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ARTICLE

Determination of Essential and Non-Essential Elements in Dietary Supplements by Microwave-Induced Plasma Optical Emission Spectrometry: *Method Development and Study of Non-Spectral Interferences*

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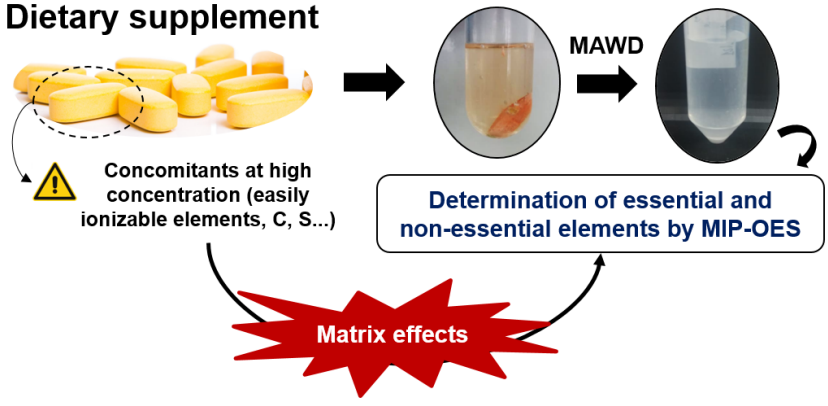

Dietary supplements have been used to overcome nutritional deficiencies and the knowledge concerning essential and non-essential elements is an important issue. In this work the suitability of microwave-induced plasma optical emission spectrometry (MIP OES) for the determination of essential and non-essential elements in dietary supplements was evaluated. Twelve dietary supplement samples of several classifications (vitamins/minerals, minerals, amino acids, and botanicals) were digested in their whole form for determination of essential (Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Na, and Zn) and non-essential (Ag, Al, B, Ba, Be, Cd, Cr, La, Li, Ni, Pb, Sr, and V) elements by MIP OES. Potential non-spectral interferences by common concomitants (C, S, K, Na, and Ca) were evaluated, as well as those by residual acidity of digests. The study of non-spectral interferences showed that a signal suppression effect is observed with higher concentrations of Ca, Na, and K. Relatively good robustness was observed considering the presence of C and S, as well as residual HNO_3. The limits of quantification (LOQs) were dependent on the sample mass used for decomposition (from 0.6 to 1.6 g in the commercial product) and on the minimum dilution factor. From the results, there was a prevalence of essential and non-essential elements in vitamins and minerals, minerals, and botanicals-based dietary supplements, whereas lower concentrations were found in the dietary supplements based on amino acids. All elements were in a concentration below the recommended dietary allowances (RDAs), exception for those with the concentration intentionally higher. Accuracy of results by

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MIP OES was evaluated by using standard reference materials (SRM) NIST 1572 and NIST 1575a. In addition, results showed no statistical difference by comparison with those by ICP OES. MIP OES proved to be a suitable technique for the determination of metals in dietary supplements, being a feasible alternative for the quality control of these products.

Keywords: dietary supplements, essential elements, non-essential elements, MIP OES, bioanalytical chemistry

INTRODUCTION

Several essential nutrients are required for the healthy functioning of the human body, such as proteins, vitamins, and minerals. Nowadays, due to the large consumption of processed foodstuffs and the lack of essential nutrients in these ones, people have been suffering from nutritional deficiencies and, consequently, from related diseases.[1] In order to overcome these nutritional deficiencies the use of dietary supplements has grown, associated with other factors, such as the carefulness of people with health care and the higher consumption by athletes and bodybuilding exercise practitioners, among others.[1,2]

The elements required by humans and provided by dietary supplements can be divided into essential and non-essential elements, depending on their known or unknown/uncertain role in the physiological system of humans, respectively.[3] In addition to those elements added to supply, both essential and non-essential elements can be introduced as contaminants, from raw materials, manufacturing, transport, and storage of the final products, moreover those introduced into botanicals-based from the environment.[2,4] In this sense, the contamination of several classes of dietary supplements by these elements has been reported.[5–7] In view of this, for monitoring the concentration of essential and non-essential elements added as a supplier in dietary supplements, as well as present as elemental contaminant, several analytical techniques have been used, with emphasis to the plasma-based spectrometric techniques, such as optical emission spectrometry (ICP OES) and mass spectrometry (ICP-MS).[2] Among these, microwave-induced plasma optical emission spectrometry (MIP OES) can be also an alternative, promoting suitable limits of detection (LOD) for quality control of essential and non-essential elements in dietary supplements, similar with those by ICP OES. However, so far, MIP OES was few explored and only one report was found for the determination of Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, V, and Zn in Spirulina dietary supplements.[8]

Elemental determination by MIP OES tends to be prone to matrix effects more than ICP OES due to the use of nitrogen as plasma gas on the current MIP OES instrumentation. This results in lower plasma temperatures compared to that achieved by argon plasma-based (about 5000 K for nitrogen-based against 10000 K for argon-based plasmas).[9] This characteristic makes essential to evaluate the non-spectral interferences in the analysis by N_2-MIP OES. However, to date, there are few studies reported about this on the current MIP OES instruments, mostly focused on non-spectral interferences caused by easily ionizable elements (EIEs, e.g. Na and K).[10–13] Either signal suppression or enhancement have been related to the high concentrations of EIEs, mainly due to changes in the physical properties of the plasma, such as excitation temperature and ionization equilibrium.[12,14] Moreover, the excitation/ionization energy of the element line also impact on the interference phenomena. Serrano et al.[12] reported that atomic lines with excitation energy below 3.26 eV had a signal enhancement with a 0.5% w w^{-1} calcium nitrate solution, while ionic lines (higher excitation/ionization energy) had a signal suppression. This same work is the only one reporting the influence of carbon and sulfur on the determination by MIP OES, despite the well-studied effects demonstrated by ICP OES.[15–17] Operating with 0.5% w w^{-1} glycerol or sulfuric acid solutions, lower effects were observed by MIP OES when compared with ICP OES. In that case, the plasma temperature was considered beneficial to reduce the physical effects caused by carbon and sulfur on the measurements by MIP OES.[12]

Thus, the purpose of this work was to evaluate the suitability of MIP OES for the determination of essential and non-essential elements in dietary supplements, aiming a method for the quality control of

elements added as a supplier, as well as those present as contaminants. For this, in order to develop a reliable method, a study of non-spectral interferences was carried out, comprising common concomitant elements present in dietary supplements (C, S, Na, K, and Ca). Moreover, non-spectral interferences caused by residual HNO_3 acidity remained from sample preparation were also investigated.

MATERIALS AND METHODS

Samples and standard reference materials

Twelve dietary supplements from different brands were purchased in the local and electronic market, originating from Brazil and the USA, in the form of tablets, capsules, and powders. The samples were coded as vitamins and minerals (VM), minerals (MN), amino acids (AM), and botanicals (BT). The characteristics of each sample are shown in Table S1 (Supplementary Material). Whole samples were used for sample digestion, without any pre-treatment procedure, by inserting the tablets, capsules, or powders directly into the digestion vessel.

The accuracy of the proposed method was evaluated using two standard reference materials (SRM): 1572 (Citrus Leaves) and 1575a (Trace Elements in Pine Needles), both from the National Institute of Standards and Technology (NIST, USA).

Instrumental

A microwave-induced plasma optical emission spectrometer (4210 MP AES, Agilent Technologies, USA) equipped with a N_2 generator (model 4107, Agilent Technologies, USA), a five-channel peristaltic pump and an inert concentric nebulizer (OneNeb® series 2, Agilent Technologies, USA) was used. Operational conditions for measurements by MIP OES are shown in Table I. The nebulizer gas flow-rate and the plasma observation position of each element were optimized automatically by the instrument software (MP Expert, Agilent Technologies, USA).

Sample preparation was performed in a microwave-assisted single reaction chamber system (Ultrawave™, Milestone, Italy). The system is composed by five quartz vessels with a capacity of 40 mL, which are placed in a rack and into a modified polytetrafluoroethylene (PTFE-TFM) vessel. The vessel is inserted in the microwave cavity chamber (1 L), which is sealed and pressurized with 40 bar of Ar (99.5%, White Martins, Brazil) before microwave irradiation. The system was set to operate at a maximum power, temperature, and pressure of 1500 W, 270 °C, and 160 bar, respectively.

Reference values for elements were obtained using an inductively coupled plasma optical emission spectrometer (Spectro Ciros CCD, Spectro Analytical Instruments, Germany). Carbon and sulfur content in digests were also determined by ICP OES. The operational conditions for the determination by ICP OES are shown in Table S2 (Supplementary Material). Argon (99.998%, White Martins, Brazil) was used as plasma, auxiliary, and nebulizer gas in ICP OES.

Determination of residual acidity in digests was performed by an automatic titration system (836, Metrohm, Switzerland) equipped with a module of automatic stirring (803 Ti Stand, Metrohm) and a combined pH electrode (6.0262.100, Metrohm).

All statistical calculations were performed using GraphPad InStat software (GraphPad InStart Inc, Version 3.06, 2007) with a confidence level of 95%.

Table I. Operational conditions for elemental determination by N_2-MIP OES

Parameter	MIP OES
Microwave frequency (MHz)	2450
Plasma power (kW)	1.0
Plasma gas flow-rate (L min^{-1})	20
Auxiliary gas flow-rate (L min^{-1})	1.0

(continues on the next page)

Table I. Operational conditions for elemental determination by N_2-MIP OES (continuation)

Parameter	**MIP OES**	
Background correction	Auto	
Replicates	3	
Read time (s)	3	
Stabilization time (s)	15	
Peristaltic pump rotation	15	
Analytes (wavelength, nm)	Nebulizer gas flow-rate (L min^{-1})	Plasma observation position
Ag(I) (328.068)	0.70	50
Al(I) (394.401)	0.35	-130
B(I) (249.677)	0.40	10
Ba(II) (493.408)	0.75	0
Be(I) (234.861)	0.50	0
Ca(II) (396.847)	0.65	-10
Cd(I) (228.802)	0.45	-10
Co(I) (340.512)	0.60	80
Cr(I) (357.868)	0.90	0
Cu(I) (324.754)	0.80	10
Fe(II) (259.940)	0.50	50
K(I) (766.461)	1.00	10
La(II) (433.374)	0.55	-10
Li(I) (670.784)	1.00	10
Mg(II) (280.271)	0.55	-10
Mn(I) (403.307)	1.00	-10
Mo(I) (386.410)	0.75	-10
Na(I) (589.592)	1.00	10
Ni(I) (341.476)	0.30	40
Pb(I) (363.957)	0.55	-10
Sr(II) (407.771)	0.60	0
V(I) (437.923)	0.95	-10
Zn(I) (213.857)	0.55	-40

(I) Atomic emission line; (II) Ionic emission line.

Reagents and standards

Water was ultra-purified in a Milli-Q system (18.2 MΩ cm, Merck Millipore, USA) and was used for the preparation of all standards, solutions, and dilutions, as well as for cleaning and washing materials.

Nitric acid (65%, Merck, Germany) and hydrochloric acid (37%, Merck) were sub-boiling distilled (DuoPur, Milestone, Italy) before use for sample digestion.

For elemental determination by MIP OES and ICP OES, analytical standards ranging from 1 to 100 μg L^{-1} were prepared by dilution of a multielement stock reference solution (SCP33MS, SCP Science, 10 mg L^{-1}, Canada) in 5% v v^{-1} HNO_3. Moreover, for the determination of analytes at higher concentration, analytical standards from 0.25 to 5 mg L^{-1} were prepared by dilution of a multielement stock reference solution (Merck IV, Merck, 1000 mg L^{-1}) in 5% v v^{-1} HNO_3. For the determination of dissolved carbon in digests by ICP OES, analytical standards (25 to 500 mg L^{-1}) were prepared by dilution of a 10 g L^{-1} stock solution, prepared with citric acid (Dinâmica, Brazil) in ultrapure water. Ytrium (Assurance, Spex CertiPrep®, 1001.5 ± 3 mg L^{-1} in 0.28 mol L^{-1} HNO_3, USA) was used as internal standard for the determination of carbon by ICP OES, being 1 mg L^{-1} added to all analytical standards, blanks, and samples. Sulfur was determined by ICP OES and analytical standards (0.25 to 5 mg L^{-1}) were prepared by dilution of a stock reference solution (Assurance, Spex CertiPrep®, 1003 ± 3 mg L^{-1}, USA) in 5% v v^{-1} HNO_3.

For the study of non-spectral interferences by MIP OES, spiked solutions containing 100 μg L^{-1} of all analytes were prepared in synthetic matrices containing 25, 250, and 5000 mg L^{-1} of C, S, Na, K, and Ca in 5% v v^{-1} HNO_3. A 10 g L^{-1} stock solution of each interferent was prepared by dissolution/dilution of citric acid, calcium nitrate (Dinâmica, Brazil), sulfuric acid (97%, Sigma Aldrich, USA), sodium nitrate (Cinética Química, Brazil), and potassium nitrate (Êxodo Científica, Brazil). Moreover, non-spectral interferences by residual HNO_3 acidity (10 to 50% v v^{-1}) were also evaluated.

Sample preparation

The procedure used for the decomposition of dietary supplements was based on previous works.[18,19] Whole samples with sample masses ranging from 0.5 to 1.6 g for tablet or capsules were used. For the powdered samples, 0.5 g was weighed and inserted into the digestion vessel. Samples were weighed directly into the digestion vessels, and then 10 mL of HNO_3:HCl (8:2) solution was added. The digestion vessels were placed in the instrument rack, which was inserted into the single reaction chamber system (lined with PTFE-TFM, containing 130 mL of water and 5 mL of HNO_3). The system was then sealed and pressurized with 40 bar or Ar. All digestions were carried out using maximum temperature, pressure, and microwave power of 270 °C, 160 bar, and 1500 W, respectively. Heating program used was: 10 min of ramp and holding for 20 min at 270 °C. After digestion, the obtained digests were transferred to volumetric flasks and made up to 25 mL with ultrapure water for further elemental determination by MIP OES, ICP OES, and ICP-MS.

Elemental determination by MIP OES and study of non-spectral interferences

The interferences caused by common concomitant elements (C, S, Na, K, and Ca) on the determination by MIP OES were evaluated. Solutions containing 100 μg L^{-1} of all analytes were spiked with 25, 250, or 5000 mg L^{-1} of each concomitant. In addition, the influence of the residual HNO_3 acidity in the digests was also evaluated, and the spiked solutions of all analytes were prepared in 10, 20, 30, 40, and 50% v v^{-1} HNO_3. Reference values for the study of non-spectral interferences were considered those for a solution containing 100 μg L^{-1} of all analytes in 5% v v^{-1} HNO_3.

In this study, acceptable spike recoveries were based on the repeatability uncertainty. In this sense, 10 replicates of a standard solution containing 100 μg L^{-1} of all analytes in 5% v v^{-1} HNO_3 were measured, and a relative standard deviation (RSD) of 4.8% was obtained. Then, an expanded uncertainty equal to 11% was estimated, which was calculated using the standard uncertainty (4.8%), multiplied by the coverage factor (k=2.2).[20] Thus, the acceptable recoveries were in the range of 89–111% and it was used for all optimizations carried out in this study.

In addition to consider spike recoveries, non-spectral interferences were also related to the E_{sum} (i.e., the sum of the excitation and ionization energy) of the lines determined by MIP OES (Table S3, Supplementary Material).

RESULTS AND DISCUSSION

Considering the complex matrices of the dietary supplements, that can come from materials from several origins and can have a mixture of matrices in their compositions and taking into account the interferences that can arise from digests in the lower temperature MIP, non-spectral interferences caused by the common concomitant elements (C, S, Na, K, and Ca) were evaluated. Moreover, non-spectral interferences from residual HNO_3 acidity remained from sample preparation were also investigated.

Study of non-spectral interferences by MIP OES

Carbon and sulfur-based non-spectral interferences by MIP OES

Dietary supplements, mainly vitamins and botanicals-based, can contain a relatively high concentration of carbon, which can cause interferences on the measurements by MIP OES. Carbon-related matrix effects on spectroscopic techniques have been widely studied.[15,21] For optical-emission techniques, such as MIP OES, effects on the signals can be induced by changes in the analyte transport and plasma ionization equilibrium.[16]

Carbon can be present in solutions as a consequence of partial digestion. In view of this, carbon-based matrix effects on the determinations by MIP OES were evaluated. Citric acid is a non-volatile carbon compound that has been normally used for carbon-based interferences studies.[18,22] Spiked solutions at 100 µg L^{-1} containing 25, 250, and 5000 mg L^{-1} C (as citric acid) were evaluated.

As the carbon content as well as the amount digested was different for each sample, dissolved carbon remained in digests ranged from 11.1 to 179 mg L^{-1} (Table S4, Supplementary Material). Spike recoveries for essential and non-essential elements are presented in Figure S1 (Supplementary Material).

The results demonstrated good robustness of MIP OES even operating with high concentration of carbon. Signal suppression for Co and Mo was observed, but at relatively high carbon concentration (5000 mg L^{-1}). It is important to note that, considering the E_{sum} of lines (Figure 1A), both Co and Mo have lower E_{sum} (3.21 and 4.05 eV, respectively) (dots between dashed lines indicate no matrix effect). Signal suppression effect by carbon have been related to lines with excitation energy lower than 6 eV, probably due to the inactivation of the excited state of the analyte by collisions with carbon atoms or radicals.[16] In another study,[12] MIP OES demonstrated to be more robust than ICP OES for the presence of 5% w w^{-1} glycerol (ca. 20 g L^{-1} of carbon), and no effects related to carbon were observed for the determination of As, Co, Cu, Mg, Mn, Mo, Sc, Se, Sr, and Zn. In general, the results in this work agree with those previous reports demonstrating a relatively suitable robustness of MIP OES to high concentrations of carbon which can be related to the lower plasma temperature that minimizes the effects (***e.g.,*** charge transfer reaction) caused by carbon in the plasma.[12]

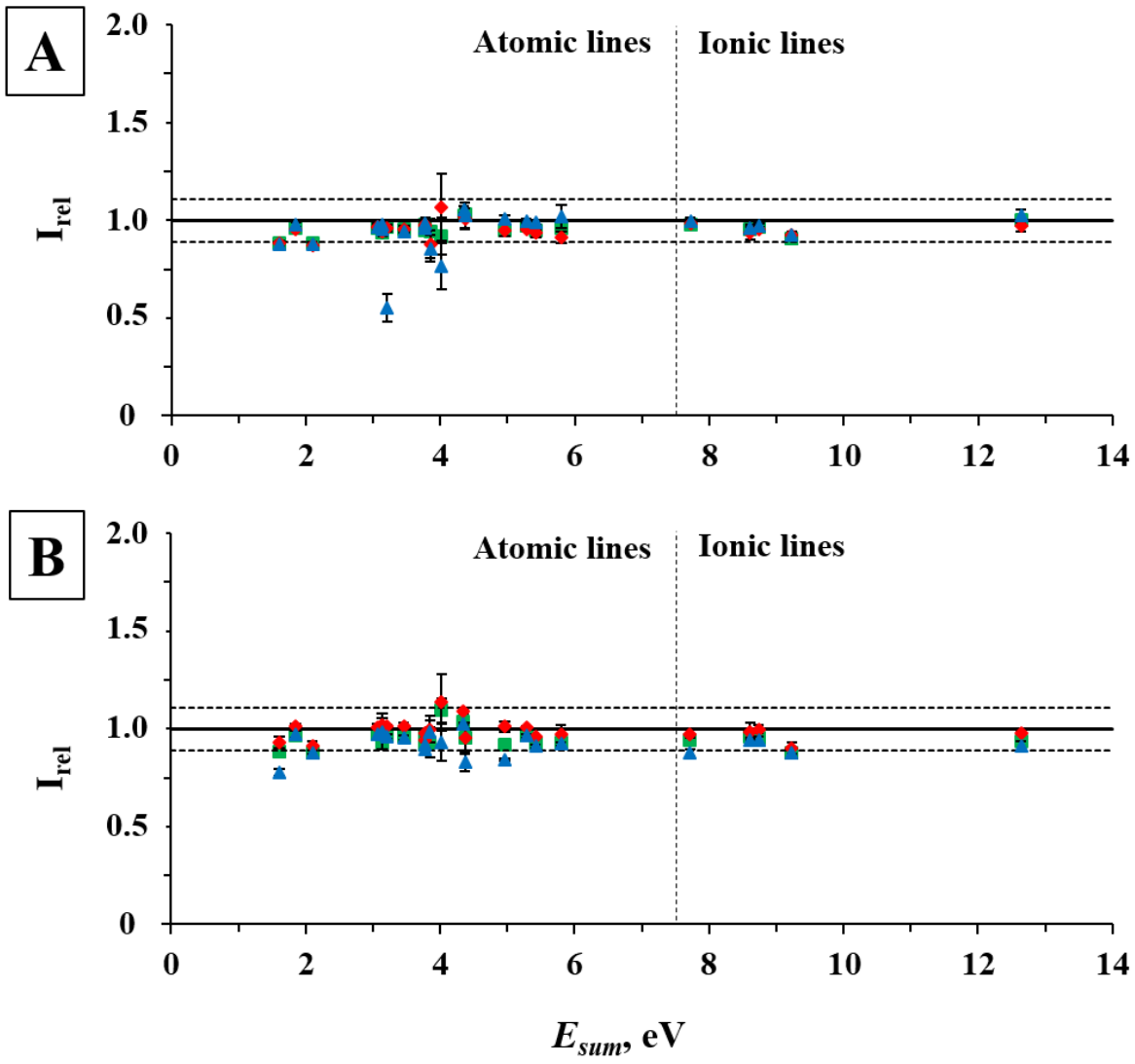

Figure 1. Relative signal intensity (I_{rel}) for lines according to E_{sum} values influenced by A) carbon (as citric acid) and B) sulfur (as sulfuric acid), with concentrations of 25 (■), 250 (◆), and 5000 (▲) mg L^{-1} by MIP OES. Continuous and dashed lines represent the 5% v v^{-1} HNO_3 reference solution value and the expanded uncertainty, respectively.

Sulfur can induce effects similar to carbon on the properties of the plasma (*i.e.*, ionization equilibrium, charge transfer reaction, etc.).[17] Due to matrix composition, sulfur content can be relatively high for some samples. As can be seen in Table S4, sulfur concentration in dietary supplements samples were in the range of 13.3 to 307 mg L^{-1}. The effect of sulfur on the determination by MIP OES was evaluated using spiked solutions containing different concentrations of sulfur (as sulfuric acid). Just as noted for carbon, low effects by sulfur were observed (Figure S2, Supplementary Material), since only the signal of K was suppressed with a relatively high sulfur concentration (5000 mg L^{-1}). It can be explained, possibly, by the lower E_{sum} of the line used for K (1.61 eV, Figure 1B) and the effect on of the excited state of elements with lower excitation energy caused by sulfur at high concentrations. As reported,[12] the poor matrix effects induced by sulfur in MIP OES were explained by the similar plasma temperatures even using a 5% w w^{-1} H_2SO_4 (ca. 16 g L^{-1} of S) solution compared to that using 1% w w^{-1} HNO_3 solution, and by the minimized physical interferences using the OneNeb® nebulizer (the same employed in this work).

Sodium-, potassium-, and calcium-based non-spectral interferences by MIP OES

High concentration of EIEs, such as sodium and potassium, induce a lower temperature and a higher electronic density in the plasma, causing changes in the ionization equilibrium.[23] Non-spectral interferences by sodium have been reported from 300 mg L^{-1}.[11] Despite fewer effects are expected for calcium due to the higher ionization energy (6.11 eV against 5.14 eV for sodium, for example), significant consequences can be observed in the presence of higher concentrations of calcium (the case of many dietary supplements).[14] For the samples investigated on this work, Na, K, and Ca concentrations were in the range of 6.27 to 128, 0.046 to 532, and 0.215 to 15851 mg L^{-1}, respectively (Table S4).

Non-spectral interferences promoted by sodium (as sodium nitrate), potassium (as potassium nitrate), and calcium (as calcium nitrate) on the determination by MIP OES were evaluated using spiked solutions containing crescent concentrations of these elements. As can be observed by spike recoveries (Figures S3 and S4, Supplementary Material), similar effects on signals were observed by both sodium and potassium, being those by sodium more significant. No interference for 25 mg L^{-1} of sodium and potassium was observed (except for Ca, which suffer a signal suppression in the presence of sodium). Absence of interferences were also observed by Baranyai et al.[11] in the determination of Ca, Cu, Fe, K, Mg, and Zn with about 30 mg L^{-1} of sodium in human blood serum. More pronounced effects were observed from 250 mg L^{-1} of sodium and potassium. Signal suppression for Ba, La, Ni, Pb, and Sr at 250 mg L^{-1} was observed. At least 20% suppression occurred for most of the analytes for 5000 mg L^{-1} of potassium and/or sodium, including total signal suppression of La, Ni, and Pb with sodium.

Regarding interferences by calcium, no effects with 25 mg L^{-1} were observed (Figure S5, Supplementary Material). From 250 mg L^{-1}, the effect of signal suppression was milder than those by sodium and potassium, and a total signal suppression for Mg and Pb occurred with 5000 mg L^{-1}. On the other hand, on the contrary of that observed for sodium and potassium, signal enhancement of some elements with lower E_{sum} (K, Li, Mo, Na, and V) was observed in the presence of higher concentration of calcium, reaching an enhancement of 130% for Na at 5000 mg L^{-1}.

As can be observed in Figure 2A and Figure 2B, atomic lines with lower E_{sum} had their signals more impacted by higher concentrations of sodium and potassium (from 5000 mg L^{-1}). However, signal suppression of ionic lines can be observed even with a concentration of 25 mg L^{-1}, which can be explained by higher energy required for the ionic lines.[14] On the other hand, different behavior occurred in the presence of calcium (Figure 2C). Whereas a signal enhancement for atomic lines with E_{sum} lower than 3.21 eV was observed (except for Al), atomic/ionic lines with E_{sum} higher than 3.46 eV had their signals suppressed. This same behavior was observed for the presence of 0.5% w w^{-1} of calcium nitrate (ca. 1.2 g L^{-1} of calcium).[12]

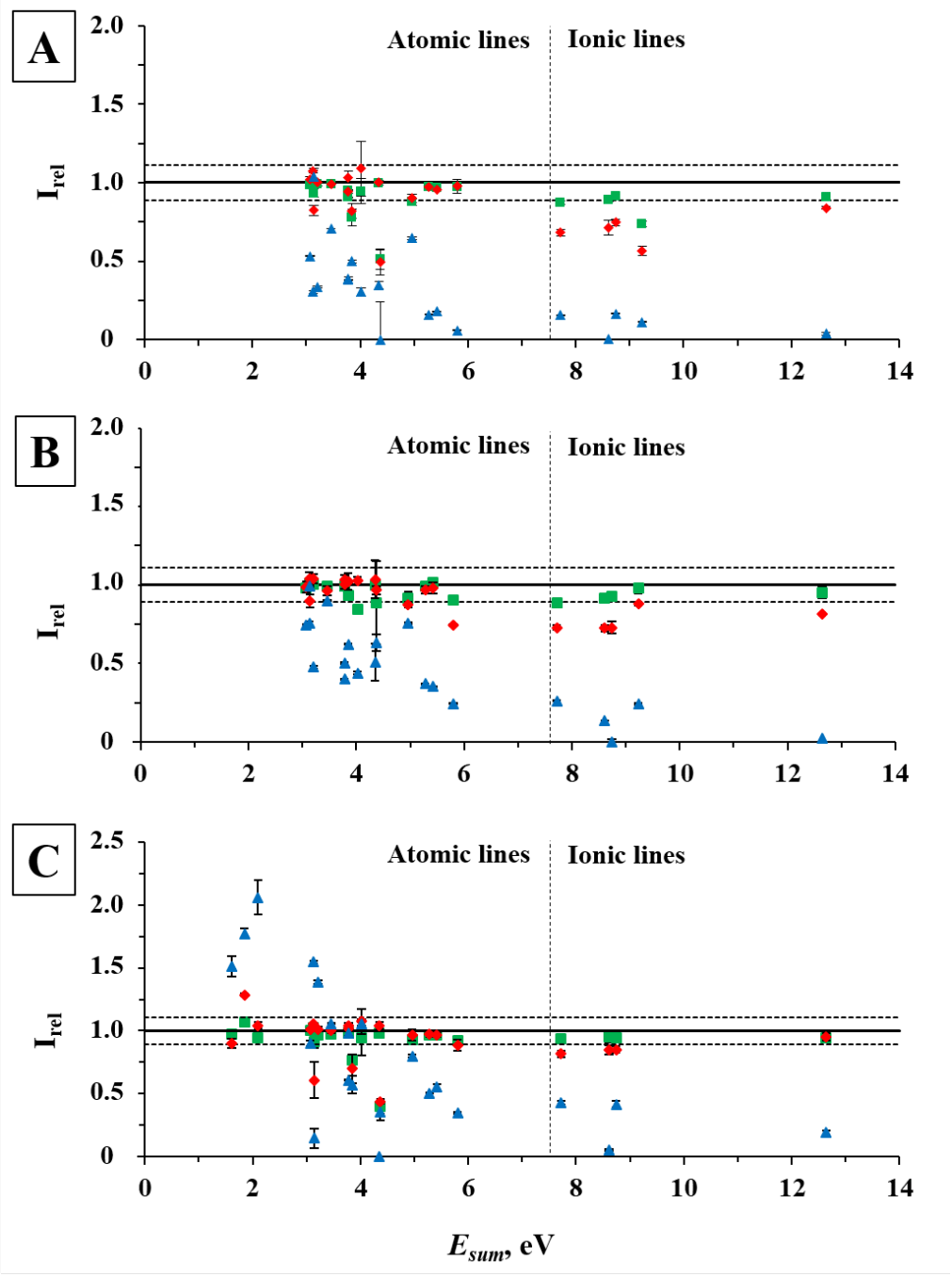

Figure 2. Relative signal intensity (Irel) for lines according to E_{sum} values influenced by A) sodium (as sodium nitrate), B) potassium (as potassium nitrate) and C) calcium (as calcium nitrate), with concentrations of 25 (■), 250 (◆), and 5000 (▲) mg L^{-1} by MIP OES. Continuous and dashed lines represent the 5% v v^{-1} HNO_3 reference solution value and the expanded uncertainty, respectively.

Influence of the residual HNO_3 acidity

It is well known that high residual acidity remained from sample preparation can induce physical non-spectral interferences on measurements by plasma-based spectrometric techniques. Changes in the analyte transport to the plasma, as well as effect in the thermal characteristics are reported.[24] However, so far, there is no study demonstrating the influence of the residual HNO_3 acidity on the determinations by MIP OES.

Thus, for this evaluation, spiked solutions containing all analytes were prepared to contain HNO_3 concentrations at 10, 20, 30, 40, and 50% v v^{-1}. The spike recoveries can be seen in Figure S6 (Supplementary Material). In general, MIP OES demonstrated a good tolerance at high HNO_3 concentrations, since the signal for most of the analytes was not damaged even when operating with a 50% v v^{-1} HNO_3 solution. On the other hand, Al, Co, K, and Pb had their signals suppressed for a 30% v v^{-1} HNO_3 solution, which is similar to the effects of residual HNO_3 acidity observed by ICP OES.[24] In this point, it is important to mention that digests of all samples, even using a powerful digestion system, presented a residual acidity in solution from 15 to 29%, except for AM-1 and AM-2 samples, in which the residual acidity was about 60% (probably due to acid hydrolysis of amino acids present), suggesting that care must be taken. Based on the results, if acidity higher than 30% is observed, a proper dilution must be performed previous to analysis.

Determination of common concomitants in dietary supplements

As observed in the study of non-spectral interferences, EIEs, such as sodium, potassium, and calcium, as well as carbon, sulfur, and residual HNO_3 acidity can bring several interferences on the determinations by MIP OES. Given this, the concentration of Na, K, Ca, S, and dissolved carbon in digests were determined by ICP OES. In addition, the residual acidity was determined by potentiometric titration. The results can be seen in Table S4.

Carbon dissolved in digests and sulfur concentration was not higher than 130 and 307 mg L^{-1}, respectively. From the study of non-spectral interferences, it is not expected interferences caused by carbon or sulfur for a concentration below 5000 mg L^{-1}. On the other hand, the maximum concentrations of sodium, potassium, and calcium in the samples were 128, 532, and 15851 mg L^{-1}, respectively. Based on the study of non-spectral interference, these concentrations interfere on several elements, mainly if synergic effects are considered. Because of this, a minimum dilution factor must be defined to the determinations by MIP OES, considering the concentration of at least sodium, potassium, and calcium. The dilutions factors employed were 10-fold for BT-2, 20-fold for VM-1 and 50-fold for VM-3, VM-4, MN-1, and MN-2 samples. Moreover, a minimum dilution factor of 4-fold was defined for samples AM-1 and AM-2 due to residual acidity, which was higher than 30%, to avoid signal suppression. Finally, it is important to emphasize that the LOQs of the method were impacted by the minimum dilution factor required, which will be further discussed.

Determination of essential and non-essential elements in dietary supplements by MIP OES after digestion by MAWD-SRC

Quality control of essential and non-essential elements added as supplier or as elemental impurities in dietary supplements is crucial. However, exception for As, Cd, Hg, and Pb, which have maximum concentrations in dietary supplements established by United States Pharmacopoeia (USP) General Chapter 2232[25] and by EC 629/2008 (except As),[26] there are not a regulation neither to other essential or non-essential elements in dietary supplements. Despite dietary supplements are not regulated as pharmaceutical products, the Q3D guideline on the elemental impurities of the International Council for Harmonization of Technical Requirements for Pharmaceuticals for Human Use (ICH-Q3D)[27] can be used as a reference for the maximum concentrations of some elements. The ICH-Q3D classified the elements in three classes, depending on their toxicity and uptake route: Class 1 (As, Cd, Hg, and Pb), Class 2A (Co, Ni, and V), Class 2B (Ag, Au, Ir, Os, Pd, Pt, Rh, Ru, Se, and Tl), and Class 3 (Ba, Cr, Cu, Li, Mo, Sb, and Sn). In addition, the recommended dietary allowance (RDA) of the elements also can be used as a limit for some essential elements (such as Ca, Fe, Zn, among others).

The concentrations of essential and non-essential elements determined in dietary supplements by MIP OES after digestion are shown in Table II. Considering the high concentration of concomitants in samples and the undesirable effects previously discussed on the study of non-spectral interferences, a minimum dilution factor was required for some samples. The LOQs obtained, related to samples masses and to minimum dilution factors are shown in Table S5 (Supplementary Material). The LOQs were estimated as

$10s + \bar{x}$, where $\bar{x}$ is the mean and *s* is the standard deviation of ten measurements of a blank.[28] The higher concentration of elements, as Na, K, and Ca required dilution that impaired the LOQs and results for Ag, Be, Co, La, Ni, and Pb were lower than the LOQ. It is noteworthy that most of the LOQs obtained for Cd and Pb not attend the maximum concentration established by USP General Chapter 2232 (0.5 μg g^{-1} for both) or EC 629/2008 (1.0 and 3.0 μg g^{-1}, respectively), except those achieved for Cd for samples without a minimum dilution factor (VM-2, AM-3, AM-4, and BT-1, LOQ was 0.290 μg g^{-1}).

As expected, essential elements are the majority in the vitamins and/or minerals dietary supplements, as well as for those botanical-based. Calcium, Fe, Na, Mg, and Zn are the elements with higher concentrations. On the other hand, lower concentrations of both essential and non-essential elements are found in amino acids dietary supplements, probably due to the few number of ingredients used in the formulation of these ones. With regard to non-essential elements in vitamins and/or minerals and botanical-based dietary supplements, Al was the element at higher concentration.

The concentration of all essential and non-essential elements determined in dietary supplements samples are below their RDAs (data not presented), except for those which concentration intentionally exceed the RDA and are labeled, cases of Cu in VM-3, Mg in MN-2, and Mn, Mo, and Zn in VM-3 and MN-2. In addition, taking into account the ICH-Q3D, the concentrations obtained were lower than that limited for V (Class 2A, 10 μg g^{-1}), Ag (Class 2B, 15 μg g^{-1}), Li, Ba, Mo, and Cr (Class 3, 55, 140, 300, and 1100 μg g^{-1}, respectively). However, the concentration of Cu (Class 3) exceed the limit established (300 μg g^{-1}) for VM-1 and VM-3 samples (442 and 1332 μg g^{-1}, respectively).

Table II. Results for essential and non-essential elements in different classes of dietary supplements after digestion and determination by MIP OES (mean ± standard deviation, n = 3)

Element	Vitamins and minerals				Minerals		Amino acids				Botanicals	
	VM-1	VM-2	VM-3	VM-4	MN-1	MN-2	AM-1	AM-2	AM-3	AM-4	BT-1	BT-2
Essential elements												
Ca, mg g^{-1}	136 ± 12	0.720 ± 0.026	159 ± 4	271 ± 18	307 ± 9	224 ± 20	< 0.044	0.094 ± 0.004	0.113 ± 0.006	< 0.037	0.386 ± 0.013	111 ± 12
Cu, µg g^{-1}	442 ± 15	< 0.455	1332 ± 67	< 22.7	< 10.5	110 ± 11	< 2.18	< 2.18	< 0.455	< 0.455	2.56 ± 0.12	14.5 ± 0.5
Fe, µg g^{-1}	178 ± 10	16202 ± 1682	11709 ± 721	293 ± 29	106 ± 8	176 ± 10	< 4.84	< 4.84	1.54 ± 0.10	14.0 ± 0.7	184 ± 11	511 ± 32
K, mg g^{-1}	< 0.173	0.054 ± 0.006	< 0.216	< 0.576	< 0.266	12.1 ± 0.9	< 0.055	< 0.055	< 0.011	0.616 ± 0.041	5.53 ± 0.22	12.6 ± 0.8
Mg, mg g^{-1}	70.9 ± 1.3	0.473 ± 0.032	62.7 ± 0.7	49.4 ± 4.4	105 ± 7	107 ± 8	< 0.010	< 0.010	0.024 ± 0.002	0.010 ± 0.001	5.66 ± 0.26	4.87 ± 0.09
Mn, µg g^{-1}	1440 ± 117	3482 ± 55	2710 ± 41	30.3 ± 0.9	40.4 ± 1.1	792 ± 23	< 0.203	0.326 ± 0.016	< 0.042	< 0.042	65.2 ± 2.6	39.5 ± 2.1
Mo, µg g^{-1}	34.3 ± 2.3	< 0.535	63.8 ± 2.4	< 26.8	< 12.4	< 12.4	< 2.57	< 2.57	< 0.535	< 0.535	< 0.535	< 5.35
Na, µg g^{-1}	562 ± 52	390 ± 28	977 ± 33	3027 ± 312	1510 ± 170	416 ± 22	357 ± 24	791 ± 15	614 ± 56	523 ± 18	1172 ± 79	306 ± 23
Zn, mg g^{-1}	9.96 ± 0.62	3.45 ± 0.18	10.8 ± 0.2	1.61 ± 0.12	4.47 ± 0.31	3.12 ± 0.17	< 0.013	< 0.013	< 0.003	< 0.003	0.020 ± 0.001	0.030 ± 0.001
Non-essential elements												
Al, µg g^{-1}	233 ± 20	73.5 ± 2.1	103 ± 7	107 ± 16	92.5 ± 9.7	73.4 ± 5.5	< 63.2	< 63.2	< 13.1	56.3 ± 1.9	316 ± 22	511 ± 32
B, µg g^{-1}	90.3 ± 6.6	< 0.826	106 ± 8	57.8 ± 4.3	7.11 ± 0.48	221 ± 18	< 3.97	< 3.97	< 0.826	< 0.826	2.13 ± 0.07	19.0 ± 0.7
Ba, µg g^{-1}	20.3 ± 1.6	0.292 ± 0.018	1.45 ± 0.13	8.46 ± 0.77	1.45 ± 0.12	18.1 ± 1.1	< 0.576	< 0.576	1.69 ± 0.11	3.75 ± 0.15	1.11 ± 0.05	20.7 ± 1.6
Cr, µg g^{-1}	18.3 ± 1.2	< 0.165	84.5 ± 4.2	1.73 ± 0.31	3.13 ± 0.07	11.4 ± 0.6	< 0.791	< 0.791	< 0.165	< 0.165	0.429 ± 0.007	3.20 ± 0.27
Li, µg g^{-1}	0.374 ± 0.015	< 0.074	0.464 ± 0.012	1.18 ± 0.08	0.509 ± 0.006	0.610 ± 0.007	< 0.357	< 0.357	< 0.074	< 0.074	0.248 ± 0.009	1.81 ± 0.12
Sr, µg g^{-1}	537 ± 24	< 0.338	28.4 ± 2.1	1058 ± 83	52.1 ± 3.9	66.7 ± 3.1	< 1.62	< 1.62	< 0.338	< 0.338	1.75 ± 0.12	53.0 ± 3.0
V, µg g^{-1}	1.35 ± 0.09	< 0.022	1.08 ± 0.09	< 1.12	0.960 ± 0.098	11.1 ± 0.6	< 0.107	< 0.107	< 0.022	< 0.022	0.219 ± 0.021	0.831 ± 0.075

Accuracy

The accuracy of the results obtained for essential and non-essential elements by MIP OES was evaluated by the digestion of two botanical SRMs (NIST 1572 and NIST 1575a) and further elemental determination by MIP OES. The results obtained are in Table III. No statistical differences (*t*-test, confidence level of 95%) were observed between found and certified values.

Table III. Results obtained for SRMs by MIP OES after wet digestion (mean ± standard deviation, n = 3)

Element	NIST 1572		NIST 1575a	
	Found value	Certified value	Found value	Certified value
Al, μg g^{-1}	96 ± 4	92 ± 15	630 ± 35	580 ± 30
B, μg g^{-1}	54.4 ± 2.4	n.i.	9.2 ± 0.3	9.6 ± 0.2
Ba, μg g^{-1}	17 ± 2	21 ± 3	5.7 ± 0.2	6.0 ± 0.2
Ca, % m m^{-1}	2.85 ± 0.19	3.15 ± 0.10	0.26 ± 0.02	0.25 ± 0.01
Cd, μg g^{-1}	< 0.14	0.03 ± 0.01	0.226 ± 0.022	0.233 ± 0.004
Co, μg g^{-1}	< 2.00	0.02[a]	< 2.00	0.061 ± 0.001
Cr, μg g^{-1}	0.5 ± 0.1	0.8 ± 0.2	< 0.4	0.3 – 0.5[a]
Cu, μg g^{-1}	15.5 ± 0.8	16.5 ± 1.0	2.5 ± 0.2	2.8 ± 0.2
Fe, μg g^{-1}	95 ± 18	90 ± 10	44 ± 2	46 ± 2
K, % m m^{-1}	1.53 ± 0.30	1.82 ± 0.06	0.425 ± 0.020	0.417 ± 0.007
Mg, % m m^{-1}	0.53 ± 0.04	0.58 ± 0.03	0.101 ± 0.011	0.106 ± 0.017
Mn, μg g^{-1}	21 ± 2	23 ± 2	442 ± 40	488 ± 12
Mo, μg g^{-1}	< 0.26	0.17 ± 0.09	0.300 ± 0.052	n.i.
Na, μg g^{-1}	134 ± 15	160 ± 20	65 ± 3	63 ± 1
Ni, μg g^{-1}	< 3.7	0.6 ± 0.3	< 3.73	1.47 ± 0.10
Pb, μg g^{-1}	12.0 ± 3.1	13.3 ± 2.4	< 2.20	0.167 ± 0.015
Sr, μg g^{-1}	88 ± 19	100 ± 2	6.01 ± 0.22	n.i.
Zn, μg g^{-1}	28 ± 2	29 ± 2	42 ± 2	38 ± 2

n.i. = not informed.

In addition, the accuracy was evaluated by comparing the results obtained for essential and non-essential elements in dietary supplements by MIP OES with those by ICP OES. The results obtained for one sample of each dietary supplement class analyzed are shown in Table S6 (Supplementary Material), and it is possible to see that they presented no statistical differences (*t*-test, confidence level of 95%). It is important to mention that the minimum dilution factor performed by MIP OES was the same used for ICP OES, impairing the LOQ.

CONCLUSIONS

In this work, the suitability of MIP OES for the determination of essential and non-essential elements in dietary supplements was evaluated. The study of non-spectral interferences demonstrated relatively

good robustness of MIP OES for elevated concentrations of carbon and sulfur since few elements were impacted and in this case for relatively high concentration of interferent (5000 mg L^{-1}). On the other hand, the study showed the great influence of EIEs on the measurements by MIP-OES. Signal suppression or enhancement effects were observed for several elements operating with a concentration from 250 mg L^{-1} of sodium, potassium, or calcium. Taking into account the high concentration of these elements normally found in dietary supplements, a minimum dilution factor should be employed to guarantee a free-interference response and reliable results by MIP OES. This directly impacts the LOQs, making difficult the determination of elements with lower concentrations.

Based on this study, it was possible to determine several essential and non-essential elements in dietary supplements by MIP OES. The accuracy was demonstrated using SRMs, and no statistical difference was observed between found and certified values (*t*-test). Thereby, the results demonstrated the feasibility of MIP OES for the quality control of metals, added as a supplier or present as elemental contaminants in dietary supplements.

Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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REFERENCES

(1) Camire, M. E.; Kantor, M. A. Dietary Supplements: Nutritional and Legal Considerations. *Food Technol.* **1999**, *53* (7), 87–96. https://www.ift.org/news-and-publications/food-technology-magazine/issues/1999/july/features/scientific-status-summary (accessed in 2022-03-15).

(2) Smichowski, P.; Londonio, A. The Role of Analytical Techniques in the Determination of Metals and Metalloids in Dietary Supplements: A Review. *Microchem. J.* **2018**, *136*, 113–120. https://doi.org/10.1016/j.microc.2016.11.007

(3) Chellan, P.; Sadler, P. J. The Elements of Life and Medicines. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2015**, *373* (2037). https://doi.org/10.1098/rsta.2014.0182

(4) Costa, J. G.; Vidovic, B.; Saraiva, N.; do Céu Costa, M.; Del Favero, G.; Marko, D.; Oliveira, N. G.; Fernandes, A. S. Contaminants: A Dark Side of Food Supplements? *Free Radic. Res.* **2019**, *53*, 1113–1135. https://doi.org/10.1080/10715762.2019.1636045

(5) Krejčová, A.; Kahoun, D.; Černohorský, T.; Pouzar, M. Determination of Macro and Trace Element in Multivitamins Preparations by Inductively Coupled Plasma Optical Emission Spectrometry with Slurry Sample Introduction. *Food Chem.* **2006**, *98* (1), 171–178. https://doi.org/10.1016/j.foodchem.2005.06.022

(6) Pereira, R. M.; Crizel, M. G.; La Rosa Novo, D.; dos Santos, C. M. M.; Mesko, M. F. Multitechnique Determination of Metals and Non-Metals in Sports Supplements after Microwave-Assisted Digestion Using Diluted Acid. *Microchem. J.* **2019**, *145*, 235–241. https://doi.org/10.1016/j.microc.2018.10.043

(7) Rzymski, P.; Budzulak, J.; Niedzielski, P.; Klimaszyk, P.; Proch, J.; Kozak, L.; Poniedziałek, B. Essential and Toxic Elements in Commercial Microalgal Food Supplements. *J. Appl. Phycol.* **2019**, *31* (6), 3567–3579. https://doi.org/10.1007/s10811-018-1681-1

(8) Neher, B. D.; Azcarate, S. M.; Camiña, J. M.; Savio, M. Nutritional Analysis of Spirulina Dietary Supplements: Optimization Procedure of Ultrasound-Assisted Digestion for Multielemental Determination. *Food Chem.* **2018**, *257*, 295–301. https://doi.org/10.1016/j.foodchem.2018.03.011

(9) Müller, A.; Pozebon, D.; Dressler, V. L. Advances of Nitrogen Microwave Plasma for Optical Emission Spectrometry and Applications in Elemental Analysis: A Review. *J. Anal. At. Spectrom.* **2020**, *35* (10), 2113–2131. https://doi.org/10.1039/d0ja00272k
(10) Berg, I.; Karlsson, S. Validation of MP-AES at the Quantification of Trace Metals in Heavy Matrices with Comparison of Performance to ICP-MS. Bachelor Diploma, Örebro University. School of Science and Technology. **2015**.
(11) Baranyai, E.; Tóth, C. N.; Fábián, I. Elemental Analysis of Human Blood Serum by Microwave Plasma—Investigation of the Matrix Effects Caused by Sodium Using Model Solutions. *Biol. Trace Elem. Res.* **2020**, *194* (1), 13–23. https://doi.org/10.1007/s12011-019-01743-1
(12) Serrano, R.; Grindlay, G.; Gras, L.; Mora, J. Evaluation of Calcium-, Carbon- and Sulfur-Based Non-Spectral Interferences in High-Power MIP-OES: Comparison with ICP-OES. *J. Anal. At. Spectrom.* **2019**, *34* (8), 1611–1617. https://doi.org/10.1039/c9ja00148d
(13) Fontoura, B. M.; Jofré, F. C.; Williams, T.; Savio, M.; Donati, G. L.; Nóbrega, J. A. Is MIP-OES a Suitable Alternative to ICP-OES for Trace Element Analysis? *J. Anal. At. Spectrom.* **2022**, *37* (5), 966–984. https://doi.org/10.1039/D1JA00375E
(14) Zhang, Z.; Wagatsuma, K. Matrix Effects of Easily Ionizable Elements and Nitric Acid in High-Power Microwave-Induced Nitrogen Plasma Atomic Emission Spectrometry. *Spectrochim. Acta - Part B At. Spectrosc.* **2002**, *57* (8), 1247–1257. https://doi.org/10.1016/S0584-8547(02)00049-6
(15) Serrano, R.; Grindlay, G.; Gras, L.; Mora, J. Insight into the Origin of Carbon Matrix Effects on the Emission Signal of Atomic Lines in Inductively Coupled Plasma Optical Emission Spectrometry. *Spectrochim. Acta - Part B At. Spectrosc.* **2021**, *177*, 106070. https://doi.org/10.1016/j.sab.2021.106070
(16) Grindlay, G.; Gras, L.; Mora, J.; de Loos-Vollebregt, M. T. C. Carbon-Related Matrix Effects in Inductively Coupled Plasma Atomic Emission Spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2008**, *63* (2), 234–243. https://doi.org/10.1016/j.sab.2007.11.024
(17) Grindlay, G.; Gras, L.; Mora, J.; de Loos-Vollebregt, M. T. C. Carbon-, Sulfur-, and Phosphorus-Based Charge Transfer Reactions in Inductively Coupled Plasma–Atomic Emission Spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2016**, *115*, 8–15. https://doi.org/10.1016/j.sab.2015.10.010
(18) Muller, A. L. H.; Oliveira, J. S. S.; Mello, P. A.; Muller, E. I.; Flores, E. M. M. Study and Determination of Elemental Impurities by ICP-MS in Active Pharmaceutical Ingredients Using Single Reaction Chamber Digestion in Compliance with USP Requirements. *Talanta* **2015**, *136*, 161–169. https://doi.org/10.1016/j.talanta.2014.12.023
(19) Avula, B.; Wang, Y. H.; Smillie, T. J.; Duzgoren-Aydin, N. S.; Khan, I. A. Quantitative Determination of Multiple Elements in Botanicals and Dietary Supplements Using ICP-MS. *J. Agric. Food Chem.* **2010**, *58* (16), 8887–8894. https://doi.org/10.1021/jf101598g
(20) JGCM. Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement; JGCM 100:2008; Bureau International Des Poids et Mesures. **2008**. https://www.bipm.org/documents/20126/2071204/JCGM_100_2008_E.pdf/cb0ef43f-baa5-11cf-3f85-4dcd86f77bd6 (accessed in 2022-04-21).
(21) Agatemor, C.; Beauchemin, D. Matrix Effects in Inductively Coupled Plasma Mass Spectrometry: A Review. *Anal. Chim. Acta* **2011**, *706* (1), 66–83. https://doi.org/10.1016/j.aca.2011.08.027
(22) Grindlay, G.; Mora, J.; de Loos-Vollebregt, M.; Vanhaecke, F. A Systematic Study on the Influence of Carbon on the Behavior of Hard-to-Ionize Elements in Inductively Coupled Plasma–Mass Spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2013**, *86*, 42–49. https://doi.org/10.1016/j.sab.2013.05.002
(23) Chan, G. C.-Y.; Chan, W.-T. Plasma-Related Matrix Effects in Inductively Coupled Plasma—Atomic Emission Spectrometry by Group I and Group II Matrix-Elements. *Spectrochim. Acta Part B At. Spectrosc.* **2003**, *58* (7), 1301–1317. https://doi.org/10.1016/S0584-8547(03)00055-7

(24) Todolí, J.-L.; Mermet, J.-M. Acid Interferences in Atomic Spectrometry: Analyte Signal Effects and Subsequent Reduction. *Spectrochim. Acta Part B At. Spectrosc.* **1999**, *54* (6), 895–929. https://doi.org/10.1016/S0584-8547(99)00041-5
(25) U. S. Pharmacopeia (USP) General Chapter <2232> Elemental Contaminants in Dietary Supplements. **2012**. https://www.uspnf.com/sites/default/files/usp_pdf/EN/USPNF/elemental_contaminants_in_dietary_supplements_m5291_3-26-2012.pdf (accessed in 2022-03-27).
(26) E. U. Comission Regulation (EC) No 629/2008. Amending Regulation (EC) No 1881/2006 Setting Maximum Levels for Certain Contaminants in Foodstuffs. Official Journal of the European Union. **2008**. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008R0629&from=EN (accessed in 2022-03-27).
(27) ICH. ICH Guideline Q3D (R1): Guideline for Elemental Impurities. **2019**. https://www.ich.org/fileadmin/Public_Web_Site/ICH_Products/Guidelines/Quality/Q3D/Q3D-R1EWG_Document_Step4_Guideline_2019_0322.pdf (accessed in 2022-08-15).
(28) IUPAC. IUPAC Compendium on Analytical Nomenclature, Definitive Rules 1997. **1998**. https://media.iupac.org/publications/analytical_compendium/ (accessed in 2022-08-15).

SUPPLEMENTARY MATERIAL

Table S1. Classification, sample code, dosage form, active ingredients, and origin of dietary supplements used in this study

Classification	Sample code	Dosage form	Active ingredientes	Origin
Vitamins and minerals	VM-1	Tablet	Vitamins A, B1, B2, B3, B5, B6, B7, B9, B12, C, D3, and K, MgO, Cr, Cu, Mb, Mn, Se, and Zn	Brazil
Vitamins and minerals	VM-2	Tablet	Vitamins A, B1, B2, B3, B6, B9, B12, C, and D, $FeSO_4$, $ZnSO_4$, $MnSO_4$, and calcium D-pantothenate	Brazil
Vitamins and minerals	VM-3	Tablet	Vitamins A, B1, B2, B5, B6, B7, B9, B12, C, D3, E, and K, $CaCO_3$, $C_4H_2FeO_4$, KI, MgO, ZnO, Na_2Se, $CuSO_4$, $MgSO_4$, $CrCl_3$, and Na_2MoO_4	USA
Vitamins and minerals	VM-4	Capsule	Vitamins D3 and E, oyster shell $CaCO_3$, $C_4H_8N_2MgO_4$, $Zn(C_2H_4NO_2)_2$, $C_5H_{11}NO_2Se$, and SiO_2	Brazil
Minerals	MN-1	Tablet	$CaCO_3$, MgO, $ZnSO_4$, $C_8H_9NaO_7$, $C_{18}H_{36}O_2$, TiO_2, and $MgSiO_3$	USA
Minerals	MN-2	Capsule	Calcium amino acid chelate, KH_2PO_4, KI, magnesium amino acid chelate, zinc amino acid chelate, $C_5H_{11}NO_2Se$, copper amino acid chelate, manganese amino acid chelate, $Cr(C_6H_4NO_2)_3$, Mo, KCl, H_3BO_3, vanadium amino acid chelate, glutamic acid, rice protein, parsley leaf, alfalfa leaf, horsetail, watercress, dandelion root, yellow dock root, and chamomile	USA
Amino acids	AM-1	Powder	Creatine monohydrate	Brazil
Amino acids	AM-2	Powder	Taurine, vitamins B6, B12, and PP, Beta-5 (*beta vulgaris L.*, powdered beet, and vitamin B5), NO2Drive (watermelon pulp, vitamin B2, vitamin B3, and calcium L-ascorbate), glucuronolactone, and caffeine	Brazil
Amino acids	AM-3	Capsule	L-leucine, L-isoleucine, and L-valine	Brazil
Amino acids	AM-4	Capsule	L-theanine	USA
Botanicals	BT-1	Capsule	Ginseng extract (*panax ginseng*), rice bran, and oat fiber	USA
Botanicals	BT-2	Capsule	Guarana (*paullinia cupana*) and açaí (*euterpe oleracea*) flavoring, catuaba (*anemopaegma mirandum*), cocoa (*theobroma cacao*), and ginseng (*panax ginseng*) extracts, vitamins A, B1, B2, B3, B5, B6, B9, B12, C, E and K2, Cu, Fe, Cr, Mn, Mo, Se, and Zn	Brazil

Table S2. Operational conditions for elemental determination by ICP OES

Parameter	ICP OES
RF power (W)	1400
Plasma gas flow-rate (L min^{-1})	15
Auxiliary gas flow-rate (L min^{-1})	0.2
Nebulizer gas flow-rate (L min^{-1})	0.7
Spray chamber, type	Cyclonic double-pass (Scott)
Nebulizer, type	Cross-flow
Analytes	Wavelength (nm)
Ag	328.068 (I)
Al	167.078 (II)
B	249.677 (I)
Ba	233.527 (II)
Be	234.861 (I)
C	193.030 (I)
Ca	396.847 (II)
Cd	228.802 (I)
Co	238.892 (II)
Cr	205.552 (II)
Cu	327.396 (I)
Fe	259.941 (II)
K	766.491 (I)
La	408.672 (II)
Li	670.780 (I)
Mg	280.270 (II)
Mn	259.373 (II)
Mo	202.095 (II)
Na	589.592 (I)
Ni	231.604 (II)
Pb	220.353 (II)
S	182.034 (I)
Sr	407.771 (II)
V	292.464 (II)
Y[a]	371.029 (II)
Zn	213.856 (I)

[a]Used as internal standard for the determination of C.

(I) Atomic emission line; (II) Ionic emission line.

Table S3. Wavelength and excitation + ionization energy (E_{sum}) values of the lines determined by MIP OES in this study

Element	Wavelength, nm	E_{sum}[a], eV
K	769.897 (I)	1.61
Li	670.784 (I)	1.85
Na	589.592 (I)	2.10
Mn	403.307 (I)	3.07
V	437.923 (I)	3.13
Al	396.152 (I)	3.14
Mo	386.410 (I)	3.21
Cr	357.868 (I)	3.46
Ag	328.068 (I)	3.78
Cu	327.395 (I)	3.78
Ni	361.939 (I)	3.85
Co	345.351 (I)	4.02
Mg	285.213 (I)	4.35
Pb	283.305 (I)	4.37
B	249.772 (I)	4.96
Be	234.861 (I)	5.28
Cd	228.802 (I)	5.42
Zn	213.857 (I)	5.80
Ba	493.408 (II)	7.72
La	433.374 (II)	8.61
Sr	407.771 (II)	8.74
Ca	396.847 (II)	9.23
Fe	259.940 (II)	12.64

[a]E_{sum} = excitation + ionization energy.

Table S4. Determination of common concomitants in dietary supplements by MIP OES (mean ± standard deviation, n = 3)

Samples	C[a], mg L^{-1}	S[a], mg L^{-1}	Na[a], mg L^{-1}	K[a], mg L^{-1}	Ca[a], mg L^{-1}	Residual acidity[b], %
VM-1	124 ± 23	51.2 ± 2.7	22.6 ± 0.3	8.64 ± 0.26	4224 ± 219	30 ± 1
VM-2	179 ± 6	300 ± 27	11.7 ± 0.3	1.27 ± 0.16	19.3 ± 0.7	26 ± 1
VM-3	129 ± 15	189 ± 2	90.5 ± 0.4	9.03 ± 0.07	11049 ± 12	15 ± 1
VM-4	16.6 ± 0.3	28.2 ± 1.0	111 ± 14	3.08 ± 0.37	8775 ± 905	29 ± 1
MN-1	11.1 ± 2.4	128 ± 7	128 ± 7	13.7 ± 0.6	15851 ± 589	15 ± 4
MN-2	16.9 ± 4.4	34.6 ± 2.6	28.3 ± 6.0	532 ± 12	11143 ± 750	17 ± 3
AM-1	50.6 ± 3.3	< 0.510	6.27 ± 0.11	0.046 ± 0.001	0.733 ± 0.008	60 ± 1
AM-2	50.3 ± 2.6	307 ± 25	15.5 ± 0.2	0.416 ± 0.007	2.02 ± 0.03	59 ± 1
AM-3	44.0 ± 4.0	13.3 ± 0.3	13.8 ± 0.4	0.120 ± 0.005	3.03 ± 0.05	24 ± 1
AM-4	50.8 ± 7.8	4.33 ± 0.07	9.44 ± 0.14	13.2 ± 0.1	0.215 ± 0.021	27 ± 2
BT-1	53.7 ± 2.0	17.5 ± 0.5	24.9 ± 1.4	122 ± 4	9.03 ± 0.25	27 ± 2
BT-2	43.5 ± 3.6	34.0 ± 1.9	7.75 ± 0.54	239 ± 38	2369 ± 364	29 ± 3

Determined by [a]ICP OES and [b]potentiometric titration.

Table S5. Limits of quantification (LOQs) obtained by MIP OES in this work

Element, μg g^{-1}	Vitamins and minerals				Minerals		Amino acids		Botanicals	
	VM-1	VM-2	VM-3	VM-4	MN-1	MN-2	AM-1 and AM-2	AM-3 and AM-4	BT-1	BT-2
Sample mass	800	600	1600	600	1300	1300	500	600	600	600
Minimum dilution factor	20	no	50	50	50	50	4	no	no	10
Ag	3.13	0.208	3.91	10.4	4.81	4.81	1.00	0.208	0.208	2.08
Al	198	13.1	247	658	304	304	63.2	13.1	13.1	132
B	12.4	0.826	15.5	41.3	19.1	19.1	3.97	0.826	0.826	8.26
Ba	1.80	0.120	2.25	6.00	2.77	2.77	0.576	0.120	0.120	1.20
Be	0.356	0.024	0.445	1.19	0.547	0.547	0.114	0.024	0.024	0.240
Ca	555	37.0	694	1850	854	854	178	37.0	37.0	370
Cd	4.36	0.290	5.45	14.5	6.70	6.70	1.39	0.290	0.290	2.90
Co	62.6	4.17	78.2	209	96.2	96.2	20.0	4.17	4.17	41.7
Cr	2.47	0.165	3.09	8.24	3.80	3.80	0.791	0.165	0.165	1.65
Cu	6.82	0.455	8.53	22.7	10.5	10.5	2.18	0.455	0.455	4.55
Fe	15.1	1.01	18.9	50.4	23.3	23.3	4.84	1.01	1.01	10.1
K	173	11.5	216	576	266	266	55.3	11.5	11.5	115
La	0.552	0.037	0.690	1.84	0.850	0.850	0.177	0.037	0.037	0.370
Li	1.12	0.074	1.40	3.72	1.72	1.72	0.357	0.074	0.074	0.740
Mg	32.0	2.13	40.0	107	49.2	49.2	10.2	2.13	2.13	21.3
Mn	0.636	0.042	0.795	2.12	0.978	0.978	0.203	0.042	0.042	0.420
Mo	8.03	0.535	10.0	26.8	12.4	12.4	2.57	0.535	0.535	5.35
Na	103	6.88	129	344	159	159	33.0	6.88	6.88	68.8
Ni	116	7.76	146	388	179	179	37.3	7.76	7.76	77.6
Pb	68.9	4.59	86.1	230	106	106	22.0	4.59	4.59	45.9
Sr	5.06	0.338	6.33	16.9	7.79	7.79	1.62	0.338	0.338	3.38
V	0.335	0.022	0.419	1.12	0.516	0.516	0.107	0.022	0.022	0.220
Zn	40.5	2.70	50.6	135	62.3	62.3	13.0	2.70	2.70	27.0

Table S6. Results for VM-2, MN-2, AM-2, and BT-1 samples by MIP OES and ICP OES (mean ± standard deviation, n = 3)

Element	VM-2		MN-2		AM-2		BT-1	
	MIP OES	ICP OES	MIP OES	ICP OES	MIP OES	ICP OES	MIP OES	ICP OES
Ag, μg g^{-1}	< 0.208	< 0.115	< 4.81	< 2.65	< 1.00	< 0.551	< 0.208	< 0.115
Al, mg g^{-1}	0.073 ± 0.002	0.071 ± 0.001	0.073 ± 0.005	0.064 ± 0.004	< 63.2	< 91.1	316 ± 22	274 ± 19
B, μg g^{-1}	< 0.826	< 1.06	221 ± 18	264 ± 21	< 3.97	< 5.08	2.13 ± 0.07	2.04 ± 0.05
Ba, μg g^{-1}	0.292 ± 0.018	0.262 ± 0.013	18.1 ± 1.1	20.6 ± 1.3	< 0.576	< 0.426	1.11 ± 0.05	1.12 ± 0.06
Be, μg g^{-1}	< 0.024	< 0.025	< 0.547	< 0.587	< 0.114	< 0.122	< 0.024	< 0.025
Ca, mg g^{-1}	0.720 ± 0.026	0.763 ± 0.021	224 ± 20	226 ± 8	94.5 ± 3.7	101 ± 4	0.386 ± 0.013	0.378 ± 0.019
Cd, μg g^{-1}	< 0.290	< 0.161	< 6.70	< 3.72	< 1.39	< 0.774	< 0.290	< 0.161
Co, μg g^{-1}	< 4.17	3.48 ± 0.11	< 96.2	< 5.11	< 20.0	< 1.06	< 4.17	0.239 ± 0.007
Cr, μg g^{-1}	< 0.165	< 0.278	11.4 ± 0.6	11.6 ± 0.4	< 0.791	< 1.34	0.429 ± 0.007	0.417 ± 0.040
Cu, μg g^{-1}	< 0.455	< 0.278	110 ± 11	129 ± 7	< 2.18	< 1.69	2.56 ± 0.12	2.77 ± 0.21
Fe, mg g^{-1}	162 ± 1.7	158 ± 10	0.176 ± 0.010	0.170 ± 0.003	< 4.84	< 11.5	184 ± 11	192 ± 9
K, mg g^{-1}	0.054 ± 0.006	0.049 ± 0.007	12.1 ± 0.9	10.8 ± 0.4	< 55.3	20.8 ± 0.3	5.53 ± 0.22	5.11 ± 0.23
La, μg g^{-1}	< 0.037	< 0.075	< 0.850	< 1.73	< 0.177	< 0.359	< 0.037	< 0.075
Li, μg g^{-1}	< 0.074	< 1.50	0.610 ± 0.007	< 34.7	< 0.357	< 7.21	0.248 ± 0.009	< 1.50
Mg, mg g^{-1}	0.473 ± 0.032	0.512 ± 0.018	107 ± 8	111 ± 3	9.23 ± 0.70	8.44 ± 0.50	5.66 ± 0.26	5.56 ± 0.20
Mn, mg g^{-1}	3.49 ± 0.05	3.54 ± 0.03	0.792 ± 0.023	0.829 ± 0.027	0.326 ± 0.016	0.358 ± 0.024	65.2 ± 2.6	63.5 ± 2.6
Mo, μg g^{-1}	< 0.535	< 0.498	< 12.4	10.9 ± 0.9	< 2.57	< 2.39	< 0.535	< 0.498
Na, mg g^{-1}	0.390 ± 0.028	0.415 ± 0.031	0.416 ± 0.022	0.413 ± 0.011	791 ± 15	777 ± 22	1172 ± 79	1040 ± 67
Ni, μg g^{-1}	< 7.76	5.36 ± 0.57	< 179	< 51.2	< 37.3	< 10.6	< 7.76	< 2.22
Pb, μg g^{-1}	< 4.59	< 3.92	< 106	< 90.5	< 22.0	< 18.8	< 4.59	< 3.92
Sr, μg g^{-1}	< 0.338	< 0.349	66.7 ± 3.1	69.9 ± 4.4	< 1.62	< 1.68	1.75 ± 0.12	1.96 ± 0.10
V, μg g^{-1}	< 0.022	< 0.366	11.1 ± 0.6	12.3 ± 1.5	< 0.107	< 1.76	0.219 ± 0.021	< 0.366
Zn, mg g^{-1}	3.45 ± 0.18	3.22 ± 0.12	3.12 ± 0.17	3.21 ± 0.16	< 13.0	< 11.8	20.2 ± 0.6	21.3 ± 0.9

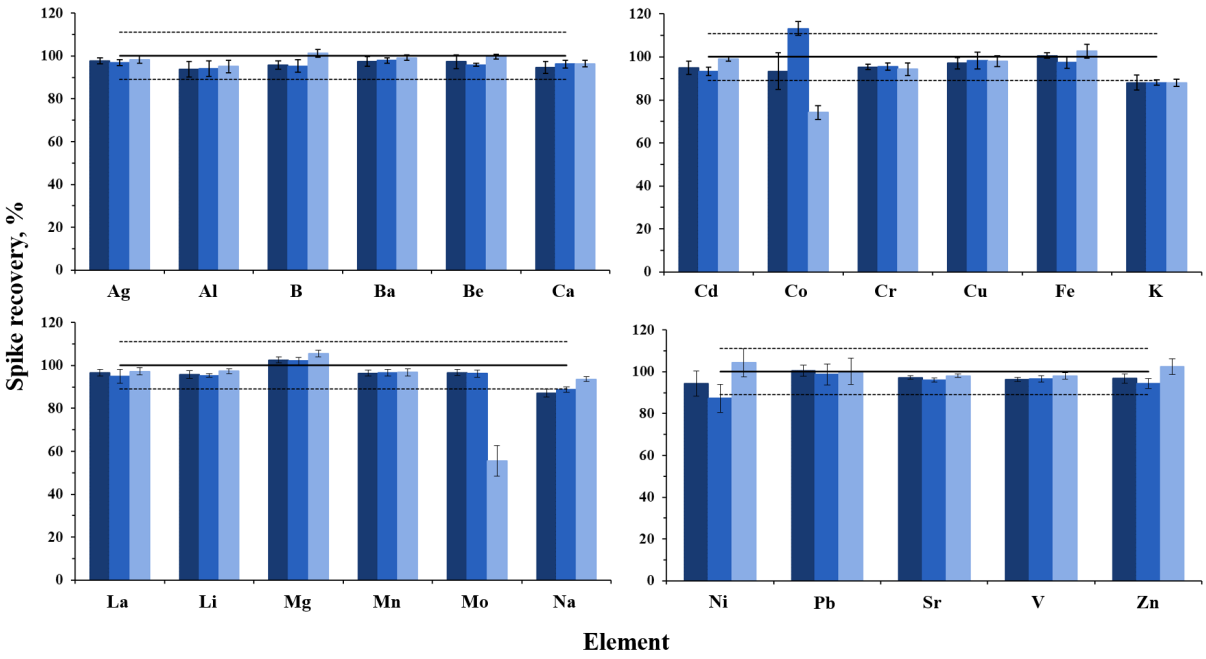

Figure S1. Spike recoveries obtained for metals (100 µg L^{-1}) with 25 (■), 250 (■), and 5000 mg L^{-1} (■) of carbon (as citric acid) by MIP OES. Continuous and dashed lines represents the reference value (100%) and the expanded uncertainty, respectively.

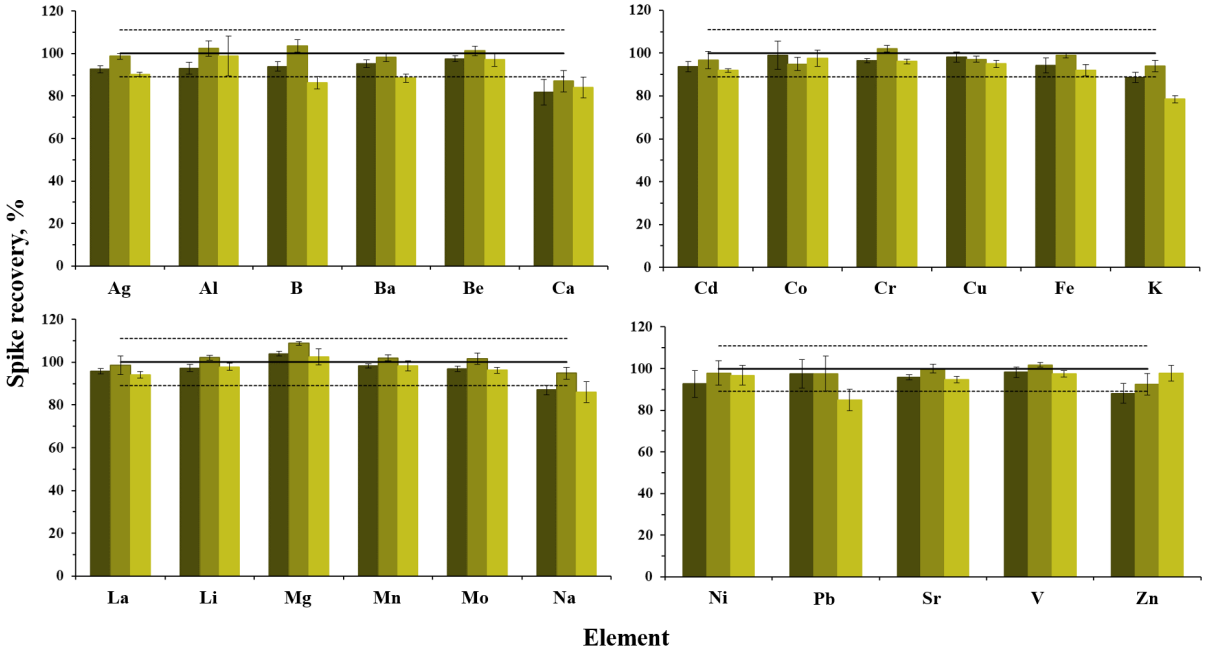

Figure S2. Spike recoveries obtained for metals (100 µg L^{-1}) with 25 (■), 250 (■), and 5000 mg L^{-1} (■) of sulfur (as sulfuric acid) by MIP OES. Continuous and dashed lines represents the reference value (100%) and the expanded uncertainty, respectively.

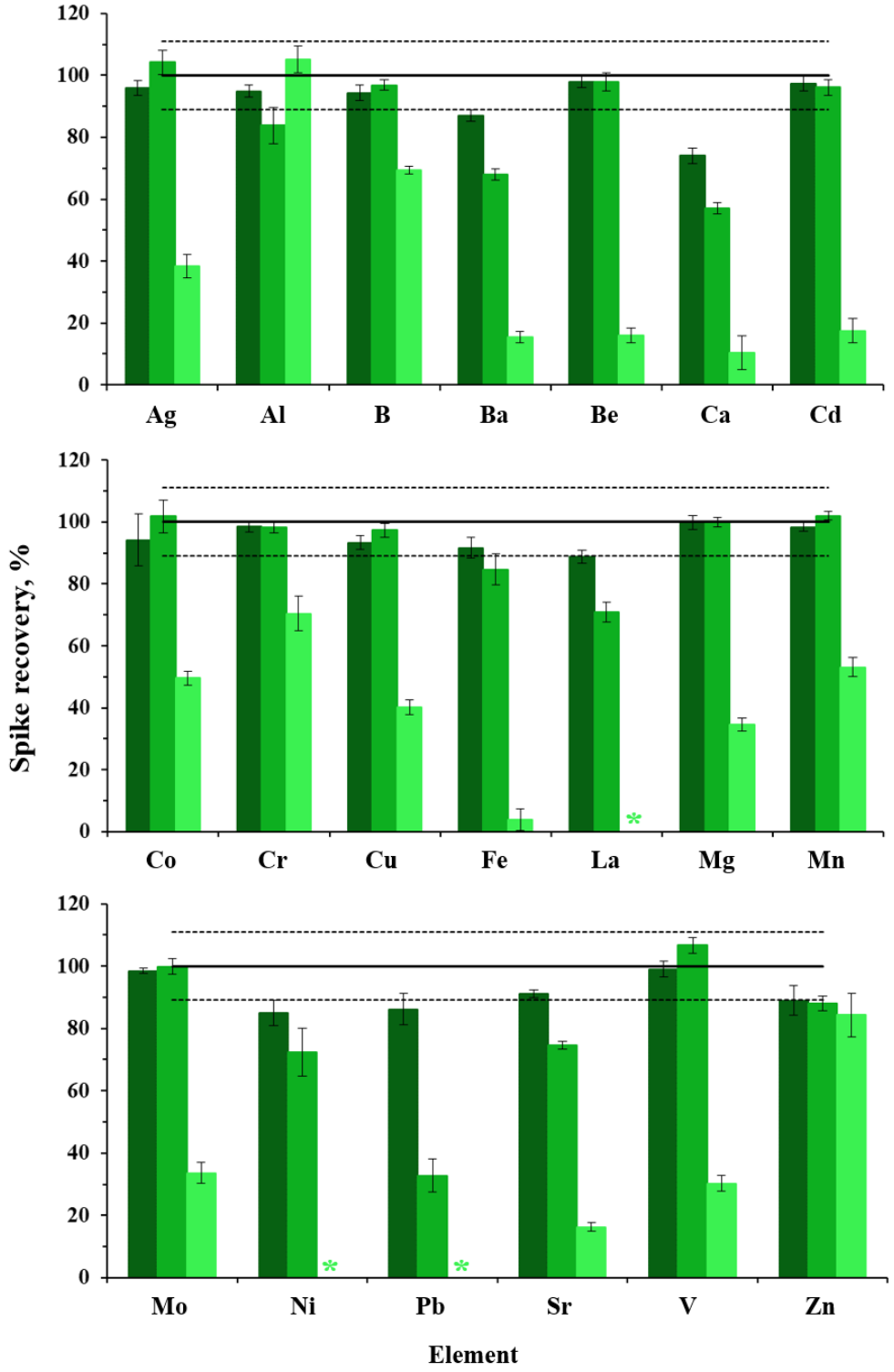

Figure S3. Spike recoveries obtained for metals (100 µg L^{-1}) with 25 (■), 250 (■), and 5000 mg L^{-1} (■) of sodium (as sodium nitrate) by MIP OES. Continuous and dashed lines represents the reference value (100%) and the expanded uncertainty, respectively. *Total signal suppression.

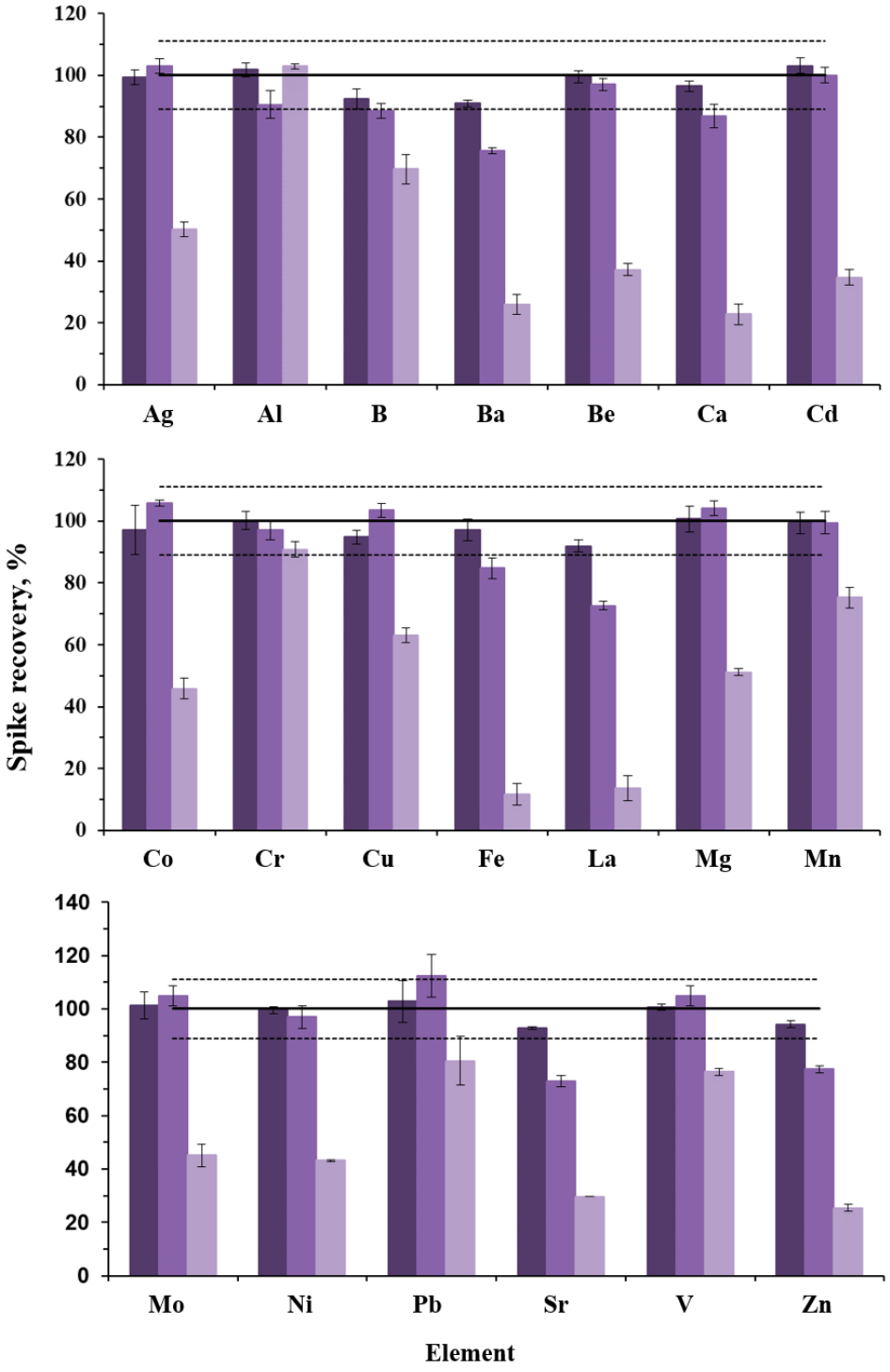

Figure S4. Spike recoveries obtained for metals (100 µg L^{-1}) with of 25 (■), 250 (■), and 5000 mg L^{-1} (■) of potassium (as potassium nitrate) by MIP OES. Continuous and dashed lines represents the reference value (100%) and the expanded uncertainty, respectively.

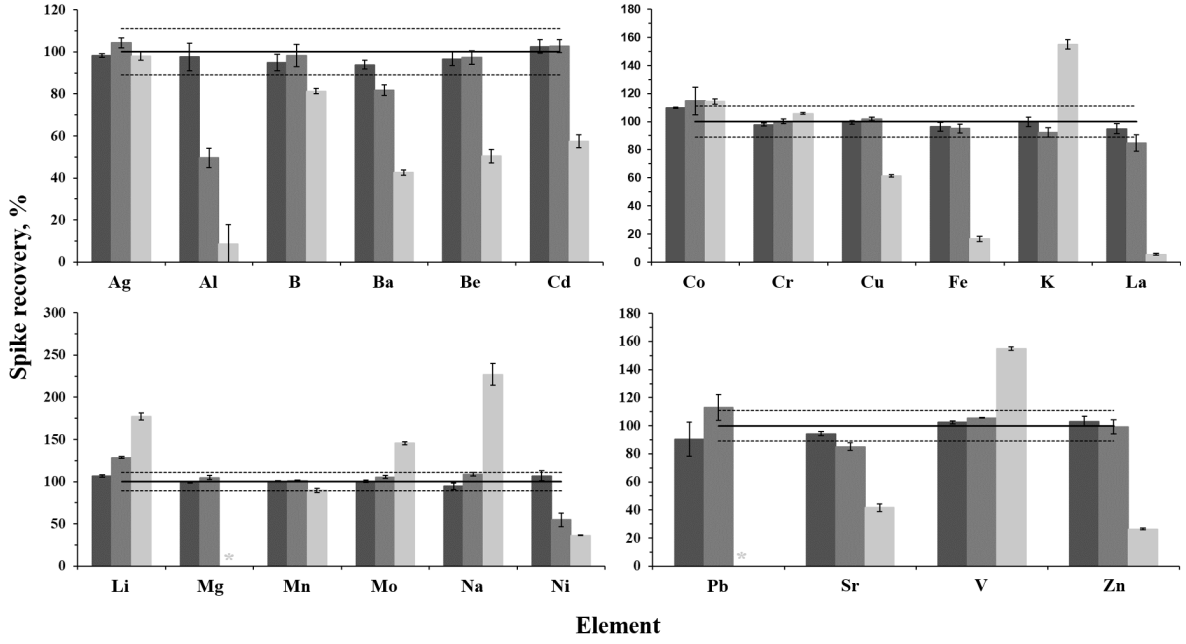

Figure S5. Spike recoveries obtained for metals (100 µg L^{-1}) with 25 (■), 250 (■), and 5000 mg L^{-1} (■) of calcium (as calcium nitrate) by MIP OES. Continuous and dashed lines represents the reference value (100%) and the expanded uncertainty, respectively. *Total signal suppression.

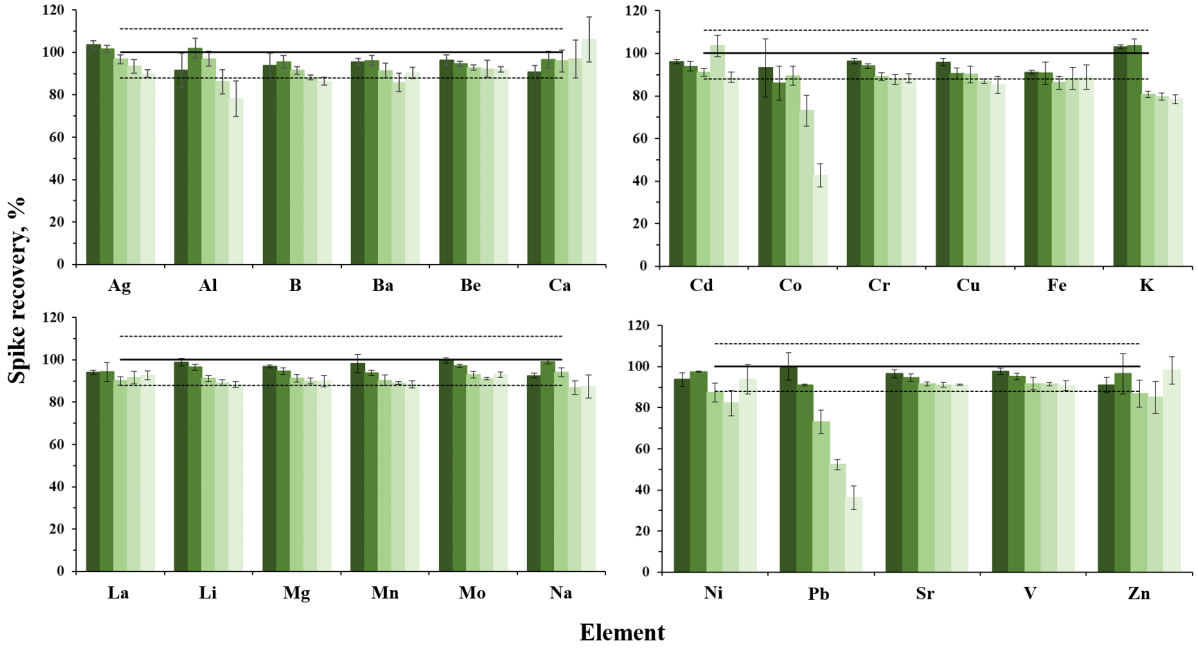

Figure S6. Spike recoveries obtained for metals (100 µg L^{-1}) with residual HNO_3 acidity at 10 (■), 20 (■), 30 (■), 40 (■), and 50% v v^{-1} HNO_3 (■) by MIP OES. Continuous and dashed lines represents the reference value (100%) and the expanded uncertainty, respectively.