Evaluation of the aluminum migration from metallic seals to coffee beverage after using a high-pressure coffee pod machine

Abstract

The availability of aluminum during coffee drink preparation through a coffee pod machine was evaluated, through its determination in capsule seals, ground coffee, and coffee drink. The coffee drink preparation through a conventional filtration system and coffee pod machines was compared, with an increase around 13% on aluminum concentration (respectively, 408 ± 6 and 459 ± 9 μg L^{-1}). The highest aluminum concentration (approximately 80%) was found in the capsule seals, and 6 mg kg^{-1} incorporated into the ground coffee during coffee drink preparation. An aluminum concentration of 0.46 mg kg^{-1} was leached to the coffee drink, indicating its strong absorption by the ground coffee. This concentration represented only 0.15% of that range recommended by the European Food Safety Authority (EFSA), indicating a safe consumption of espresso coffee (5 cups/day). However, the reuse of ground coffee is of great concern, once approximately 3.5 times higher aluminum content was found in this sample.

Keywords: aluminum availability, coffee drink, coffee pod machine, leaching, inorganic mass spectrometry

1. Introduction

According to Thesaurus dictionary (Soanes, 1999), the coffee drink can be defined as “a beverage consisting of a decoction or infusion of the roasted ground or crushed seeds (coffee beans) of the two-seeded fruit (coffee berry) of a certain coffee tree”. Still, the popular saying also defines, more gracefully, the coffee drink as “a dark, magical substance that turns leave me alone into good morning honey”. However, whatever is the definition, coffee is an important raw material in the global economy, becoming one of the most valuable products in our daily life. In fact, the coffee drink is one of the most consumed and appreciated beverages in the world due to its organoleptic properties (odor and taste), and, mainly, for presenting potential effects on human health, such as antioxidant (Espinelli Junior et al., 2020; Verzelloni et al., 2011; Isac-Torrente et al., 2020), and physiological and psychological properties, with the stimulating effect being the most desired to improve the ability to concentrate, increase body energy, as well as reducing drowsiness and tiredness (Lima et al., 2010; Esquivel & Jiménez, 2012).

The roasted coffee bean has a very complex chemical composition, and it is estimated there are more than 2000 components - such as caffeine, minerals, phenolic compounds, amino acids, diterpenes, sterols, β-carbolines, among many others - some of these responsible for positively interfering with cognitive and psychomotor performance, as well as delaying the development of certain diseases, including type II diabetes, asthma, alcoholic cirrhosis and some types of cancer (Espinelli Junior et al., 2020; Alves et al., 2009; Martini et al., 2016).

Besides organic compounds, more than 30 different elements can be found in green, roasted, ground coffees, and infusions. These elements can be divided into three groups: macronutrients, micronutrients, and trace elements. Some of the trace elements, for example, aluminum, present in coffee (Koch et al., 1989; Santos & Oliveira, 2001; Stahl et al., 2017) or its infusions at excessive levels, can be toxic to health (Santos & Oliveira, 2001; Exley, 2016; Isac-Torrente et al., 2020; Martinez et al., 2018; Windisch et al., 2020) and therefore the concentrations of these elements in the final product and during coffee production must be strictly controlled to verify information about exposure to these elements.

The launch of the coffee capsule segment gave rise to innovation and sophistication associated with this product, changing the habits of the consumers, and also the coffee taste. The high amount of coffee flavors offered in capsules aroused the curiosity of consumers to try more than 25 different flavors grouped into aromatic families, intensities, and varieties (Nespresso, 2018). The search for quality products, fast preparation, and mono portions, which provide a differentiated experience, transformed this coffee segment into one of the greatest growth potentials in the Brazilian coffee market, and worldwide (ABIC, 2019; Fior Markets, 2019).

As it is a natural product with beneficial and protective actions, at first, moderate coffee consumption does not, in general, seem to be contraindicated (Alves et al., 2009). However, in view of preparation for consumption under conditions of high temperature and pressure (up to 19 bar, in fact, the highest in the market) (Nespresso, 2019) submitted by home espresso machines, and also due to the fact that the product packaging can also contribute to the contamination and introduction of elemental impurities, the hypothesis of this work arises that such conditions may foster the transfer of aluminum from metallic seals to coffee drink, once these seals are perforated by the machine during the coffee extraction (Pohl et al., 2012; Vega-Carrillo et al., 2002; Stahl et al., 2017; Windisch et al., 2020). To this end, the presence and magnitude of aluminum when the coffee drink is prepared using coffee pod machines are evaluated in this work through three different samples, including ground coffee, capsule seals, and the own coffee drink.

2. Experimental

2.1 Reagents and solutions

For microwave-assisted acid decomposition tests and standard/sample dilutions, sub-boiling nitric acid was obtained from a sub-boiling device (Berghof, Eningen, Germany), while hydrochloric and sulfuric acids, and hydrogen peroxide were purchased from Merck KGaA (Darmstadt, Germany). The standard stock solution (1000 mg L^{-1}) of Al employed for ICP-MS measurements was purchased from Merck KGaA. Working solutions were prepared with deionized water (≥ 18.2 MΩ cm) from a Milli-Q Direct-Q® 5UV water purification system (Millipore, Bedford, USA).

All materials used were made of polypropylene (PP) to avoid aluminum leaching from the glassware, usually composed of sodium borosilicate glass with aluminum oxide. Before use, all materials were cleaned with 10% (v/v) HCl, and then, rinsed three times with deionized water.

2.2 Instrumentation

Quantification of the total content of Al in the ground coffee, capsule seals, and coffee drink were performed by an inductively coupled plasma quadrupole mass spectrometer ICP-MS (ICPMS 2030, Shimadzu Scientific Instruments, Maryland, USA), equipped with a mini torch, a concentric nebulizer (Meinhard®), and a cyclonic nebulization chamber cooled at a constant temperature of 5 ºC, and incorporated an octapole collision cell with He as a collisional gas. The experimental conditions used in all analyses are shown in Table 1. The daily ICP-MS quality-control calibration was carried out using a multielemental standard solution containing the following species: Be at 10 µg L^{-1}, In, Bi and Ce at 2 µg L^{-1}, and Co and Mn at 5 µg L^{-1}.

Table 1 should be inserted here.

For sample preparation aimed at the determination of total aluminum content, all the samples (capsule seals, ground coffee, and coffee drink) were decomposed in a

DGT-100 microwave oven (Provecto Analitica, Jundiaí, Brazil) equipped with a magnetron of 2450 ± 13 MHz, operated at 1200W (nominal power) using Teflon® vessels.

2.3 Sample preparation and evaluation of the total Al content

The coffee capsules were acquired in a local market (Nespresso stores). The coffee drink (Arpeggio flavor) was prepared along this work using the Nespresso® *Essenza Mini* machine, equipped with a unique extraction system that guarantees pressure up to 19 bar and prepared as espresso (40 mL per cup). Deionized water was used to prepare the coffee drink. Subsequently, those three kinds of samples (ground coffee, seals, and coffee drink) were treated differently according to the following sections. Figure 1 illustrates the workflow with the general steps of the experimental procedure.

Figure 1 should be inserted here.

2.3.1 Capsule seals

Two types of metallic seals were analyzed: unused ones (pre) and those perforated after coffee extraction (post). Four seals (n=4) of each type were removed from the capsules, weighed separately (64 ± 3 mg for both pre and post seals), and transferred to Teflon flasks of the microwave oven. These samples were subjected to a microwave-assisted acid decomposition process with 250 μL sub-boiling HNO_3, 3 mL HCl and 750 μL deionized water, using the following microwave oven program: 6 min @ 400 W and 5 min @ 800 W. After microwave digestion, all samples were transferred to volumetric flasks and the volume made up to 50 mL with deionized water. Before analysis, the samples and blanks were diluted 20 times with 1.0% (v/v) HNO_3, and the total Al content determined by ICP-MS.

In this task, several sample preparation procedures were evaluated. The most representative microwave-assisted sample decomposition protocols are visualized in Table 2.

Table 2 should be inserted here.

2.3.2 Ground coffee

Likewise, in the previous section, two types of ground coffee were analyzed: unused (pre) and extracted (post). The contents of the coffee capsules were homogenized and dried at 37°C to constant mass. Then, 200 mg of ground coffee pre and post were weighted separately (n=3), microwave decomposed with 3 mL sub-boiling HNO_3, 1 mL HCl, 500 μL H_2SO_4, and 2 mL 30% (w/v) H_2O_2, with the resulting digests dried almost to dryness, and the volume replaced up to 5mL with 1.0 % (v/v) HNO_3. Finally, the samples were properly diluted, and the total element content determined by ICP-MS.

For quality control purposes and validation of the method, the microwave decomposition of ground coffee detailed above was applied to the certified reference material (SRM 1568a rice flour) for the trueness check.

Several microwave-assisted sample decomposition programs were evaluated as shown in Table 3.

Table 3 should be inserted here.

2.3.3 Coffee drink

A total of 10 capsules (n=10) from the same lot were prepared sequentially using the coffee machine (ca. 40 mL drink each) so as to perform a pool for minimizing outliers. After reaching room temperature and homogenization, 3 mL of this pool were transferred to Teflon flasks of the microwave oven, as well as specific volumes of an Al standard. Here the standard addition method was used to check any contamination or Al loss during the sample preparation step, as well as to build-up the analytical curve on the sample matrix for further determination of Al concentration in the coffee drink. The samples were subjected to a microwave-assisted acid decomposition process with 5 mL sub-boiling 20 % (v/v) HNO_3, 1 mL 20 % (v/v) HCl and 1 mL 30% (w/v) H_2O_2 using the following microwave oven program: 10 min @ 250 W; 10 min @ 400 W; 40 min @ 800 W and 10 min @ 0 W. The decomposed samples were diluted by adding 14.5 mL of deionized water, and, after proper dilution, the total element concentration was determined by ICP-MS. The most representative microwave-assisted sample decomposition methods studied for the coffee drink are compiled in Table 4.

Table 4 should be inserted here.

2.4 Statistical analysis

Statistical analyses of data were performed with the OriginPro 8 software (OriginLab Corporation, USA). Total aluminum concentrations from capsule seals pre- and post-extraction, certified reference material, pre- and post-extraction ground coffee, coffee drinks with- and without cleaning the machine between replicates as well as, coffee drinks prepared by filtration and coffee pod machine were tested separately assuming equivalent variances (checked by F-test at $\alpha = 0.05$) by Student's t-test. All statistical evaluations were carried out at 0.05 significance level (95 % confidence level).

3. Results and discussion

According to Figure 1, the experimental workflow was carried out to evaluate the aluminum concentration in the ground coffee, capsule seal, and coffee drink, so as to get insight into the aluminum sources. For the sake of clarity, the determination of aluminum is herein presented in separate samples: seal, ground coffee, and drink.

3.1. Capsule seals

The optimization of the microwave-assisted method for the capsule seals obtained pre- and post-coffee preparation was adapted from early acid digestion methods used for aluminum alloys (Arruda, 2007; Chen et al., 2008; Molnár et al., 2000). In fact, it should be noted that some methods used hydrofluoric acid (HF), however, considering safety handling aspects, initial tests without HF were then performed. Table 3 shows three different methods employed (A - C). For method A, it was visually noticed that the seal was only partially decomposed, which may be due to the high amount of weighted mass, and mild microwave conditions. Then, as seen in method B (Table 2), a lower amount of seal mass, a higher volume of the acids, and more drastic conditions for sample preparation (microwave time and power) were used. With these new conditions, a great improvement in the qualitative aspects of the sample after decomposition was observed. However, for improving, even more the microwave conditions, a further reduction of the sample mass was then chosen, such mass corresponding to a hole capsule shell (*ca*. 65 mg), with readaptation of the proportion of the reagents for appropriate solid to liquid ratio and adopting a longer method with enhanced microwave power (program C in Table 2). With this procedure, a complete dissolution was then possible, guaranteeing clear and homogeneous samples.

After optimizing the conditions, the total aluminum contents in capsule seals pre- and post-extraction for coffee drink preparation using the coffee machine were calculated as 800 ± 25 and 794 ± 11 mg g^{-1} Al, respectively. Although these results are statistically equivalents (according to the Student's *t*-test at 0.05 significance level and 95% confidence level) it is easy to rationalize that minute amounts of aluminum may be transferred to the ground coffee, during coffee extraction, thus explaining the results found in the section below.

3.2. Ground coffee

Preliminary tests were conducted for visualization of the microwave digests described in Table 3 by qualitative aspect. For the majority of programs (A to F), the presence of gelatinous precipitates was noted after sample preparation of ground coffee, thus indicating poor decomposition efficiency. Due to the presence of a high number of fibers, proteins, and lipids in the ground coffee (Murthy & Naidu, 2012), the use of more drastic conditions for sample preparation is herein justified. In this way, sulfuric acid was incorporated as a suitable acid for decomposing fat, lipids, and proteins (Arruda, 2007). Methods G, H, and I (Table 3) were proposed, and after sample preparation, the samples presented a better aspect than those already obtained from methods A to F. However, only method I presented a completely transparent solution after sample preparation.

For the validation of the parameters for sample preparation using method I (Table 3), the SRM 1568a rice flour with a certified concentration of 4.4 ± 1.0 mg kg^{-1} Al was analyzed. After applying the microwave-assisted acid digestion program, a concentration of 4.1 ± 0.2 mg kg^{-1} Al was found, indicating an analytical recovery factor of 86±8% (according to the Student's *t*-test at 0.05 significance level and 95% confidence level). In addition, this recovery lies within the range of acceptance of 80-110% as endorsed by MAPA (2019).

After analyzing the pre- and post-extraction ground coffee samples using the coffee pod machine, the results were 2.5 ± 0.9 and 8.5 ± 2.0 mg kg^{-1} Al, respectively. These results indicate an increase of *ca*. 3.5 times of the aluminum concentration in the ground coffee after coffee preparation using such machines (according to the Student's *t*-test at 0.05 significance level and 95% confidence level). This increase might be explained by the leaching of aluminum from the seal to the ground coffee once the aluminum seal of the capsule is perforated during the extraction for coffee drink preparation. Although such increase does not represent a great concern regarding the intake of aluminum, the coffee ground wastes have been reused for several purposes, such as to exfoliate the skin, grow mushrooms, remove smells from hands, absorb odors from fridges, among others (Healthline, 2018; NewScientist, 2016). Therefore, such reuse must be carefully considered, once it is reasonable to think that part of the aluminum available in such a matrix may be then transferred to the soil, to the crops, or to the hands, thus, acting as a potential contaminant on account of concentrations as high as few mg/kg in the material.

3.3 Coffee drink

Considering the results from ground coffee, where a significant increase of Al amount was found in the post-extraction ground coffee samples due to the Al leaching from the seal, the concentration of such metal was also determined in the coffee drink to investigate the Al role in this sample.

It is important to emphasize that the coffee drink sample was initially prepared as a simple infusion (Szymczycha-Madeja et al., 2016), using different centrifugation conditions, filters (PDVF and Nylon), dilutions (from 1:5 to 1:35 range), or ultrasound extraction. However, such strategies of sample preparation were discarded due to the residual sample matrix content, e.g. high organic matter, which prevented an adequate sample nebulization (even after dilution), thereby causing saturation and destabilization of the plasma source of ICP-MS.

As in the previous sections, the coffee drink was also decomposed using microwave technology, and some acid digestion methods were tested as shown in Table 4. In fact, these methods were initially based on that proposed for tea infusion decomposition (CEM, 2019), employing hydrochloric acid (for stabilizing high contents of Al) and steady power increasing steps to prepare the coffee drink sample. With such changes, a transparent sample was obtained, without staining, and free of particles that could obstruct the nebulization process of the ICP-MS equipment. Method D (Table 4) was chosen, once the best conditions were found, taking into account the qualitative aspect (clear sample, without coloring, free from particles and homogeneous), and the quantitative ones (decreased matrix effect with a stronger sample decomposition).

As previously mentioned, the standard addition method was considered to perform the analytical curve (Fig. 2) on the sample matrix where analytical linear regressions were obtained, thus, proving this strategy suitable for Al determination in the coffee drink samples free of significant contamination and analyte loss. Two procedures were established for checking the aluminum role in the coffee drink prepared from a coffee pod machine. The first involved collecting a pool of 10 coffee drinks (40 mL each) without cleaning the machine between replicates, and the second, cleaning the machine by passing 3 times ultrapure water between replicates to check if the system could represent an input itself of Al in the coffee drink. The results obtained with and without cleaning were 407 ± 15 and 394 ± 4 μg L^{-1} Al, respectively. No statistically significant differences were found (according to the Student's *t*-test at 0.05 significance level and 95% confidence level), thus revealing that cleaning or not the machine between the replicates of the preparation of the coffee drink resulted in a similar content of aluminum in the coffee drink. In fact, aluminum concentration of *ca*. 400 μg L^{-1} was already reported in the literature (Fraňková et al., 2009) for a coffee drink. However, different values of aluminum concentration can also be found in the literature, such as 13.9 and 18.26 μg L^{-1} (Isaac-Torrente et al., 2020; Windisch et al. 2020), but different origin of the coffee, coffee machine, or sample preparation were used.

In addition to this test, in order to demonstrate that, in fact, there is aluminum leaching from the capsule to the drink consumed, the coffee drink prepared at high pressure by the coffee machine was analyzed along that obtained by the conventional filtration system (at environmental pressure). It should be noted that analytical paper filters were used for the conventional system, and the same content of the capsule ground coffee was added. The infusion was made with water preheated in a water bath at 80ºC, which is equivalent to the temperature of the water ejected from the pod machine. Four capsules (n=4) of coffee from the same batch were processed in each method and the contents of aluminum of the drinks prepared by filtration and coffee pod machine were 408 ± 6 and 459 ± 9 μg L^{-1} Al, respectively. This result indicates an increase of *ca*. 13 % of the aluminum content when the coffee is prepared with a coffee pod machine against that of the filtration system (according to the Student's *t*-test at 0.05 significance level and 95% confidence level). This difference in aluminum concentration in the beverage could be, in fact, due to the high pressure used by the

Nespresso machine (19 bar) for coffee drink preparation, providing a better extraction, not only for those organoleptic organic compounds but also for unwanted aluminum, as quantified through ICP-MS.

3.4 Summarizing the results

For the sake of clarity, Table 5 summarizes all the aluminum concentrations determined in the coffee-related samples evaluated through this work. In fact, the highest aluminum content (*ca*. 80%) is found in the metallic seal of the capsules, and this sample is contributing to the incorporation of *ca*. 0.001% aluminum in the ground coffee after coffee drink preparation through the coffee pod machine. However, it is curious that despite the high aluminum concentration in the capsule seal, only 0.46 mg kg^{-1} of aluminum was found in the coffee beverage. A possible explanation for this fact is that ground coffee is adsorbing most of the leached aluminum from the capsule seal during coffee drink preparation, thus, resulting in low aluminum concentration in the coffee infusion. Our results corroborate this hypothesis, since an increase of *ca.* 6 mg kg^{-1} of aluminum is observed in the ground coffee after beverage preparation through the coffee machine, thereby, suggesting that ground coffee is acting as a natural adsorbent. In fact, ground coffee waste has been extensively employed as a biosorbent for removing several contaminants from aqueous media, including toxic metals (Cherdchoo et al., 2019; Alvarez et al., 2018; Babu et al., 2018; Anastopoulos et al., 2017).

Table 5 should be inserted here.

Additionally, based on the *Agence Française de Securité Sanitaire des Aliments* (AFSSA, 2003), the packaging and utensils marketed for food storage are usually responsible for the migration from 4 to 12 mg of the metal per kg of food. In fact, the value found *ca*. 6 mg kg^{-1} is inside this range. The Environmental Protection Agency (EPA) has recommended a secondary maximum contaminant level (SMCL) of 0.05 to 0.2 mg L^{-1} of aluminum in drinking water, which is significantly lower than the aluminum concentration found in the coffee drink (*ca*. 0.46 mg L^{-1}). However, and considering espresso coffee, it is really difficult for one adult to drink one liter of this beverage per day. Taken into account the recommendation from the European Food Safety Authority (EFSA, 2008), the range of weekly intake of aluminum in adults ranges from 0.2 to 1.5 mg/kg bw/per week. Considering our results in the coffee drink (*ca*. 460 µg L^{-1}), and a maximum amount of 5 cups of espresso/day (40 mL each), this represents 91.8 µg Al/day. By taking an adult weight of 70 kg, the aluminum content is then 1.31 µg/kg bw/day, being this result far from the range preconized by EFSA. It is interesting to note that all data refer to the total amount of aluminum, without considering the percentage of bioaccessibility. In fact, the bioaccessible pools of aluminum in the body from coffee drink prepared from coffee pod machines may be significantly lower than the total aluminum content in the beverage.

4. Conclusions and perspectives

The main objective of this work was successfully attained. It was clear that the coffee drink prepared through machines at high pressures contributes to the increase of aluminum content in the beverage (*ca*. 13%), compared to that from conventional filtration systems at environmental pressure. Although the capsule seals are a great source of aluminum, and the process for coffee drink preparation through coffee machines damage such seals, the leaching of aluminum from the seal to coffee drink is only marginal, acting the particles of the ground coffee as natural sorbents for aluminum.

From our results, and their comparison with those preconized by some food and environmental protection agencies, it is easy to rationalize that a daily normal consumption of coffee drink (*ca*. 5 cups of espresso/day) prepared from these machines does not represent a serious health risk of aluminum contamination by coffee consumers.

Anyway, the reuse of ground coffee as recommended in a diversity of propaganda is of great concern, once the increase of aluminum content is *ca*. 3.5 times higher in the ground coffee after coffee drink preparation by coffee pod machines, and thus this potential recycling strategy should be discouraged.

Possible perspectives of this work are to establish the bioaccessibility and bioavailability of aluminum, in body fluids after drinking the coffee prepared from a high-pressure coffee machine. Additionally, other important elements to life, such as calcium, magnesium, phosphorus, potassium, and others could be also evaluated by ICP-MS for improving the comprehension of their intake after drinking coffee prepared through these high-pressure coffee pod machines.

CRediT authorship contribution statement

Isabelle Pereira Squizzato: Undergraduate student who carried out the analysis. **Rodrigo Moretto Galazzi:** One of the supervisors of the research student facilitated analytical work. **Manuel Miró:** One of the supervisors of the research student**. Marco Aurélio Zezzi Arruda:** The senior supervisor and the overall coordinator of the research project. Involved in all aspects of the research from the beginning.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors (IS and MAZA) thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, São Paulo, Brazil, 2018/25207-0), and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brasília, Brazil, 401170/2016-0) for financial support and fellowships. Additionally, the author MM acknowledges financial support from the Spanish Ministry of Science, Innovation and Universities (MCIU) and the Spanish State Research Agency (AEI) through project CTM2017-84763-C3-3-R (MCIU/AEI/FEDER, EU).

References

ABIC - Associação brasileira da indústria de café. (2019). Tendências do Mercado de Cafés em 2019. Retrieved August 13, 2020 from: http://abic.com.br/estatisticas/pesquisas/pesquisa-tendencias-de-consumo/.

Alvarez, N. M. M., Pastrana, J. M., Lagos, Y., Lozada, J. J. (2018). Evaluation of mercury (Hg^{2+}) adsorption capacity using exhausted coffee waste. *Sustainable Chemistry and Pharmacy*, *10*, 60-70.

Alves, R. A., Casal, S., & Oliveira, B. (2009). Benefícios do café na saúde: mito ou realidade? *Química Nova*, *32*, 2169-2180.

Anastopoulos, I., Karamesouti, M., Mitropoulos, A. C., & Kyzas, G. Z. (2017). A review for coffee adsorbents. *Journal of Molecular Liquids*, *229*, 555-565.

Arruda, M. A. Z. (Ed.). (2007). *Trends in Sample Preparation*. (1st ed.). New York. Nova Publishers, (Chapter IX).

Babu, A. N., Reddy, D. S., Kumar, G. S., Ravindhranath, K., Mohan, G. V. K. (2018). Removal of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent. *Journal of Environmental Management*, *218*, 602-612.

CEM. (2019). MARS 6 Method Note Compendium. CEM Corporation, Matheus, NC, US. Retrieved August 13, 2020 from: http://cem.com/en/mars-6-method-note-compendium.

Chen, L., Song D., Tian, Y., Ding, L., Yu, A., & Zhang, H. (2008). Application of on-line microwave sample-preparation techniques. *Trends in Analytical Chemistry*, *27*, 151-159.

Cherdchoo, W., Nithettham, S., Charoenpanich, J. (2019). Removal of Cr (VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea. *Chemosphere*, *221*, 758-767.

EFSA - European Food Safety Authority. (2008). EFSA Advises on the Safety of Aluminium in Food. Retrieved March 5, 2021 from: https://www.efsa.europa.eu/en/news/efsa-advises-safety-aluminium-food.

EPA - Environmental Protection Agency. Secondary Drinking Water Standards: Guidance for Nuisance Chemicals. Retrieved July 1, 2020 from: https://www.epa.gov/sdwa/secondary-drinking-water-standards-guidance-nuisance-chemicals.

Espinelli Junior, J. B. S., Da Silva, G. B. M. D., Bastos, R. B., Furlong, E. B., Carapelli, R. (2020). Evaluation of the influence of cultivation on the total magnesium concentration and infusion extractability in commercial arabica coffee. *Food Chemistry*, *327*, 127012.

Esquivel, P., Jiménez, V. M. (2012). Functional properties of coffee and coffee by-products. *Food Research International*, *46*, 488-495.

Exley, C. (2016). The toxicity of aluminium in humans. *Morphologie, 100*, 51-55.

Fior Markets. (2019). Global Coffee Pod and Capsule Market by Product Type (Coffee Capsules, Coffee Pods), Application Type (Coffee Beans, Coffee Powder), Material (Conventional Plastic, Others), Region Global Industry Analysis, Market Size, Share, Growth, Trends, and Forecast 2018 to 2025. Retrieved May 14, 2021 from: https://www.fiormarkets.com/report/global-coffee-pod-and-capsule-market-by-product-375940.html.

Fraňková A., Drábek, O., Havlík, J., Száková, J., & Vaněk, A. (2009). The effect of beverage preparation method on aluminium content in coffee infusions. *Journal of Inorganic Biochemistry*, *103*, 1480–1485.

Healthline. (2018). 16 Creative ways to use old coffee grounds at Home. Retrieved August 13, 2020 from: https://www.healthline.com/nutrition/uses-for-coffee-grounds.

Institut de Veille Sanitaire. AFSSA. (2003). Évaluation des risques sanitaires liés à l'exposition de la population francaise à láluminium. 191p. Retrieved August 13, 2020 from: https://www.santepubliquefrance.fr/docs/evaluation-des-risques-sanitaires-lies-a-l-exposition-de-la-population-francaise-a-l-aluminium.-eaux-aliments-produits-de-sante.

Isac-Torrente, L., Fernandez-Gomez, B. & Miguel, M. (2020). Coffee capsules: implications in antioxidant activity, bioactive compounds, and aluminum content. *Eur Food Res Technol*, 246, 2335–2347.

Windisch, J., Keppler, B. K., & Jirsa, F. (2020). Aluminum in Coffee. *ACS Omega*, 5(25), 15335–15343.

Koch, K. R., Pougnet, M. A. B., & Villiers, S.D. (1989). Determination of Aluminum Levels in Tea and Coffee by Inductively Coupled Plasma Optical Emission

Spectrometry and Graphite Furnace Atomic Absorption Spectrometry. *Analyst*, *114*, 911-913.

Lima, A. R., Pereira, R. G. F. A., Abrahão, S. A., Duarte, S. M. S., & Paula, F. B. A. (2010). Compostos bioativos do café: atividade antioxidante in vitro do café verde e torrado antes e após a descafeinação. *Química Nova*, *33*, 20-24.

MAPA - Ministério da Agricultura, Pecuária e Abastecimento. (2019) Guia de Validação e Controle de Qualidade Analítica. Retrieved August 10, 2020 from: http://www.agricultura.gov.br/assuntos/laboratorios/arquivos-publicacoes-laboratorio/guia-de-validacao-controle-de-qualidade-analitica.pdf.

Martini, D., Del Bo', C., Tassotti, M., Riso, P., Del Rio, D., Brighenti, F., & Porrini, M. (2016). Coffee Consumption and Oxidative Stress: A Review of Human Intervention Studies. *Molecules*, 21(8), 979.

Martinez CS, Uranga-Ocio JA, Peçanha FM, Vassallo DV, Vera G, Miguel M, & Wiggers GA. (2018). Aluminum exposure for 60 days at an equivalent human dietary level promotes peripheral dysfunction in rats. *J Inorg Biochem*, 181, 169–176.

Molnár, G., Borossay, J., Varga, Z. B., Balloák, M., & Barth, A. (2000). Microwave Digestion of Thermoluminescent Aluminium-Oxide Powders and Determination of Trace Impurities by Inductively Coupled Plasma Optical Emission Spectroscopy, *Microchimica Acta*, *134*, 193-197.

Murthy, P. S., & Naidu, M. M. (2012). Sustainable management of coffee industry by-products and value addition—A review. *Resources, Conservation and Recycling*, *66*, 45-58.

Nespresso. (2018). Variedades de café em cápsula. Retrieved August 11, 2020 from: https://www.nespresso.com/br/pt/capsulas-cafe#!/por-variedades.

Nespresso. (2019). Manual Essenza Mini. Retrieved July 21, 2020 from: https://www.nespresso.com/shared_res/manuals/essenza-mini/2017/UM_NESPRESSO_ESSENZA_MINI_BREVILLE_PROD_WEB_2017_02_20.pdf.

NewScientist. (2016). Recycled coffee grounds could make roads smoother and greener. Retrieved September 1, 2020 from: https://www.newscientist.com/article/2086510-recycled-coffee-grounds-could-make-roads-smoother-and-greener/.

Pohl, P., Stelmach, E., Welna, M. & Szymczycha-Madej, A. (2012). Determination of the Elemental Composition of Coffee Using Instrumental Methods. *Food Analytical Methods*, *6*, 598–613.

Santos, E. J., & Oliveira, E. (2001). Determination of Mineral Nutrients and Toxic Elements in Brazilian Soluble Coffee by ICP-AES. *Journal of Food Composition and Analysis*, *14*, 523-531.

Soanes, C. (1999). *The Oxford Dictionary and Thesaurus: American Edition*. (3rd Ed.) United Kingdom: Oxford University Press.

Stahl T, Falk S, Rohrbeck A, Georgii S, Herzog C, Wiegand A, Hotz S, Boschek B, Zorn H, & Brunn H. (2017). Migration of aluminum from food contact materials to food-a health risk for consumers? Part I of III: exposure to aluminum, release of aluminum, tolerable weekly intake (TWI), toxicological effects of aluminum, study design, and methods. *Environ Sci Eur.*, 29(1), 19.

Szymczycha-Madeja, A., Pohl, P., Welna, M., Stelmach, E., & Jedryczko, D. (2016). The evaluation of the suitability of different alternative sample preparation procedures prior to the multi-elemental analysis of brew of ground roasted and instant coffees by FAAS and ICP OES. *Food Research International*, 89, 958-966.

Vega-Carrillo, H. R., Iskander, F. Y., & Manzanares-Acuna, E. (2002). Elemental content in ground and soluble/instant coffee. *Journal of Radioanalytical and Nuclear Chemistry*, *252*, 75–80.

Verzelloni, E., Tagliazucchi, D., Del Rio, D., Calani, L., & Conte, A. (2011). Antiglycative and antioxidative properties of coffee fractions. *Food Chemistry*, *124*, 1430-1435.

Tables

Table 1. Optimized ICP-MS operational conditions for Al measurement.

Cyclonic nebulization chamber	Cyclonic
Nebulizer	Concentric
RF power (W)	1200
Plasma gas flow-rate (L min^{-1})	8.0
Auxiliary gas flow-rate – Ar (L min^{-1})	1.1
Nebulizer gas flow-rate – Ar (L min^{-1})	0.7
Cell voltage (V)	-21
Replicates	5
Collision cell gas flow (mL min^{-1})	6.0
Energy filter (V)	7.0
Correction equation	Non-used
Monitored m/z	^{27}Al

Table 2. Microwave acid digestion programs tested for sample preparation of capsule metallic seals.

Method	***Sample (mg)***	***HNO_3 (mL)***	***HCl (mL)***	***H_2O (mL)***	***Microwave oven programs (time @ power)***
A	300	0.1	4.0	1.0	1º: 3min @ 400W 2º: 3min @ 0W
B	100	2.0	6.0	1.0	1º: 6 min @ 400W 2º: 3 min @ 200W
C	65	0.25	3.0	0.75	1º: 6 min @ 400W 2º: 5 min @ 800W

Table 3. Microwave acid digestion programs tested for sample preparation of ground coffee.

Method	***HNO_3 (mL)***	***HCl (mL)***	***H_2O_2 (mL)***	***H_2SO_4 (mL)***	***Microwave oven programs (time @ power)***
A	3.0	-	1.0	-	1º: 10min @ 300W 2º: 15min @ 800W
B	4.0	-	1.0	-	1º: 10min @ 400W 2º: 20min @ 800W
C	1.0	3.0	2.0	-	1º: 10min @ 400W 2º: 20min @ 800W
D	3.0	1.0	2.0	-	1º: 10min @ 400W 2º: 20min @ 800W
E	3.0	1.0	2.0	-	1º: 10min @ 400W 2º: 30min @ 800W
F	3.0	1.0	2.0	-	1º: 10min @ 400W 2º: 40min @ 800W
G	3.0	1.0	2.0	0.5	1º: 10min @ 400W 2º: 20min @ 800W
H	3.0	1.0	2.0	0.25	1º: 10min @ 400W 2º: 40min @ 800W
I	3.0	1.0	2.0	0.5	1º: 10min @ 400W 2º: 40min @ 800W

Table 4. Microwave acid digestion programs tested for sample preparation of coffee drink.

Method	***Sample (mL)***	***HNO_3 (mL)***	***HCl (mL)***	***H_2O_2 (mL)***	***Microwave oven programs (time @ power)***
A	3.0	5.0	-	2.0	1º: 10min @ 400W 2º: 40min @ 800W
B	5.0	5.0	-	2.0	1º: 10min @ 400W 2º: 40min @ 800W
C	5.0	4.5	0.5	-	1º: 10min @ 250W 2º: 10min @ 400W 3º: 40min @ 800W 4º: 10min @ 0W
D	3.0	*5.0	*1.0	1.0	1º: 10min @ 250W 2º: 10min @ 400W 3º: 40min @ 800W 4º: 10min @ 0W

*Diluted acids to 20% (v/v).

Table 5. Al concentrations in the three types of samples as determined by ICP-MS and percentage leached from the metallic seals to ground coffee, and coffee drink.

Samples[1]	**Metallic seals* (n=4)**		**Ground coffee* (n=3)**		**Coffee drink**[2] **(n=10)**
Portion	Pre	Post	Pre	Post	Post
Concentration	(80.0±2.5)[3]	(79.4±1.1)[3]	(2.5±0.9)[4]	(8.5±2.0)[4]	(0.46±0.09)[5]
Leachate (%)	---		(0.001)		(7.67)

[1]All samples came from the same batch; [2]Prepared without cleaning, as usually done by the consumers; [3]Values as % (m/m); [4]Values as mg kg^{-1}; [5]Values as mg L^{-1}; *Student's *t*-test at 0.05 significance level.

Figure Captions

Figure 1. General outline of the experimental workflow.

Figure 2. Representative analytical average curve (n=3) using standard addition method for Al determination in coffee drink samples.

Figures

Figure 1

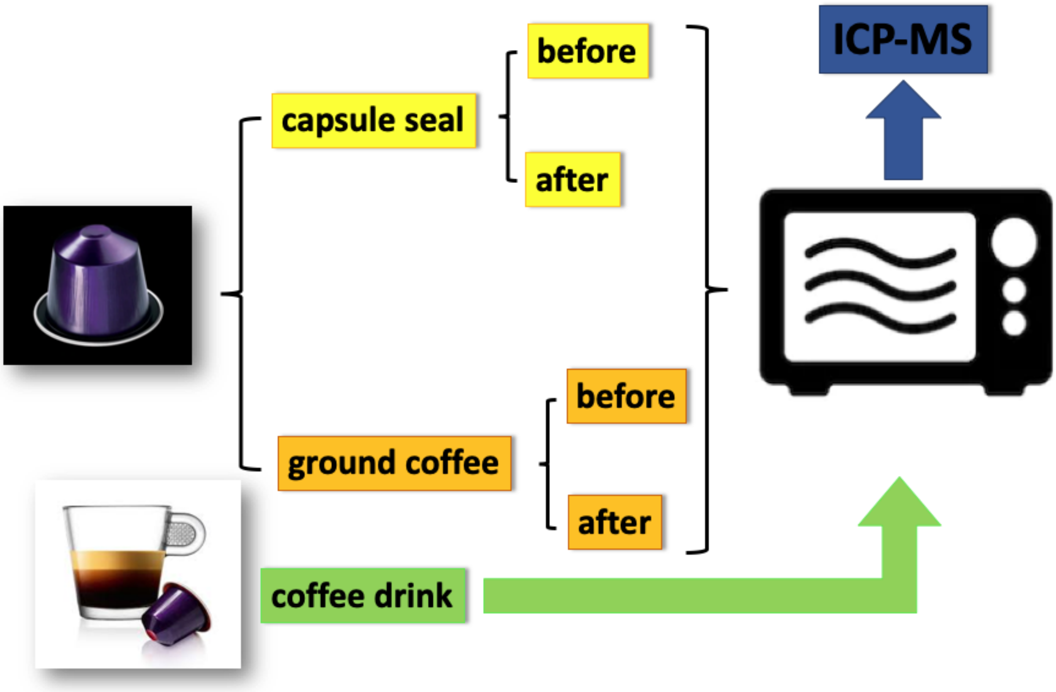
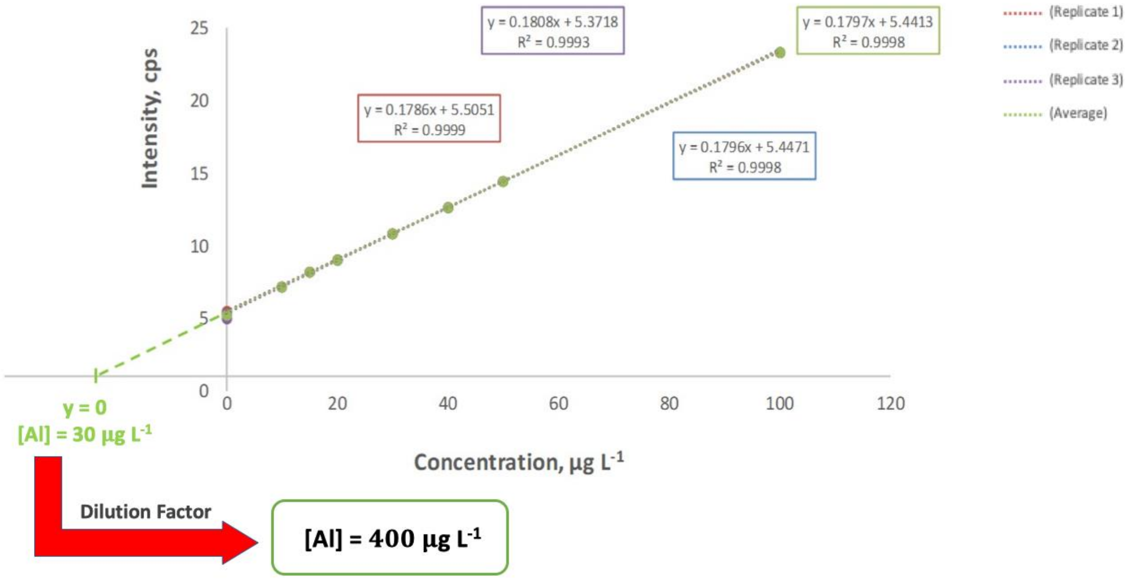


Figure 2



Intensity, cps
Concentration, µg L-1
y = 0.1808x + 5.3718
R² = 0.9993
y = 0.1797x + 5.4413
R² = 0.9998
y = 0.1786x + 5.5051
R² = 0.9999
y = 0.1796x + 5.4471
R² = 0.9998
(Replicate 1)
(Replicate 2)
(Replicate 3)
(Average)
y = 0
[Al] = 30 µg L-1
Dilution Factor
[Al] = 400 µg L-1