ± 19	282 ± 23	0.041 ± 0.003	0.049 ± 0.002	0.083 ± 0.001	0.091 ± 0.003	nd	nd
Bread	0.37 ± 0.03	0.41 ± 0.02	387 ± 32	367 ± 25	0.75 ± 0.03	0.82 ± 0.04	0.10 ± 0.02	0.12 ± 0.02	nd	2.5 ± 0.2
Sugar	0.022 ± 0.001	0.025 ± 0.002	123 ± 8	110 ± 6	0.12 ± 0.02	0.16 ± 0.01	0.15 ± 0.03	0.13 ± 0.02	nd	nd
Vegetables	0.28 ± 0.03	0.32 ± 0.05	150 ± 9	164 ± 10	0.57 ± 0.03	0.65 ± 0.03	0.043 ± 0.004	0.052 ± 0.001	nd	nd
Cheese	0.081 ± 0.001	0.075 ± 0.002	312 ± 10	291 ± 17	4.2 ± 0.2	3.8 ± 0.1	0.17 ± 0.03	0.14 ± 0.02	23.1 ± 1.2	20.3 ± 1.0
Milk (powder)	0.038 ± 0.002	0.045 ± 0.002	101 ± 10	112 ± 10	1.3 ± 0.1	1.2 ± 0.2	0.035 ± 0.03	0.032 ± 0.004	32.2 ± 2.4	34.4 ± 1.2
Butter	0.045 ± 0.003	0.042 ± 0.001	53 ± 4	49 ± 2	0.073 ± 0.001	0.068 ± 0.003	0.12 ± 0.01	0.10 ± 0.01	nd	nd
Wheat	0.020 ± 0.002	0.021 ± 0.001	312 ± 23	289 ± 12	0.32 ± 0.03	0.35 ± 0.03	0.091 ± 0.003	0.083 ± 0.001	nd	nd
Pear	0.010 ± 0.001	0.011 ± 0.001	110 ± 10	99 ± 6	0.081 ± 0.002	0.075 ± 0.001	0.045 ± 0.002	0.049 ± 0.002	nd	nd
Brazil nut	0.031 ± 0.002	0.038 ± 0.002	532 ± 35	480 ± 32	212 ± 10	189 ± 15	1.3 ± 0.1	1.5 ± 0.1	nd	nd
Coffee	0.019 ± 0.001	0.022 ± 0.001	71 ± 3	64 ± 3	0.92 ± 0.02	0.99 ± 0.02	0.087 ± 0.004	0.095 ± 0.002	nd	nd
Chocolate	0.14 ± 0.01	0.17 ± 0.02	398 ± 37	432 ± 21	1.1 ± 0.1	1.4 ± 0.1	0.44 ± 0.03	0.42 ± 0.07	nd	nd
Biscuit	0.14 ± 0.03	0.11 ± 0.01	300 ± 13	282 ± 12	0.054 ± 0.002	0.060 ± 0.002	0.15 ± 0.02	0.15 ± 0.01	nd	nd
Pasta	0.033 ± 0.001	0.034 ± 0.001	121 ± 7	109 ± 9	0.32 ± 0.03	0.35 ± 0.02	0.057 ± 0.002	0.053 ± 0.001	nd	nd

The value given is the mean ± standard deviation (n = 5).
nd = not detected.

Table 6
Analytical performance for the determination of toxic elements in different types of food samples: comparison between AAS and ICP-MS (proposed method)

Sample	GF AAS Cd (ng/g)	This method Cd (ng/g)	GF AAS Pb (ng/g)	This method Pb (ng/g)	GF AAS Al (μg/g)	This method Al (μg/g)	GF AAS Ni (μg/g)	This method Ni (μg/g)	GF AAS As (ng/g)	This method As (ng/g)	CV AAS Hg (ng/g)	This method Hg (ng/g)
Rice	5.6 ± 0.9	4.8 ± 0.2	nd	5.0 ± 0.1	0.71 ± 0.06	0.61 ± 0.02	0.032 ± 0.002	0.031 ± 0.002	nd	12.1 ± 0.2	15.4 ± 0.5	13.5 ± 0.2
Bean	nd	2.1 ± 0.1	nd	7.3 ± 0.2	12.1 ± 1.2	10.1 ± 0.6	0.020 ± 0.002	0.016 ± 0.001	nd	8.9 ± 0.2	nd	nd
Egg	nd	1.1 ± 0.1	nd	18.4 ± 0.2	0.26 ± 0.04	0.31 ± 0.03	0.12 ± 0.01	0.091 ± 0.003	nd	10.2 ± 0.2	6.1 ± 0.4	5.5 ± 0.2
Meat	nd	0.21 ± 0.01	nd	15.6 ± 0.2	0.12 ± 0.01	0.15 ± 0.01	0.019 ± 0.001	0.021 ± 0.001	nd	5.7 ± 0.1	10.9 ± 0.4	12.0 ± 0.2
Fish	12.3 ± 1.4	9.1 ± 0.7	99.1 ± 8	104.4 ± 0.8	0.32 ± 0.03	0.29 ± 0.01	0.055 ± 0.002	0.052 ± 0.001	61.5 ± 0.3	59.1 ± 0.3	109 ± 21	134 ± 15
Bread	nd	0.22 ± 0.01	nd	12.9 ± 0.2	1.0 ± 0.1	0.92 ± 0.02	0.036 ± 0.002	0.032 ± 0.001	nd	5.2 ± 0.1	nd	nd
Sugar	13.5 ± 1.0	12.5 ± 0.2	86.4 ± 8.9	74.4 ± 0.2	2.0 ± 0.1	2.3 ± 0.1	0.057 ± 0.004	0.054 ± 0.002	nd	7.4 ± 0.2	9.9 ± 0.6	10.1 ± 0.4
Vegetables	nd	6.3 ± 0.1	nd	6.2 ± 0.1	0.10 ± 0.01	0.12 ± 0.01	0.030 ± 0.003	0.032 ± 0.001	nd	nd	nd	nd
Cheese	nd	0.64 ± 0.03	nd	19.3 ± 0.3	0.11 ± 0.01	0.09 ± 0.01	0.041 ± 0.001	0.043 ± 0.002	nd	5.4 ± 0.3	7.3 ± 0.9	6.3 ± 0.4
Milk (powder)	nd	0.35 ± 0.02	nd	14.4 ± 0.2	0.20 ± 0.01	0.18 ± 0.01	0.060 ± 0.004	0.056 ± 0.002	nd	6.3 ± 0.2	5.2 ± 0.4	4.6 ± 0.3
Butter	nd	0.89 ± 0.02	nd	22.3 ± 0.2	0.081 ± 0.003	0.09 ± 0.01	0.039 ± 0.002	0.034 ± 0.001	nd	23.2 ± 0.3	6.3 ± 0.3	6.9 ± 0.6
Wheat	nd	1.2 ± 0.1	82.4 ± 5.9	87.8 ± 1.4	0.78 ± 0.03	0.82 ± 0.03	0.073 ± 0.003	0.067 ± 0.002	nd	6.12 ± 0.06	nd	nd
Pear	nd	nd	nd	12.1 ± 0.1	0.093 ± 0.001	0.10 ± 0.01	nd	0.013 ± 0.001	nd	nd	nd	nd
Brazil nut	nd	4.6 ± 0.2	nd	nd	0.43 ± 0.05	0.39 ± 0.01	4.0 ± 0.4	4.6 ± 0.2	nd	5.3 ± 0.1	nd	nd
Coffee	nd	0.28 ± 0.01	nd	nd	0.32 ± 0.01	0.35 ± 0.02	nd	0.012 ± 0.001	nd	nd	nd	nd
Chocolate	nd	1.9 ± 0.1	nd	14.6 ± 0.3	3.2 ± 0.3	2.93 ± 0.04	0.54 ± 0.03	0.59 ± 0.03	nd	nd	nd	nd
Biscuit	nd	2.2 ± 0.2	nd	14.2 ± 1.4	0.18 ± 0.01	0.23 ± 0.05	nd	0.023 ± 0.001	nd	1.2 ± 0.1	nd	nd
Pasta	nd	0.44 ± 0.01	nd	12.7 ± 0.2	0.15 ± 0.02	0.18 ± 0.01	nd	0.032 ± 0.001	nd	4.3 ± 0.2	nd	nd

The value given is the mean ± standard deviation $n = 5$).
nd = not detected.

0.5, 30, 16, 12, 1.0, 5.0, 60, 4.0, 35, 5.0, 10, 7.0 ng/g, respectively. The LODs were determined as 3 SD of the 20 consecutive measurements of the reagent blanks multiplied by the dilution factor used for sample preparation (250 mg of sample/50 mL).

The accuracy of the proposed method was evaluated by analyzing five Certified Reference Materials from the National Institute of Standards and Technology (NIST). The obtained results are shown in Table 3 and Table 4 for essential and toxic elements, respectively. Additional validation were provided by the analyses of 18 different types of food samples (rice, bean, egg, meat, fish, bread, sugar, vegetables, cheese, powder milk, butter, wheat, pear, brazil nut, coffee, chocolate, biscuits and pasta) analyzed by the proposed method and using comparative methods with AAS as detector (Tables 5 and 6).No significant statistical differences at 95% confidence level were observed between certified values and found levels for Certified Reference Materials analysis by applying paired *t*-test.. Moreover, the values found by using comparative methods (AAS detector) and by using the proposed method (for ordinary sample analysis) were in good agreement (Tables 5 and 6). It demonstrates the accuracy of the proposed method. The between- and within-batch precision for most of the elements analyzed were lower than 12% and 8%, respectively ($n = 10$, Whole Egg Powder 8415). However, between- and within-batch precision for mercury and arsenic were lower than 20% and 15%, respectively ($n = 10$, Whole Egg Powder 8415). An explanation for that could be the low levels of mercury and arsenic in the Whole Egg Powder 8415 Certified Reference Material.

4. Conclusion

The proposed method showed to be reliable for the determination of 16 elements in different types of food samples by inductively coupled plasma mass spectrometry. The good agreement between found values and the certified or reference values of CRMs samples indicates effective recovery of analytes after digestion and subsequent accurate detection. Considering the time for sample digestion (digestion, cooling and dilution), and the scanning conditions used in this method and showed in Table 1, at least 30 samples can be routinely analyzed per day in triplicate measurements for each sample (8h/day). Moreover, when compared to other studies in the literature when ICP-OES or AAS were used as detectors the proposed simultaneous method present better detection limits (ppt-ppb level) and similar or better precision.

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