

ARTICLE



Rapid Elemental Analysis of Sugarcane Spirits by Inductively Coupled Plasma: Optical Emission Spectrometry

Raquel Fernanda Milani^a , Marcelo Antonio Morgano^a  and Késia Diego Quintaes^b 

^aInstitute of Food Technology, Campinas, Brazil; ^bOuro Preto Federal University (UFOP), Nutrition School (ENUT), Campus Morro do Cruzeiro, s/n, Ouro Preto, Brazil

ABSTRACT

A simple, direct, and rapid method was developed and employed to determine arsenic, cadmium, copper, lead, and nickel in sugarcane spirits by inductively coupled plasma – optical emission spectrometry (ICP-OES). The samples were analyzed directly, avoiding the need for sample treatment or the use of toxic chemicals in agreement with the green chemistry principles. The accuracy was evaluated using spiked trials at three levels for each contaminant, with recoveries between 83 and 115%. High sensitivity was obtained, with limits of detection less than 0.008 mg L^{-1} for all elements but copper (0.05 mg L^{-1}), in agreement with Brazilian and The Common Market of the South regulations. Low values of coefficient of variation were also observed, 0.4 to 7.7% for all analytes. The analysis time and sample amount required for the direct method were lower than methods that use sample treatment procedures, which is very positive for routine laboratory analysis.

ARTICLE HISTORY

Received 12 March 2018
Accepted 3 May 2018

KEYWORDS

Alcoholic beverage; direct analysis; inductively coupled plasma – optical emission spectrometry; inorganic contaminants; sugarcane spirits

Introduction

Frequently known as *cachaça*, sugarcane spirits are a popular alcoholic beverage consumed in Brazil. Brazilian annual production is around 1.4 billion liters in 2015 (Expocachaça 2017) and the Brazilian Ministry of Agriculture, Livestock and Food Supply defines sugarcane spirits as a beverage obtained by fermented sugarcane distillation, containing 38–48% alcohol at 20°C (Brazilian Ministry of Agriculture, Livestock and Food Supply 2005). Main physical–chemical characteristics consist of 75–82% of water and 15–24% of sugars (fructose, glucose, and sucrose), proteins, amino acids, and inorganic solids (Penteado and Masini 2009; Silva et al. 2009; Capobiango, Oliveira, and Cardeal 2013).

Inorganic contaminants may be introduced to this alcoholic beverage by different sources such as raw material (sugarcane for *cachaça*) and the plantation and harvesting environment; additives; process equipment (vessel materials and barrels); aging and storage (Ibanez et al. 2008). Brazilian and The Common Market of the South (MERCOSUR) have established threshold for some contaminants, such as arsenic (0.10 mg kg^{-1}), cadmium (0.02 mg kg^{-1}), lead (0.20 mg kg^{-1}) (The Common Market of the South 2011; Resolução RDC n° 42 2013) and nickel (3.00 mg kg^{-1}) (Decreto n° 55.871 1965) in fermented-distilled

CONTACT Marcelo Antonio Morgano  morgano@ital.sp.gov.br  Institute of Food Technology, Campinas, Brazil.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lanl.

alcoholic beverages and for arsenic (0.1 mg L^{-1}), copper (5.0 mg L^{-1}), and lead (0.2 mg L^{-1}) in sugarcane spirits (Brazilian Ministry of Agriculture, Livestock and Food Supply 2005).

Simple, fast, and low-cost methods of analysis are desirable and some groups have devoted their efforts to developing methods for alcoholic samples. Donati et al. (2013) proposed the determination of some metals (Cr, Pb, and V) in ethanol fuel by microwave plasma optical emission spectrometry (MIP OES) using dilution in 1% HNO_3 . A recent paper by this group is described by Virgilio et al. (2015) which proposed an innovative method for As, Cr, P, Pb, Si, and V in ethanol fuel using simple dilution (10-fold with 1% HNO_3) and direct analysis by inductively coupled plasma tandem mass spectrometry. In this method, the authors used a matrix-matching strategy and spiked experiments provided accuracy ranged between 84 and 109% for all analytes. Some elements such as Cr, P, and Si were considered to be challenging elements to determine in ethanol samples, exemplified for P and Si: only the tandem mass spectrometry mode allowed quantifying.

Nevertheless, for alcoholic beverages, a few studies have been reported, most concerning wine samples. Fiket, Mikac, and Kniewald (2011) performed a study of several trace elements (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn) in nine brands of wine from Croatia using sample dilution strategy (10-fold) using 2% HNO_3 and In as an internal standard. The technique used in their study was high resolution inductively coupled plasma mass spectrometry. On the topic of spirit samples, Caldas et al. (2011) studied the multivariate optimization of a spectrophotometric method for copper determination in sugarcane spirits using the Doehlert design. The methodology for the copper determination was based on the reaction of Cu (II) ions with phenylfluorone in the presence of cetylpyridinium chloride. This procedure provided a limit of detection of $3.4 \mu\text{g L}^{-1}$.

Miranda, Dionísio, and Pereira-Filho (2010) also proposed a simple method for Cu determination by flame atomic absorption spectrometry (FAAS). The authors evaluated several internal standards. The use of silver provides a method with a limit of detection of $15 \mu\text{g L}^{-1}$. Fiket, Mikac, and Kniewald (2011) reported a sample treatment method consisting of a twofold dilution with 1.0 mol L^{-1} HNO_3 . A multielemental study was performed by Jurado et al. (2007) in aniseed beverages by graphite furnace atomic absorption spectrometry. The group applied a 10-fold dilution in samples purchased from Spanish liquor retailer and markets and observed the need of a matrix matching for cadmium quantification. A previous study by our group determined inorganic contaminants using an acid decomposition strategy as sample treatment to verify the contaminant transference from new soapstone glasses to sugarcane spirits (Fernandes et al. 2013).

Considering these aspects, this work reports a simple, fast, and multielemental method for the direct determination of arsenic, cadmium, copper, lead, and nickel in sugarcane spirits by inductively coupled plasma – optical emission spectrometry (ICP-OES). Since there is little reported in the literature dealing with direct determination of these contaminants in sugarcane spirits, the aim of this work was the optimization of the ICP-OES conditions to allow the direct determination of these contaminants. Method validation was performed based on the guidelines of the Brazilian National Institute of Metrology, Quality and Technology (INMETRO) (Brazilian National Institute of Metrology, Quality & Technology 2016) and the Association of Official Analytical Chemists (AOAC) (Association of Official Analytical Chemists 2013).

Materials and methods

Instrumentation

An emission spectrometer with a plasma source and inductive coupling (ICP-OES) (5100 VDV, Agilent Technologies, Tokyo, Japan) was used for the simultaneous determination of As, Cd, Cu, Ni, and Pb. The conditions used were: axial viewing equipped with a 27 MHz radio frequency source, a charged coupled device solid state simultaneous multielemental detector, a quartz torch for volatile organics (0.8 mm i.d. injector), a peristaltic pump, a nebulization chamber, and a Seaspray nebulizer. The ICP Expert software controlled the system and 99.996% pure argon (Air Liquid, SP, Brazil) was used as the plasma gas.

The ICP OES parameters optimized included the radio frequency source power; nebulization flow rate, plasma flow rate, auxiliary argon flow rate, and read time. These were studied employing a 2^{5-1} fractional factorial design for screening the variables that could significantly affect the plasma, taking into account possible interactions between these variables. Then, a 2^3 central composite design was carried out to refine the experimental conditions. For both designs, the response was the plasma robustness, defined by the Mg(II)/Mg(I) ratio, where Mg (I) was at 285.213 nm and Mg (II) was at 280.270 nm (Mermet 1991). The conditions are described in detail in Table 1 and 2. All measurements were performed randomly using a spiked sample containing 1 mg L^{-1} of a magnesium standard (Merck, Darmstadt, Germany). The statistical evaluations were carried out employing the Statistica software (Stat Soft, Tulsa, OK, USA).

The experimental conditions were: radio frequency source power (1.45 kW); nebulization flow rate (0.25 L min^{-1}); plasma flow rate (12.0 L min^{-1}); auxiliary gas flow rate (0.45 L min^{-1}); background correction (2 points); stabilization time (15 s); read time

Table 1. 2^{5-1} fractional design employed for ICP-OES optimization.

| Variable | (-1) | (+1) |
|---|------|------|
| (a) Radio frequency source power (kW) | 1.30 | 1.50 |
| (b) Nebulizer flow rate (L min^{-1}) | 0.30 | 0.60 |
| (c) Auxiliary gas flow rate (L min^{-1}) | 0.40 | 0.60 |
| (d) Plasma flow rate (L min^{-1}) | 12.0 | 15.0 |
| (e) Read time (s) | 10 | 20 |

| Experiment | (a) | (b) | (c) | (d) | (e) | Plasma robustness |
|------------|-----|-----|-----|-----|-----|-------------------|
| | | | | | | Mg(II)/Mg(I) |
| 1 | -1 | -1 | -1 | -1 | +1 | 6.45; 6.45 |
| 2 | +1 | -1 | -1 | -1 | -1 | 6.85; 6.83 |
| 3 | -1 | +1 | -1 | -1 | -1 | 3.27; 3.24 |
| 4 | +1 | +1 | -1 | -1 | +1 | 3.89; 3.99 |
| 5 | -1 | -1 | +1 | -1 | -1 | 6.33; 6.31 |
| 6 | +1 | -1 | +1 | -1 | +1 | 6.64; 6.61 |
| 7 | -1 | +1 | +1 | -1 | +1 | 2.88; 2.91 |
| 8 | +1 | +1 | +1 | -1 | -1 | 3.70; 3.77 |
| 9 | -1 | -1 | -1 | +1 | -1 | 6.52; 6.49 |
| 10 | +1 | -1 | -1 | +1 | +1 | 6.53; 6.64 |
| 11 | -1 | +1 | -1 | +1 | +1 | 3.09; 3.15 |
| 12 | +1 | +1 | -1 | +1 | -1 | 3.91; 3.90 |
| 13 | -1 | -1 | +1 | +1 | +1 | 6.34; 6.35 |
| 14 | +1 | -1 | +1 | +1 | -1 | 6.66; 6.63 |
| 15 | -1 | +1 | +1 | +1 | -1 | 2.91; 2.90 |
| 16 | +1 | +1 | +1 | +1 | +1 | 3.75; 3.80 |

Table 2. Central composite design employed for ICP-OES optimization.

| Variable | $-\sqrt{3}$ | (-1) | 0 | (+1) | $+\sqrt{3}$ |
|--|-------------|------|------|------|-------------|
| (a) Radio frequency source power (kW) | 1.44 | 1.45 | 1.47 | 1.49 | 1.50 |
| (b) Nebulizer flow rate (L min ⁻¹) | 0.22 | 0.25 | 0.30 | 0.35 | 0.38 |
| (c) Auxiliary gas flow rate (L min ⁻¹) | 0.32 | 0.35 | 0.40 | 0.45 | 0.48 |

| Experiment | (a) | (b) | (c) | Plasma robustness Mg(II)/Mg(I) |
|------------|-------------|-------------|-------------|-----------------------------------|
| 1 | -1 | -1 | -1 | 6.67; 6.74 |
| 2 | -1 | -1 | +1 | 6.66; 6.65 |
| 3 | -1 | +1 | -1 | 6.32; 6.33 |
| 4 | -1 | +1 | +1 | 6.27; 6.27 |
| 5 | +1 | -1 | -1 | 6.72; 6.75 |
| 6 | +1 | -1 | +1 | 7.14; 6.74 |
| 7 | +1 | +1 | -1 | 6.35; 6.36 |
| 8 | +1 | +1 | +1 | 6.31; 6.31 |
| 9 | $-\sqrt{3}$ | 0 | 0 | 6.53; 6.52 |
| 10 | $+\sqrt{3}$ | 0 | 0 | 6.71; 6.70 |
| 11 | 0 | $-\sqrt{3}$ | 0 | 6.17; 6.13 |
| 12 | 0 | $+\sqrt{3}$ | 0 | 6.02; 6.04 |
| 13 | 0 | 0 | $-\sqrt{3}$ | 6.65; 6.69 |
| 14 | 0 | 0 | $+\sqrt{3}$ | 6.58; 6.58 |
| 15 | 0 | 0 | 0 | 6.57; 6.58; 6.59 |

(10 s); number of replicates (3), and wavelengths of As (193.696 nm), Cd (214.439 nm), Cu (324.754 nm), Ni (221.648 nm), and Pb (220.353 nm). The method was validated based on Brazilian National Institute of Metrology, Quality and Technology (2016) guidelines for specificity, linearity, detection and quantification limits, precision, and accuracy. Statistical analyses were performed using Statistica (StatSoft, Tulsa, OK, USA) considering a 95% confidence level.

Reagents and samples

Materials used in analysis were previously decontaminated using 5% (v/v) HNO₃ bath for at least 12 h and then rinsed with deionized water. Reverse osmosis-purified water (Gehaka, São Paulo, Brazil, 18.2 MΩ cm) was applied for all solutions. Analytical curves were prepared by external and standards addition calibration. Successive dilutions of 1000 mg L⁻¹ certified standard solutions (Merck, Darmstadt, Germany) were applied and ranges were established using the Brazilian and The Common Market of the South regulations: 0.005 to 0.50 mg L⁻¹ for As; 0.0025 to 0.05 mg L⁻¹ for Cd; 0.05 to 25 mg L⁻¹ for Cu; 0.005 to 5.0 mg L⁻¹ for Ni and 0.025 to 0.50 mg L⁻¹ for Pb in 48% (v/v) ethanol (Merck, Darmstadt, Germany) for external calibration and in a sugarcane spirit sample for standard addition calibration. For both methods, five standard solutions were employed.

The direct method was successfully applied to samples of sugarcane spirits purchased in Minas Gerais (southeastern Brazil) and all analyses were carried out in triplicate.

Results and discussion

Preliminary measurements

An evaluation of the ICP OES parameters that may influence the plasma robustness was crucial to obtain adequate conditions for analyses in an alcoholic sample and hardware

parameters must be evaluated. 2.0, 1.2, and 0.8 mm internal diameter (i.d.) quartz torches and Seaspray and conical nebulizers were evaluated. A stable plasma was only obtained using 0.8 mm (i.d.) torch and the Seaspray nebulizer. For sample preparation, an evaluation of signal and background were carried out using different additions of nitric acid in ethanoic solutions containing the analytes. Figure 1a exemplifies the behavior observed for all contaminants: the presence of nitric acid did not provide an expressive improvement in the method sensitivity.

A preliminary measurement was also carried out to verify the effect with the alcohol content variation (38 to 48% alcohol at 20 °C) in sugarcane spirits (Brazilian Ministry of Agriculture, Livestock and Food Supply 2005). Figure 1b shows that it was possible to verify the insignificant effect in the method sensitivity employing the lowest and the highest allowed alcohol content also demonstrated by copper spectra.

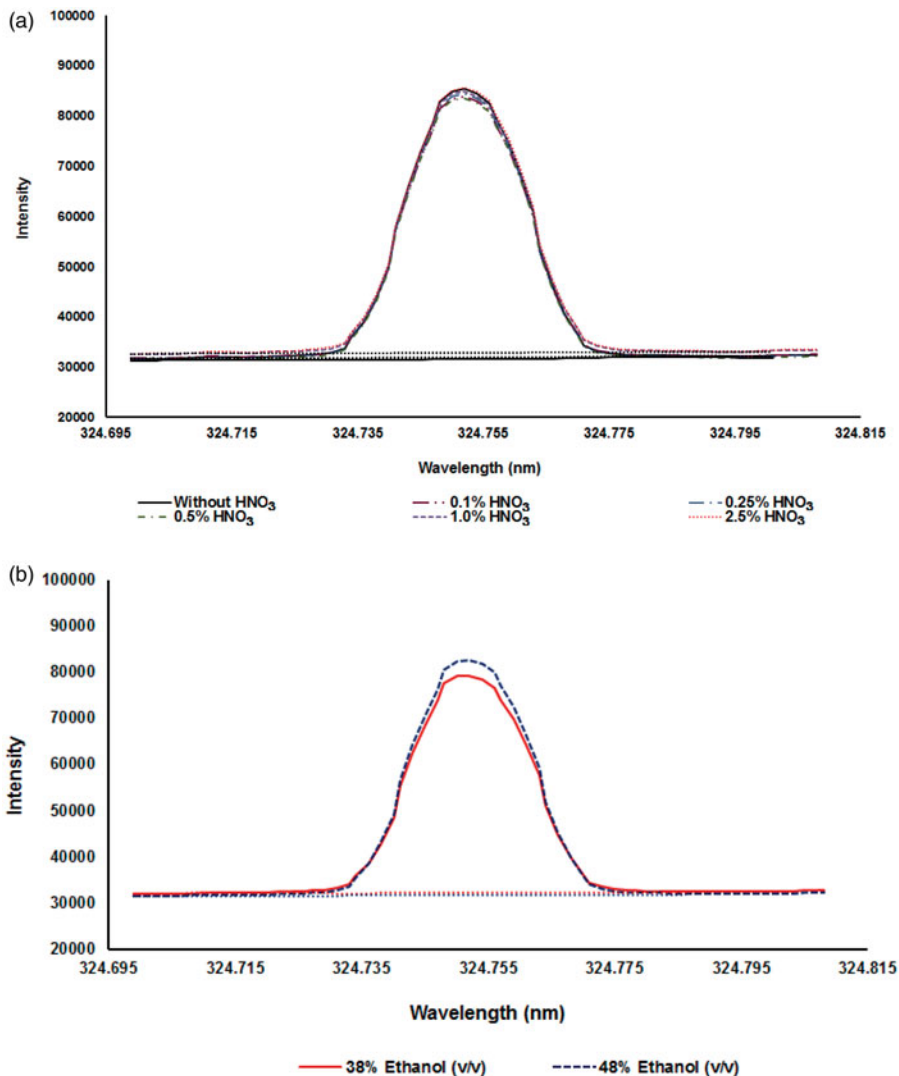


Figure 1. Copper spectrum from solutions spiked with 1 mg L⁻¹ of copper standard solution with (a) 48% ethanol + different concentrations of HNO₃ (v/v) and (b) varying ethanol composition.

Experimental design

The plasma robustness is a parameter that allows verification of optimum conditions for operation. This is usually expressed as an ICP OES condition when matrix variations cannot compromise analytical results. The influence of the parameters radio frequency source power; nebulization flow rate, plasma flow rate, auxiliary gas flow rate, and read time were evaluated using a 2^{5-1} fractional design. The experiments were randomly performed and the results are presented in Table 1.

From Table 1 it is evident that classical plasma robustness was not achieved in these experiments, since values for the Mg(II)/Mg(I) ratio were below eight (Mermet 1991). Nevertheless, the maximum values for the Mg(II)/Mg(I) ratio were observed in experiments 2 and 14 which have the high values (+1) for radio frequency source power and low values (−1) for nebulizer flow rate and read time. The lowest values were verified in experiments 7 and 15 which presented the lowest values (−1) for radio frequency source power.

From a Pareto Chart (Figure 2), the variables of radio frequency source power, nebulizer flow rate and auxiliary gas flow rate had a significant effect, considering a 95% confidence level, and for this reason these variables were chosen for further analysis. A central composite design was employed and the results are shown in Table 2 and Figure 3.

In Table 2, the maximum values for Mg(II)/Mg(I) ratio were observed in experiments 5 and 6 which presented the high values (+1) for radio frequency source power and the lowest values were seen in experiments 11 and 12. From Figure 3 it is evident that the maximum Mg(II)/Mg(I) ratio was achieved using a radio frequency source power of 1.45 kW; nebulization flow rate of 0.25 L min^{-1} and auxiliary gas flow rate of 0.45 L min^{-1} .

Therefore, the optimized experimental conditions for ICP OES were achieved using a radio frequency source power of 1.45 kW; nebulization flow rate of 0.25 L min^{-1} ; plasma flow rate of 12 L min^{-1} ; auxiliary gas flow rate of 0.45 L min^{-1} , and read time of 10 s.

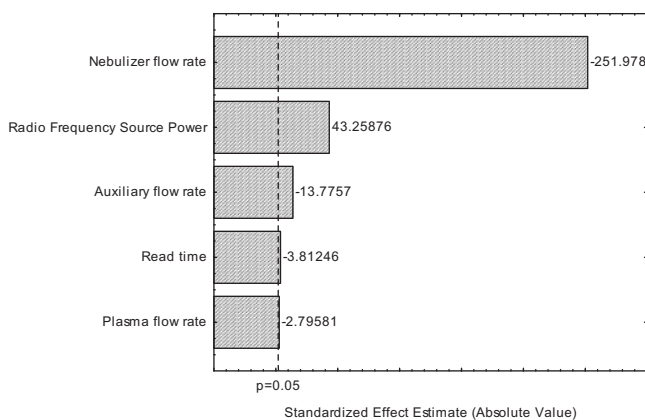


Figure 2. Pareto chart for 2^{5-1} fractional factorial design. Conditions: radio frequency source power (1.30 and 1.50 kW); nebulizer flow rate (0.30 and 0.60 L min^{-1}); auxiliary gas flow rate (0.40 and 0.60 L min^{-1}); plasma flow rate (12.0 and 15.0 L min^{-1}) and read time (10 and 20 s). Sample: sugarcane spirits spiked with 1 mg L^{-1} of magnesium standard.

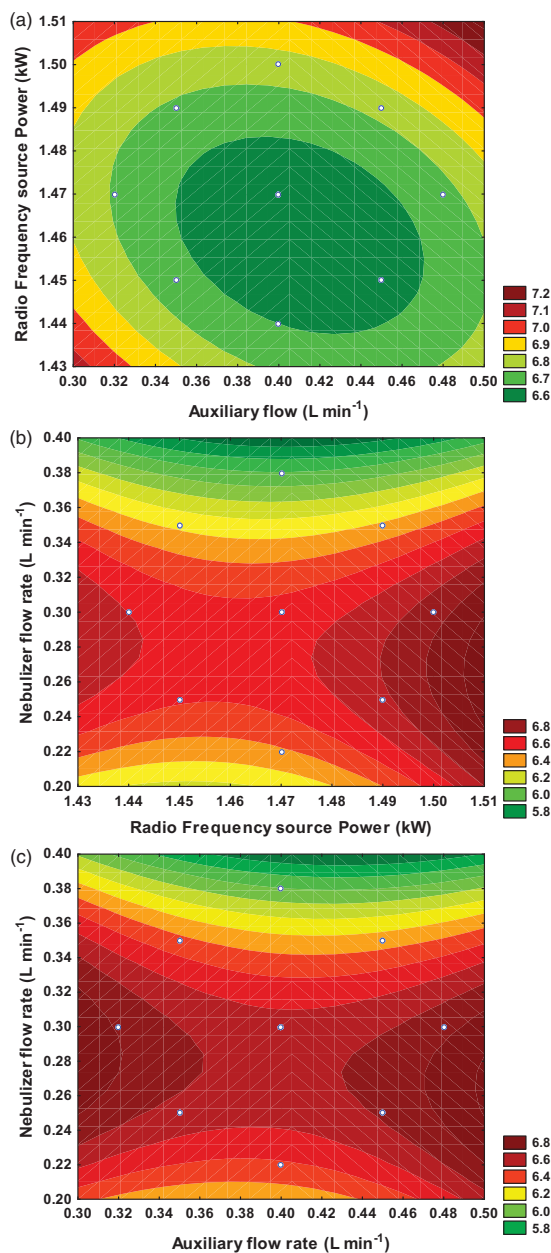


Figure 3. Surfaces obtained from central composite design: (a) auxiliary flow rate vs. radio frequency source power; (b) nebulizer flow rate vs. radio frequency source power; and (c) Nebulizer flow rate vs. auxiliary flow rate. Conditions: radio frequency source power (1.44, 1.45, 1.47, 1.49, and 1.50 kW); nebulizer flow rate (0.22, 0.25, 0.30, 0.35, and 0.38 L min⁻¹); auxiliary gas flow rate (0.32, 0.35, 0.40, 0.45, and 0.48 L min⁻¹); plasma flow rate (12.0 L min⁻¹); and read time (10 s). Sample: Sugarcane spirits spiked with 1 mg L⁻¹ of magnesium standard.

Method validation

The method was validated considering the Brazilian National Institute of Metrology, Quality and Technology (2016) recommendations. The figures of merit evaluated were linearity (considering correlation coefficients); specificity (preparing curves by standards addition and external calibration); limits of detection and quantification (calculated as 3 s and 10s, respectively, where “s” means standard deviation of eight blank experiments); accuracy (calculated using the recovery of spiked experiments; and precision (verified using the coefficient of variation of seven independent replicates). The results are presented in Table 3.

For accuracy, the recovery ranged between 83 and 115% for all inorganic contaminants and were adequate considering the Association of Official Analytical Chemists (2013) and Brazilian National Institute of Metrology, Quality and Technology (2016) recommendations of 80–110%.

The specificity or matrix effect was verified comparing the angular coefficients values in curves prepared by standards addition (sugarcane spirit sample) and external calibration (in 48% v/v ethanol). From the results presented in Table 3, it is possible to infer that there are no matrix effects in inorganic contaminant determination using external calibration curves, since the variation between angular coefficients was lower than 7.5%. The absence of interference in the selected emission lines was also confirmed by the analysis of inorganic contaminant spectra.

Linearity was achieved in the analytical curves ranges (0.005 to 0.50 mg L⁻¹ for As; 0.0025 to 0.05 mg L⁻¹ for Cd; 0.05 to 25 mg L⁻¹ for Cu; 0.005 to 5.0 mg L⁻¹ for Ni, and 0.025 to 0.50 mg L⁻¹ for Pb) and may be observed by *r* values above 0.999. For arsenic, cadmium, copper, and nickel, the lowest concentration of the analytical curves presented elevated relative standard deviations ranging from 21% to 28%. Precision was evaluated by coefficient of variation (CV) of seven replicates of sugarcane spirits and ranged between 0.4% (Cd) and 7.7% (As). The limits of detection and quantification were below to 0.008 and 0.026 µg L⁻¹, respectively, for all inorganic contaminants, except for Cu (0.05 and 0.17 µg L⁻¹, respectively). These values are adequate for alcoholic beverage analysis considering the values established by Brazilian and The Common Market of the South regulations (Decreto n° 55.871 1965; Brazilian Ministry of Agriculture, Livestock and Food Supply 2005; The Common Market of the South 2011; Resolução RDC n° 42 2013).

The values observed in present work are similar to those found by Fiket, Mikac, and Kniewald (2011) who studied wine samples from eastern Croatia using sample treatment procedures and quantification by high resolution inductively coupled plasma sector-field mass spectrometry. Low values of limits of detection were observed in the study of Jurado et al. (2007), which performed the direct determination of Cd, Cu, and Pb using direct determination by electrothermal atomic absorption spectrometry. Nevertheless, in this study for Cd analysis, the authors employed standard addition curve due to matrix effects. A previous paper from our group (Fernandes et al. 2013) obtained similar sensitivity for all elements using soft ICP OES operational conditions that required a sample treatment procedure.

Table 4 compares the present study results with recent values reported in literature for spirit samples.

Table 3. Analytical parameters for inorganic contaminant determination in spirit samples by ICP-OES.

| Element | Analytical curve | | | | Accuracy | | | Limit of Detection (mg L ⁻¹) | Limit of Quantification (mg L ⁻¹) |
|---------|------------------------------------|---|--|------------------------------------|--|---|---------------|--|---|
| | Linear range (mg L ⁻¹) | Ethanol 48% (v/v) | Standard addition | Spiked level (mg L ⁻¹) | Result (mg L ⁻¹) | Recovery (%) | Precision (%) | | |
| Arsenic | 0.005–0.50 | $y = (1216 \pm 21)x + 141(\pm 3)$ $r = 0.9990$ | $y = (1148 \pm 33)x + 142(\pm 3)$ $r = 0.9979$ | 0.025 0.050 0.25 0.025 | 0.029 ± 0.004 0.042 ± 0.005 0.22 ± 0.02 0.0024 ± 0.0000 | 115 ± 16 83 ± 10 87 ± 7 95 ± 1 | 7.7 | 0.008 | 0.026 |
| Cadmium | 0.0025–0.05 | $y = (33132 \pm 262)x + 74(\pm 7)$ $r = 0.9998$ | $y = (32153 \pm 343)x + 178(\pm 9)$ $r = 0.9995$ | 0.025 0.050 | 0.0025 0.023 ± 0.000 0.049 ± 0.001 | 94 ± 2 97 ± 2 | 0.4 | 0.001 | 0.003 |
| Copper | 0.05–25 | $y = (26438 \pm 108)x + 2927(\pm 1047)$ $r = 0.9999$ | $y = (24894 \pm 209)x + 96726(\pm 2029)$ $r = 0.9996$ | 0.50 2.50 25.0 | 0.53 ± 0.02 2.52 ± 0.04 23.8 ± 0.4 | 106 ± 4 101 ± 2 95 ± 2 | 5.8 | 0.05 | 0.17 |
| Lead | 0.025–0.5 | $y = (4434 \pm 56)x + 732(\pm 12)$ $r = 0.9996$ | $y = (4103 \pm 51)x + 730(\pm 13)$ $r = 0.9994$ | 0.025 0.050 | 0.021 ± 0.001 0.042 ± 0.003 | 83 ± 3 84 ± 5 | 2.9 | 0.005 | 0.018 |
| Nickel | 0.005–5.0 | $y = (1772 \pm 7)x + 107(\pm 6)$ $r = 1.0000$ | $y = (1727 \pm 11)x + 110(\pm 11)$ $r = 0.9998$ | 0.025 0.050 | 0.23 ± 0.01 0.022 ± 0.002 0.050 ± 0.006 2.44 ± 0.04 | 93 ± 3 88 ± 8 100 ± 11 97 ± 2 | 0.9 | 0.003 | 0.011 |

The recovery is the percentage between the measured and spiked concentration levels.

Table 4. Recent methods reported for inorganic contaminant determination in sugarcane spirits.

| Matrix | Sample treatment | Technique | Recovery (Precision) | Limit of detection (mg L^{-1}) | | | | | Reference |
|------------------|--|--|----------------------|---|---------|--------|-------|--------|---|
| | | | | As | Cd | Cu | Ni | Pb | |
| Sugarcane spirit | 1 mL sample + 10 mL borate buffer (0.10 mol L^{-1}) + $1.5 \text{ mL } 1.0 \times 10^{-4} \text{ mol L}^{-1}$ phenylfluorone + 1.5 mL 0.01 mol L^{-1} cetylpyridinium chloride + 2.5 mL 0.1 mol L^{-1} Triton X-100 to a 25 mL volumetric flask using purified water | Ultraviolet-visible spectrophotometry | 80–109% (5.4%) | – | – | 0.0034 | – | – | Caldas et al. (2011) |
| Sugarcane spirit | Acid digestion at 95°C : 5 mL of the sample + 1.25 mL HNO_3 65%; final solution diluted to a 25 mL volumetric flask using purified water | Inductively coupled plasma – optical emission spectrometry | 97–118% (1–4%) | 0.006 | 0.002 | 0.003 | 0.002 | 0.003 | Fernandes et al. (2013) |
| Aniseed spirit | 10-fold dilution of sample using water/ethanol/nitric acid (58:40:2) mixture | Electrothermal atomic absorption spectrometry | 96–104% (2.85–5.08) | – | 0.00004 | 0.0006 | – | 0.0007 | Jurado et al. (2007) |
| Sugarcane spirit | 5 mL of sample + 400 μL of 50 mg L^{-1} Ag standard (internal standard) to a 10 mL flask using 1.0 mol L^{-1} HNO_3 | Fast sequential flame atomic absorption spectrometry | 99–102% (0.3–2.4%) | – | – | 0.015 | – | – | Miranda, Dionísio, and Pereira-Filho (2010) |
| Sugarcane spirit | Direct determination | Inductively coupled plasma – optical emission spectrometry | 83–115% (0.4–7.7%) | 0.008 | 0.001 | 0.05 | 0.003 | 0.005 | This study |

Table 5. Inorganic contaminants levels in sugarcane spirits samples using the direct method by ICP OES.

| Sample | | Inorganic contaminant (mg L ⁻¹) | | | | |
|--------------------------------------|------------------------------|---|---------|--------|--------|--------|
| | | Arsenic | Cadmium | Copper | Lead | Nickel |
| Sugarcane spirit A (43% v/v alcohol) | Mean | <0.008 | 0.0035 | 3.95 | <0.005 | <0.003 |
| | Standard deviation | – | 0.0001 | 0.02 | – | – |
| | Coefficient of variation (%) | – | 1.7 | 0.6 | – | – |
| Sugarcane spirit B (46% v/v alcohol) | Mean | <0.008 | <0.003 | 2.40 | <0.005 | 0.024 |
| | Standard deviation | – | – | 0.03 | – | 0.000 |
| | Coefficient of variation (%) | – | – | 1.4 | – | 0 |
| Sugarcane spirit C (46% v/v alcohol) | Mean | 0.016 | <0.001 | 4.00 | 0.040 | <0.003 |
| | Standard deviation | 0.003 | – | 0.02 | 0.001 | – |
| | Coefficient of variation (%) | 18 | – | 0.4 | 3.6 | – |
| Sugarcane spirit D (46% v/v alcohol) | Mean | <0.008 | <0.001 | 4.70 | <0.005 | <0.003 |
| | Standard deviation | – | – | 0.04 | – | – |
| | Coefficient of variation (%) | – | – | 0.9 | – | – |
| Sugarcane spirit E (46% v/v alcohol) | Mean | <0.008 | <0.001 | 2.79 | <0.005 | <0.003 |
| | Standard deviation | – | – | 0.02 | – | – |
| | Coefficient of variation (%) | – | – | 0.9 | – | – |

Similar results were obtained by Caldas et al. (2011) that verified recoveries from 80 to 109% and precision of 5.4% performing 10 measurements of a 20 µg L⁻¹ Cu solution. Fernandes et al. (2013), who also studied As, Cd, Cu, Ni, and Pb in sugarcane spirits, observed recoveries and precision between 97 and 118% and 1 and 4%, respectively.

From Table 4, it is also possible to note the good results obtained in this study considering the limits of detection, recovery and precision values, and the absence of sample treatment steps. These characteristics are particularly essential for routine analysis.

Application to sugarcane samples commercialized in Brazil

The proposed method was applied in five sugarcane spirits commercialized in Minas Gerais, southeastern Brazil. The analysis was performed in triplicate and the results are presented in Table 5.

Table 5 shows that low levels for As, Cd, Ni, and Pb were observed in sugarcane spirits purchased in Brazil, ranging from <0.008 to 0.016 mg L⁻¹, <0.003 to 0.0035 mg L⁻¹, <0.003 to 0.024 mg L⁻¹, and <0.005 to 0.040 mg L⁻¹, respectively. The results provided by this study are in a good agreement with those found by Fernandes et al. (2013) who also characterized samples from Brazil. In their study, the authors found levels between 0.006 and 0.039 mg L⁻¹ for As; 0.002 and 0.004 mg L⁻¹ for Cd; 0.002 and 0.020 mg L⁻¹ for Ni, and 0.003 and 0.070 mg L⁻¹ for Pb in 18 samples of sugarcane spirits. Penteadó and Masini (2009) also reported very low Cd and Pb levels in sugarcane spirits that were below the detection limit of the method.

Copper levels were from 2.40 to 4.70 mg L⁻¹ and presented a lower variation than the results reported by Miranda, Dionísio, and Pereira-Filho (2010) and Penteadó and Masini (2009), who verified levels with variation of 10× and 20×, ranging between 0.66 and 6.64 mg L⁻¹ and 0.371 and 6.068 mg L⁻¹, respectively. This metal is widely employed in stills and contributes to color, flavor, and taste of sugarcane spirits (Penteadó and Masini 2009).

Regarding the maximum levels allowed for inorganic contaminants in alcoholic beverages, the results demonstrated that no levels were found above the thresholds established

by Brazilian and The Common Market of the South regulations for As (0.10 mg kg^{-1}), Cd (0.02 mg kg^{-1}), Pb (0.20 mg kg^{-1}) (The Common Market of the South 2011; Resolução RDC n° 42 2013); for Ni (3.00 mg kg^{-1}) in fermented-distilled alcoholic beverages (Decreto n° 55.871 1965) and for As (0.1 mg L^{-1}) Cu (5.0 mg L^{-1}) and Pb (0.2 mg L^{-1}) in sugarcane spirits (Brazilian Ministry of Agriculture, Livestock and Food Supply 2005).

Conclusions

A direct method of analysis was extensively evaluated and was shown to be simple, fast, and accurate for quantifying arsenic, cadmium, copper, lead, and nickel levels in sugarcane spirits by ICP-OES. The ICP-OES parameters were optimized using two experimental designs by evaluating radio frequency source power, nebulization flow rate, plasma flow rate, auxiliary gas flow rate, and read time. The proposed method presented high sensitivity, with limits of detection below 0.008 mg L^{-1} for all contaminants except for Cu (0.05 mg L^{-1}) and accuracy near to 100% using spiked samples. Comparing to methods with sample treatment procedures, the presented method offers rapid analysis with a 10 s read time and low chemical consumption in agreement with the green chemistry concept. The proposed method was applied to samples commercialized in Brazil and no levels were observed above the maximum limits established by Brazilian and The Common Market of the South (MERCOSUR) for inorganic contaminants.

Acknowledgement

The authors are grateful to Craig A. Dedini for English revision.

Funding

This work was supported by the FAPEMIG under Grants [APQ-02246-14 and APQ-01007-10].

ORCID

Raquel Fernanda Milani  <http://orcid.org/0000-0002-2403-960X>

Marcelo Antonio Morgano  <http://orcid.org/0000-0001-8332-3953>

Késia Diego Quintaes  <http://orcid.org/0000-0001-5022-1571>

References

- Association of Official Analytical Chemists. 2013. *Guidelines for dietary supplements and botanicals*. Maryland: Association of Official Analytical Chemists.
- Brazilian Ministry of Agriculture, Livestock and Food Supply. 2005. Instrução Normativa n° 13, de 29 de junho de – Regulamento técnico para fixação dos padrões de identidade e qualidade para aguardente de cana e para cachaça. Diário Oficial da União. <http://extranet.agricultura.gov.br/sislegis-consulta/consultarLegislacao.do?operacao=visualizar&id=12386> (Accessed April 30, 2018).
- Brazilian National Institute of Metrology, Quality and Technology (INMETRO). 2016. Orientação Sobre Validação de Métodos Analíticos (DOQ-CGCRE-008), revision 05:1-31.

- Capobianco, M., E. S. Oliveira, and Z. L. Cardeal. 2013. Evaluation of methods used for the analysis of volatile organic compounds of sugarcane (cachaça) and fruit spirits. *Food Analytical Methods* 6 (3):978–88. doi:10.1007/s12161-012-9550-z.
- Caldas, L. F. S., B. B. A. Francisco, A. D. Pereira Netto, and R. J. Cassella. 2011. Multivariate optimization of a spectrophotometric method for copper determination in Brazilian sugar-cane spirits using the Doehlert design. *Microchemical Journal* 99 (1):118–24. doi:10.1016/j.microc.2011.04.008
- Decreto n° 55.871, de 26 de março de 1965. Modifica o Decreto n° 50.040, de 24 de janeiro de 1961, referente a normas reguladoras do emprego de aditivos para alimentos, alterado pelo Decreto n° 691, de 13 de março de 1962. Diário Oficial da União. <http://www2.camara.leg.br/legin/fed/decret/1960-1969/decreto-55871-26-marco-1965-396122-norma-pe.html> (Accessed April 30, 2018).
- Donati, G. L., R. S. Amais, D. Schiavo, and J. A. Nóbrega. 2013. Determination of Cr, Ni, Pb and V in gasoline and ethanol fuel by microwave plasma optical emission spectrometry. *Journal of Analytical Atomic Spectrometry* 28 (5):755–9. doi:10.1039/c3ja30344f.
- Expocachaça. 2017. 27th Expocachaça (June 8th to 11th held in Belo Horizonte, Brazil). <http://www.expocachaca.com.br/numeros-da-cachaca.php> (Accessed December 28, 2017).
- Fernandes, I. C., M. A. Fausto, O. M. P. A. B. Bezerra, K. D. Quintaes, M. A. Morgano, and I. B. Cerqueira. 2013. Níveis de contaminantes inorgânicos em cachaças da região do quadrilátero ferrífero armazenadas em copos in natura de esteatito (pedra-sabão). *Química Nova* 36 (9):1360–5. doi:10.1590/S0100-40422013000900014.
- Fiket, Ž., N. Mikac, and G. Kniewald. 2011. Arsenic and other trace elements in wines of Eastern Croatia. *Food Chemistry* 126 (3):941–7. doi:10.1016/j.foodchem.2010.11.091.
- Ibanez, J. G., A. Carreon-Alvarez, M. Barcena-Soto, and N. Casillas. 2008. Metals in alcoholic beverages: a review of sources, effects, concentrations, removal, speciation, and analysis. *Journal of Food Composition and Analysis* 21 (8):672–83. doi:10.1016/j.jfca.2008.06.005.
- Jurado, J. M., M. J. Martín, F. Pablos, A. Moreda-Piñeiro, and P. Bermejo-Barrera. 2007. Direct determination of copper, lead and cadmium in aniseed spirits by electrothermal atomic absorption spectrometry. *Food Chemistry* 101 (3):1296–304. doi:10.1016/j.foodchem.2006.01.027.
- Mermet, J. M. 1991. Use of magnesium as a test element for inductively coupled plasma atomic emission spectrometry diagnostics. *Analytica Chimica Acta* 250 :85–94. doi:10.1016/0003-2670(91)85064-Y.
- Miranda, K., A. G. G. Dionísio, and E. R. P. Pereira-Filho. 2010. Copper determination in sugar cane spirits by fast sequential flame atomic absorption spectrometry using internal standardization. *Microchemical Journal* 96 (1):99–101. doi:10.1016/j.microc.2010.02.011.
- Penteado, J. C. P., and J. C. Masini. 2009. Multivariate analysis for the classification differentiation of Brazilian sugarcane spirits by analysis of organic and inorganic compounds. *Analytical Letters* 42 (17):2747–57. doi:10.1080/00032710903060727.
- Resolução RDC n° 42, de 29 de agosto de 2013. Dispõe sobre o Regulamento Técnico MERCOSUL sobre Limites Máximos de Contaminantes Inorgânicos em Alimentos. Diário Oficial da União. http://bvsmms.saude.gov.br/bvs/saudelegis/anvisa/2013/rdc0042_29_08_2013.html (Accessed April 30, 2018).
- Silva, P. H. A., J. O. Santos, L. D. Araújo, F. C. Faria, A. F. Pereira, V. A. De Oliveira, M. A. Vicente, and R. L. Brandão. 2009. Avaliação cromatográfica de compostos voláteis de cachaças produzidas com leveduras de diferentes procedências. *Ciência e Tecnologia De Alimentos* 29 (1):100–6. doi:10.1590/S0101-20612009000100016.
- The Common Market of the South (MERCOSUR). 2011. Resolução GMC n. 12/2011 - Regulamento técnico MERCOSUL sobre limites máximos de contaminantes inorgânicos em alimentos (Revogação das RES. GMC N° 102/94 e N° 35/96). <http://gd.mercosur.int/SAM/GestDoc/pubweb.nsf/Normativa?ReadForm&lang=POR&id=AD4E9EB61FB91B7E032578C00059A780> (Accessed: April 30, 2018).
- Virgilio, A., R. S. Amais, D. Schiavo, and J. A. Nóbrega. 2015. Dilute-and-shoot procedure for determination of As, Cr, Pb, Si, and V in ethanol fuel by inductively coupled plasma tandem mass spectrometry. *Energy & Fuels* 29 (7):4339–44. doi:10.1021/acs.energyfuels.5b00434.