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Analysis of Caffeine, Ash, Water and Coffee Extract Levels On Commercial Ground Coffee Samples

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Abstract. Caffeine is a secondary metabolite compound derived from the alkaloid group with its characteristic bitter taste. This study aims to analyze the water content, ash content, coffee extract and caffeine test using the High-Performance Liquid Chromatography (HPLC) method on ground coffee with six different types of ground coffee. The method used for ground coffee analysis refers to SNI 01-3542-2004. In the caffeine content test, the method used refers to SNI 2983:2014 concerning instant coffee. Caffeine was extracted from the sample with water at 90ºC in the presence of magnesium oxide after filtering, the caffeine content in the extract was determined using the HPLC method on the RP-18 column using isoratic elution with UV light detection at a wavelength of 272 nm. Caffeine levels in ground coffee are 1.71%, 2.43%, 0.23%, 2.10%, 2.58% and 6.02%. Ash Levels in ground coffee are 4.57%, 5.27%, 3.25%, 2.03%, 3.35% and 4.10%. Water levels in ground coffee are 0.25%, 0.58%, 1.62%, 0.32%, 0.43% and 2.60%. The maximum amount of caffeine content that is allowed for public consumption per day based on SNI is 0.9-2%.

Keywords : HPLC, Coffee Powder, Caffeine Content, Isoratic Elution.

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Introduction

Coffee is one of the many types of drinks that are most popular throughout the world. Coffee is usually consumed when relaxing and increasing energy [1]. Its rich and distinctive aroma, its uplifting substance content and its availability have made coffee popular [2]. The main ingredients of coffee are caffeine, tannins, fixed oils, carbohydrates and protein. Its content contains 2-3% caffeine, 3-5% tannins, 13% protein and 10-15% fixed oil [3].

Coffee is one of the plantation commodities that plays an important role in Indonesia's economy as a foreign exchange earner besides gas and oil. In addition to export opportunities, the existence of the domestic coffee market is still quite large. Indonesia's natural coffee exports cover five continents, namely Asia, Africa, Australia, America and Europe. The impact of the world community's passion for coffee has made the economic value of Indonesian coffee quite high as shown by the volume of exports to the United States reaching 54.49 thousand tons or 14.36% of the total volume of Indonesian coffee exports with a value of US$ 202.45 million in 2020 [4].

The widespread development of coffee plantations in Indonesia has made various types and brands of ground coffee spread throughout Jambi Province. So that the feasibility of ground coffee food commodities with various types of coffee and brands needs to be tested and standardized according to predetermined product quality standards. Standardization of food products is very important in local and global trade [5]. A standard is a technical specification or something that is standardized including procedures and methods that have been prepared related to taking into account the requirements for safety, security, health, environmental ecosystems, science and technology developments as well as current and future developments to obtain the maximum benefit [6]. The purpose of standardization is as an effort to protect society from the aspects of safety, occupational security, health and environment (K3L), contribute to increasing competitiveness and encourage national products to be able to compete in the global market [7].

As the fourth largest coffee producing country in the world, Indonesia has many opportunities to develop ground coffee products that are supported by a standard as a reference for product quality. To find out the quality of various types and brands of ground coffee circulating in Jambi Province, chemical testing can be done. This research was conducted to find out whether commercial ground coffee complied with the applicable SNI, namely SNI 01-3542-2004 on the analysis of water content, ash content and coffee extract and SNI 2983:2014 on the analysis of caffeine content. There are several test parameters that can be carried out, namely testing for water content, ash content, coffee extract test and caffeine test using the High-Performance Liquid Chormatography (HPLC) method. The testing process is carried out in accordance with the Indonesian National Standard (3542-2004) regarding the Quality Standards for Ground Coffee. Through this study, the authors hope to be able to provide recommendations for the quality criteria for pure ground coffee products by taking into account quality assurance so that the setting of product quality standards is in accordance with the Indonesian National Standard in an effort to improve HSE and increase the competitiveness of local products in the global market.

Experimental

HPLC Method Sample Preparation

All coffee samples were weighed as much as 0.3 g and put into a 250 mL volumetric flask. Bring to a boil and wait for the solution to reach 90ºC. The coffee sample was weighed as much as 0.3 g, put into a 250 mL Erlenmeyer. Then add 200 mL of aquabides and let stand for 30 minutes for the extraction process and then cool. Filtered using Whatman filter paper no.1. 1 mL of the filtrate was taken into a 10 mL measuring flask and measured with aquabides. The solution was filtered with a 0.2 µm microfilter syringe and put into a vial. HPLC determination. HPLC was prepared under the following conditions: mobile phase flow rate of 1 mL/min, UV detector installed at a wavelength of 272 nm, then ensured that the sensitivity range of the detector matched the peak on the standard. Then let the system equilibrate at the mobile phase flow rate and pressure for at least 10 minutes to stabilize. Inject 10µL of

standard solution into the column using a syringe. Followed by the same volume of extraction of the test sample. Then inject standard solution at regular intervals when a single standard solution is used. The HPLC system and column were rinsed with 50% by volume of the methanol and water fraction after each analysis stage and the column was released for further storage.

Gravimetry methods preparation

The weight of the coffee sample is weighed as much as 2 g and put into a 500 mL glass cup or porcelain cup. Water content. Weigh a sample weight of 2 g in a glass cup of known weight. Dry in the oven at 105ºC for 3 hours. Removed from the oven and desired in a desiccator. Then weigh and repeat this procedure until a constant weight is obtained. Ash Content. Weigh the sample weight as much as 2 g and put it into a porcelain cup whose weight is known. Charcoal over the burner flame, then ashed in the furnace at a temperature of 550ºC until complete ashing. Cooled in a desiccator then weighed until the weight remains. Extract Coffee. Weigh the sample weight as much as 2 g and put it into a 500 mL beaker. Then added 200 mL of boiling water, let stand for 1 hour. Filter the solution into a 500 mL volumetric flask and rinse with hot water until the solution is clear. Let the solution come to room temperature, then add water and make sure it is up to the line mark. Pipette 50 mL of the solution into a porcelain dish of known weight. Heated on a water bath until dry. Put in the oven at 105ºC for 2 hours. Then cooled in a desiccator and weighed until the weight remains constant.

Basically HPLC is a development of the column chromatography method.

HPLC allows the use of particles with a very small size with a larger surface area so that the interactions will be even greater. This will make the separation system work better. The working principle of HPLC is to separate the analyte components based on their polarity, each mixture that comes out will be detected with a detector and will be recorded in the form of a chromatogram. In HPLC instruments there is a stationary phase and a mobile phase where the stationary phase used is a chromatographic column in the form of a c18 octadesil silica (ODS) column where this column is most popularly used in HPLC. While the mobile phase used is aquabidest:methanol with a ratio of 60:40. In HPLC instruments there is a stationary phase and a mobile phase where the stationary phase used is a chromatographic column in the form of a c18 octadesil silica (ODS) column where this column is most popularly used in HPLC. While the mobile phase used is aquabidest:methanol with a ratio of 60:40. The method in this study used the HPLC method to test caffeine content and the gravimetric method to test water content, ash content and coffee extract. The tools used for HPLC are HPLC units, chromatography columns for HPLC, glassware, balances, ultrasonic baths, water baths and whatman filter paper no.1. While the tools used for gravimetry are glassware, excitators, ovens, balances, furnaces, water baths and porcelain dishes. The main ingredients used in this study were six types of pure ground coffee, standard solutions of caffeine, methanol, aquabides and distilled water.

The types of detectors used in HPLC instruments are UV-Vis detectors, fluorescence detectors, mass spectrometers, refractive index detectors and electrochemical detectors. However, the HPLC used uses a UV-Vis detector.

Results and Discusion

Water Content Test Results

Moisture content is the amount (in %) of water contained in coffee grounds. Testing the water content of pure coffee grounds is carried out using the oven method, with the gravimetric principle. Analysis of the water content with the principle of gravimetry is to evaporate the water present in the material by heating, then weighing the material until a constant weight means that all the water has been evaporated. In general, the determination of moisture content is carried out by drying the material in an oven at a temperature of 105-110°C for 3 hours or until a constant weight is obtained (fixed weight).

The initial stage of testing the water content of pure coffee powder is sample preparation, where the sample is weighed as much as 2 grams in a glass cup whose weight is known. Place in the oven at 105ºC for 3 hours. Then cool in a desiccator. The purpose of cooling in a desiccator for approximately 30 minutes is that during the weighing process the weights obtained are fixed and do not change. Weigh and repeat the oven process for about 30 minutes so that the weight obtained remains constant. The following are the results of the water content test obtained. Following are the results of testing the water content of the 6 samples.

Ash Content Test Results

As with the previous water content test, the ash content test is the amount (in %) of the ash content in the coffee grounds. This test is carried out based on the SNI 01-3542-2004 reference. The working principle of the ash content test is that organic substances are decomposed into water and CO2, but not inorganic materials. The ash content test process begins by weighing 2 g of sample weight and placing it in a porcelain cup of known weight. Charcoal over the burner flame, then ashes in an electric furnace at a temperature of 550ºC until complete ashing (occasionally the furnace door is

Tabel 1. Water Content Test

No	Empty Cup Weight	Cup Weight + Sample (g)	Sample Weight (4-3) (g)	Cup Weight + Sample after heating (g)		Water Weight (4-6) (g)	Water Content (%)	Avarage (%)
				I	II			
A	26,8746	28,8746	2,0000	28,8574	28,8692	0,0054	0,27	0,25
	33,0937	35,0943	2,0006	35,0806	35,0896	0,0047	0,23	
B	27,1151	29,1156	2,0005	29,1002	29,1009	0,0147	0,73	0,58
	24,8886	26,8891	2,0005	26,8740	26,8806	0,0085	0,42	
C	47,8573	49,8573	2,0000	49,8373	49,8298	0,0275	1,38	1,62
	45,7620	47,7628	2,0008	46,7540	46,7256	0,0372	1,86	
D	26,0878	28,0885	2,0007	28,0794	28,0819	0,0066	0,33	0,32
	24,2125	26,2132	2,0007	26,1942	26,2069	0,0063	0,31	
E	29,1522	31,1526	2,0004	31,1460	31,1509	0,0017	0,08	0,43
	26,9455	28,9460	2,0005	28,9311	28,9304	0,0156	0,78	
F	27,3650	29,3656	2,0006	29,3102	29,3108	0,0548	2,74	2,60
	22,4902	24,4905	2,0003	24,4345	24,4412	0,0493	2,46	

The water content test was carried out based on SNI 01 -3542-2004. Where based on SNI 01-3542-2004 the maximum limit of water content in ground coffee is 7% wb. At harvest, the water content of the coffee beans can be up to 60%, so a drying process is carried out to reduce the water content. Apart from drying in the sun, other factors that affect the water content of the coffee grounds are the processing and storage processes where this will affect the water content and taste of the coffee [7]. Based on the results above, it can be seen that the water content of the six tested samples met the quality requirements of SNI 01-3542-2004, namely 7%.

opened slightly, so that oxygen can enter). The purpose of the coagulation process on the burner flame is to remove the water content contained in the sample so that when the combustion is carried out, the flame does not occur. Meanwhile, the purpose of opening the electric furnace door occasionally so that oxygen enters is to optimize the oxidation process where oxygen acts as an oxidizer in the combustion process, so that the sample can be completely burned to ashes.

Ash content is an organic residue obtained from the ashing process of organic materials found in foodstuffs. In general, ash content is a parameter used when conducting tests to see the mineral content contained in a

food ingredient. If the ash content is higher, the mineral content in the food will be higher, conversely if the ash content is lower, the mineral content in the food will be lower as well. There are several factors that cause foodstuffs to have a low ash content, namely increased brittleness during the roasting process so that the mineral content decreases which causes the ash content to decrease [8].

Based on the Indonesian National Standard SNI 01-3542-2004 the maximum limit of ash content in ground coffee is 5% wb. Based on table 2 of the ash content test results in samples A, B, C, D, E, F, the ash content was obtained respectively 4.57%, 5.27%, 3.25%, 2.03%, 3.35% and 4.10%. In samples A, C, D, E, and F the results of the analysis showed that the ash content of pure coffee grounds was in accordance with SNI 01-3542-2004 regarding the maximum ash content in coffee grounds, namely 5% wb. However, the analysis results obtained in sample B had results that were not in accordance with SNI, namely 5.27%. This can occur due to the length of the roasting process that is carried out and the temperature used during roasting which can affect the ash content of the coffee grounds. In addition, the high mineral content in the coffee grounds can also result in a high ash content in the coffee grounds.

Coffee Extract Test Results

What is meant by coffee essence is the fraction of ground coffee dissolved in water. The coffee essence contained in coffee grounds is a composition of organic and inorganic chemical compounds, such as sugar, acid, caffeine, chlorogenic acid, melanoidin, triglonelin and minerals. The juice content is also affected by the roast level. The level of ground coffee essence is directly proportional to the level of roast. The higher the roasting level, the more complex organic compounds in the coffee beans decompose thermically into simple organic compounds. Following are the test results of the coffee extract which can be seen in table 3.

Based on these results, it indicates that the smaller the value of the coffee essence, the sample has a higher purity of coffee than other samples because the content of coffee essence varies depending on the type of coffee, the level of ripeness of the fruit at harvest time and the addition of other ingredients to pure ground coffee.

Tabel 2. Ash Content Test

No	Empty Cup Weight	Cup Weight + Sample (g)	Sample Weight (4-3) (g)	Cup + Ash Ash Weight		Ash Content (%)	Avarage (%)
A	37,7529	39,7531	2,0002	37,8440	0,0911	4,55	4.57
	31,9782	33,9787	2,0005	32,0700	0,0918	4,59	
B	31,5128	32,5130	1,0002	31,5666	0,0538	5,38	5,27
	28,1175	30,1178	2,0003	28,2206	0,1031	5,15	
C	35,0735	37,0738	2,0003	35,1340	0,0605	3,02	3,25
	38,4005	40,4007	2,0002	38,4700	0,0695	3,47	
D	28,9657	30,9660	2,0003	29,0065	0,0408	2,04	2,03
	30,5694	32,5696	2,0002	30,6097	0,0403	2,01	
E	28,1665	30,1667	2,0002	28,2278	0,0613	3,06	3,35
	39,1962	41,1965	2,0003	39,2691	0,0729	3,64	
F	40,2728	42,2729	2,0001	40,3722	0,0994	4,97	4,10
	35,5465	37,5469	2,0004	35,6113	0,0648	3,24	

In testing coffee extract has a very close relationship with solubility. Coffee essence content is the amount of a substance dissolved in water during coffee brewing. If the particle size of the coffee is getting smaller, the value of the coffee essence content obtained will be higher. and vice versa, if the particle size of the coffee is getting bigger, then the value of the coffee essence content obtained will be lower. This happens because the smaller the size of the coffee particles will result in an increase in surface area, so that the amount of dissolved solids will increase [9].

The chromatogram results in Figure 1 above are the results of an analysis of caffeine content using HPLC. Can be seen in Figure 1 is the chromatogram of the standard solution and some of the samples analyzed. In Figure 1 it can be seen that the samples analyzed have a retention time of 4.410 minutes. Retention time is the time required by the sample component compounds to pass through the column to the detector. The retention time is calculated from the time the sample is injected to the peak of the maximum reading on the detector. The analysis that can be carried out on the peak chromatogram is by observing peaks that have the same retention

Tabel 3. Extract Coffee Test

No	Empty Cup Weight (g)	Cup Weight + Sample (g)	Sample Weight (g)	Porcelain Cup Weight (g) B. Porcelain Cup + Sample Extract (g)		Extract Weight (g)	Extract Coffee (%)	Avarage (%)
A	93,8399	95,8403	2,0004	78,7499	78,8210	0,0711	35,5429	34.34
B	94,2353	96,2358	2,0005	69,9429	69,9979	0,0550	27,4931	
B	98,3058	100,3061	2,0003	81,4730	81,5265	0,0535	26,7460	27.12
C	93,6627	95,6635	2,0008	70,6306	70,6848	0,0542	27,0892	
C	100,4720	102,4728	2,0008	67,2958	67,3484	0,0526	26,2895	26.69
D	99,6960	101,6961	2,0001	72,8927	72,9422	0,0495	24,7488	
D	95,5515	97,5520	2,0005	75,1785	75,2315	0,0530	26,4934	25.62
E	93,9590	95,9595	2,0005	71,6406	71,6906	0,0500	24,9938	
E	102,2796	104,2798	2,0002	77,1262	77,1785	0,0523	26,1474	25.57
F	97,3255	99,3264	2,0009	70,0830	70,2712	0,1882	94,0577	
F	98,0160	100,0165	2,0005	68,9803	69,1668	0,1865	93,2267	33.16
	22,4902	24,4905	2,0003	24,4345	24,4412	0,0493	2,46	

Caffeine Test

The caffeine content test was analyzed using HPLC (High Performance Liquid Chromatography). HPLC analysis was carried out to find out whether caffeine was present in the ground coffee samples. Following are the results of the chromatograms obtained.

In the column a separation process will occur where the mixed components will be retained by the stationary phase and then dissolved by the mobile phase which is continuously flowing so that it passes through the column to the detector. Polar compounds contained in the components of the mixture through the column will stick longer to the polar silica (stationary phase) compared to non-polar compounds which will pass through the column faster (stationary phase).

time and observing the area of the peak. Because the standard solution is a caffeine solution, the caffeine content in it is the largest compared to other components such as impurities. The presence of these impurities shows that there is more than one peak on the chromatogram. Each compound will have a different retention time. For some compounds, the retention time will vary greatly and depend on the pressure applied, the conditions of the stationary phase, the composition of the solvent and the temperature of the column. Polar compounds contained in the components of the mixture through the column will stick longer to the polar silica (stationary phase) compared to non-polar compounds which will pass through the column faster (stationary phase). The cause of the presence of impurity peaks on the chromatogram can be caused by several factors, namely sample preparation that is not thorough and careful, resulting in impure

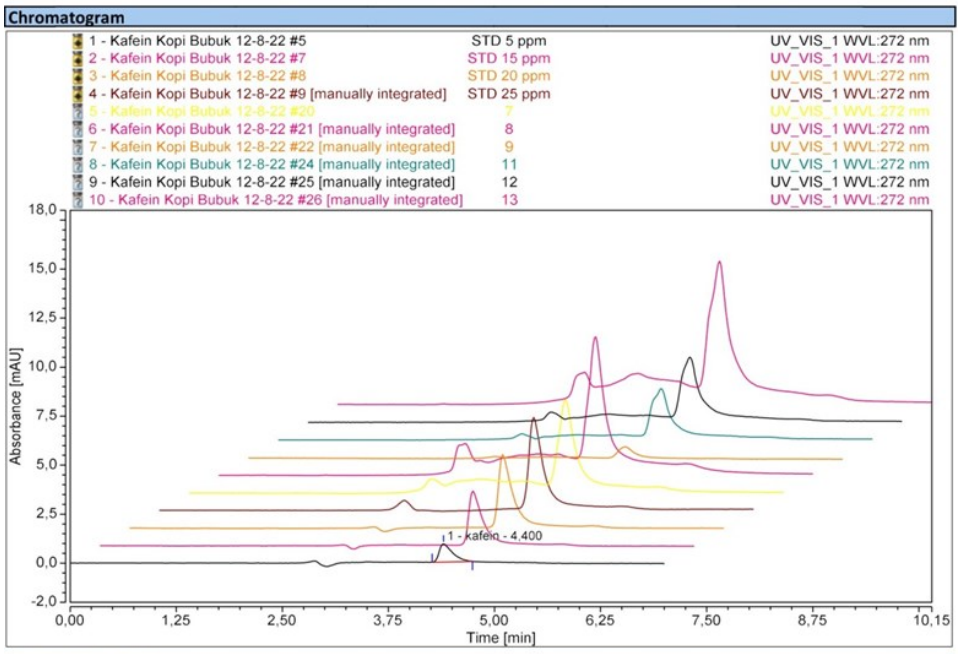
samples to be analyzed. In addition, the conditioning of the tool can also cause impurity peaks on the chromatogram. This can happen because when the mobile phase (eluent) flows into the stationary phase (column) there is gas/ bubbles which are then detected by the detector as an impurity. Quantitative analysis was carried out by calculating the caffeine content contained in ground coffee A, B and C. Determination of caffeine content was calculated based on SNI 2983: 2014

Caffeine content is the percentage of caffeine content contained in a material to be analyzed, namely coffee grounds. In testing the caffeine content, the standard solution to be used has several concentrations, namely 5 ppm, 15 ppm, 20 ppm and 25 ppm. The following table contains the concentration of standard caffeine solutions.

Tabel 4. Extract Caffein Standard Solution Concentration

No	Standard Concentration	Area
1	5 ppm	0,167
2	15 ppm	0,533
3	20 ppm	0,745
4	25 ppm	0,929

Table 4 is the concentration of the standard caffeine solution used. The purpose of carrying out variations of standard solutions is to make a standard curve first with a series of standard solutions whose concentrations vary.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount ppm
1	kafein	4,400	0,167	0,921	100,00	100,00	5,1094
Total:			**0,167**	**0,921**	**100,00**	**100,00**	

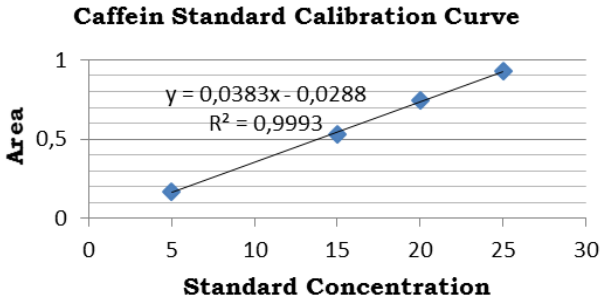


Figure 2. Caffein Standard Calibration Curve

In Figure 2, the calibration curve above is made by plotting each standard solution with different concentrations on the peak area of the caffeine content from the analysis results so that a straight line is obtained. We can see from the caffeine standard calibration curve image above with the standard solution concentrations used are 5 ppm, 15 ppm, 20 ppm and 25 ppm. So the equation obtained from the regression value y = 4.0042x + 2.375 with a value of R = 0.9995. The value (r) is close to 1, indicating that the calibration curve created has formed a linear straight line, which indicates that the graph obtained is good. The levels of caffeine obtained are as follows.

According to SNI 2983-2014 regarding coffee quality requirements [10].

Table 5. Caffein Content

No	Sample Code	Caffein Content (%)
1	A	1,71
2	B	2,43
3	C	0,23
4	D	2,10
5	E	2,58
6	F	6,02

caffeine content in coffee. Allowed caffeine content is 0.9-2%. Based on the table above, it can be seen that the caffeine content obtained in samples A, B, C, D, E and F were 1.71%, 2.43%, 0.23%, 2.10%, 2 respectively. .58%, and 6.02%. Referring to SNI 2983-2014 regarding the allowable caffeine content in ground coffee, the coffee sample that is included in the quality requirements of SNI 2983 is sample A with a caffeine content of 1.71%. In sample C, the caffeine content was below the SNI quality requirements, namely 0.23%, while samples B, D, E and F had caffeine levels above the SNI quality requirements. Calculation of caffeine content was carried out using SNI 2983:2014 instant

There are several factors that cause varying levels of caffeine in coffee, namely drying and roasting. In the process of roasting coffee beans, a small part of the coffee beans will evaporate and form other components such as acetone, furfural, ammonia, trimethylamine, formic acid, and acetic acid [11]. The influence of heat and cold also greatly affects the levels of caffeine in coffee. Caffeine contained in cold coffee is higher than the caffeine content contained in hot coffee.

Conclusion

Based on the research that has been done, it has been shown that the water content and coffee essence tests of the six samples found that the six samples met the quality requirements according to SNI 01-3542-2004 (7% wb water, 36% coffee extract). In the ash content test, it can be seen that sample B exceeds the quality requirements of SNI 01-3542-2002 (5%) which is 5.27% wb. Whereas in the caffeine content test the samples that met the quality requirements of SNI 2983 -2014 (0.9-2%) were sample A which was 1.71%.

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