

Ecofriendly and low-cost sample preparation methods for magnesium determination in beer

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ARTICLE INFO

Article history:

Received: December 14, 2020

Accepted: February 09, 2021

Published: July 01, 2021

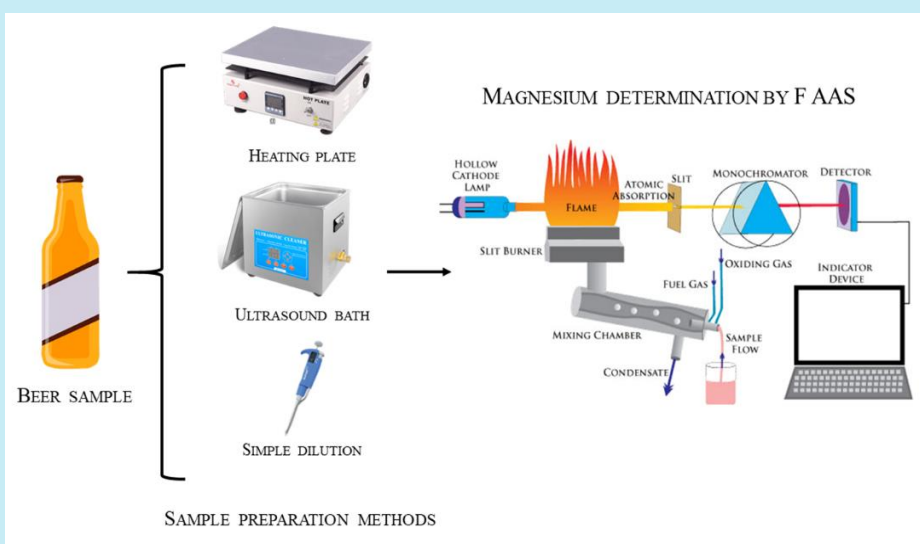
Section Editor: Paulo Clairmont Feitosa de Lima Gomes

Keywords

1. Magnesium
2. beer
3. ultrasound-assisted extraction
4. direct analysis
5. flame atomic absorption spectrometry

ABSTRACT: Ultrasound-assisted extraction and direct analysis were compared with total digestion for magnesium determination in beer samples by flame atomic absorption spectrometry. The method for total digestion used concentrated nitric acid under plate heating. In optimized instrumental conditions, validation of the analytical method was promoted, with good linear range (0.06 to 0.5 mg L⁻¹), low limits of detection and quantification (0.04 and 0.12 µg g⁻¹, respectively), good precision, relative standard deviation (RSD) < 3.4%, and accuracy (recovery levels of 91.5 to 99.0%).

The characteristic concentration (C₀) was 9 µg L⁻¹. The extraction procedure was performed in a 1:1 nitric acid solution for 55 min in an ultrasonic bath at 60 °C, while the direct analysis involved a dilution of the samples in a 2% v/v nitric acid solution. The different sample preparation methods were applied to 13 beer samples and at a 95% confidence level, no significant differences were observed. Thus, direct analysis proved to be more suitable for quality control routines of beer samples in the industry.



1. Introduction

Beer is one of the most popular drinks worldwide and the third most consumed, after water and tea (Pai et al., 2015; Sampaolesi et al., 2019). Historical reports date back to their production by Sumerians and Assyrians around 8,000 years ago (Rosa and Afonso, 2015), while the Egyptians were responsible for spreading their production among the eastern people in the Mediterranean basin and from there to the rest of Europe (Ferreira et al., 2011). Beer is traditionally produced with malted barley because of its high enzymatic content, which allows for the rapid conversion of starch into fermentable sugars that give rise to alcohol, carbon dioxide and flavor compounds during yeast fermentation (*Saccharomyces cerevisiae*) (Omari et al., 2020). In addition, hops are used in the fermentation process to add a characteristic bitterness and distinct aroma to the beer (Kishimoto et al., 2020).

The composition of beer varies according to style, however, the presence of minerals, such as Ca, K, Mg, P and Zn (Rosa and Afonso, 2015; Sleiman et al., 2010), has already been reported, which can correspond to up to 10% of the recommended daily intake values. Moderate beer consumption is associated with several benefits, ranging from diuretic properties and antioxidant action to positive effects against several cardiovascular risk factors, including an increase in high density lipoprotein (HDL) cholesterol and a lower risk of ischemic stroke (Arranz et al., 2012; Gaetano et al., 2016; Lordan et al., 2019). These factors may be related to the presence of moderate levels of magnesium in beer, influencing the quality of the drink. Magnesium is an essential micronutrient associated with more than 300 enzymatic processes in the body (Rosanoff, 2013). In beer, when associated with calcium it helps in the kinetics of the isomerization reaction of α -acids in cis and trans-iso- α -acids, constituents responsible for the bitterness of beer (Wietstock et al., 2015).

Different methods of analysis have been used to determine magnesium in several types of samples, including colorimetry (Shishov et al., 2019), liquid chromatography (Paull et al., 1997), electrochemistry (Akhter et al., 2020), capillary electrophoresis (Sako et al., 2018), flame atomic absorption spectrometry (F AAS) and graphite furnace atomic absorption spectrometry (GF AAS) (Santos et al., 2019; Seeger et al., 2019), inductively coupled plasma optical emission spectrometry (ICP OES) (Souza et al., 2019) and inductively coupled plasma mass spectrometry (ICP-MS) (Moreda-Piñeiro et al., 2018). The methods recommended by the American Society of Brewing

Chemists for determining magnesium in beer samples are based on the spectrophotometry, F AAS, GF AAS and ICP OES techniques (ASBC). Among these, the one with the lowest cost and most adequate is the F AAS, as it presents good selectivity, precision, robustness, high analytical frequency associated with the low cost of acquisition and maintenance of equipment and analysis (Khajeh and Sanchooli, 2010; Pohl and Sergiel, 2010).

The optimization of sample preparation conditions, which is a critical step that involves from simple dilution to partial or total solubilization, are essential for the development of analysis methods (Santos et al., 2019). Currently, the main objective is focused on obtaining the best results in the shortest time, with minimum error, low consumption of reagents and minimum generation of residues, the latter two topics being associated with green chemistry. However, the methods commonly used for this purpose are digestion using concentrated acids under heating (heating plate and microwave oven) and alkaline solubilization, both methods require massive volume of reagent, high energy consumption and generate toxic waste (Mketo et al., 2016). Excellent alternatives to this problem are the use of ultrasound-assisted extraction (UAE) and direct analysis, as demonstrated by the scientific literature (Adolfo et al., 2020; Ferreira et al., 2014; Oliveira et al., 2017; Santos et al., 2018; Szymczycha-Madeja et al., 2013; Welna et al., 2014).

Thus, the present work aims to develop and compare different methods of preparing samples by digestion in heating plate, UAE and simple dilution to evaluation of magnesium levels in beer samples by F AAS.

2. Experimental

2.1 Materials, reagents and samples

All measurements were performed on a flame atomic absorption spectrometer (Thermo Scientific, model SOLAAR Serie M5; USA). A magnesium hollow cathode lamp (Photron Lamps; USA) was used, operating with a maximum current of 4 mA and a wavelength of 285.2 nm. The acid digestion was performed on a heating plate (Warmnest, model DB-IVA). The extraction was performed in an ultrasonic bath with power 220 W and frequency of 40 kHz, temperature control (30 to 60 °C) and volume 9.5 L (Unique, model USC-2800A). All reagents used were of analytical grade. The solutions were prepared using deionized water with resistivity of at least 18.2 M Ω cm

(Elga Purelab Option-Q, model LA611; UK). Nitric acid (Sciavicco Comércio e Indústria Ltda, 65% v/v) was used to prepare samples and solutions. The analytical curve was prepared from a stock solution of Mg 1000 mg L⁻¹ (Vetec Química Fina Ltda). All glassware used was cleaned in at 10% (v/v) nitric acid bath for at least 24 h, then washed with deionized water at least three times and dried at room temperature. The 13 samples of beer of different brands were purchased on the local market, named A01 to A13.

2.2 Sample preparation

Initially, the samples were subjected to a degassing process through sonication in an ultrasonic bath for 15 min to remove CO₂ (Blanco et al., 2010). The acid digestion of the samples was performed on a heating plate using beakers and watch glasses as a reflux system. The procedure was carried out in the exhaust hood. Initially, about 500 mg of degassed sample was weighed, then 10.0 mL of concentrated HNO₃ was added. After this stage, the mixture was taken to a heating plate at 90 °C until the release of nitrous vapors ceases.

For the extraction procedure in ultrasonic bath, 500 mg of the sample and 5.0 mL of diluted HNO₃ solution (1:1) were added in a polypropylene tube. The tubes were positioned under the support and sonicated for 55 min at a controlled temperature of 60 °C. All samples were transferred to volumetric flasks of 25.0 mL and completed volume with deionized water.

For direct analysis, 125 mg of sample was weighed and diluted to 25.00 mL in a volumetric flask with HNO₃ solution (2% v/v).

2.3 Instrumental conditions optimization of F AAS

Instrumental optimization was performed according to the recommendation of the equipment manual. The gas flow was evaluated from 1.0 to 1.3 L min⁻¹, the spectral bandpass from 0.1 to 1.0 nm and the burner height from 6.8 to 7.2 mm. The optimization studies were performed in a univariate manner and all measurements were performed in triplicate.

2.4 Figures of merit

All analytical parameters were validated according to the Resolution RDC No. 166 of July 24, 2017, of the National Health Surveillance Agency (Anvisa), which

provides for the validation of methods analytical and other measures (Anvisa, 2017). The linearity of the analytical curve, homoscedasticity and normality of the data were verified using the analysis of variance tests (ANOVA), Cochran and Shapiro–Wilk, respectively, at a 95% confidence level. The limit of detection (LOD) and limit of quantification (LOQ) of the method were calculated by multiplying the value of the standard deviation (10 measurements of absorbance signal of the blank digestions on a heating plate) by 3.3 (LOD) or 10 (LOQ), then the result was divided by the slope of the analytical curve. The limits obtained by the previous calculation were corrected by a factor where they were multiplied by the final volume of the analysis solutions (0.025 L) and divided by the mass of samples (approximately 0.5 g), obtaining LOD and LOQ in µg g⁻¹, as already demonstrated by Mimura et al. (2016).

Regarding the method detectability, sensitivity was evaluated by calculating the characteristic concentration (*C₀*) (Welz and Sperling, 1999). The precision of the method was verified using the relative standard deviation (RSD). Spike tests were also performed in order to evaluate the accuracy. These were performed at three levels of concentration. The analytes were added, as solutions, to the samples immediately after weighing. For the first level, the concentrations of Mg in the samples were 10 mg L⁻¹. For the second level, the concentrations of Mg in the samples were 20 mg L⁻¹. For the third level, the concentrations were 30 mg L⁻¹. Blank samples were also evaluated at a concentration level of 10 mg L⁻¹. After sample preparation, dilution processes were necessary for magnesium quantification in the concentration range of the analytical curve.

3. Results and discussion

3.1 Instrumental conditions optimization

The development of methods for determining mineral elements by F AAS requires a step of optimizing instrumental conditions. Generally, it is recommended to evaluate parameters such as gas flow, burner height and spectral bandpass. Magnesium, as well as other alkaline-earth metals, is more sensitive to slightly reducing flames, where maximum temperatures are obtained from 2100 to 2200 °C (Welz and Sperling, 1999). With the increase in the flow of acetylene gas, the flame increases its reducing power, which directly influences to obtain flames with milder temperatures and lower gradients. Thus, it is expected

to reduce the absorbance signal, as shown in Fig. 1a. The adjustment of the burner height (observation height), associated with analytical sensitivity, is important for the residence time of the metal in the fundamental state in the gas phase. In this sense, as evidenced by Fig. 1b, the positioning of the burner influenced the absorption conditions of the radiation beam that passes through the flame. There was an increase in analytical signal up to 7.0 mm, from this value less analytical sensitivity and considerable loss of precision was observed, showing a significant fluctuation of the atomic absorption signals. In atomic absorption spectrometry (AAS), the monochromator has the exclusive task of separating the analytical line from other emission lines from the source. The saturation of the detector can often be observed from certain values of the spectral bandpass, as shown in Fig. 1c, where from 0.2 nm the measured absorbance remains practically constant. However, in very narrow bandpass, the small amount of radiation reaching the detector also compromises sensitivity. Table 1 shows the experimental conditions optimized for the analyses.

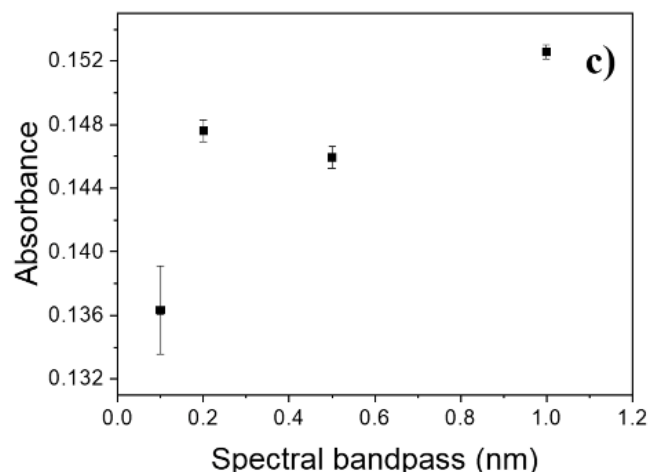
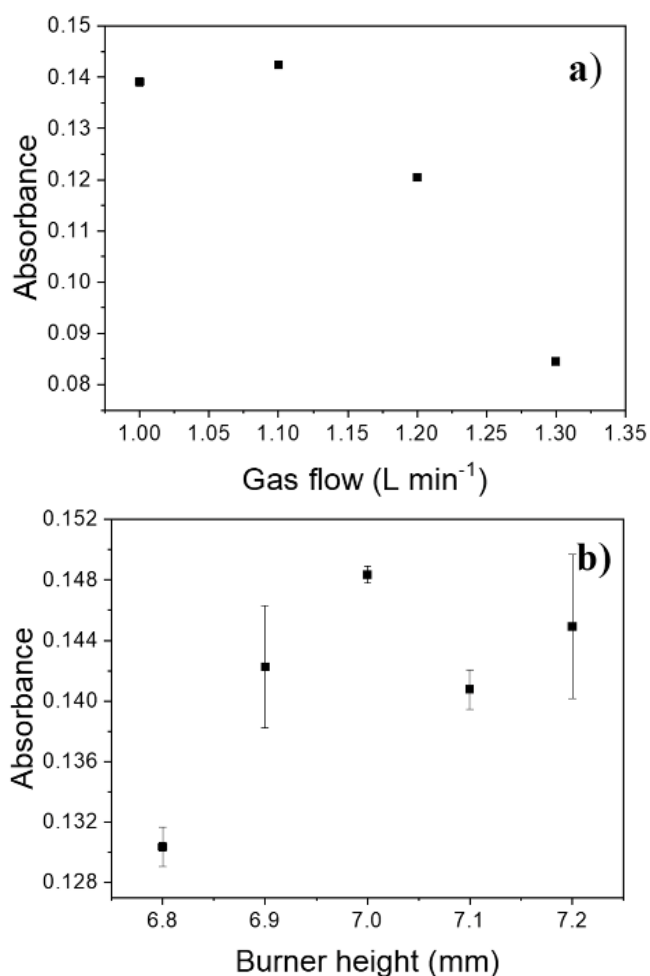


Figure 1. Optimization curves for instrumental conditions related to the magnesium determination in beer samples by flame atomic absorption spectrometry. **a)** gas flow; **b)** observation height; and **c)** spectral bandpass. Conditions: the optimizations were performed using a standard solution with a concentration of 0.3 mg L^{-1} , according to instructions in the equipment manual. Optimal gas flow 1.1 L min^{-1} ; burner height 7.0 mm ; spectral bandpass 0.2 nm .

Table 1. Instrumental conditions for magnesium determination in beer samples by F AAS.

| Parameters | Conditions |
|----------------------------------|---------------|
| Gas flow (L min^{-1}) | 1.1 |
| Spectral bandpass (nm) | 0.2 |
| Burner height (mm) | 7.0 |
| Wavelength (nm) | 285.2 |
| Gas mixture | Air/acetylene |

3.2 Figures of merit

Linearity was evaluated through ANOVA for an external analytical calibration curve with the concentration ranging from 0.06 to 0.5 mg L^{-1} , constructed under previously optimized conditions. The analytical curve showed good linearity, with a linear correlation coefficient (R) greater than 0.99 , as shown in Fig. 2. The regression showed no lack of fit for $\alpha = 0.05$ ($F_{calc} = 0.617 < F_{tab} = 3.26$), and it was highly significant and useful for prediction purposes. The homoscedasticity and normality of the data were verified using the Cochran ($C_{calc} = 0.606 < C_{tab} = 0.616$) and Shapiro–Wilk ($W_{calc} = 0.938 > W_{tab} = 0.897$) tests, respectively, at a 95% confidence level. The test results indicated that the data were distributed homogeneously and according to a normal function.

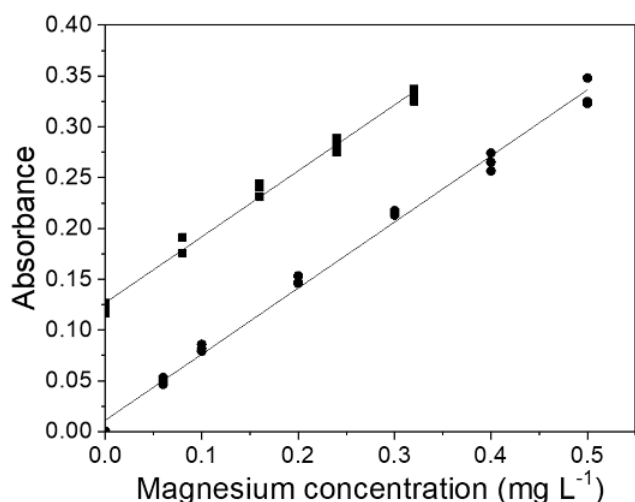


Figure 2. External calibration curve (●) ($y = 0.650x + 0.011$, $R^2 = 0.99$) and standard addition curve (■) ($y = 0.649x + 0.127$, $R^2 = 0.99$) for determining Mg in beer samples.

The matrix effect in determinations using F AAS can be evaluated by comparing the external calibration with the standard addition curves. Figure 2 shows the calibration curves for beer samples with concentration ranging from 0.06 to 0.50 mg L⁻¹ for external calibration curve and from 0.08 to 0.32 mg L⁻¹ for standard addition curve. The concentration variances determined by both methods, Tab. 2, were compared using the F test (Fisher–Snedecor). The calculated F value (6.45) was greater than the critical F value (3.44), which indicates that the calculation for comparing the means must be performed using the t-test with ungrouped variances. The t-test was calculated at a 95% confidence level and, since the calculated t-value (0.93) was less than the critical t-value (2.23), it can be said that there is no significant evidence of differences between the different calibration methods, indicating that the established method presents satisfactory selectivity, with no matrix effect on the determinations.

Table 2. Magnesium concentrations in beer samples obtained by F AAS using an external calibration curve and standard addition curve. Concentration \pm standard deviation (sd), $n = 3$.

| Samples | Magnesium concentration ($\mu\text{g L}^{-1}$) | |
|---------|--|-------------------------|
| | External calibration curve | Standard addition curve |
| 1 | 172 ± 1 | 193 ± 3 |
| 2 | 156 ± 1 | 143 ± 2 |
| 3 | 178 ± 6 | 195 ± 9 |

The spike tests, carried out at three concentration levels, allowed to evaluate the accuracy of the method. It should be noted that the standard solution was added to the samples prior to the digestion process and the blank sample was also prepared at a concentration level for control. The recovery percentages were 98.0 ± 0.1 , 99.0 ± 2.0 and $99.0 \pm 3.0\%$ for levels 1, 2 and 3, respectively; while for the blank sample, the percentage of recovery was $91.5 \pm 0.5\%$. These recovery values close to 100% indicate that the method, digestion in heating plate, presented good accuracy for magnesium determination in beer samples.

The precision of the measurements was also evaluated using repeatability tests ($n = 10$). For beer samples, this value was 3.4%. Considering the concentration level in the reading solution (approximately 0.24 mg L⁻¹), it can be inferred that the measurements were highly precise. The LOD and LOQ calculated for the method were 0.04 and 0.12 $\mu\text{g g}^{-1}$, respectively. The analytical sensitivity expressed as the characteristic concentration (C_0) was 9 $\mu\text{g L}^{-1}$. The value found is close to values in the literature, such as that obtained by Ieggli et al. (2010; 2011). for chocolate samples (19 $\mu\text{g L}^{-1}$) and emulsified egg samples (14 $\mu\text{g L}^{-1}$).

3.3 Application and comparison of methods

After validation of the method involving total digestion, the UAE method and dilutions for direct analysis were performed. The results, shown in Tab. 3, were compared using the IBM SPSS Statistics 21 software. The first assumption evaluated was normality through the Shapiro–Wilk test and the results obtained indicate that the residues showed normal distribution, since the significance presented a value higher than the p-value (0.05). The homoscedasticity was evaluated by Levene test and similarly it was found that showed significant p-value greater than the value (0.05). The independence was evaluated using the Durbin–Watson (DW) test, to test for the presence of autocorrelation in the errors of a regression model and since the calculated DW value is within the critical range ($dU < DW < 4 dU$, that is, $1.38 < DW < 2.62$), it can be said that, at a 95% confidence level, the residues are independent. Thus, regression analysis of the methods (ANOVA, single factor) was performed and it was found that at a 95% confidence level the calculated F value (0.050) is less than the critical F value (3.259) and, therefore, it can be said that the results are statistically equivalent.

Table 3. Results for magnesium determination in mg g^{-1} by F AAS in beer samples using different sample preparation techniques. Concentration \pm sd, $n = 3$.

| Samples | Heating plate digestion ($\mu\text{g g}^{-1}$) | Ultrasound-assisted extraction ($\mu\text{g g}^{-1}$) | Direct analysis ($\mu\text{g g}^{-1}$) |
|---------|--|---|--|
| A01 | 113 \pm 3 | 101 \pm 8 | 114 \pm 3 |
| A02 | 82 \pm 4 | 93 \pm 5 | 89 \pm 3 |
| A03 | 71 \pm 4 | 74 \pm 5 | 70 \pm 5 |
| A04 | 74 \pm 1 | 77 \pm 2 | 86 \pm 5 |
| A05 | 72 \pm 7 | 69 \pm 1 | 88 \pm 6 |
| A06 | 70 \pm 7 | 72 \pm 3 | 65 \pm 8 |
| A07 | 46 \pm 3 | 44 \pm 2 | 49 \pm 7 |
| A08 | 62 \pm 4 | 55 \pm 1 | 54 \pm 3 |
| A09 | 60 \pm 2 | 58 \pm 5 | 67 \pm 1 |
| A10 | 68 \pm 5 | 69 \pm 4 | 65 \pm 5 |
| A11 | 85 \pm 4 | 85 \pm 2 | 85 \pm 2 |
| A12 | 81 \pm 4 | 78 \pm 6 | 71 \pm 2 |
| A13 | 92 \pm 6 | 93 \pm 7 | 90 \pm 1 |

ANOVA: p -value = 0.952, $F = 0.050$ Residual normality test (Shapiro–Wilk test): p -value = 0.517Residual homoscedasticity test (Levene test): p -value = 0.780Residual independence test (Durbin–Watson test): p -value = 1.747

Both methods of sample preparation proved to be adequate for the evaluation of magnesium levels in beer samples. Highlighting in relation to the procedures recommended by the American Society of Brewing Chemists, demand for lower consumption of concentrated acid reagents, time and analytical cost, providing even less operational risk to the analyst (ASBC). Thus, among the methods evaluated, direct analysis is shown to be the best cost-effective alternative for monitoring magnesium in beers.

The magnesium levels in beer samples ranged from 44 to 114 $\mu\text{g g}^{-1}$ and their source may be related to the malt used in the production process, as reported by Omari et al. (2020) and Styburski et al. (2018). Similar results are described in the scientific literature involving different sample preparation methods and instrumental techniques. Leão et al. (2018) used a mixture of nitric acid and hydrogen peroxide for digestion in digesting block with determination by microwave-induced plasma optical emission spectrometry (MIP-OES), with magnesium levels ranging from 46 to 97 $\mu\text{g g}^{-1}$ (Leão et al., 2018). On the other hand, Marcano et al. (2010) used direct analysis associated with ICP OES, with magnesium levels ranging from 29 to 85 $\mu\text{g g}^{-1}$. In general, the method developed in the present work has more attractive characteristics, either due to the simplicity of sample preparation or the instrumental and operational cost of the analysis technique.

4. Conclusion

The sample preparation methods developed proved to be adequate for the magnesium determination in beer samples by flame atomic absorption spectrometry. The detection and quantification limits were 0.04 and 0.12 $\mu\text{g g}^{-1}$, respectively, making it possible to determine the levels of this micronutrient in 13 samples, with adequate precision and accuracy. It is noteworthy that the observed levels are in accordance with other works reported.

The method involving direct analysis proved to be promising, since it requires minimal handling, reducing the risk of analyte losses and/or contamination, with low demand for samples, reagents and expensive instrumentation. Thus, it is shown as a viable alternative for implementation in routine analyzes for the quality control of beers in the industry.

Authors' contribution

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Methodology: Lisboa, T. P.

Project administration: Lisboa, T. P.; Farias, D. M.; Matos, M. A. C.; Silva, J. C. J.; Oliveira, M. A. L.

Resources: Matos, M. A. C.; Silva, J. C. J.; Oliveira, M. A. L.

Software: Not applicable.

Supervision: Lisboa, T. P.; Faria, L. V.; Matos, M. A. C.; Silva, J. C. J.; Oliveira, M. A.

Validation: Lisboa, T. P.; Faria, L. V.

Visualization: Lisboa, T. P.; Faria, L. V.

Writing – original draft: Lisboa, T. P.; Faria, L. V.

Writing – review & editing: Lisboa, T. P.; Faria, L. V.; Matos, M. A. C.; Silva, J. C. J.; Oliveira, M. A.

Data availability statement

All data sets were generated or analyzed in the current study.

Funding

Not applicable.

Acknowledgments

The authors would like to thank Professors Dr. Renato Camargo Matos and Dr. Rafael Arromba de Sousa for making the laboratory and equipments availables.

References

Adolfo, F. R.; do Nascimento, P. C.; Leal, G. C.; Bohrer, D.; Viana, C.; de Carvalho, L. M. Simultaneous determination of Fe and Ni in guarana (*Paullinia cupana* Kunth) by HR-CS GF AAS: Comparison of direct solid analysis and wet acid digestion procedures. *J. Food Compos. Anal.* **2020**, *88*, 103459. <https://doi.org/10.1016/j.jfca.2020.103459>.

Agência Nacional de Vigilância Sanitária (Anvisa). Resolução RDC nº 166, de 24 de julho de 2017. Dispõe sobre a validação de métodos analíticos e dá outras providências; Ministério da Saúde, 2017.

Akhter, F.; Nag, A.; Alahi, M. E. E.; Liu, H.; Mukhopadhyay, S. C. Electrochemical detection of calcium and magnesium in water bodies. *Sens Actuators. A: Phys.* **2020**, *305*, 111949. <https://doi.org/10.1016/j.sna.2020.111949>.

American Society of Brewing Chemists (ASBC). ASBC Methods of Analysis. <https://www.asbcnet.org/methods/pages/default.aspx> (accessed 2020-12-01)

Arranz, S.; Chiva-Blanch, G.; Valderas-Martínez, P.; Medina-Remón, A.; Lamuela-Raventós, R. M.; Estruch, R.

Wine, Beer, Alcohol and Polyphenols on Cardiovascular Disease and Cancer. *Nutrients* **2012**, *4* (7), 759–781. <https://doi.org/10.3390/nu4070759>.

Blanco, C. A.; Sancho, D.; Caballero, I. Aluminium content in beers and silicon sequestering effects. *Food Res. Int.* **2010**, *43* (10), 2432–2436. <https://doi.org/10.1016/j.foodres.2010.09.017>.

Ferreira, B. L.; Chaves, E. S.; Vialich, J.; Sauer, E. Extração assistida por ultrassom para determinação de Fe, K e Na em amostras de achocolatado em pó. *Braz. J. Food Technol.* **2014**, *17* (3), 236–242. <https://doi.org/10.1590/1981-6723.1514>.

Ferreira, R. H.; Vasconcelos, M. C. R. L.; Judice, V. M. M.; Neves, J. T. R. Inovação na fabricação de cervejas especiais na região de Belo Horizonte. *Perspect. Ciênc. Inf.* **2011**, *16* (4), 171–191. <https://doi.org/10.1590/S1413-99362011000400011>.

Gaetano, G. de; Costanzo, S.; Di Castelnuovo, A.; Badimon, L.; Bejko, D.; Alkerwi, A.; Chiva-Blanch, G.; Estruch, R.; La Vecchia, C.; Panico, S.; Pounis, G.; Sofi, F.; Stranges, S.; Trevisan, M.; Ursini, F.; Cerletti, C.; Donati, M. B.; Iacoviello, L. Effects of moderate beer consumption on health and disease: A consensus document. *Nutr. Metab. Cardiovasc. Dis.* **2016**, *26* (6), 443–467. <https://doi.org/10.1016/j.numecd.2016.03.007>.

Ieggli, C. V. S.; Bohrer, D., do Nascimento, P. C.; de Carvalho, L. M.; Garcia, S. C. Determination of sodium, potassium, calcium, magnesium, zinc, and iron in emulsified egg samples by flame atomic absorption spectrometry. *Talanta* **2010**, *80* (3), 1282–1286. <https://doi.org/10.1016/j.talanta.2009.09.024>.

Ieggli, C. V. S.; Bohrer, D.; do Nascimento, P. C.; de Carvalho, L. M. Determination of sodium, potassium, calcium, magnesium, zinc and iron in emulsified chocolate samples by flame atomic absorption spectrometry. *Food Chem.* **2011**, *124* (3), 1189–1193. <https://doi.org/10.1016/j.foodchem.2010.07.043>.

Khajeh, M.; Sanchooli, E. Optimization of Microwave-Assisted Extraction Procedure for Zinc and Iron Determination in Celery by Box–Behnken Design. *Food Anal. Methods* **2010**, *3*, 75–79. <https://doi.org/10.1007/s12161-009-9086-z>.

Kishimoto, T.; Teramoto, S.; Fujita, A.; Yamada, O. Principal Component Analysis of Hop-Derived Odorants Identified by Stir Bar Sorptive Extraction Method. *J. Am. Soc. Brew. Chem.* **2020**, 1–9. <https://doi.org/10.1080/03610470.2020.1843926>.

Leão, P. R. P. de; Medina, A. L.; Vieira, M. A.; Ribeiro, A. S. Decomposição de amostras de cerveja com sistema de refluxo para determinação monoelementar por F AAS/AES e

- determinação multielementar por MIP OES. *Braz. J. Food Technol.* **2018**, *21*, e2017062. <https://doi.org/10.1590/1981-6723.6217>.
- Lordan, R.; O'Keeffe, E.; Dowling, D.; Mullally, M.; Heffernan, H.; Tsoupras, A.; Zabetakis, I. The *in vitro* antithrombotic properties of ale, lager, and stout beers. *Food Biosci.* **2019**, *28*, 83–88. <https://doi.org/10.1016/j.fbio.2019.01.012>.
- Marcano, E.; Gómez, C.; Benzo, Z.; Laine, J. Estudio preliminar sobre la determinación de elementos traza en cervezas venezolanas por ICP-OES. *Quím. Nova* **2010**, *33* (3), 653–655. <https://doi.org/10.1590/S0100-40422010000300032>.
- Mimura, A. M. S.; Oliveira, M. A. L.; Ciminelli, V. S. T.; Silva, J. C. J. Optimization of Ultrasound-Assisted Extraction of Cr, Cu, Zn, Cd, and Pb from Sediment, Followed by FAAS and GFAAS Analysis. *J. AOAC Int.* **2016**, *99* (1), 252–259. <https://doi.org/10.5740/jaoacint.15-0090>.
- Mketo, N.; Nomngongo, P. N.; Ngila, J. C. An overview on analytical methods for quantitative determination of multi-element in coal samples. *TrAC Trends Analyt. Chem.* **2016**, *85* (Part C), 107–116. <https://doi.org/10.1016/j.trac.2016.09.002>.
- Moreda-Piñeiro, J.; Sánchez-Piñero, J.; Mañana-López, A.; Turnes-Carou, I.; Alonso-Rodríguez, E.; López-Mahía, P.; Muniategui-Lorenzo, S. Multi-element determinations in foods from Amazon region by ICP-MS after enzymatic hydrolysis assisted by pressurisation and microwave energy. *Microchem. J.* **2018**, *137*, 402–409. <https://doi.org/10.1016/j.microc.2017.11.018>.
- Oliveira, T. M. de; Peres, J. A.; Felsner, M. L.; Justi, K. C. Direct determination of Pb in raw milk by graphite furnace atomic absorption spectrometry (GF AAS) with electrothermal atomization sampling from slurries. *Food Chem.* **2017**, *229*, 721–725. <https://doi.org/10.1016/j.foodchem.2017.02.143>.
- Omari, I. O.; Charnock, H. M.; Fugina, A. L.; Thomson, E. L.; McIndoe, J. S. Magnesium-Accelerated Maillard Reactions Drive Differences in Adjunct and All-Malt Brewing. *J. Am. Soc. Brew. Chem.* **2020**, *79* (2), 145–155. <https://doi.org/10.1080/03610470.2020.1795437>.
- Pai, T. V.; Sawant, S. Y.; Ghatak, A. A.; Chaturvedi, P. A.; Gupte, A. M.; Desai, N. S. Characterization of Indian beers: chemical composition and antioxidant potential. *J. Food Sci. Technol.* **2015**, *52* (3), 1414–1423. <https://doi.org/10.1007/s13197-013-1152-2>.
- Paull, B.; Macka, M.; Haddad, P. R. Determination of calcium and magnesium in water samples by high-performance liquid chromatography on a graphitic stationary phase with a mobile phase containing *o*-cresolphthalein complexone. *J. Chromatogr. A* **1997**, *789* (1–2), 329–337. [https://doi.org/10.1016/S0021-9673\(97\)00660-2](https://doi.org/10.1016/S0021-9673(97)00660-2).
- Pohl, P.; Sergiel, I. Direct determination of the total concentrations of copper, iron and manganese and their fractionation forms in freshly ripened honeys by means of flame atomic absorption spectrometry. *Microchim. Acta* **2010**, *168*, 9–15. <https://doi.org/10.1007/s00604-009-0266-8>.
- Rosa, N. A.; Afonso, J. C. A Química da Cerveja. *Quím. Nova Esc.* **2015**, *37* (2), 98–105. <https://doi.org/10.5935/0104-8899.20150030>.
- Rosanoff, A. The high heart health value of drinking-water magnesium. *Med. Hypotheses* **2013**, *81* (6), 1063–1065. <https://doi.org/10.1016/j.mehy.2013.10.003>.
- Sako, A. V. F.; Spudeit, D. A.; Dupim, M.; Filho, W. P. O.; Saint'Pierre, T. D.; de Oliveira, M. A. L.; Mücke, G. A. Dual-opposite end multiple injection method applied to sequential determination of Na⁺, K⁺, Ca⁺², Mg⁺² ions and free and total glycerol in biodiesel by capillary zone electrophoresis. *J. Chromatogr. A* **2018**, *1570*, 148–154. <https://doi.org/10.1016/j.chroma.2018.07.079>.
- Sampaolesi, S.; Gamba, R. R.; De Antoni, G. L.; León Peláez, Á. M. Potentiality of yeasts obtained as beer fermentation residue to be used as probiotics. *LWT* **2019**, *113*, 108251. <https://doi.org/10.1016/j.lwt.2019.108251>.
- Santos, J. M. dos; de Andrade, J. K.; Galvão, F.; Felsner, M. L. Optimization and validation of ultrasound-assisted extraction for the determination of micro and macro minerals in non-centrifugal sugar by F AAS. *Food Chem.* **2019**, *292*, 66–74. <https://doi.org/10.1016/j.foodchem.2019.04.037>.
- Santos, J. M. dos; Quináia, S. P.; Felsner, M. L. Fast and direct analysis of Cr, Cd and Pb in brown sugar by GF AAS. *Food Chem.* **2018**, *260*, 19–26. <https://doi.org/10.1016/j.foodchem.2018.03.106>.
- Seeger, T. S.; Muller, E. I.; Mesko, M. F.; Duarte, F. A. Magnesium and calcium determination in desalted crude oil by direct sampling graphite furnace atomic absorption spectrometry. *Fuel* **2019**, *236*, 1483–1488. <https://doi.org/10.1016/j.fuel.2018.09.108>.
- Shishov, A.; Trufanov, I.; Nechaeva, D.; Bulatov, A. A reversed-phase air-assisted dispersive liquid-liquid microextraction coupled with colorimetric paper-based analytical device for the determination of glycerol, calcium and magnesium in biodiesel samples. *Microchem. J.* **2019**, *150*, 104134. <https://doi.org/10.1016/j.microc.2019.104134>.
- Sleiman, M.; Venturini Filho, W. G.; Ducatti, C.; Nojimoto, T. Determinação do percentual de malte e adjuntos em cervejas comerciais brasileiras através de análise isotópica.

Ciênc. Agrotec. **2010**, *34* (1), 163–172.
<https://doi.org/10.1590/S1413-70542010000100021>.

Souza, S. O.; Costa, S. S. L.; Brum, B. C. T.; Santos, S. H.; Garcia, C. A. B.; Araujo, R. G. O. Determination of nutrients in sugarcane juice using slurry sampling and detection by ICP OES. *Food Chem.* **2019**, *273*, 57–63.
<https://doi.org/10.1016/j.foodchem.2018.03.060>.

Styburski, D.; Janda, K.; Baranowska-Bosiacka, I.; Łukomska, A.; Dec, K.; Goschorska, M.; Michalkiewicz, B.; Ziętek, P.; Gutowska, I. Beer as a potential source of macroelements in a diet: the analysis of calcium, chlorine, potassium, and phosphorus content in a popular low-alcoholic drink. *Eur. Food Res. Technol.* **2018**, *244*, 1853–1860. <https://doi.org/10.1007/s00217-018-3098-0>.

Szymczycha-Madeja, A.; Welna, M.; Pohl, P. Determination of Elements in Energy Drinks by ICP OES with Minimal Sample Preparation. *J. Braz. Chem. Soc.* **2013**, *24* (10), 1606–1612. <https://doi.org/10.5935/0103-5053.20130202>.

Welna, M.; Szymczycha-Madeja, A.; Pohl, P. Improvement of Determination of Trace Amounts of Arsenic and Selenium in Slim Coffee Products by HG-ICP-OES. *Food Anal. Methods* **2014**, *7*, 1016–1023.
<https://doi.org/10.1007/s12161-013-9707-4>.

Welz, B.; Sperling, M. *Atomic Absorption Spectrometry*; Wiley-VCH, Weinheim, 1999.
<https://doi.org/10.1002/9783527611690>.

Wietstock, P. C.; Kunz, T.; Waterkamp, H.; Methner, F. J. Uptake and Release of Ca, Cu, Fe, Mg, and Zn during Beer Production. *J. Am. Soc. Brew. Chem.* **2015**, *73* (2), 179–184.
<https://doi.org/10.1094/ASBCJ-2015-0402-01>.