

## Chemometrical analysis of Fourier Transform Infrared Spectrum profile of Indonesia's black tea products (*Camellia sinensis* L.)

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### ABSTRACT

Black tea (*Camellia sinensis* L.) is one of the most popular beverage ingredients in Indonesia. Generally, tea quality assessment is done by tea taster using the organoleptic method with evaluation based on shape, color, aroma, and taste. In this research, an alternative method of testing black tea product quality with FTIR (Fourier Transform Infrared) was developed. The variability of chemical composition is an important factor that determines flavor (taste and aroma) and health benefits. The sample of black tea tested came from 12 products circulating in Indonesia. A chemometric analysis of Principal Component Analysis and Cluster Analysis was used to support the analysis of specific differences of each FTIR spectra of samples. The analysis results of water and ethanol extract showed that the two solvents extracted the different of the variety of metabolite contents. Analysis of volatile compounds was also performed which also showed that each sample contained the different volatile compounds; which then is predicted can be investigated further to determine the black tea's quality.

**Keywords:** Black tea; Quality; FTIR; Chemometric.

### 1. INTRODUCTION

Black tea is made from the process of fermenting the tea leaves (*Camellia Sinensis* L.), which is known as the most popular beverage in the world [1]. This type of tea is very in demand because it has a special taste and aroma. Some advantageous chemicals are consisted, such as caffeine, theobromine, theophylline, tannins, adenine, essential oils, polysaccharides, amino acids, lipids, vitamins (such as vitamin C), quercetin, naringenin, and polyphenol [2]. Black tea also has health benefits because of the various secondary metabolite's activities to overcome diabetes, lung cancer, prostate cancer, breast cancer, anti-ulcer, and respiratory disorders. In addition, this simplicia has antioxidant activity [3].

Black tea consumption in Indonesia is 0.61 kg / capita / year, circulating in various brands [4]. The presence of these brands allows there is a difference in quality, which can be affected by the variability of chemical composition. The chemical composition of the tea depends on the place of growth, soil, the height of planting, picking, sorting, processing, extraction, drying, and storage [5, 6, 7].

Generally, the determination and quality assessment of a black tea product is done by tea taster using the organoleptic method. Organoleptic assessment methods include flavor, aroma, color, and shape. However, since this method is strongly influenced by

subjective factors, the inconsistency and uncertainty of the evaluation results are high. The factors of tea taster such as individual variability decreased sensitivity due to prolonged exposure, fatigue, mental states, and others [8, 9, 10, 11, 12]. In purpose to overcome the problem, then will be done the instrumental approach. One tool that can be selected is FTIR (Fourier Transform Infrared) [13, 14, 15, 16, 17, 18, 19, ] FTIR can exhibit a measurement and distinct spectrum (fingerprint), but in reality, the FTIR spectrum of sample measurements often shows relatively similar shapes. Therefore, it needs to be further analyzed using the chemometrics method [20, 21]. Chemometrics is the science that connects measurements made through a chemical process or system through mathematical and statistical approaches. Chemometric analysis can be a powerful method for exploring large data sets derived from biological systems that contain many variables and can group them [22, 23].

The method was used in this study to classify samples based upon their chemical content. Research conducted by Chew et al in 2002 showed that Principal Component Analysis (PCA) chemo metric analysis can distinguish the quality and variety of various herbal medicines [17]. Therefore, this method is applied to the grouping of compounds in Indonesian black tea products.

### 2. MATERIALS AND METHODS

**2.1. Instruments.** Thermo Scientific® Nicolet iS5 FTIR spectrometer, Holder of ZnSe iD3 ATR (Attenuated Total Reflectance), Thermo Gass Cell FTIR.

**2.2. Tools.** In this study the tools that will be used include evaporating cup, measuring flask, micropipette, beaker glass,

erlenmeyer, thermometer, stirring rod, spatter, parchment paper, filter paper, water bath, and measuring cup.

**2.3. Materials.** Black tea samples used in black tea products circulating in Bandung, the sample code is A, B, C, D, E, F, G, H, I, J, K, and L. In addition, supporting materials are used such as aquadest and ethanol (Merck).

**2.4. Software.** In this study chemometric analysis was carried out using the Minitab software.

## 2.5. Research methods.

### 2.5.1. Tea Sample Preparation.

#### a. Water Extract

Each sample of black tea was weighed as much as 10 g, then dissolved in 100 mL (w/v) aquadest heat (100°C) and allowed to stand for 15 minutes. The tea juice is then evaporated to form a thick extract.

#### b. Ethanol Extract

Each sample of black tea was weighed as much as 10 g, then dissolved in 100 mL (w/v) ethanol and allowed to stand (soaked) for 24 hours, then filtered. The tea juice is evaporated to form a thick extract.

**2.5.2. Determination of FTIR Spectrum Profile of Black Tea Extract.** FT-IR measurements were carried out in the wave number range 650 - 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  with 16 scans. A small sample is placed on the surface of the ZnSe ATR FTIR holder. The sample is pressed with a die. Next, select the

collect sample option on the OMNIC Spectra® application. Repeated measurements were taken three times. Each sample that has been tested is cleaned thoroughly before being replaced with a different sample.

**2.5.3. Spectrum Analysis using the Minitab Black Tea Extract application.** The spectrum obtained from each sample is analyzed by looking at the typical peaks in each spectrum that appears. Then the spectrum of various functional groups is observed in the corresponding wave number. The results are compared with the literature. Minitab is used for PCA (Principal Component Analysis) and cluster analysis of the FTIR spectrum obtained.

**2.5.4 Analysis of Volatile Black Tea Compounds with FTIR.** Each sample of black tea was weighed 15 g, put into a 500 mL flask and added 300 mL of distilled water. The flask is heated, the water vapor that is formed is allowed to be conditioned, while the gas formed flows to the transmit gass holder. Furthermore, the gas is analyzed using FTIR. The resulting FTIR spectrum is grouped by the PCA method and cluster analysis.

## 3. RESULTS

### 3.1. Water Extract.

In general, black tea is served by brewing it with hot water and soaking it for a few minutes before being consumed. The following yields water extracts from 12 black tea samples: A 24.20%; B 25.03%; C 25.79%; D 28.28%; E 26.57%; F 26.09%; G 26.29%; H 29.90%; I 27.20%; J 23.26%; K 27.36%; and L 27.62% the average extract yield of 26.46% (w/w). The smallest yield was obtained from the J ample with a percentage of 23.16%, while the largest yield was obtained from the H sample with a percentage of 29.90%. Brewed black tea with a time of 25 seconds to 2 minutes can extract chemical metabolites such as total phenolics, catechins, alkaloids, phenolic acids, teaflavins, flavonol glycosides, and flavones [24].

### 3.2. Ethanol Extract.

In this study extraction of black tea was also carried out using 96% ethanol. The following yields ethanol extracts from 12 black tea samples: A 21.31%; B 14.73%; C 16.64%; D 18.33%; E 14.15%; F 14.27%; G 18.72%; H 17.74%; I 18.18%; J 16.62%; K 18.08%; and L 18.25%.

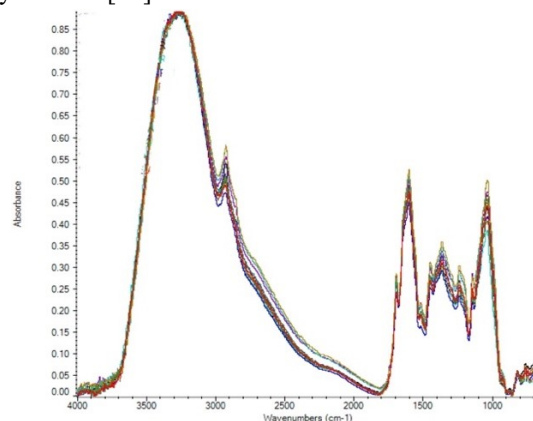
The results of the average extract yield of 17.25% (w/w). The smallest yield was obtained from F samples with a percentage of 14.15%, while the largest yield was produced by A samples with a percentage of 21.31%. The yield of the sample extracted with ethanol is smaller than the sample extracted with water.

### 3.3. PCA and Cluster Analysis Water Extract.

The FTIR (Fourier Transform Infrared) spectrum results from 12 black tea samples produced a pattern and shape of the spectrum that was relatively the same, but had different absorption intensities. There are 10 peaks that appear in the area of 800 - 3400  $\text{cm}^{-1}$ , with moderate and strong intensity. The FTIR spectrum can be seen in Figure 1.

The peak that appears on the FTIR spectrum is the result of absorption (vibration) of the metabolites contained in the sample. Broad spectrum peaks in the area of 3247  $\text{cm}^{-1}$ , indicating stretching O-H uptake of hydroxyl groups (alcohols, phenols). The peak that appears in the 2927  $\text{cm}^{-1}$  region shows the stretching vibration of the C-H bond of the alkane and carboxylic acid

groups. The peak at 1693  $\text{cm}^{-1}$  shows the stretching vibration of C=O (carbonyl) bonds from flavonoids, polyphenols, and catechins. Uptake in the area of 1515  $\text{cm}^{-1}$  shows the vibration of the C=C bond of aromatic compounds. Uptake in the area of 1450  $\text{cm}^{-1}$  shows stretch vibrations of aromatic compounds. Medium intensity peaks in the 1238  $\text{cm}^{-1}$  region indicate CN bond vibrations from aliphatic amine groups, while peaks with strong and sharp intensities in the 1037  $\text{cm}^{-1}$  region show stretching vibrations of CO bonds from alcoholic compounds, esters, and carboxylic acids [25].



**Figure 1.** Spectrum FTIR of water extract of the black tea samples.

In Figure 1, the resulting FTIR spectrum showed no significant difference in absorption intensity if observed visually. Observation of differences in spectrum between samples is difficult to see with the naked eye, so to help observe the variability of peak intensity can be done by chemometric statistical methods [17]. The chemometric statistical methods include PCA and Cluster Analysis. Both of these methods can be used for sample grouping and observe the grouping relationships between samples based on differences in the peak absorption intensity of the FTIR spectrum of each sample. In PCA analysis and Cluster Analysis there are 10 top FTIR spectrum choices that can be seen in Table 1 below.

**Table 1.** Peaks of the FTIR spectrum of water extracts.

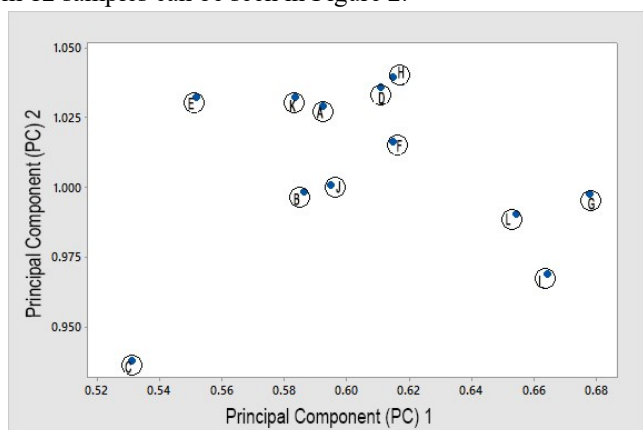
Sample	Wavelength (cm <sup>-1</sup> )									
	1037	1141	1238	1365	1450	1515	1604	1693	2927	3247
A	0.4355	0.2446	0.2523	0.3080	0.2622	0.1836	0.4670	0.2360	0.4830	0.8790
B	0.4214	0.2215	0.2431	0.2980	0.2590	0.1798	0.4527	0.2313	0.5228	0.8621
C	0.3582	0.2086	0.2351	0.2830	0.2488	0.1748	0.4270	0.2487	0.4826	0.8301
D	0.4513	0.2413	0.2596	0.3115	0.2683	0.1830	0.4725	0.2376	0.4970	0.8789
E	0.4223	0.2214	0.2351	0.2956	0.2538	0.1646	0.4529	0.2358	0.4786	0.8971
F	0.4491	0.2374	0.2551	0.3110	0.2680	0.1833	0.4684	0.2444	0.5005	0.8603
G	0.4698	0.2603	0.2716	0.3222	0.2829	0.1947	0.4783	0.2565	0.5404	0.8271
H	0.4381	0.2413	0.2631	0.3140	0.2770	0.1933	0.4791	0.2628	0.5085	0.8922
I	0.4503	0.2492	0.2725	0.3219	0.2795	0.1945	0.4740	0.2576	0.5237	0.8033
J	0.4287	0.2281	0.2568	0.3079	0.2637	0.1797	0.4698	0.2441	0.4798	0.8503
K	0.4180	0.2368	0.2478	0.3030	0.2690	0.1904	0.4687	0.2398	0.5037	0.8952
L	0.4437	0.2663	0.2726	0.3140	0.2779	0.2026	0.4712	0.2624	0.5206	0.8325

The PCA results produce 10 new variables which are the correlation values of the previous variables. PCA can reduce multivariate data (multivariable) which converts (transforms) a data matrix into a set of fewer linear combinations but absorbs most of the variants from the initial data, in this case the peak intensity of the FTIR spectrum is the variable [23]. The new variable is called the Principle Component (PC).

The Eigenvalue value shows how much influence a variable has on the formation of new matrix characteristics. PC1 gives the largest proportion of eigenvalue with a value of 0.0018976 or 58.2% of the total variance. Meanwhile, PC2 gives the second largest proportion of eigenvalue with a value of 0.0009548 or 29.3%. The eigenvalue values of PC1 and PC2 give cumulative proportions of 87.5%, indicating that the formation of 2 new variants (PC1 and PC2) has represented 87.5% of the total variant data formed.

The PCA results in addition to providing an overview of the proportion of each main component formed. Besides that, it can also display the coefficient value of each wave number variable from each PC. The coefficient value is the value of the matrix constant of the previous variables.

The graph of the PC1 coefficient on PC2 is called the score plot. The score plot shows the sample position in the PC1 and PC2 regions, if the position between the plots (samples) that are close together can explain that the sample has similar physical and chemical properties. Graphs of plot scores between PC1 and PC2 from 12 samples can be seen in Figure 2.



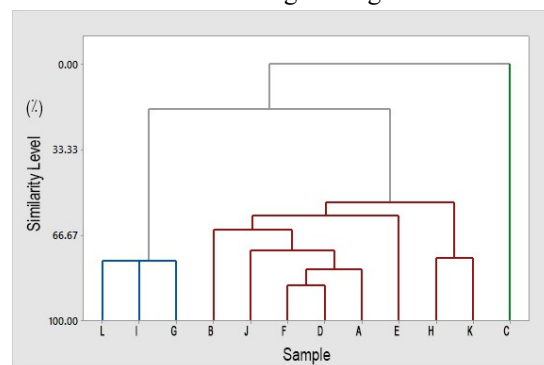
**Figure 2.** Graph of plot scores between PC1 and PC2.

In Figure 2 the graph of the plot score between PC1 and PC2 shows that the sample is H with D, as well as the K sample with A, and B samples with J, each located in an adjacent position. The C sample is a sample that is located in the furthest position of the plot, compared to other samples. The proximity of the plot position can give an illustration, that between these samples have the same secondary metabolites. Likewise, the further the location

of the plot position of a sample shows that the sample has secondary metabolites which are increasingly different. The plot score can provide information about the similarity and proximity of the metabolite content between samples but has not been able to provide an overview of the relationships between groups. Then, the grouping was done with Cluster Analysis.

Cluster Analysis is used to divide a group of objects (samples) into a class, so that similar objects are in the same class. As with PCA, groups of objects are obtained from mathematical analysis and no assumptions are made regarding the distribution of variables from each object. Cluster Analysis looks for adjacent objects in variable space [26].

From Figure 3, it can be seen that the highest similarity percentage was found in the F and D samples, which amounted to 86.55%. While the smallest percentage similarity is found in L and C samples with a percentage of 0%, which shows that the two samples do not have similarities. Cluster Analysis used in research based on hierarchical methods. The grouping carried out in this method by starting grouping two or more objects that have the closest similarity, then passed on to other objects and so on until the cluster will form a kind of 'tree' where there is a clear level (hierarchy) between objects, from the most similar to the least similar. The tool that helps to clarify this hierarchy process is called a dendrogram. To see the relationship between groups and sub groups is illustrated in the dendrogram Figure 3.



**Figure 3.** Dendrogram 12 Cluster Analysis of Water Extract Samples.

Figure 3 shows the dendrogram resulting from cluster analysis of 12 black tea samples. In dendrogram cluster analysis, the X axis shows the relationship between sample groups, and the Y axis shows the percentage value of the similarity of the formed subgroups.

Based on the results of the cluster analysis the water extract sample was divided into 3 clusters. Cluster 1 consists of samples from L, I, and G. Cluster 2 has the most population, consisting of B, J, F, D, A, E, H, and K. In cluster 2 there are sub-groups that are interrelated between one another. Meanwhile, cluster 3 only consists of one sample, C.

### 3.4. PCA and cluster analysis ethanol extract.

The FTIR spectrum of 12 samples extracted with ethanol solvent produced relatively similar patterns and shapes. Measurement of FTIR ethanol extract was carried out in the wave number area of 800-3400 cm<sup>-1</sup>. The FTIR spectrum of ethanol extract has 18 peaks which appear with moderate and strong intensity. These peaks can provide information about the functional group and the class of compounds found in the sample.



FTIR spectrum extracts of ethanol, when compared with water extracts have more spectrum peaks, especially in areas of 1000-1800  $\text{cm}^{-1}$ . A broad spectrum peak at an area of 3255  $\text{cm}^{-1}$  indicates the vibration of stretching hydroxyl groups (alcohols and phenols). The peak in the area of 2923  $\text{cm}^{-1}$  and 2854  $\text{cm}^{-1}$  indicates the presence of stretch vibration from the C-H bond of the alkane and carboxylic acid groups. Peak with strong and sharp intensity in the area of 1693  $\text{cm}^{-1}$  shows vibrations of stretching bond C=O (carbonyl) from flavonoids, alkaloids, polyphenols, and catechins. Medium intensity peaks in the area of 1515  $\text{cm}^{-1}$  indicate vibrations of C=C bonds of aromatic compounds. Medium intensity peaks at an area of 1450  $\text{cm}^{-1}$  indicate the presence of stretching vibrations of aromatic compounds. Medium intensity peaks in the 1292  $\text{cm}^{-1}$  area indicate the presence of C-O bond vibrations from alcohol. Medium intensity peaks in the area of 1234  $\text{cm}^{-1}$  indicate the presence of CN bond vibrations from aliphatic amine groups, as well as peaks with strong and sharp intensity at 1029  $\text{cm}^{-1}$ , indicating the presence of stretching vibrations of CO bonds from alcoholic, ester, and carboxylic acids [25].

Some of the FTIR spectral peaks of water and ethanol extracts that appear in the same wave number region show a similarity in the content of the metabolites extracted in both solvents.

Like the FTIR spectrum of water extract, the FTIR spectrum form of ethanol extract is also difficult to observe directly so it is necessary to do statistical analysis to facilitate observation. The chemometric statistical method is chosen to analyze an object (sample) that has many variables. In this study, the variable is the peak that appears in the FTIR spectrum. Table 2 shows the choice peaks and intensity of FTIR spectrum absorption of 12 samples of ethanol extract black tea.

PCA results produce 18 new variables which are the correlation values of the previous variables. The profile of eigenvalue values and the proportion of 18 new variants.

PC1 gives the largest proportion of eigenvalue with a value of 0.016270 or 90% of the total value of the new variant, while PC2 gives the value of the second largest proportion with a proportion of 5.65%. The two new variants can provide a cumulative proportion of 95.6% of the total variants formed. The plot scores of 12 ethanol extract samples are seen in Figure 4.

**Table 2.** Peak FTIR Spectrum Ethanol Extract.

Absorption on Wavenumbers (cm <sup>-1</sup> )									
Sample	1030	1142	1207	1234	1292	1338	1361	1412	1450
A	0.3612	0.2773	0.2584	0.2555	0.1918	0.2187	0.2223	0.1620	0.2368
B	0.4439	0.3013	0.3066	0.3249	0.2546	0.2913	0.2973	0.2353	0.3092
C	0.3767	0.2836	0.2934	0.3078	0.2431	0.2807	0.2824	0.2264	0.2957
D	0.4398	0.2981	0.2952	0.3087	0.2405	0.2822	0.2834	0.2166	0.2887
E	0.4540	0.3060	0.2964	0.3109	0.2449	0.2821	0.2836	0.2143	0.2954
F	0.4500	0.2960	0.2912	0.3104	0.2441	0.2896	0.2902	0.2244	0.2932
G	0.4562	0.3132	0.3093	0.3217	0.2546	0.3036	0.3014	0.2373	0.3125
H	0.4514	0.3027	0.2995	0.3158	0.2438	0.2925	0.2894	0.2200	0.2975
I	0.4446	0.3057	0.3082	0.3195	0.2515	0.2965	0.2938	0.2222	0.3012
J	0.4290	0.3096	0.3107	0.3265	0.2525	0.2888	0.2921	0.2243	0.3049
K	0.4487	0.2831	0.2739	0.2912	0.2327	0.2634	0.2743	0.2120	0.2802
L	0.4187	0.2809	0.2661	0.2762	0.2106	0.2449	0.2486	0.1895	0.2567

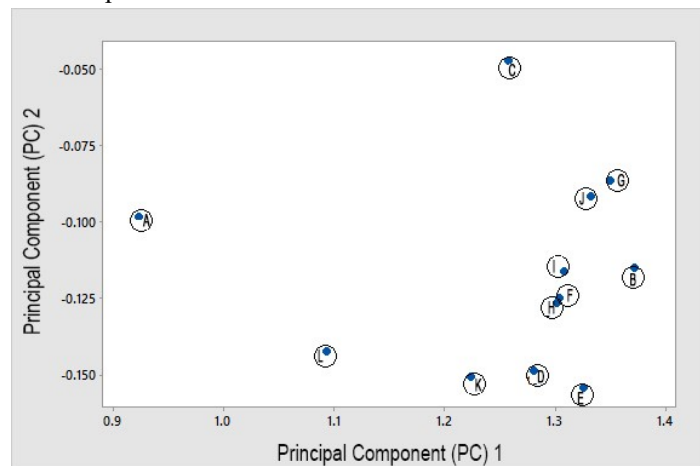
  

Absorption on Wavenumbers (cm <sup>-1</sup> )									
Sample	1500	1516	1554	1604	1628	1693	2854	2924	3255
A	0.1185	0.1271	0.1415	0.3288	0.3138	0.2375	0.4372	0.6064	0.5544
B	0.1783	0.1821	0.2540	0.4777	0.4677	0.3352	0.4269	0.5557	0.8457
C	0.1799	0.1797	0.2354	0.4285	0.4298	0.3451	0.4090	0.5288	0.7510
D	0.1602	0.1702	0.2120	0.4458	0.4247	0.2918	0.4203	0.5516	0.8069
E	0.1681	0.1726	0.2124	0.4586	0.4459	0.3178	0.4097	0.5419	0.8386
F	0.1708	0.1769	0.2252	0.4518	0.4387	0.3141	0.3916	0.5138	0.7945
G	0.1887	0.1943	0.2486	0.4717	0.4652	0.3448	0.4089	0.5347	0.7916
H	0.1696	0.1777	0.2200	0.4546	0.4363	0.3174	0.4121	0.5474	0.7953
I	0.1717	0.1818	0.2257	0.4618	0.4344	0.3148	0.4107	0.5459	0.7930
J	0.1792	0.1845	0.2379	0.4706	0.4605	0.3375	0.4141	0.5470	0.8012
K	0.1585	0.1615	0.1969	0.4180	0.4115	0.2937	0.4174	0.5536	0.7666
L	0.1359	0.1415	0.1655	0.3747	0.3653	0.2662	0.4067	0.5519	0.6811

Figure 4 shows several samples located in positions (points) that are close together such as the H, I, and F samples.

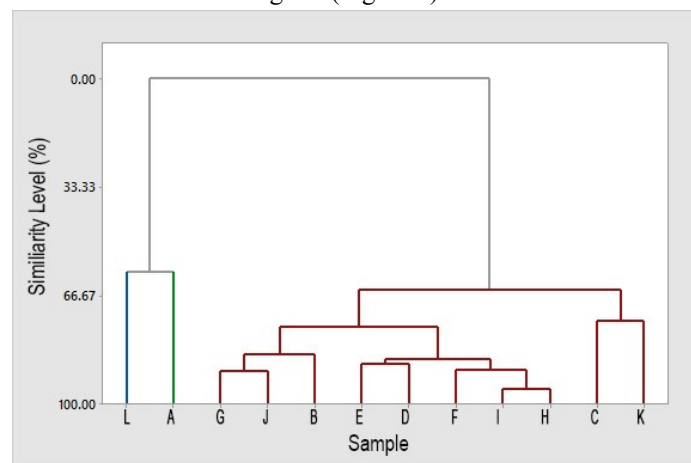
The three samples are in one group. In addition, J samples with G are located in positions that are close together. The A sample was in the furthest position from 11 other samples. The position of A can provide information that the sample has the most different chemical properties and content from 11 other samples.

Like the water extract sample, the Cluster Analysis sample was also carried out in ethanol extract samples to divide the sample into classes based on the proximity between objects in the variable space.



**Figure 4.** Graph of plot scores between PC1 and PC2.

From Figure 5, it can be seen that the highest similarity percentage was found in the I and H samples, which amounted to 95.64%, while the smallest percentage was found in L and G samples with a percentage of 0%, which showed that the two samples did not have similarities between groups and sub groups can be seen in the dendrogram (Figure 5) below.



**Figure 5.** Dendrogram of ethanol extract back tea samples.

Analysis Cluster results divide the sample into 3 clusters. Clusters 1 and 3 each have only one population, L and A, while cluster 2 has the most sample population. The samples contained in cluster 2 include G, B, C, E, J, F, I, H, D, and K.

### 3.5. PCA and Gas Cluster Analysis (Volatile Compounds).

The content of volatile tea compounds or often called Volatile Flavor Compounds (VFC) has proven to be a parameter of the quality of tea products. VFC can be divided into two groups [27]. Group 1 consists of compounds of fatty acid degradation products during the process of making black tea which gives an undesirable aroma of greenish flavor such as 1-penten-3-ol, *n*-hexanal, *n*-hexanol, *cis*-3-hexenal, *trans*-2-hexenal, *cis*-3-hexenol,

*trans*-2-hexenol, and pentanol. Group II consists of compounds that give sweet flowery aroma to black tea, mainly derived from glycoside side compounds from terpenoids such as linalool compounds, linalool oxides, methyl salicylate, phenylacetaldehyde, geraniol, benzyl alcohol, 2-phenylethanol, benzaldehyde,  $\alpha$ -ionone, and  $\beta$ -ionone [28].

In general, the quality of tea that has good aroma and taste has a very high rating, and vice versa and for poor tea quality, both of these attributes have an equally bad rating. aroma or taste is often used as a single attribute in the assessment of tea quality [29, 30].

Measurement of FTIR samples was carried out in the range of wave numbers 1000-4000  $\text{cm}^{-1}$  and produced a peak spectrum with different intensities. Peak spectrum can provide information on the volatile compound content of each sample. The peaks that appear at 3444  $\text{cm}^{-1}$  can indicate the presence of hydroxyl groups (alcohols, phenols, and carboxylic acids) and amines (primary, secondary and tertiary). The peak in the area of 1650-1750  $\text{cm}^{-1}$  with strong and sharp intensity shows the vibration of stretching carbonyl groups derived from amides, esters, aldehydes, ketones, and carboxylic acids. In addition, there are peaks in the area of 1450-1600  $\text{cm}^{-1}$  can provide information that in the sample there is a C=C (aryl) bond or it can indicate a buckling vibration of the C-H bond [25].

Visual observation is difficult to see the differences and similarities of each sample spectrum. As with the samples of water extracts and ethanol, the FTIR gas analysis spectrum is also carried out by PCA and Cluster Analysis.

PCA results produce 18 new variables which are the correlation values of the previous variables. The profile of eigenvalue values and the proportion of 18 new variants can be seen in Table 3.

PC1 has an eigenvalue value of 0.0022275 or gives 85.9% the proportion of the total value of the new variant formed PC2 gives the second largest eigenvalue with a proportion of 8.5% of the total value of the new variant. The eigenvalue values of PC1 and PC2 give cumulative proportions of 94.3%, indicating that the formation of 2 new variant matrices (PC1 and PC2) has represented 94.3% of all variant data formed.

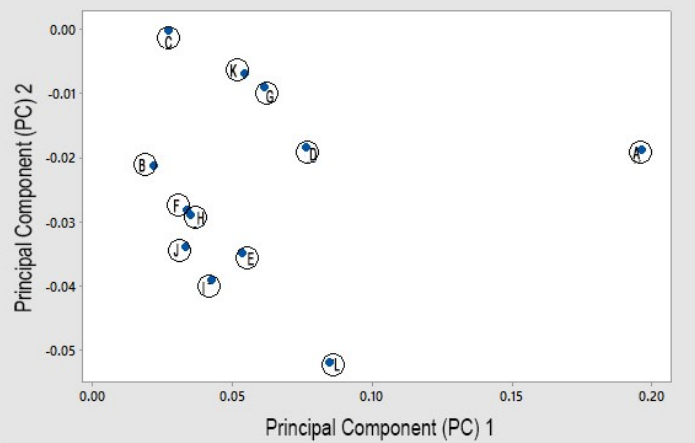
**Table 3.** Peak of FT-IR Spectrum Results of Gas Analysis.

Sample	Absorption on Wavenumbers ( $\text{cm}^{-1}$ )									
	1338	1396	1421	1458	1520	1539	1649	1699	1741	1793
A	0.0048	0.0103	0.0107	0.0163	0.0331	0.0318	0.0639	0.0333	0.0189	0.0087
B	0.0017	0.0043	0.0042	0.0068	0.0140	0.0127	0.0095	0.0103	0.0082	0.0046
C	0.0028	0.0026	0.0026	0.0035	0.0058	0.0052	0.0047	0.0046	0.0063	0.0026
D	0.0039	0.0082	0.0084	0.0124	0.0237	0.0219	0.0179	0.0187	0.0212	0.0091
E	0.0065	0.0101	0.0101	0.0139	0.0247	0.0234	0.0190	0.0187	0.0164	0.0100
F	0.0030	0.0064	0.0063	0.0098	0.0188	0.0171	0.0145	0.0141	0.0114	0.0066
G	0.0026	0.0059	0.0061	0.0091	0.0173	0.0157	0.0128	0.0137	0.0167	0.0067
H	0.0025	0.0059	0.0059	0.0096	0.0198	0.0179	0.0142	0.0148	0.0122	0.0063
I	0.0040	0.0087	0.0087	0.0133	0.0256	0.0236	0.0188	0.0188	0.0152	0.0086
J	0.0038	0.0074	0.0075	0.0114	0.0219	0.0198	0.0150	0.0160	0.0130	0.0074
K	0.0022	0.0049	0.0049	0.0075	0.0141	0.0128	0.0130	0.0116	0.0124	0.0055
L	0.0052	0.0113	0.0118	0.0184	0.0371	0.0349	0.0347	0.0290	0.0220	0.0116

Sample	Absorption on Wavenumbers ( $\text{cm}^{-1}$ )									
	1828	1867	1919	3444	3566	3599	3616	3649	3743	3836
A	0.0051	0.0037	0.0037	0.0042	0.1060	0.0897	0.0841	0.0562	0.0311	0.0192
B	0.0030	0.0022	0.0017	0.0023	0.0039	0.0056	0.0081	0.0073	0.0134	0.0086
C	0.0015	0.0011	0.0009	0.0012	0.0055	0.0190	0.0166	0.0053	0.0148	0.0035
D	0.0054	0.0039	0.0030	0.0041	0.0169	0.0445	0.0412	0.0184	0.0429	0.0150
E	0.0074	0.0061	0.0054	0.0063	0.0134	0.0211	0.0227	0.0155	0.0281	0.0162
F	0.0046	0.0034	0.0027	0.0036	0.0084	0.0101	0.0128	0.0110	0.0175	0.0114
G	0.0038	0.0027	0.0020	0.0028	0.0118	0.0395	0.0356	0.0136	0.0364	0.0107
H	0.0040	0.0029	0.0022	0.0030	0.0079	0.0106	0.0138	0.0113	0.0205	0.0127
I	0.0059	0.0045	0.0035	0.0046	0.0097	0.0114	0.0156	0.0137	0.0229	0.0152
J	0.0050	0.0038	0.0030	0.0040	0.0065	0.0083	0.0122	0.0113	0.0196	0.0129
K	0.0035	0.0026	0.0023	0.0028	0.0142	0.0334	0.0297	0.0114	0.0253	0.0075
L	0.0075	0.0055	0.0041	0.0057	0.0304	0.0284	0.0324	0.0254	0.0346	0.0225

Samples that are in a position (plot) close together can explain that between these samples have similar physical properties and chemical metabolites. The graph of the gas analysis score plot is seen in Figure 6 below.



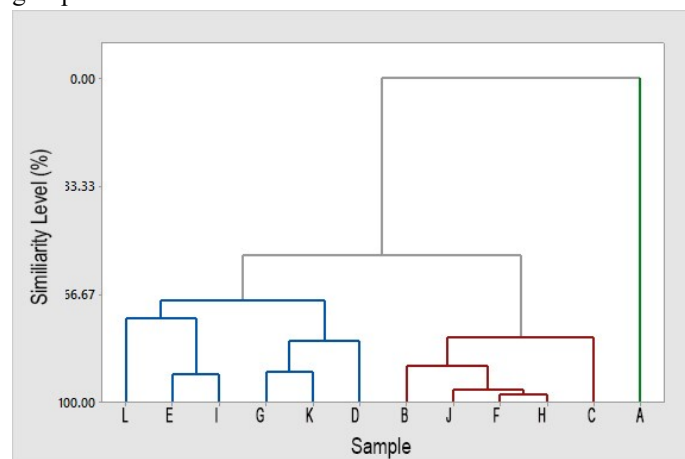
**Figure 6.** Graph Plots of PC1 and PC2 Score Results of Gas Analysis.

The plot score between PC1 and PC2 shows several samples located in adjacent positions. Samples located close together indicate that the sample has the same volatile compound content. The graph shows that the F sample with H is located in the closest position compared to other samples. In addition, the G sample with K is also located in an adjacent position. Samples located in adjacent positions can be called a group. The score plot graph can provide an illustration, that the farther the distance between plots (samples) shows the higher differences in physical properties and volatile compound content between the samples. The A sample which was in the farthest position compared to the other 11 samples, indicated that the A sample had the most different volatile compounds compared to the other 11 samples.

Cluster Analysis is also carried out to divide the sample into classes. Cluster Analysis results show the level of similarity and grouping stages between samples which can be seen in Figure 7.

In Figure 7, it can be seen that the highest similarity percentage was found in F and H samples, which amounted to 97.62%. Sub group I, F and J also have a high similarity, with a percentage of 96.21%. While the smallest percentage similarity is found in L and A samples with a percentage of 0%, which shows that the two samples do not have similarity in volatile compound content.

The dendrogram profile results from cluster analysis can be seen in Figure 7. The results of the dendrogram can provide a pattern of grouping and relationships between groups and sub groups.



**Figure 7.** Dendrogram Results of FTIR Gas Cluster Analysis.

The results of cluster analysis of gas compounds (volatiles) are shown in the dendrogram to divide the sample into 3 groups. Cluster 1 consists of 6 samples, L, G, E, I, D, and K. Cluster 2

consists of 5 samples, B, C, J, F, and H. Meanwhile, cluster 3 only consists of A samples.

#### 4. CONCLUSIONS

The results of this study indicate that FTIR can be used to test the quality of black tea semi-quantitatively elaborated by chemometric. Water and ethanol extracts from black tea showed different secondary metabolites, as seen from the differences in the FTIR spectrum, as well as the results of Principal Component

Analysis (PCA) and Cluster Analysis. In PCA and Cluster Analysis on the spectrum of volatile compounds containing 12 black tea samples, the volatile content varies. Thus, the PCA and Cluster Analysis are proven and can be used to see the specific differences of 12 black tea samples circulating in Indonesia.

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