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In situ digestion for the determination of Ca in beverages by tungsten coil atomic emission spectrometry

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ABSTRACT

Tungsten coil atomic emission spectrometry (WCAES) is employed for the determination of calcium in juice, mineral and coconut water samples. A sample aliquot of 20 μL is placed directly on the coil and a constant-voltage power source is used to dry and atomize the sample, as well as to promote Ca atomic emission. Analytical signals are resolved and detected using a Czerny–Turner spectrometer and a charge coupled device detector. Some experimental parameters such as coil position related to the spectrometer entrance slit and integration time are critically evaluated. A heating program with relatively constant drying temperatures is used in all measurements. An *in situ* digestion procedure is used to partially decompose organic matrices and improve WCAES precision and accuracy. By adding an oxidizing mixture to the sample and including a digestion step in the heating cycle, no statistical difference was observed between WCAES and ICP OES results for Ca in juice and coconut water samples. Mineral water samples were simply diluted with 1% v v^{-1} HNO_3 before analysis and no significant interference was observed for concomitants such as Na and K. Despite severe positive interference caused by Mg, good agreement was obtained between WCAES and ICP OES results for Ca in several mineral water samples. Limits of detection and quantification obtained were 0.02 and 0.07 mg L^{-1}, respectively. The method precision, calculated as the relative standard deviation for 10 consecutive measurements of a 2.5 mg L^{-1} Ca solution, is 3.8%.

1. Introduction

Considering the role of minerals in human metabolism and nutrition, the determination of food mineral composition has become increasingly important. Calcium is present in various foods, especially milk and dairy products. It provides rigidity to the skeleton and plays an important role in several metabolic processes. The World Health Organization recommends a dairy calcium intake of 1 g for an adult [1]. Though milk is a well-known source of calcium, some beverages such as fruit juices contain considerable amounts of this element and may be used in nutritional supplementation. Thus, the development of simple, fast and effective methods to be applied in beverage quality control is highly desirable.

The number of analytical techniques suitable for such application is rather ample and varied. For Ca, for example, the most common methods are based on flame atomic absorption spectrometry (FAAS) [2,3] or inductively coupled plasma optical emission spectrometry (ICP OES) [4–6]. Flames, arcs, and plasmas are commonly employed in atomic emission spectrometry, however limitations related to power requirements and the use of large volumes of gases prevent their application in portable methods.

On the other hand, since its introduction in 2005 [7], tungsten coil atomic emission spectrometry (WCAES) has been successfully used in potentially portable methods to determine several elements in different samples [8,9]. A typical WCAES system employs a tungsten filament extracted from mass-produced, commercially available 150 W light bulbs, simultaneously as atomizer and excitation source. Due to the coil small mass and tungsten low specific heat, no cooling system is needed to bring the atomizer back to room temperature after the atomization step, which contributes for small, light-weight systems. In the first work described by Rust et al. [7], the emission signals were monitored with a high resolution Czerny–Turner spectrometer and a charge coupled device (CCD) detector. Power was supplied by a small solid state constant-current source and limits of detection below the μg L^{-1} level were obtained for Ca, Ba and Sr. In another work by the same authors, Al, Cr, Mn and K were determined in a standard reference material (trace elements in water) with limits of detection also at the μg L^{-1} level [10]. Some advantages of the method such as the possibility of field applications and multi-element determinations were emphasized in these works. More recently, Gu et al. [11] evaluated a portable system and determined fifteen elements in water and soil samples. A 24 V, 250 W tungsten coil, and a 400 W solid state power supply were used in this work,

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which provided higher temperatures, resulting in low limits of detection. In order to improve the analytical sensitivity, a new metallic cell was proposed by Donati et al. [12]. The new design allows denser atomic clouds and smaller background signals, resulting in better sensitivities. The same atomization cell was used in a new system [13] with reduced dimensions, which allowed multi-element determinations at trace levels in the field.

Although presenting several attractive characteristics such as simplicity, low cost, and portability, some limitations hinder a broader application of WCAES. One critical aspect is related to the open nature of the atomizer, which may cause a pronounced gas phase temperature gradient and severe matrix-related interferences. It was demonstrated that the gas phase temperature can drop by up to 250 °C for every millimeter away from the coil surface [14]. At lower temperatures, negative interferences can be caused by recombination processes, for instance. In this case, reactions between the analyte and concomitant species present in the gas phase may significantly reduce the original analytical signal [15]. To minimize such interferences, different strategies have been proposed such as the use of two atomizers to increase the gas phase temperature [16] and the re-design of the atomization cell for a more homogeneous atomization atmosphere [12].

A different approach for reducing matrix interferences may be applied at the sample preparation step. In this strategy, matrix effects may be mostly minimized by using a suitable sample decomposition procedure and by manipulating the atomizer heating program. Sample preparation methods such as closed-vessel microwave-assisted acid digestion have been successfully used to totally decompose organic matrices while avoiding contamination and analyte losses by volatilization [17]. Despite its advantages, sample preparation is frequently the most time consuming step and the bottleneck of the whole analytical process [18]. One of the most interesting characteristics of any electrothermal atomic absorption spectrometric method (ETAAS) is the possibility of performing *in situ* sample decompositions, directly on the atomizer surface. It has been demonstrated that high carbon content matrices can be eliminated in graphite furnace atomic absorption spectrometry (GFAAS) by using a strong oxidizing mixture and optimizing the heating program [19]. A mixture of hydrogen peroxide and nitric acid, for example, has been used to minimize matrix interferences caused by organic compounds in milk samples [20] and biological fluids [21] during the GFAAS heating cycle. Naozuka and Oliveira [22] used the same strategy to determine Al, Cu and Fe in coconut water samples. In addition to reducing matrix interferences, a 75% increase in graphite tube lifetimes was observed since less carbon residues were formed on the tube surface.

In the work here described, WCAES is used to determine calcium in juice, mineral and coconut water samples. Interference effects on Ca caused by Na, K and Mg, which are major concomitants in these samples, are investigated. An *in situ* digestion method based on matrix decomposition under strong oxidizing conditions with hydrogen peroxide and nitric acid is also evaluated. The method accuracy is checked by comparing the results with those obtained by direct analyses using ICP OES.

2. Experimental

2.1. Instrumental

A schematic diagram of the WCAES system is presented in Fig. 1. The atomizer is a ten-turn, commercially available tungsten coil (Osram, Pullach, Germany) connected to two copper electrodes (Fig. 1). The filament was housed inside a borosilicate glass atomization chamber with fused silica windows. A constant potential, solid state power supply (Anacom Cientifica, São Bernardo do Campo, SP, Brazil) was employed to resistively heat the coil during solvent vaporization and atomization. A purge gas composed of 10% H_2 plus 90% Ar was used to prevent coil oxidation and to improve atomization. The radiation emitted about 1 mm above the atomizer was collected by a fused silica lens and imaged onto the entrance slit of a handheld spectrometer (Ocean Optics, HR 4000, Dunedin, FL, USA). The CCD detector consists of a two-dimensional array of 3648 pixels. The system provides a spectral window of approximately 100 nm depending upon the selection of the central wavelength. A fixed 50 μm entrance slit was employed throughout.

The detector software provides user selectable integration times as low as 3.8 ms. For Ca, the best signal-to-noise ratios (S/N) were obtained using an integration time of 200 ms. Adopting this value, the maximum emission intensities were generally observed during the 2nd spectrum, with the analytical signal returning to baseline after 800 ms. Considering variations in synchronization between the heating program and the detector software, 15 successive spectra were collected at the beginning of the atomization step to ensure that the whole of the emission signal was recorded.

2.2. Reagents and samples

All glassware was kept in 10% $\mathrm{v\,v^{-1}}$ HNO_3 for 24 h and then rinsed with distilled-deionized water. Ultrapure water was obtained using a Milli-Q® system (Millipore, Bedford, MA, USA). Reagent-grade concentrated nitric acid (Synth, Diadema, SP, Brazil) and hydrogen peroxide 30% $\mathrm{m\,m^{-1}}$ (Synth) were employed in *in situ* digestions carried out directly on the atomizer surface. Calcium, Mg, Na and K reference solutions were prepared by diluting 1000 $\mathrm{mg\,L^{-1}}$ stock solutions (Titrisol®, Merck, Darmstadt, Germany).

Mineral water samples from five different Brazilian states (Alagoas, Bahia, Rio de Janeiro, Minas Gerais, and São Paulo) were analyzed. Sample aliquots of 5.0 mL were diluted to 10.0 mL with HNO_3 (Carlo Erba, Italy) and ultrapure water for a final acid concentration of 1% $\mathrm{v\,v^{-1}}$. Three coconut water and three fruit juice samples were purchased in local markets. A semi-quantitative analysis was performed to determine Ca concentration ranges and adequate the sample solutions to the linear dynamic range of the analytical calibration curve. In this case, 20 μL of the original sample were placed on the coil and the heating program presented in Table 1 was applied. Calcium concentrations in each sample were then estimated based on signal comparisons with previously determined standard solutions. From the semi-quantitative results, appropriate volumes of each sample were transferred to 10.0 mL volumetric flasks, and 5 mL of an oxidizing mixture containing 15% $\mathrm{v\,v^{-1}}H_2O_2$ and 1% $\mathrm{v\,v^{-1}}$ HNO_3 were added. Finally the mixture was diluted to the mark with distilled-deionized water. One dilution and three consecutive determinations ($n=3$) were carried out for each sample.

2.3. WCAES measurements

A sample aliquot of 20 μL was directly placed on the atomizer using a micropipette (Eppendorf 10–100 μL, Brinkman, Westbury, NY, USA). The purge gas flow rate was kept at 1.0 $\mathrm{L\,min^{-1}}$ and a heating program appropriated to each type of sample was applied. Four increasingly lower potential steps, followed by a high power atomization step were used in all experiments. The gradual potential decrease during the drying step was adopted to keep a constant temperature both during and after the complete solvent removal, as demonstrated by Oliveira et al. [23]. On the other hand, the tungsten coil characteristic fast heating rate allowed a rapid atomization step and the formation of a dense atomic cloud with enough thermal energy to promote excitation

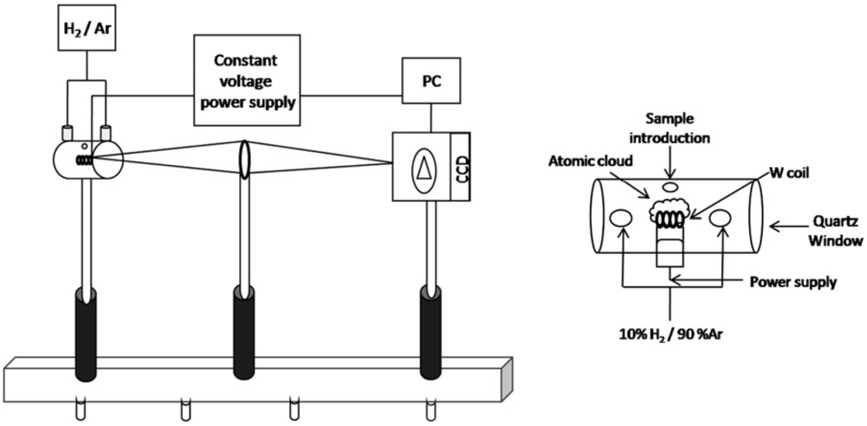

Fig. 1. Schematic representation of the WCAES system setup.

Table 1
Heating program used for the tungsten coil atomizer.

Step	Applied voltage (V)	Time (s)	Read
1	0.70[a]/0.80[b]	20[a]/10[b]	No
2	0.65	10	No
3	0.60	10	No
4	0.50	10	No
5	14.0[c]	3	Yes

[a] Mineral water.
[b] Coconut water and juice samples.
[c] Estimated atomizer temperature: 3100 K [14].

of a fraction of the calcium ground state population before reaching maximum intensity of the background spectrum. Data were collected at this step. To promote the sample partial digestion and reduce matrix interferences, a 0.80 V, 10 s first step was used for juice and coconut water samples. For mineral water samples, a longer, lower potential first step was employed. Table 1 presents the experimental conditions adopted.

2.4. ICP OES analysis

For comparison purposes, all samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP OES with axial viewing configuration, Vista PRO-CCD, Varian, Mulgrave, Australia) using standard operating conditions. In this case, samples were diluted similarly as the WCAES method described above. However, no oxidation mixture was added and all samples were diluted with HNO_3 to a final acid concentration of 2% v v^{-1} [24].

3. Results and discussion

3.1. Instrumental parameters

Monitoring atomic emission lines in WCAES is highly dependent on the coil positioning [10]. The tungsten coil atomizer is well-characterized as a non-isothermal system [14], so finding the position with high gas phase temperatures, where the energy is enough to promote atomization and excitation processes is critical in atomic emission determinations. Another factor to be considered is the intense blackbody radiation emitted by the atomizer during the atomization step. The high background signals can saturate the detector before any analytical signal is collected [9]. Thus obtaining a position of compromise, where the background signal is minimal and the gas phase temperature is the highest possible, is of fundamental importance in WCAES. In this work, the influence of the coil position relatively to the spectrometer entrance slit was investigated to improve the method sensitivity for Ca determinations. Different coil orientations were evaluated based on signal intensities for a 50 mg L^{-1} Ca solution.

While using the vertical orientation, analytical signals were only observed at the position represented in Fig. 2(a). Fig. 3(a) shows a spectrum obtained at this atomizer position. Due to Ca high concentration in the test solution, a double peak, indicative of self-absorption can be observed in Fig. 3(a). This phenomenon has been previously reported by other authors in atomic emission determinations with metallic atomizers [25]. Therefore a 15 mg L^{-1} test solution was used in further studies. For the horizontal orientation, emission signals were observed at all evaluated positions. However, relatively low emission signals were obtained in regions close to the purge gas inlet, which is probably a temperature-related effect. At the spectrometer entrance slit center, background signal increased and caused saturation of the detector. On the other hand, adequate analytical signals were obtained for regions slightly above the atomizer (opposite to the purge gas inlet). Considering the highest S/N values for Ca, the filament was fixed so that its image was positioned as represented in Fig. 2(b) (horizontal orientation). Fig. 3(b) shows a spectrum obtained with a 2.5 mg L^{-1} Ca solution at this position.

The analytical integration time was also evaluated and emission signals obtained with values ranging from 100 to 500 ms were compared to determine the best S/N. The highest values were obtained using 200 ms. Longer integration times resulted in more intense background signals which compromised the S/N and, consequently, sensitivity.

3.2. Heating cycle

The heating programs comprising the stages of solvent vaporization and analyte atomization are critical in the development of electrothermal atomization-based methods. It is especially

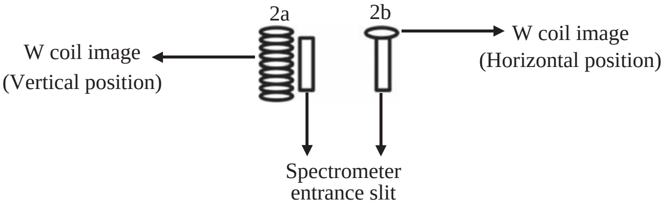

Fig. 2. Schematic representation of the atomizer position relative to the spectrometer entrance slit. (a) Atomizer vertical position. (b) Atomizer horizontal position.

important in open systems such as WCAES, where analyte losses prior to the atomization step can compromise sensitivity and accuracy.

A heating program with relatively constant drying temperatures [23] was used for all Ca determinations. The program basically consisted of drying and atomization steps. The applied voltage followed an inverted ramp cycle in all experiments. The potential applied to the atomizer in the initial heating steps supply energy to vaporize the solvent. After complete removal of the solvent, all applied voltage is consumed to heat the atomizer, which can cause analyte losses due to overheating. To prevent sensitivity, accuracy and precision problems, gradually smaller voltages were applied to the atomizer to prevent overheating and compensate for temperature variations throughout the drying process. Another important parameter evaluated was the atomization potential applied. In this case, the best results were obtained with 14 V. As expected, a higher voltage provides more energy for atomization and excitation of the analyte. At this applied potential, atomizer surface temperatures exceed 3000 K [14], but gas phase temperatures as low as 1800 K may be expected 1 mm above the coil surface [16]. Thus, considerably smaller Ca signals, which may hinder the method applicability, were obtained for values lower than 14 V. Table 1 shows the heating program used in this work, which was optimized for a 20 μL sample aliquot.

3.3. Analytical figures of merit

The analytical figures of merit for Ca determined by WCAES were calculated. Considering the spectral window used in this work, two Ca emission lines at 393.3 and 422.7 nm [26] were observed, and the more intense one (422.7 nm) was used in all experiments. The limit of detection ($3\times S_{\text{blank}}$/slope) and limit of quantification ($10\times S_{\text{blank}}$/slope) were calculated as 0.02 and 0.07 mg L^{-1}, respectively. The standard deviation of the analytical blank solution, composed of 5 mL of ultrapure water and 5 mL of an oxidizing mixture containing 15% v v^{-1} H_2O_2 and 1% v v^{-1} HNO_3, was determined in 20 consecutive measurements. The linear dynamic range and linear correlation coefficient of the analytical curve were 0.1–10 mg L^{-1} and 0.9980, respectively. The analytical sensitivity is equal to 2300 ± 700 counts L mg^{-1} and the uncertainty of the measurements of the linear dynamic range is equal to 14%.

The method repeatability and precision were evaluated by determining the relative standard deviation (RSD) of 10 consecutive measurements of a 2.5 mg L^{-1} Ca solution, and two samples of juice and coconut water. The values obtained were 3.8% (repeatability), and 4.8 and 4.4% (precision), respectively. The precision for samples not submitted to the *in situ* digestion procedure was also established and values of 7.9 and 9.2% were obtained for juice and coconut water, respectively (n=10). The efficiency of the *in situ* digestion procedure may be inferred from these results. To check the method accuracy, Ca concentrations determined in different samples (coconut waters, juice and mineral waters) were compared with results obtained by ICP OES. Inductively coupled plasma OES determinations followed the procedure proposed by Souza et al. [24]. A recovery study also was performed and results are shown in Table 2.

A matrix interference study was also carried out to evaluate the effect of major concomitants, *i.e.*, K, Mg and Na (10.0 and 100.0 mg L^{-1}) on Ca analytical signals. From Fig. 4, it can be observed that the most critical interfering concomitant is Mg, which can cause severe positive interference even when it is present at a concentration 10-fold higher than Ca (Fig. 4).

3.4. Sample analysis

The heating program presented in Table 1 was used to determine Ca in all mineral water samples. No sample pyrolysis

Table 2
Calcium concentrations in juices, mineral and coconut waters determined by WCAES and ICP OES (mean ± standard deviation, n=3).

Sample[a]	Added (mg L^{-1})	WCAES (mg L^{-1})	Recovery (%)	ICP OES (mg L^{-1})
MW$_1$	0	2.1 ± 0.2	–	1.9 ± 0.2
	5.0	7.8 ± 0.4	110	–
MW$_4$	0	1.8 ± 0.2	–	1.2 ± 0.1
	5.0	5.9 ± 0.1	87	–
MW$_5$	0	2.1 ± 0.1	–	1.8 ± 0.1
	5.0	7,7 ± 0.2	108	–
MW$_6$	0	6.6 ± 0.1	–	5.8 ± 0.3
	5.0	10.5 ± 0.5	90	–
MW$_7$	0	1.9 ± 0.1	–	1.4 ± 0.1
	5.0	6.1 ± 0.3	88	–
MW$_8$	0	8.7 ± 0.6	–	7.8 ± 0.5
	5.0	14.8 ± 0.4	108	–
MW$_9$	0	6.0 ± 0.6	–	6.6 ± 0.3
	5.0	10.2 ± 0.3	93	–
MW$_{10}$	0	4.3 ± 0.4	–	3.5 ± 0.2
	5.0	10.5 ± 0.6	113	–
MW$_{11}$	0	15 ± 1	–	16 ± 1
	5.0	21.8 ± 1	109	–
MW$_{12}$	0	17 ± 1	–	16 ± 1
	5.0	23.7 ± 2	108	–
CW$_1$	0	160 ± 10	–	150 ± 10
	5.0	173 ± 10	105	–
CW$_2$	0	290 ± 10	–	290 ± 10
	5.0	283 ± 11	96	–
CW$_3$	0	210 ± 10	–	200 ± 10
	5.0	207 ± 9	96	–
J$_1$	0	800 ± 10	–	790 ± 10
	5.0	823 ± 12	102	–
J$_2$	0	23 ± 2	–	24 ± 1
	5.0	32 ± 1	114	–
J$_3$	0	20 ± 2	–	20 ± 1
	5.0	29 ± 3	116	–

[a] MW=mineral water; CW=coconut water; J=Juice.

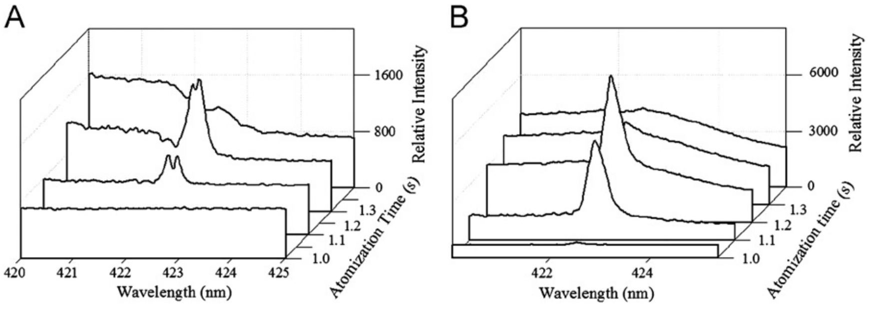

Fig. 3. Analytical signals for calcium solution. (a) Atomizer vertical position (Ca 50 mg L^{-1}). (b) Atomizer horizontal position (Ca 15 mg L^{-1}).

or pretreatment was necessary, especially considering the simplicity of the matrix. On the other hand, severe matrix effects were observed for diluted fruit juice and coconut water samples, which resulted in lower Ca recoveries when compared with ICP OES results (not shown). In addition to affecting the analytical signal, the organic matrix reduced the atomizer lifetime. The filament became brittle after a few heating cycles, probably due to the formation of tungsten carbides [27]. Because even a short pyrolysis step was not practical due to analyte losses, a sample preparation procedure capable of destroying the organic matrix was required to improve both the method accuracy and the coil lifetime.

A sample *in situ* digestion was carried out directly on the coil surface to overcome these difficulties. The procedure is based on a previous work by Naozuka and Oliveira [22] which used an oxidizing mixture of 15% v v^{-1}H_2O_2 and 1% v v^{-1} HNO_3 to promote the digestion of coconut water samples in a graphite furnace tube. In this work, the authors reported matrix decomposition at the early stages of the heating program, at temperatures varying between 20 and 130 °C. This procedure was adapted for a tungsten coil atomizer simply by adding 0.1 V to the heating program first step and reducing its time from 20 to 10 s (Table 1). A higher potential applied for less time was required to promote better matrix decomposition and prevent analyte losses from possible atomizer overheating. Thus, different sample volumes (for different Ca concentrations) were added to 5 mL of a 15% v v^{-1}H_2O_2 and 1% v v^{-1} HNO_3 mixture [22], and the volume was made up to 10 mL. Aliquots of 20 μL were then placed directly on the coil surface and the simultaneous sample digestion and solvent vaporization, followed by Ca atomization was carried out by applying the heating program presented in Table 1. Using this strategy it was possible to eliminate organic-related interfering effects and obtain adequate accuracy. Fig. 5 shows the spectra obtained for a 2.5 mg L^{-1} Ca standard solution and for a coconut water sample with the same Ca concentration before and after the application of the *in situ* digestion procedure. A significant reduction in Ca signal intensity can be observed for the untreated sample, which probably is caused by matrix effects (Fig. 5(a)). The digestion process may be considered efficient since no significant difference is observed between the signals from the reference solution and the *in situ* digested coconut sample (Fig. 5(b)).

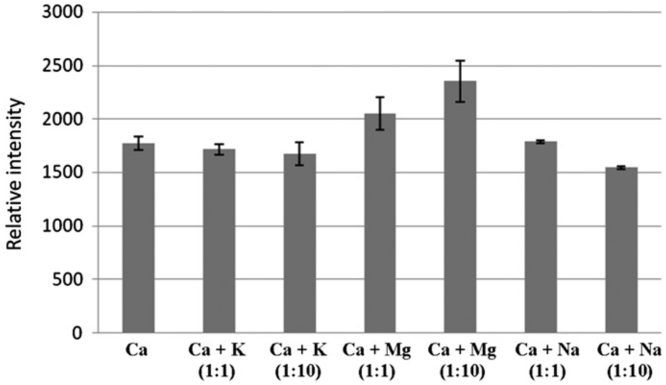

Fig. 4. Effects of some major concomitants on Ca analytical signal.

Additional evidence of the *in situ* digestion efficiency may be observed in Table 2, which presents the results for Ca determinations in juice, mineral and coconut water samples by WCAES ($n=3$). Most Ca concentrations determined by the method described are not significantly different from those determined by ICP OES at a 95% confidence level.

4. Conclusions

Tungsten coil AES provides adequate accuracy and precision to determine Ca in beverage samples. Using a small power supply, a tungsten filament extracted from commercially available light bulbs, and a handheld detector, this method represents a simple, economical alternative to more traditional, less portable atomic spectrometric methods. For mineral water samples, no pretreatment is required and a simple dilute-and-shoot procedure can provide precise and accurate results. Little interference on Ca was observed for most common concomitants in these samples, i.e., Na and K. On the other hand, some positive interference was caused by Mg, which could be responsible for some overestimated results when compared to ICP OES.

From Ca preliminary results in juice and coconut water samples, it was evident the occurrence of negative interference on WCAES analytical signals caused by organic compounds in the matrix, which resulted in lower recoveries when compared with ICP OES results. This interference was minimized by adding an oxidizing mixture to the sample and modifying the heating program so that the organic matrix was partially decomposed before the total solvent vaporization. Using the proposed *in situ* digestion procedure, no statistically significant difference was observed between WCAES and ICP OES results for Ca in both juice and coconut water samples.

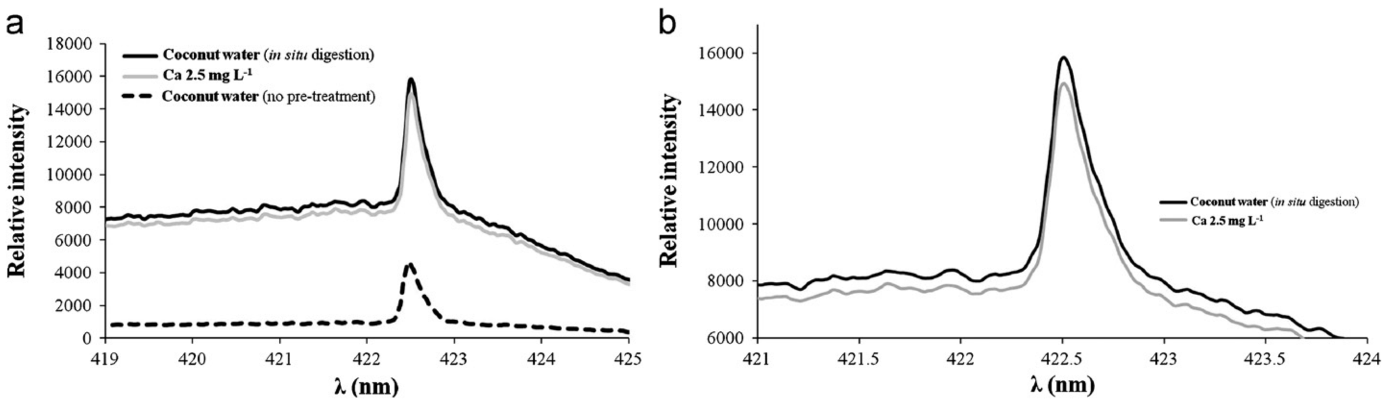

Fig. 5. WCAES spectra obtained for a 2.5 mg L^{-1} Ca reference solution and a coconut water sample with the same Ca concentration before and after the application of the *in situ* digestion procedure (a). Expanded scale spectra for the reference solution and the coconut water sample submitted to *in situ* digestion (b).

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