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The Effect of Solvent-to-Coffee Ratio on Caffeine Content in Ethyl Acetate Extracts of Arabica Gayo Coffee Beans

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Abstract. This paper studies the optimal ratio that gives the highest caffeine amount and improves the efficiency and quality of extraction from *Arabica Gayo* coffee beans. No previous studies have explored the best ratio of *Gayo Arabica* coffee beans to ethyl acetate solvent for extracting caffeine. The paper explains the method used, which has four main steps: preparing materials, extracting and measuring caffeine, and analyzing the results. The paper presents the experimental findings and discusses how different ratios affect caffeine content in *Arabica Gayo* coffee beans. It uses statistics to show significant differences between the ratios and compares them using Tukey tests. The paper concludes that the best solvent-to-coffee ratio for maximizing caffeine in ethyl acetate extracts is 1:5, resulting in a concentration of 1411.1 ppm. This ratio gives the best balance between caffeine yield and solvent usage.

Keywords: *Solvent-to-coffee ratio, caffeine extraction, Arabica Gayo coffee beans*

Abstrak. Penelitian ini bertujuan untuk menemukan rasio optimal yang dapat menghasilkan jumlah kafein tertinggi, meningkatkan efisiensi, dan meningkatkan kualitas ekstraksi dari biji kopi Arabika Gayo. Sebelumnya, belum ada penelitian yang dilakukan untuk mencari rasio terbaik antara biji kopi Arabika Gayo dan pelarut jenis etil asetat dalam ekstraksi kafein. Metode penelitian terdiri dari empat langkah utama, yaitu persiapan bahan, ekstraksi dan pengukuran kafein, serta analisis hasil. Penelitian ini memberikan temuan eksperimental dan membahas bagaimana rasio antara biji kopi dan berbagai jenis pelarut dapat mempengaruhi kandungan kafein dalam biji kopi Arabika. Analisis statistik digunakan untuk menunjukkan perbedaan signifikan antara rasio tersebut, dan uji Post hoc Tukey digunakan untuk membandingkan hasilnya. Berdasarkan penelitian ini, disimpulkan bahwa rasio pelarut-kopi terbaik untuk mencapai konsentrasi kafein tertinggi dalam ekstrak etil asetat adalah 1:15, dengan konsentrasi sebesar 1411,1 ppm. Rasio ini memberikan keseimbangan terbaik antara jumlah kafein yang dihasilkan dan penggunaan pelarut.

Kata kunci: *Rasio pelarut ke kopi, ekstraksi kafein, biji kopi Arabika Gayo.*

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INTRODUCTION

Coffee has a rich history and is enjoyed worldwide. Extensive research has been conducted to investigate the potential health benefits of coffee. Studies have found that regular consumption of coffee is associated with a reduced risk of type 2 diabetes (Nakajima et al., 2010). Coffee consumption has been

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linked to maintaining or improving kidney function as indicated by the estimated glomerular filtration rate (eGFR) (Nakajima et al., 2010). Additionally, evidence suggests that coffee may have a protective effect against liver cancer (Shimazu et al., 2005). These findings highlight the potential positive impact of coffee on our health.

Caffeine has drawbacks despite its potential performance benefits. Individual variations in sport and exercise performance may arise from caffeine consumption due to genetic, physical, and psychological factors (Guest et al., 2021). Sleep disturbances and anxiety can also result from caffeine intake (Guest et al., 2021). Excessive caffeine consumption can lead to intoxication and serious side effects (Alfaifi et al., 2022). There are conflicting findings regarding caffeine's impact on hydration levels (Georgalas et al., 2021). Notably, caffeine and smoking often go hand in hand, and both have links to mental health issues (Schellhas et al., 2021). Lastly, caffeine can adversely affect cardiac function, causing arrhythmias (Porta et al., 2011).

Based on the preceding paragraph, it is essential to explore a decaffeination process to address the numerous drawbacks associated with caffeine. Some previous work on caffeine extraction from coffee beans using solvents has been conducted by several researchers. The type of coffee beans, solvent used, and optimum solvent-to-coffee ratio vary among these studies. One study focused on the roasting process of coffee beans and analyzed the chemical composition of coffee bean extracts using nuclear magnetic resonance (NMR) (Wei et al., 2012) . However, this study did not specifically investigate caffeine extraction using solvents. Another study examined the decaffeination process of green coffee bean extract (Song et al., 2014). While the study mentioned the decrease in caffeine content during the roasting and decaffeination processes, it did not provide specific details about the solvent used or the solvent-to-coffee ratio investigated the extraction of caffeine from whole coffee beans using supercritical carbon dioxide (Peker et al., 1992). They studied the decaffeination rates as a function of CO_2 flow rate, temperature, and pressure. However, they did not mention the specific type of coffee beans or the optimum solvent-to-coffee ratio compared nine common coffee extraction methods and found that different coffee beans contained varying amounts of caffeine per cup of coffee (Gloess et al., 2013). They did not specifically mention the kind of solvent used or the solvent-to-coffee ratio mentioned that solvents such as chloroform, dichloromethane, ethyl acetate, and supercritical carbon dioxide can be used for caffeine extraction from coffee beans (Belay, 2010). However, they did not provide specific information about the optimum solvent-to-coffee ratio used ethyl lactate, water, and ethyl lactate + water mixtures for the pressurized liquid extraction of caffeine and catechins from green tea leaves (Bermejo et al., 2015). It was reported a caffeine/catechin recovery ratio of 2.0, but the specific coffee beans or the solvent-to-coffee ratio was not mentioned. Supercritical carbon dioxide is considered a green solvent for caffeine extraction. They did not provide information about the specific solvent-to-coffee ratio (Saotome & Imai, 2018).

Supercritical CO_2 decaffeination is often described as solvent-free (Welton, 2015). However, this study does not provide specific information about the solvent-to-coffee ratio.

(De Azevedo et al., 2008) studied the extraction of caffeine, chlorogenic acids, and lipids from green coffee beans using supercritical carbon dioxide and co-solvents. They did not mention the specific solvent-to-coffee ratio. (Crozier et al., 2012) quantified caffeine in coffee infusions using reversed phase HPLC. They did not mention the specific solvent or the solvent-to-coffee ratio. (Yuniarti et al., 2019) used a natural deep eutectic solvent (NADES) called choline chloride-sorbitol to extract caffeine and chlorogenic acid from green coffee beans. They aimed to determine the optimum method for extraction and tested three different preparations of the NADES. However, they did not mention the specific type of coffee beans or the solvent-to-coffee ratio. In a review article by (Kumar et al., 2006), two basic methods for producing decaffeinated coffee using solvents were mentioned: direct solvent extraction of the beans and water extraction of the beans followed by solvent extraction of the caffeine from the water extract. However, this review did not provide specific details about the type of coffee beans or the solvent-to-coffee ratio.

Overall, the previous work on caffeine extraction from coffee beans using solvents has provided valuable insights into the decaffeination process. However, there is a lack of consensus on the specific type of coffee beans, solvent, and optimum solvent-to-coffee ratio. Further research is needed to determine the most effective and efficient method for caffeine extraction from coffee beans using solvents. The solvent-to-coffee ratio is an important factor that affects the extraction efficiency, quality, and cost of caffeine extraction processes. A higher solvent-to-coffee ratio may result in higher caffeine yield, but also higher solvent consumption and waste generation. A lower solvent-to-coffee ratio may result in lower caffeine yield, but also lower solvent consumption and waste generation. Therefore, there is a need to optimize the solvent-to-coffee ratio for caffeine extraction using ethyl acetate to achieve the best balance between caffeine yield and solvent consumption.

This research aims to investigate the influence of different solvent-to-coffee ratios on the caffeine content obtained from Arabica coffee beans using ethyl acetate as the solvent. The study seeks to determine the optimum ratio that yields the highest caffeine content, enhancing the efficiency and quality of caffeine extraction processes. This paper aims to contribute valuable insights into the extraction process, ultimately aiding in the production of caffeine-rich extracts for various applications.

MATERIAL AND METHODS

Materials

Materials in this study were arabica Gayo coffee beans from Aceh Indonesia, ethyl acetate 70% (Merck), and standar caffeine (Merck).

We used a spectrophotometry UV-VIS (Evolution 350) to validate the caffeine content, waterbath, analytical balance, erlenmeyer flask (Pyrex), volumetric flask (Iwaki), sieving, measuring cylinders (Iwaki), filter paper, alumunium foil, spatula, and bottles.

Procedure

The methodology in this research consists of four primary stages, as following: materials preparation, caffeine extraction and quantification, and result statistical analysis.

Preparation

In the initial stage of material preparation, Arabica Gayo coffee beans were procured from a reliable supplier and preserved carefully in an airtight container at room temperature to maintain its quality. A reputable chemical supplier provided technical-grade ethyl acetate. Furthermore, the research necessitated the use of various indispensable tools and materials, which included a Soxhlet apparatus, a rotary evaporator, a digital balance, a volumetric flask, a pipette, a UV spectrophotometry, and distilled water. Each of these items played an important role in making the experiments run smoothly and effectively.

Caffein extraction

For the extraction of caffeine, the coffee beans were carefully crushed using a coffee grinder until they achieved the smallest attainable particle size. Subsequently, the resulting powdered coffee underwent sieving through a 60-mesh sieve to ensure uniformity (Putu et al., 2018). The precise weight of the strained coffee powder was measured using a digital scale and subsequently moved into thimble to proceed with the subsequent extraction procedures. To start extracting caffeine, an exact amount of ethyl acetate was measured using a measuring flask and cautiously transferred into a round-bottom flask. The coffee powder, wrapped in filter paper then placed in the round-bottom flask along with the ethyl acetate. The flask was sealed tightly and placed in a water bath at a consistent temperature of 50 degrees Celsius. The process of dissolving to extract caffeine from ethyl acetate was uninterrupted for 2 hours before stopped. The extraction duration was affected by the solvent-to-coffee ratio investigated. The study examined five distinct ratios as follows: 1:5, 1:7.5, 1:10, 1:12.5, and 1:15 (w/v). To ensure preciseness and consistent results, each experiment was carried out as a single batch.

Caffein quantification

After extracting caffeine with ethyl acetate, the solution was heated until only solid remained. The weight of the extracted solid caffeine was measured carefully by digital balance. The concentration of caffeine in ethyl acetate was given by dividing the weight of extract caffeine with volume of ethyl acetate used during the extraction process. To validate the caffeine content in the ethyl acetate extracts, a standardized method utilizing UV spectrophotometry with a wavelength of 275 nm was employed. A calibration curve was established by dissolving predetermined quantities of pure caffeine in ethyl acetate and measuring their corresponding absorbance values. This curve established a relationship between absorbance values and caffeine concentration which was subsequently employed in linear regression to estimate the caffeine concentration in the ethyl acetate extracts.

Statistical Analysis

The results were evaluated utilizing statistical techniques, specifically employing a one-way analysis of variance (ANOVA) to determine the significance of discrepancies and a post-hoc Tukey test to find significant variations between pair of ratios. These statistical techniques were computed using the Real Statistics Resource Pack software (*Released* 8.7) developed by Charles Zaiontz as Add-in in Microsoft Excel 2019. In this evaluation any p-value below 0.05 was deemed have statistical significance.

RESULT AND DISCUSSION

The experimental results are presented in Table 1, showing the caffeine concentration obtained from Arabica coffee beans through the utilization of different solvent-to-coffee ratios as measured UV Spectrometry. Figure 1 shows a bar graph with the average values and measurement errors for each set of solvent-to-coffee ratios.

Table 1. Concentration of caffeine extracted from *arabica coffee* beans using different solvent-to-coffee ratios

Time (min)	Concentration (ppm)				
	1:15	1:12.5	1:10	1:7.5	1:5
0	0.000	0.000	0.000	0.000	0.000
20	3.380	5.188	9.361	11.562	7.782
40	4.001	5.119	9.774	13.872	13.876
60	4.450	6.680	11.752	14.967	18.694
80	7.471	9.304	7.735	11.687	20.229
100	4.683	6.220	14.155	20.906	19.425
120	4.684	6.578	9.015	18.667	18.769

The findings reveal that the caffeine concentration extracted from Arabica coffee beans using ethyl acetate as the solvent varies based on the solvent-to-coffee ratio utilized. As the ratio increases, the caffeine extract concentration also increases, suggesting that a greater amount of caffeine is extracted from the coffee beans with a higher quantity of solvent. The descriptive statistics presented in Table 2 provide further insights into the characteristics of each group. They reveal the variations and trends within each group as visualized in Figure 1 through histograms illustrating the variance and standard error for each group set. The results of the ANOVA test as shown in Table 3 that there is a significant difference in caffeine content among the different solvent-to-coffee ratios (F(4,30) = 5.063, $p < 0.05$).

The results in Table 4 provide an overview of the pairwise comparisons and p-values obtained from the post-hoc Tukey test. Based on the test, 1:5 solvent-to-coffee ratio demonstrates a significantly higher caffeine content compared to ratio 1:15 and 1:12.5 ($p < 0.05$ for all comparisons). Likewise, the solvent-to-coffee ratio of 1:7.5 exhibits a significantly higher caffeine content in comparison to 1:15 ($p < 0.05$ for all comparisons). These findings highlight that 1:5 possesses the highest caffeine content among all the ratios since it significantly higher than 2 groups of solvent-to-coffee ratio. Importantly, there are no significant disparities in caffeine content between any pair of groups with p-values of 0.05 or greater.

The findings suggest that the solvent-to-coffee ratio has a significant influence on the caffeine extraction efficiency using ethyl acetate as the solvent. This corresponds to the research conducted by (Putu et al., 2018) stating that the caffeine content can be influenced by several factors, namely, the high concentration of the solvent in dissolving caffeine components and the extraction temperature used; caffeine compounds tend to dissolve in polar solvents. The optimum solvent-to-coffee ratio for maximizing caffeine content in ethyl acetate extracts is ratio 1:5, which yields a concentration of 1411.1 ppm.

This ratio provides the best balance between caffeine yield and solvent consumption.

Meanwhile, there is no significant difference within ratio 1:10, 1:7.5, and 1:5 (p > 0.05). The possible underlying mechanism happens when caffeine dissolves in ethyl acetate and mixes with coffee solids is coffee solids have substances like oils, acids, sugars, and proteins that affect how well caffeine dissolves in ethyl acetate. These components may interact with ethyl acetate and reduce its ability to dissolving caffein. Therefore, the more solvent may cause less caffeine dissolves, reducing extraction efficiency.

Table 2. Descriptive statistics for different groups

DESCRIPTION			Alpha		0.05
Group	*Count*	*Mean*	*Variance*	*SS*	*Std Err*
1:15	7	409.6	4.918	29.505	1.969
1:12.5	7	558.4	7.998	47.986	1.969
1:10	7	882.7	19.545	117.269	1.969
1:7.5	7	1309.4	45.330	271.979	1.969
1:5	7	1411.1	57.934	347.601	1.969

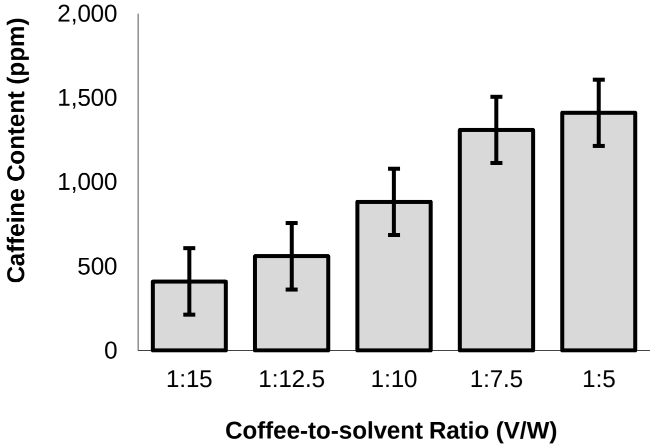

Figure 1. Mean values and standard errors for each group of solvent-to-coffee ratios

Table 2. The results of the ANOVA test

Sources	*SS*	*df*	*MS*	*F*	*P value*
Between Groups	5497348.9	4.0	1374337	5.063	0.003
Within Groups	814340	30.0	271446,7		
Total	13640749,5	34.0	401198.5		

Table 4. P-Values for pairwise comparisons in variable groups

p-value	1:15	1:12.5	1:10	1:7.5	1:5
1:51	-	0.983	0.450	**0.023**	**0.009**
1:12.5	0.983	-	0.771	0.078	**0.035**
1:10	0.983	0.771	-	0.551	0.341
1:7.5	**0.023**	0.078	0.551	-	0.996
1:5	**0.009**	**0.035**	0.341	0.996	-

CONCLUSION

The caffeine content extracted from *Arabica Gayo* coffee beans using ethyl acetate varies with the solvent-to-coffee ratio. Higher ratios result in increased caffeine concentration. Descriptive statistics and ANOVA tests confirm significant differences among the ratios. Ratio 1:5 exhibits the highest caffeine content, followed by 1:7.5. The optimum ratio for maximum caffeine extraction is 1:5, yielding 1411.1 ppm. Ratio 1:10, 1:7.5, and 1:5 show no significant differences.

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