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Biochemical and Sensory Evaluation of Arabica Coffee and Chickpea Blend: A Caffeine Reduced Alternative

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Abstract: ***This study explores the potential of blending 60% Arabica coffee with 40% chickpea to reduce caffeine content while maintaining key biochemical and sensory properties. The caffeine concentration, acidity, pH, total polyphenols, flavonoids, antioxidant activity, and organoleptic qualities were analyzed. Results show that the chickpea blend reduces caffeine content while retaining a flavor profile comparable to pure Arabica coffee. The blend offers a promising alternative for consumers seeking lower caffeine consumption without compromising sensory experience.***

Keywords: coffee, chickpea, caffeine reduction, sensory analysis, antioxidant activity

1. Introduction

In human nutrition, coffee is a product consumed by all segments of society (A. Baycar, 2021), being consumed without complying with the principles of rational nutrition, resulting in the formation of a body dependence called "coffeeism". The primary reason coffee is consumed at any time, at various meetings, parties, etc. is represented by the caffeine content that supplies the body with numerous benefits (energy boosting while reducing fatigue, increased mental attention, improved physical performance, reducing the time period until the sensation of sleep appears etc.). While coffee offers benefits, it also has negative effects like insomnia, restlessness, and anxiety. The withdrawal syndrome when consumption is stopped (decreased alertness - depressed mood, headaches, fatigue, etc.) (R.. M. van Dam, 2020). This is one reason why coffee blended with a substitute has started to be consumed to reduce the concentration of caffeine. The beginning of the consumption of chickpea as a substitute for coffee is known since the time of the Ottoman Empire, when the consumption of coffee was prohibited (A. Baycar 2021, Y. Demir and B. Serkan 2023) and with the beginning of the Second World War, when there was an increase in the consumption of chickpea together with black cumin (N. Koca and A. Ersoz Tugen 2020).

Substitutes from plants such as chicory, dandelion, artichoke and roasted sugar beet roots (deprived of caffeine) (M. Samsonowicz et al., 2018) but rich in polyphenols (chlorogenic acid also present in coffee) have been used in the manufacture of coffee substitutes either alone or in blends. In addition, the roasting process is known to have a great effect on the enrichment of beverages with antioxidants, due to the Maillard reaction, which leads to the formation of new compounds (melanoidin) and the formation of a wide range of volatile substances, (pyrazines, furans, ketones and aldehydes) which mimics the aroma of roasted coffee to some extent (H. H. Fadel et al., 2008).

Chickpea, through its chemical composition rich in bioactive components (D. Rachwa-Rosiak et al., 2015, N. Begum et al., 2023) (amino acids, phenolic compounds with antioxidant activity, proteins, carbohydrates, fatty acids) represents an alternative source of substitute that, when blended with coffee, presents an alternative to reducing caffeine consumption with organoleptic qualities very similar to regular coffee.

The scholarly literature presents a multitude of data published by various authors in connection with the chemical composition of chickpea and its contribution to human health, from which we note the following: ***Protein content:*** 22.7% (D. Rachwa-Rosiak et al., 2015), 11.3-17.6% (V. Dragicevic et al., 2015), 14.9-24.6 g/100 g (E. A. S. Ali, 2016), 19.47-21.27% (D. Ihsanullah et al., 2008), 19.82 g/100 g (X. Shiqi et al., 2023); ***The content of oil:*** 6.35 g/100 g (H. Shiqi et al., 2023), 5.68-9.01 g/100 g B. S. Shashibhushan et al., 2020), 4.44% (V. Dragicevic et al., 2015). ***Fatty acids (unroasted chickpea)*****:** *oleic acid* 26.32%, (X. Shiqi et al., 2023), 21.0-22.0% (D. Rachwa-Rosiak et al., 2015); *palmitic acid* 12.23% (X. Shiqi et al., 2023), 18.9-20.21% (D. Rachwa-Rosiak et al., 2015), 9.7% A. Madurapperumage et al., 2021); *linoleic acid* 57.3% (A. Madurapperumage et al., 2021), 54.7-56.2% (D. Rachwa-Rosiak et al., 2015); *linolenic acid* 0.59-0.9% (D. Rachwa-Rosiak et al., 2015), 1.6% (A. Madurapperumage et al., 2021); *stearic acid* 1.587% (X. Shiqi et al., 2023) and 1.3-1.7% (D. Rachwa-Rosiak et al., 2015). **Fatty acids (roasted chickpeas):** *oleic acid* 28.27%, *linoleic acid* 50.12%, *linolenic acid* 12.0%, *palmitic acid* 10.1% (A. Madurapperumage et al., 2021). ***Amino acids content:*** *chickpea is an important source of esential amino acids :* 6.92 g/100 g and unesential amino acids 13.46 g/100 g having total amino acids of 13.48 g/100 g (X. Shiqi et al., 2023). D. Ihsanullah et al., (2008) found a content in esential amino acids of 50.21 mg/100 g in raw chickpea and in roasted chickpea of 48.01 mg/100 g and in unesential amino acids of 48.01 mg/100 g in raw chickpea and of 47.98 mg/100 g in roasted chickpea. ***Vitamin content*****:** folic acid 206.5 mg/100 g; vitamin C 1.65 mg/100 g; tiamin (B_1) 0.29

mg/100 g; riboflavin (B_2) 0.21 mg/100 g; 0.312-0.33 mg/100 g (E. A. S. Ali, 2016), A. K. Jucanti et al., 2012). ***Mineral constituent:*** **Fe** 6.24 mg/100 g (UDSDA), 4.59 mg/100 g (D. Rachwa-Rosiak et al., 2015), 2.93 mg/100 g raw chickpea, 2.71 g/100 g chickpea roasted (D. Ihsanullah et. al., 2008), 6.1 mg/100 g (X. Shiqi et al., 2023); **Mn** 2.20 mg/100 g (USDA), 3.81 mg/100 g (D. Rachwa-Rosiak et al., 2015), 1.93 mg/100 g raw chickpea and 1.87 mg/100 g roasted chickpea (D. Ihsanullah et al., 2008); **Cu** 0.847 mg/100 g (USDA) 11.37 mg/100 g raw chickpea and 11.30 mg/100 g roasted chickpea (D. Ihsanullah et al., 2008); **Zn** 3.43 mg/100 g (USDA); 6.87 mg/100 g raw chickpea, 6.70 mg/100 g roasted chickpea, (X. Shiqi et al., 2023); **Ca** 105 mg/100 g (USDA), 165 mg/100 g (D. Rosiak et al., (2015); 194 mg/100 g raw chickpea and 193.7 mg/100 g roasted chickpea (D. Ihsanullah et al., 2008); **Mg** 115 mg/100 g (USDA) 169 mg/100 g (D. Rachwa-Rosiak et al., 2015), 214.87 mg/100 g (X. Shiqi et al., 2023); **Na** 100.3 mg/100 g raw chickpea and 99 mg/100 g roasted chickpea (D. Ihsanullah et al., 2008); **K** 575.0 mg/100 g (USDA), 994.5 mg/100 g (D. Rachwa-Rosiak et al., 2015); **P** 365 mg/100 g (USDA). ***Sterols:*** campesterol 12.06-13,67%; Δ^7-avenasterol 0.79-1.21%, Δ^5-avenasterol 3.12-5.72%, Stigmasterol 0.492-5.38%**,** β-sitosterol 73.12-76.1%, clerosterol 1.94-4.01% (A. G. Gopala Krishna et al., 1997), M. Zia-ul-Haq et al., 2009). ***Tocopherols:*** α-3.94 mg/100 g**;** β-1.87 mg/100 g; γ-186.17 mg/100 g**;** δ-8.3 mg/100 g **(**Gopola Krishna et al., 1997), M. Zia-ul-Haq et al., 2009). ***Tocotrienols***: γ- 3.67 mg/100 g Gopola Krishna et al (1997). ***Polyphenols****:* polyphenols total 1.44-10.84 mg GAE/g (A. C. de Camargo et al., 2019), N. Begum et al., 2023); flavonoids 12848.9 µg/g (X. Shiqi et al., 2023), N. Begum et al., 2023). Chickpea also contain important quantities of ***alcaloids***: 22.25 mg/g, **fenols**: 29.75 mg/g, ***saponins***: 18.75 mg/g, ***tanin and is carotenoids***: 37.19 mg/kg (β-carotene) (N. Begum et al., 2023).

2. Material and Method

2.1 Chemicals

Folin-Ciocâlteu reagent, ethanol, aluminium chloride, dichloromethane were purchased from Merck Germany, gallic acid, 2,2-diphenil-1-picryl-hydrazine, sodium carbonate, quercitin were purchased from Sigma-Aldrich. All rewagent were of analitytical grade. For the experiment, green Arabica coffee beans and Desi chickpeas that reached maturity, whole and relatively equal in size, and without the smell of mould, were used. Green coffee beans and chickpeas were commercially purchased.

2.2Coffee beans and chickpea roasting

The operation of roasting Arabica coffee beans and chickpea was carried out in a discontinuous roaster equipped with a Rombat-type perforated horizontal drum. The roasting time of Arabica coffee beans and chickpea was 15 min at a temperature of 220°C. After the roasting process, whole beans with a glossy surface and evenly roasted appearance were obtained. Arabica coffee beans as well as chickpea were ground using a Viacenza 200 machine adjusted so that the diameter of the coffee and chickpea particles was between 1-1.20 mm. The working samples were constituted in two variants: one from 100% Arabica coffee and another from a 60% Arabica coffee and 40% chickpea blend. The samples were placed in sealed aluminium bags and kept at a temperature of 6°C until use.

2.3 Determination of the caffeine content

The determination of the caffeine content of the 100% Arabica coffee sample as well as of the 60% Arabica coffee and 40% chickpea blend was carried out according to the procedure described by Ihsan et al., (2023) with minor modifications.

50 mg of sample together with 100 mL of distilled water were introduced separately into 200 mL flasks. The flasks were heated to 90°C and stirred for 30 min. using a magnetic stirrer. After extraction, the samples were filtered on Whatman filter paper no. 1 and the obtained filtrates were collected in 100 mL flasks and brought to the mark with distilled water. In a separation funnel, 25 mL of the obtained extract and 25 mL of dichloromethane were introduced, stirring for 5 min. After separating the aqueous phase from the organic phase, the organic phasewas extracted again 3 times using 25 mL of dichloromethane for each extract. The collected organic phase was introduced into a 100 mL flask and brought to the mark with dichloromethane and analysed using the spectrophotometry method at 275 nm wavelength. The results were expressed as % w/w using the equation y = 0.043x + 0.2096, R^2 = 0.9986 based on the calibration curve, (Figure 1).

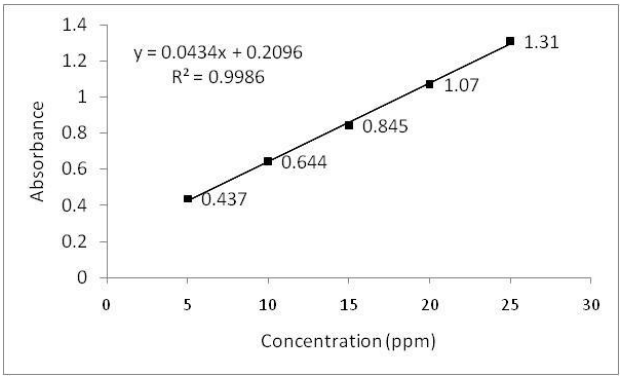

Figure 1: Standard calibration curve of caffeine

2.4 Determination of the acidity of aqueous coffee extracts

15 g of the 100% Arabica coffee sample as well as of the 60% Arabica coffee and 40% chickpea blend were placed separately in 250 mL Erlenmayer flasks containing 100 mL distilled water. The flasks were heated to 90°C and stirred for 30 min using a magnetic stirrer. After extraction, the samples were filtered on Whatman filter paper no. 1 and the obtained filtrates were collected and subjected to acidity determination. The acidity of the extracts was determined by titrating them with a 0.01 N sodium hydroxide solution using methyl orange as an indicator (M. G. Bita and M. Preda, 2008). Acidity, expressed in grams of sulfuric acid per litre of aqueous coffee extract, was calculated with the formula:

Acidity = (V1 · T)/V2 · 1.225 · 103 g H_2SO_4/L extract (1)

where:
V_1 - the number of mL of NaOH 0.01 N solution used for the titration; V_2 - the sample volume used,mL; T - the titre of the NaOH solution used in the titration, g/L; 1.225 - the ratio of the chemical equivalent of H_2SO_4 and NaOH.

2.5 Determination of pH

Determination of pH of the aqueous extracts of Arabica coffee and of the 60% Arabica coffee and 40% chickpea blend was carried out using a HANNA electronic pH-meter.

2.6 Determination of total phenolic

This method is based on the reduction of phosphomolybdates and phosphotungstates from the Folin-Ciocâlteu reagent by the phenolic compounds from the extract obtained from Arabica coffee and the 60% Arabica coffee and 40% chickpea blend. 80% methanol (1:20 g/v) was added to the ground powder (100% Arabica coffee and the 60% Arabica coffee and 40% chickpea blend) and the extraction time was 2 hours at room temperature with sonic stirring. The obtained extract was filtered on Whatman paper no. 1 and subject to analysis. 50 µL of each extract was mixed with 250 µL of Folin-Ciocâlteu reagent and 2.5 mL of distilled water for 3 min. Then, 750 µL of 20% Na_2CO_3 solution were added, stirring for 60 min. at room temperature, after which absorbances were measured using the spectrophotometry method at 765 nm wavelength (M. G. Dumitru, 2016), (X. P. Fu et al., 2021). The results were expressed as mg (GAE)/g using the following equation based on the calibration curve, Figure 2:
y = 0.0134x + 0.0171, R2 = 0.9981

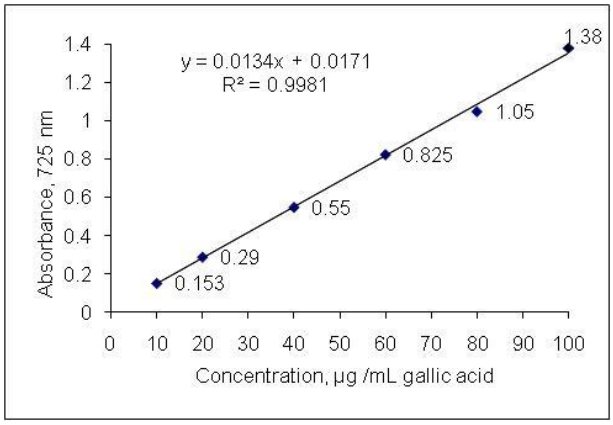

Figure 2: Standard calibration curve of gallic acid

2.7 Determination of total flavonoids (TFC)

TFC of the extracts were determined according to the colorimetric assay following the procedure of Fatemeh et al., (2012) with some modification. Mainly, the procedure is related to the formation of a complex between flavonoids and $AlCl_3$ coloured yellow, measuring the absorbance using the spectrophotometry method at 510 nm wavelength. The flavonoid contents were calculated according to the following equation that was obtained from the standard quercetin graph: y = 0.002x + 0.0314, R2 = 0.9984, Figure,. 3. The TFC was expressed as mg (QE)/g.

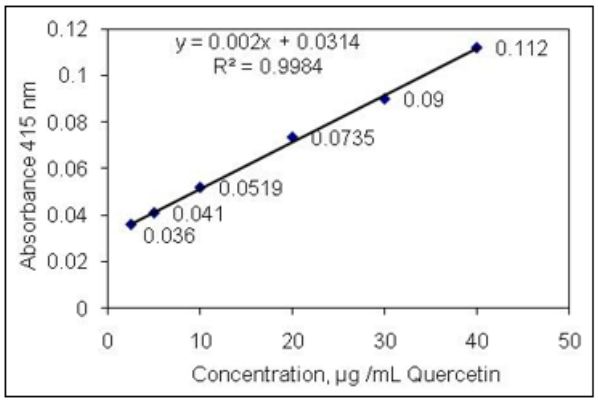

Figure 3: Standard calibration curve of quercetin

2.8 Antioxidant activity by DPPH method

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical neutralization activity was used to measure the antioxidant activity according to the method of T. Bouphun et al., 2023). The DPPH solution (oxidized form) was prepared in absolute ethanol to obtain a final absorbance of 0.8 - 1.0. Next, 100 µL of sample was added to 900 µL of DPPH radical solution. After vigorous shaking, the blend was incubated for 30 min in the dark at room temperature. The radical neutralizing capacity was determined by spectrophotometric measurement of the absorbance at 517 nm wavelength. The inhibition percentage of the samples was calculated using the equation C. Sungpud et al., (2020): % inhibition = [(Abscontrol – Abs_{sample} $Abs_{control}$] × 100 (2). where $Ab_{scontrol}$ is the absorbance of DPPH radical + methanol; Abs_{sample} is the absorbance of DPPH radical + sample extract.

2.9 Organoleptic analysis of the extracts

The organoleptic analysis was carried out using as tasters a number of 30 students from the specializations Chemistry, Biochemistry and Food Processing Technology to whom the aqueous extracts obtained from 100% Arabica coffee and a 60% Arabica coffee and 40% chickpea blend were presented (10 g sample and 90 mL water), served in disposable glasses, without sugar and first thing in the morning. Each student filled out a form and the result of the organoleptic analysis is presented in Table 1. The group was divided into smokers and non-smokers of both sexes. The group was divided into smokers and non-smokers of both sexes.

3. Results and Discussion

Following the experiment for the extracts obtained from roasted 100% Arabica coffee beans and a 60% Arabica coffee and 40% chickpea blend, the following results were obtained: the caffeine content of the extract obtained from 100% Arabica coffee beans was 1.10%, a value that is in agreement with the results obtained by A E. Lamri et al., (2022) at the three degrees of roast of 100% Arabica coffee (light, medium and dark) while in the extract obtained from the 60% Arabica coffee and 40% chickpea blend, the caffeine concentration was 0.61%. A decrease in caffeine content of 0.49% is noted, caused by the lack of caffeine content in chickpea. Acidity is an important factor in coffee quality. It is mainly given by organic acids and chlorogenic acids (S. E. Yager et al., 2021). Organic acids give coffee

taste and contribute to the formation of the aroma, being also its precursors. The aroma is closely related to the degree of roastof the coffee beans and the composition of the organic acids contained (R. Birke et al., 2023). Following the study carried out on five samples of high-quality 100%

Arabica coffee (R. Birke et al.,2023) concluded that coffee acidity should be viewed as a more holistic concept rather than considering the perceived acidity to have a simple linear response to the acid concentration of either all acids or specific individual acids. The titratable acidity values for the two samples were 0.81 g H_2SO_4/L for the extract obtained from 100% Arabica coffee and 0.62 g H_2SO_4/L for the extract obtained from the 60% Arabica coffee and 40% chickpea blend.

Determination of pH

The pH of the aqueous coffee extracts was determined with a HANNA electronic pH-meter. The determination performed on the extract obtained from 100% Arabica coffee beans had a pH value of 4.11, the value that falls within those entioned by R. Birke et al., (2023) (pH 3.97, pH 4.10 and pH 4.25), depending on the degree of roast of the coffee beans (light, medium, dark). The extract obtained from the 60% Arabica coffee and 40% chickpea blend had a pH of 5.10.

Determination of total phenolics (TPC)

Phenolic compounds are secondary metabolites that appear in nature and are distributed in the vegetable kingdom in different quantities. In the human diet, hydroxycinnamic acids, hydroxybenzoic acids, proanthocyanidins and flavonoids are the most common. In coffee, the main polyphenols are those derived from these acids following the processes that take place during roasting, reaching up to 11.3% of the weight of the dry beans (F. B. Aline et al., (2022). Following the determination of total polyphenols in the 100% Arabica coffee extract, a value of total polyphenols (TPC) of 33.2 mg GAE/g was obtained, a value that is in accordance with the result obtained by V. Matus et al (2020) of 34.06-38.43 mg GAE g/g. The total polyphenol content of the extract from the 60% Arabica coffee and 40% chickpea blend was 30.8 mg GAE/g. The great variability of total polyphenols (TPC) found in the literature confirms the variation of the content of these phytochemicals either related to the varieties, the modality of cultivation as well as the origin of the coffee.

Determination of total flavonoids

Flavonoids are phenolic compounds with an appreciable weight in plants. In the study, the content of flavonoids was determined according to a modified method based on the procedure by S. R. Fatemeh et al (2012) using quercetin as a standard. The flavonoid content was expressed in mg (QE)/g. The value obtained for the 100% Arabica coffee extract was 14.3 mg (QE)/g, a value close to that obtained by A. Nartea et al., 2022). The extract obtained from the 60% Arabica coffee and 40% chickpea blend was 12.4 mg (QE)/g. In plants, the bioactive compounds with a role in the formation of the antioxidant activity are mainly phenols. This property is given by the aromatic ring that allows the stabilization and relocation of unpaired electrons from their structure with the donation of hydrogen atoms and electrons from their hydroxyl groups (N. Chaves et al., 2020).

During the roasting process, a degradation of polyphenols also occurs, but this is compensated by the formation of other compounds following the Maillard reaction (S. E. W. Opitz et al., 2014). The presence of directly formed melanoidins compensates for the loss of phenolic compounds during roasting (V. Matus et al., 2020). The determination of the antioxidant activity by the DPPH method of the extract obtained from 100% Arabica coffee had a value of 79.8%, a value close to that obtained by J. Pokorna et al., (2015) of 60.4%, J. Hudakova et al., (2016) of 82.5%, A.Daniel and M. Worhnef (2017) of 73.33-84.16%. The extract from the 60% Arabica coffee and 40% chickpea blend had an antioxidant value of 69.1%.

Organoleptic analysis

The organoleptic analysis of the 2 extracts led to the following result:

1) The extract obtained from 100% Arabica coffee was appreciated by the groups of respondents consisting of smoking and non-smoking male and female respondents as having an excellent aroma, very deep, excellent, fine flavour, without astringency, and a slight bitter taste. The smell is strong, specific to coffee, well pronounced, spreading very discreetly a chocolate aroma;

2) The extract obtained from the 60% Arabica coffee and 40% chickpea blend was appreciated by the groups of respondents consisting of non-smoking male and female respondents as having a good, very deep, slightly sweet, fine, velvety taste, and a caramelized sugar aroma. The smell is weak, of coffee, but perceptible enough to highlight the presence of coffee in the extract. A pleasant smell of toast is also felt. There is a difference in the appreciation of the extracts by the respondents as follows: the *very good* rating was granted to the extract obtained from 100% Arabica coffee by the two groups of smoking and nonsmoking male and female respondents, in percentages of 70% and 60% compared to the results obtained by the extract obtained from the 60% Arabica coffee and 40% chickpea blend, of 33.3% and 43.3%. The same respondents granted the *good* rating in percentages of 20% and 33.3% to the extract obtained from 100% Arabica coffee and 46.6% and 50% to the extract obtained from the 60% Arabica coffee and 40% chickpea blend. The *acceptable* rating was granted by the same respondents in percentages of 10% and 6.6% for the extract obtained from 100% Arabica coffee and 10% and 6% for the extract obtained from the 60% Arabica coffee and 40% chickpea blend. The only *fail* rating was granted by the group of smoking male and female respondents to the extract obtained from the 60% Arabica coffee and 40% chickpea blend. The ratings granted by the respondents highlight the role played by chickpea in the coffee extract. The fact that the groups of male and female respondents, smokers and non-smokers, gave a fairly high percentage to the extract from the 60% Arabica coffee and 40% chickpea blend, close to the values of 100% Arabica coffee, certifies the use of chickpea blended with coffee in obtaining an extract agreeable to people who want reduced caffeine consumption.

Table 1: The result of the organoleptic analysis

Coffee Arabica 100%		Coffee Arabica 60%+chickpea 40%	
Boys and girls smokers		Boys and girls smokers	
Qualificative		Qualificative	
Very well	70%	Very well	33.3%
Well	20%	Well	46.6%
Acceptable	10%	Acceptable	10%
Rejected	0	Rejected	10%
Coffee Arabica 100%		Coffee Arabica 60%+chickpea 40%	
Boys and girls nonsmokers		Boys and girls nonsmokers	
Qualificative		Qualificative	
Very well	60%	Very well	43.3%
Well	33.3%	Well	50%
Acceptable	6.6%	Acceptable	6%
Rejected	0	Rejected	0

The differences in ratings by the groups of smokers and non-smokers can also be attributed to the taste buds that are more excited in non-smokers than in smokers, which we believe led to the 10% *fail* percentage of the extract obtained from the 60% Arabica coffee and 40% chickpea blend. The organoleptic analysis of the extract obtained from the 60% Arabica coffee and 40% chickpea blend highlights its qualities that do not differ much from the extract obtained from 100% Arabica coffee. Although the organoleptic analysis features numerous influences of subjectivity, it is very important in establishing the quality of a product.

4. Conclusions

Corroboration of the experimental data in the determinations made on the extract obtained from 100% Arabica coffee: acidity 0.81 g H2SO4/L; pH 4.11; total polyphenols (TPC) 33.2 mg GAE/g; flavonoids 14.3 mg (QE)/g; antioxidant activity 79.8% and the data obtained for the extracts from 60% Arabica coffee and 40% chickpea: acidity 0.62 g H2SO4/L; pH 5.10; total polyphenols 30.8 mg GAE/g; flavonoids 12.4 mg (QE)/g; antioxidant activity 69.1%, converge towards the idea of using chickpeas to obtain an extract with qualities similar to natural coffee and with a low caffeine content. Along with the decrease in caffeine concentration, chickpea presents, through its chemical composition, bioactive components and a fortifier for the extract. Scholarly literature proves the nutritional potential of chickpea for health. Scientific studies have provided some evidence to support the potential beneficial effects of chickpea components in lowering the risk of various chronic diseases.

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