DETECTION OF WHITE RICE ADULTERANTS IN LAMPUNG ROBUSTA COFFEE EXTRACT USING FT-IR METHOD BY FINGERPRINT ANALYSIS AND PRINCIPAL COMPONENT ANALYSIS

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Submitted: May 5, 2024 Revised: June 22, 2024 Accepted: June 27, 2024

ABSTRACT

Lampung Province has 3 areas that produce coffee: West Lampung, Tanggamus, and Waykanan, which can produce 51,484 tons of coffee annually. The high demand for coffee and limited harvest are some factors that cause the addition of adulterants to coffee products such as corn, soybeans, rye, coffee beans, and rice. This study aims to detect rice adulterants in Lampung robusta coffee using the FTIR spectrophotometric method combined with chemometric analysis using the PCA (Principal Component Analysis) method. FTIR spectrophotometric method combined with chemometric analysis using PCA (Principal Component Analysis) method. The PCA method was validated using the cross-validation method. Samples were taken from 3 Lampung coffees on the market. The extraction process was carried out on Lampung coffee and Lampung rice from 3 regions using 96% ethanol. After concentrating, the coffee and rice extracts were measured using FTIR and read in the 4000-650 cm-1 wave number range. Different wave number curves were obtained between coffee and rice. A pre-processing chemometric analysis was performed, which resulted in the classification of Robusta coffee and rice using PC1 and PC2 (50% and 24%). The results of PCA analysis showed that PC1 and PC2 in the three Lampung coffee samples, samples A and C, did not contain adulterants, while sample B was suspected of containing white rice.

Keywords: Alduteran, FTIR, Chemometrics, PCA, Lampung Robusta Coffee.

INTRODUCTION

Lampung Province is the highest Robusta coffee producer, one of which is the West Lampung, Tanggamus and Waykanan regions, with Robusta coffee yields reaching 51,484 tons/year. Located in the hilly areas of West, South, and North Lampung Province, which are included in climate zones B1 (7-9 wet months and 2 dry months) and C1 (5-6 wet months and 2 dry months), it is a major coffee production center according to Oldman. These climate zones are ideal for growing Robusta coffee plants, which require about 2000 mm of rain spread over nine to ten months each year. The selling price of coffee in bean form (green coffee) is stable and cheaper than coffee in powder form (Wang et al., 2009). Processed coffee will be different, whereas coffee processing consists of drying, roasting, milling, and packaging.

White rice is often added in the roasting process for certain Lampung regions. According to (Daniel et al., 2018), this is done to increase the volume of coffee produced so that coffee that has become powder is very difficult to distinguish between white rice and Robusta coffee; this process is called adulteration. With the high demand for coffee, many irresponsible farmers deliberately add or replace cheaper ingredients to increase their profits; this is called adulteration.

Coffee is one of the products often adulterant to increase profits for coffee sellers. Alduteran in coffee is usually added with rice, corn, soybeans, rye, and coffee stems. This can decrease coffee quality, but the price remains expensive (Toci et al., 2016). According to a barista, it has its own way of determining the quality of coffee, namely from the aroma of fragrant coffee, coffee that does not smell burnt aroma, and the colour of coffee after it has become a black drink that is not too thick. However, there is still a brownish colour because the deep black is believed to be burnt coffee.

From this, researchers want to know if the quality of coffee on the market contains adulterants. So, to do this research, there are several methods to detect adulterants in coffee: spectroscopic methods of chromatography, HPLC, uv-vis, mass spectrophotometry, and FT-IR/NIR (Pauli et al., 2014).

In this study, the method used in finding coffee adulterants is the FT-IR Spectroscopy method, which is an instrument often used to detect functional groups based on the interaction of infrared light with vibrations of chemical bonds in a correlated compound (Mauricio-Sánchez et al., 2018). This FTIR spectrum can be analyzed quickly and non-destructively and requires simple sample preparation (Liu & Kim, 2017). Because the infrared spectrum of the information obtained is complex, the generic chemical properties of the sample can be used to explain it. then the difference between one plant and another can be seen using this infrared spectrum (Andriansyah et al., 2021). The technique is very sensitive and simple to distinguish vibrations due to electrostatic interactions between functional and ionic groups (Mauricio-Sánchez et al., 2018). The results obtained are still in the form of large data; therefore, it is necessary to use the chemometric method.

Chemometric analysis is the Principal Component Analysis (PCA) method. The Principal Component Analysis (PCA) method is a validation method used in chemometric analysis (Rose & Smith, 2002). Principal Component Analysis (PCA) facilitates the interpretation of results when the number of matrix variables is lowered to introduce new variables while maintaining data information (Andriansyah et al., 2021). A statistical technique is used to study the relationship between variables in order (Rose & Smith, 2002). We will identify coffee against white rice by fingerprint analysis using the FT-IR method from this exposure.

This study aimed to analyze rice adulterant in raw materials for coffee preparations in the trade by Fourier transform infrared (FT-IR) method combined with chemometric analysis using principal method analysis (PCA).

RESEARCH METHODS

Equipment and Materials

This research was conducted to detect rice in Lampung robusta coffee raw materials using the Fourier transform infrared (FT-IR) method. The samples used in this study were taken from three different brands of coffee products. Sample preparation, making extracts, and measuring IR spectra analysed by PCA.

The raw materials used in this research are robusta coffee from West Lampung, Waykana and Tanggamus (determination number 49/HB/05/2024 in Padjadjaran University). In addition, rice from West Lampung, Waykanan, and Tanggamus is a model of adulterants used in coffee. Then, there are coffee samples from three different brands on the market.

Robusta coffee beans are roasted and then ground into powder, white rice samples are dried and ground into powder, and packaged coffee powder samples from three different manufacturers.

Samples of dried robusta coffee thick extract, samples of dried white rice thick extract, samples of dried packaged coffee thick extract from three different manufacturers, 96% ethanol solvent and silica gel.

The research method consists of two sub-chapters: the equipment and materials and the course of the research. If the data analysis is specific or the method is new, then a sub-chapter on Data Analysis can be added. The sub-chapter is written without numbering or bullet points.

Research Procedure

1. Sample preparation

Green beans taken directly from Robusta Coffee farmers have already been roasted, and varying temperatures and times have resulted in substantial chemical changes. The temperature used is 196-205°C (dark roast). In the initial stage of roasting, the moisture content of the roasted coffee beans is reduced to 100°C. The roasting process lasts 5-30 minutes. Then, the grinding process is carried out until the shape changes from beans to powder (Fadri et al., 2019).

Coffee and rice powder were extracted using 96% ethanol solvent by maceration method. A total of 100 grams of sample was put into the macerator, and then 300 ml of 96% ethanol was added and soaked every 6 hours while occasionally stirring. Then, the sample was allowed to stand for 24 hours. The macerate was separated and transferred to another Erlenmeyer, while the pulp was treated the same as 3 times maceration. The macerate obtained from the extraction was then concentrated using a rotary evaporator until a thick extract was obtained.

The coffee beans used were Robusta coffee beans, Rice, and various brands of coffee circulating in the trade. Robusta coffee beans were collected from West Lampung, Tanggamus, and Waykanan regions. Rice preparations were collected from three regions: West Lampung, Tanggamus, and Waykanan. Green coffee and rice are roasted first at a temperature of 196-205 C (dark roast) for 30 minutes, then ground into coffee powder and rice powder, after which the extraction process is carried out using 96% ethanol (Fadri et al., 2019).

2. FT-IR spectrum measurement

Samples from several regions were prepared using an FT-IR instrument, measuring infrared spectra with FT-IR (Agilent Cary 630 FT-IR) and Micro lab Expert application. Spectra were scanned in the infrared region (400-4000 cm-1) and 4 cm resolution, with the reflectance measurement technique measuring radiation absorption. That is, taking 1-2 mg of solid sample/powder and placing it on top of the ATR crystal on the FT-IR tool can be directly measured to get an infrared spectrum. Measurements produce a functional group region and a typical infrared fingerprint region in the spectrum; more precise and realistic information can be obtained from the fingerprint spectrum pattern to detect a desired compound (Coates, 2000).

3. Validation of Principal Component Analysis (PCA) method

This chemometric analysis uses Principal Component Analysis (PCA), a statistical technique, as a validation tool to sequentially examine the relationship between variables and identify the structure that controls them. PCA consists of statistics and matrix algebra (eigenvalues and eigenvectors, PCA fundamental matrix).

RESULTS AND DISCUSSION

FTIR Spectrum

Measurement of FTIR ATR spectra using the Micro lab Expert application. This study measured the coffee thick extract sample at wave numbers 4000-650 cm-1. The wave numbers are commonly used to detect the authenticity of organic compounds at 4000-1400 cm-1 and for detecting its components at wave numbers 1500-900 cm-1. The y-axis is the absorption intensity, and the x-axis is the wave number indicating the functional group. The wave numbers will be responded by the FTIR spectrometer to analyse and identify the type of functional groups present in the sample. In this study, one robusta coffee and rice raw material from each preparation was analysed to facilitate the interpretation of the FTIR spectrum. The results of the FTIR of the raw materials show the differences in the figure below.

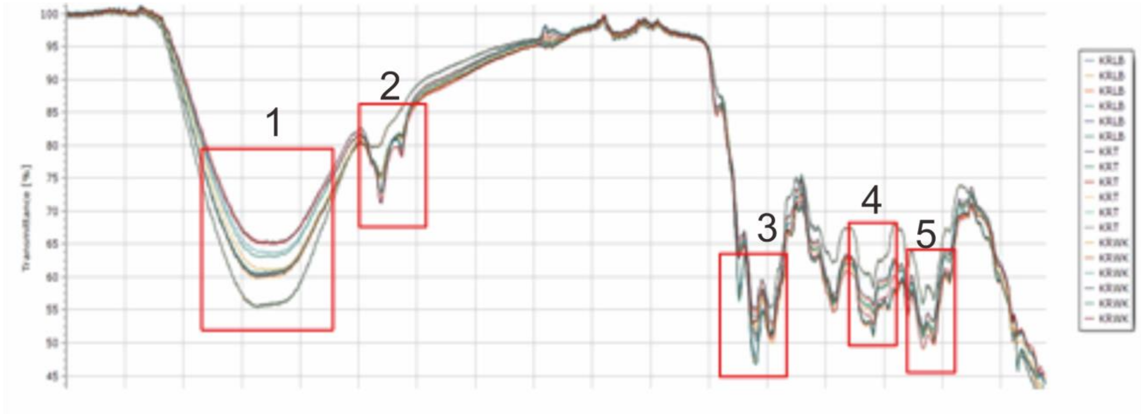

Figure 1. **FTIR Spectrum Overlay of Robusta Coffee Raw Materials from West Lampung, Tanggamus and Waykanan Regions**

The spectra of robusta coffee raw materials from West Lampung, Tanggamus and Waykanan regions were taken at wave numbers 4000-650 cm-1. They showed similar spectral patterns to each other with only differences in the transmittance values. Based on **Figure 1**. Observations between the spectra of rice raw material preparations from three regions have similar spectra marked in column (1) around the wave number area of 1022-988 cm-1 which identifies the presence of C-O vibrations, 1238-1195 cm-1, column number (2) identifies the presence of C-N vibrations, 1674-1616 cm-1, column number 3 identifies the presence of C=C vibrations, 2966-2888 cm-1, column number (4) identifies the presence of C-H vibrations and in column (5) 3400-3207 cm-1 identifies the presence of O-H vibrations. This happens because each region has its own characteristics in terms of coffee content. Based on the literature, the peak analyzed has a functional group bond. the similarity of absorption intensity occurs due to several factors, such as the area where the rice grows and the type of rice used (Govindaraju et al., 2022).

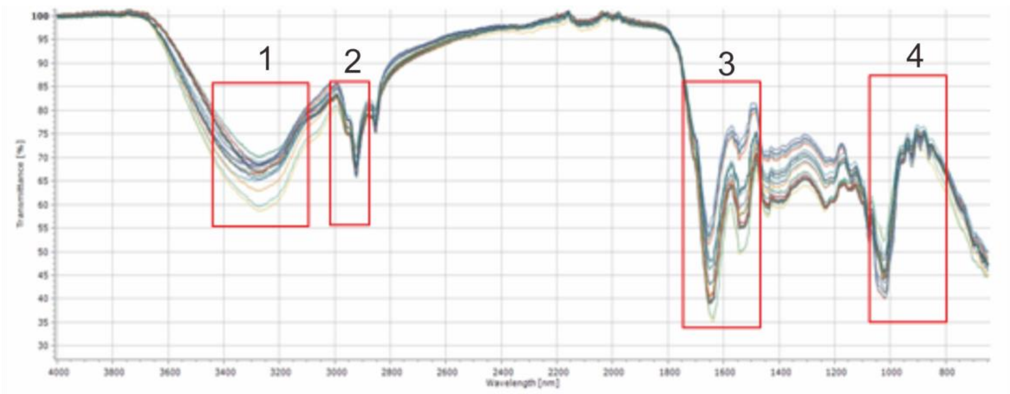

Figure 2. **FTIR Spectra Overlapped the Raw Material Preparations of West Lampung, Tanggamus, and Waykanan Rice**

The spectra of robusta coffee raw materials from West Lampung, Tanggamus and Waykanan regions were taken at wave numbers 4000-650 cm-1. They showed similar spectral patterns to each other, with only differences in their respective transmittance values. Based on **Figure 2**. Observations between the spectra of rice raw material preparations from three regions have similar spectra marked in column (1) around the wave number area 1022-988 cm-1, which identifies the presence of C-O vibrations, 1238-1195 cm-1, column number (2) identifies the presence of C-N vibrations, 1674-1616 cm-1, column number 3 identifies the presence of C=C vibrations, 2966-2888 cm-1, column number (4) identifies the presence of C-H vibrations and column (5) 3400-3207 cm-1 identifies the presence of O-H vibrations.

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PCA Analysis (Principal Component Analysis)

The results of the FTIR spectrum analysis were further analysed using PCA. FTIR spectrum data with a wave number range of 4000 - 650 cm-1 and 15 repetitions in the group and sample group were combined into one dataset. The FTIR spectrum dataset contained 900 data samples and was input into PCA. 10 sample types (15 data samples = 1 sample type).

Furthermore, the sample name was described in abbreviated form to facilitate the PCA process. In the Robusta coffee preparation group, there are KRLB (West Lampung), KRT (Tanggamus), and KRWK (Waykanan). While in the Rice preparation group, there are BT (Tanggamus), BLB (West Lampung), and BWK (Waykanan). In the sample group of coffee brands available in the market, there are KCJ (Sample B), KCBD (Sample A), and KCK (Sample C).

Cross-validation on PCA Output

In this study, cross-validation was used to evaluate the performance of the PCA model in clustering the data. The data were validated using the 2-fold method from the robusta coffee and rice preparation groups.

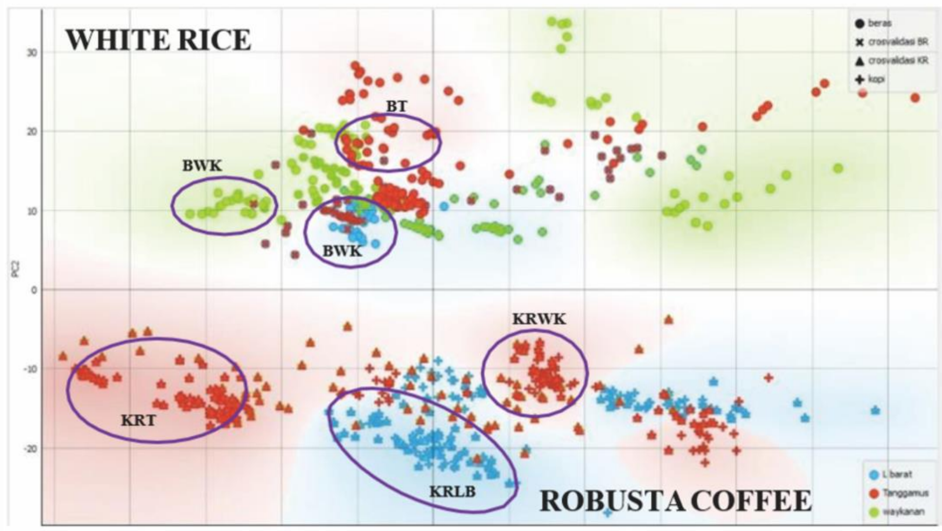

Figure 3. Scatter Plot of Robusta Coffee and Rice Preparations

Figure 3, shows the results of the confusion matrix. Judging from the confusion matrix results using the cross-validation method, it shows a grouping between fellow robusta coffee preparations and groups of rice preparations. This grouping shows that the data used is valid.

Scatter Plot

The results of this PCA analysis will show the grouping of samples based on PC1 and PC2 values in the form of a scatter plot visualisation.

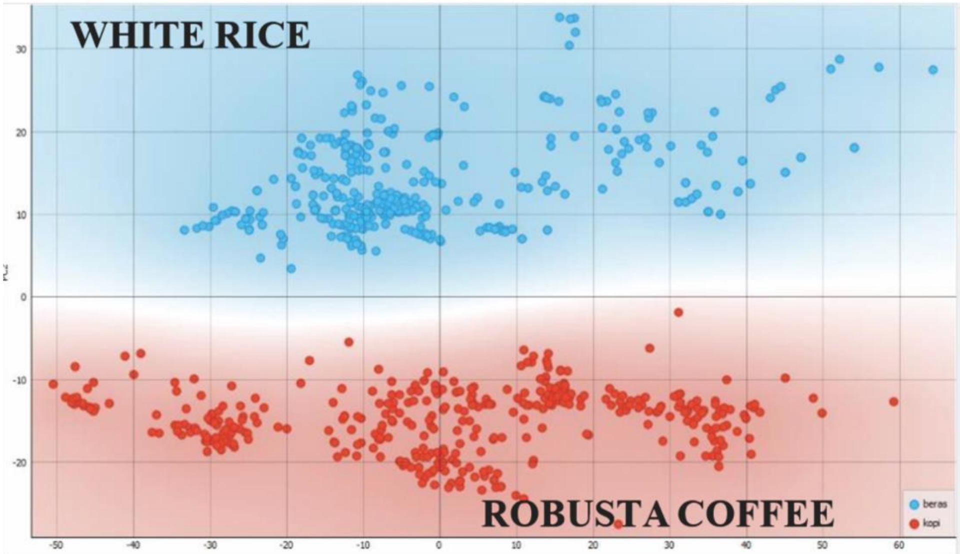

Figure 4. Scatter Plot of PC1 50% and PC2 24%

From **Figure 4**, PC1 can explain 50% of the component variation, while PC2 can explain 24% of the component variation. Thus, the total PC value associated with the robusta coffee and rice preparation groups reached 74%. The success of PCA scatter plot modelling can be seen from the high PC value, which can explain 74% of the FTIR spectrum data. In the figure, it can be seen that the rice preparation group plot is separated from the robusta coffee preparation group plot. Thus, this can facilitate testing on coffee samples suspected of being mixed with rice.

FTIR Spectrum Sample Testing

In this study, three samples of coffee brands circulating in the market were tested to evaluate their purity qualitatively. This was done by visualizing the PC1 and PC2 of each sample onto plots of robusta coffee preparation and rice preparation.

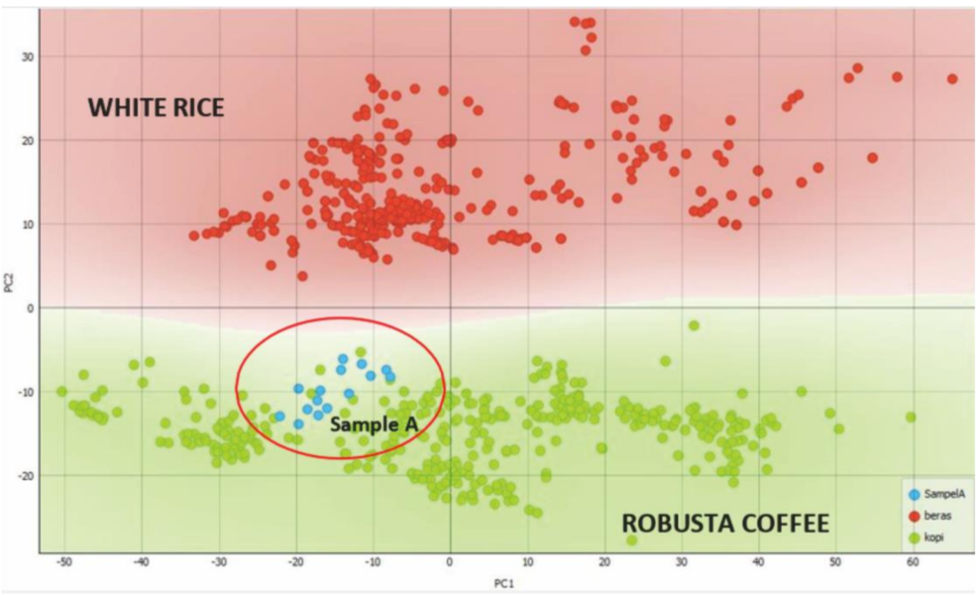

Figure 5. Scatter Plot of Raw Material Testing with Sample A

Based on **Figure 5**. The results of the Scatter Plot curve against PC 1 (50%) against PC 2 (24%) represent a cumulative variance of 74%. The combined results of robusta coffee raw materials, white rice and sample A, all sample A plots are in the robusta coffee preparation plot area. This indicates the possibility that sample A contains robusta coffee and no adulterant was detected.

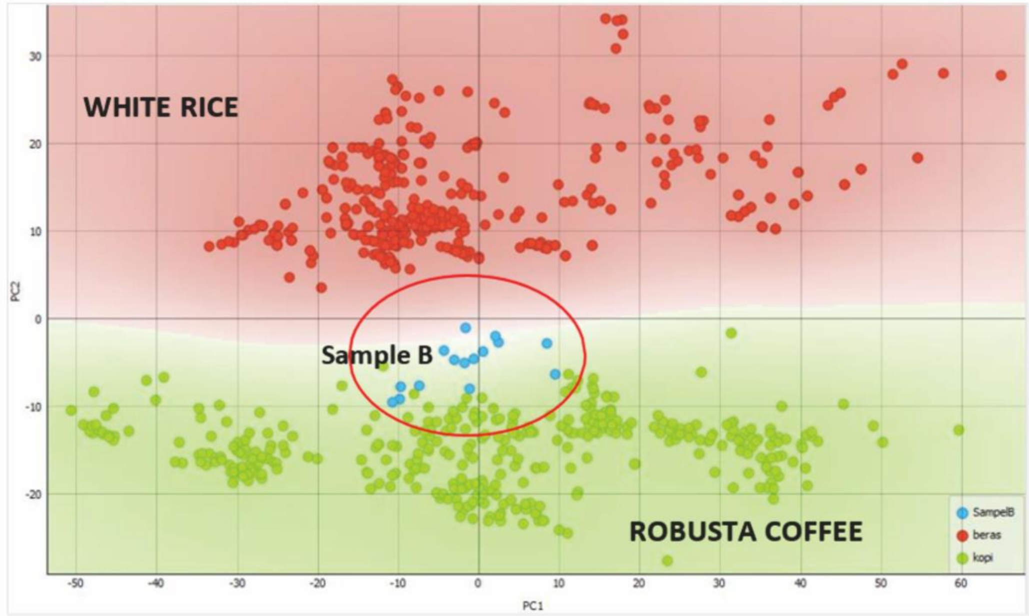

Figure 6. **Scatter Plot of Raw Material Testing with Sample B**

Based on **Figure 6**. The results of the Scatter Plot curve against PC 1 (49%) and PC 2 (24%) represent a cumulative variance of 73%. The combined results of the raw materials of robusta coffee, white rice, sample B, and all plots of sample B are between the quotients of robusta coffee and rice preparations. This indicates the possibility that sample B may contain white rice adulterant but with a small composition of white rice.

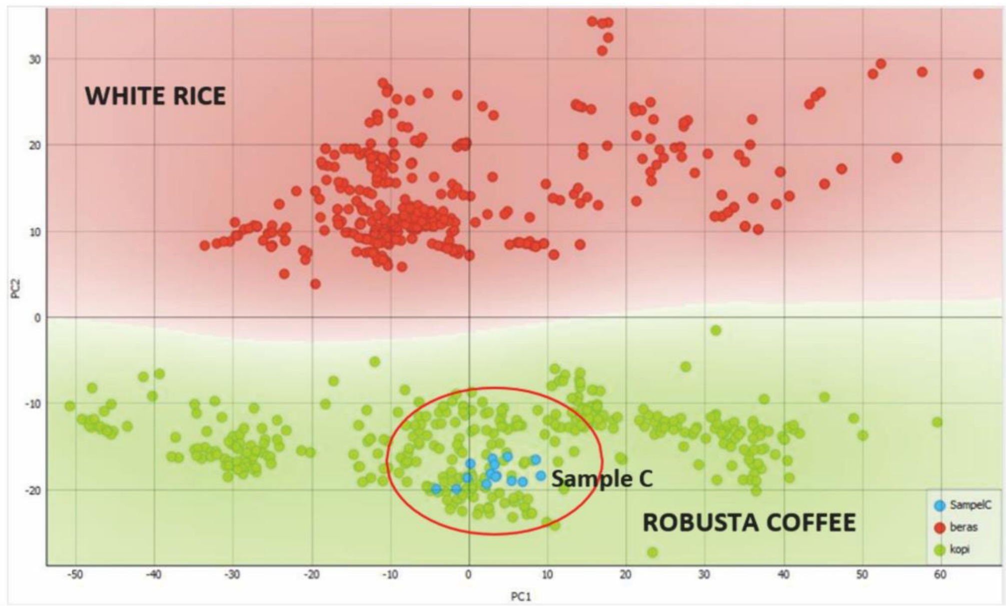

Figure 7. **Scatter Plot of Raw Material Testing with Sample C**

Based on **Figure 7**, the results of the Scatter Plot curve against PC 1 (49%) and PC 2 (25%) represent a cumulative variance of 74%. The combined results of robusta coffee raw materials, white rice and sample C, all sample C plots are in the robusta coffee preparation plot area. This indicates the possibility that sample C contains robusta coffee, and no adulterants were detected.

CONCLUSION

The results of PCA analysis showed that PC1 and PC2 in three Lampung coffee samples, A and C, did not contain adulterants. In contrast, sample B was suspected of containing white rice adulterant. PCA can detect adulterants in coffee that spread in the west of Sumatra.

ACKNOWLEDGMENT

Thanks to LPPM Bhakti Kencana University for providing an internal research grant number 013/14.LPPM/PE.I/UBK/2023 so that this research can be carried out properly.

REFERENCES

Andriansyah, I., Wijaya, H. N. M., & Purwaniati, P. (2021). Analysis of adulteration of Luwak coffee using Fourier Transform Infrared (FTIR) spectroscopy. *Jurnal Kimia Riset*, *6*(1), 26–38.

Coates, J. (2000). Interpretation of infrared spectra, a practical approach. *Encyclopedia of Analytical Chemistry*, *12*, 10815–10837.

Daniel, D., Lopes, F. S., Dos Santos, V. B., & do Lago, C. L. (2018). Detection of coffee adulteration with soybean and corn by capillary electrophoresis-tandem mass spectrometry. *Food Chemistry*, *243*, 305–310.

Fadri, R. A., Sayuti, K., Nazir, N., & Suliansyah, I. (2019). Review of coffee roasting process and formation of acrylamide related to health.

Govindaraju, I., Zhuo, G.-Y., Chakraborty, I., Melanthota, S. K., Mal, S. S., Sarmah, B., Baruah, V. J., Mahato, K. K., & Mazumder, N. (2022). Investigation of structural and physico-chemical properties of rice starch with varied amylose content: A combined microscopy, spectroscopy, and thermal study. *Food Hydrocolloids*, *122*, 107093.

Liu, Y., & Kim, H.-J. (2017). Fourier transform infrared spectroscopy (FT-IR) and simple algorithm analysis for rapid and non-destructive assessment of developmental cotton fibers. *Sensors*, *17*(7), 1469.

Mauricio-Sánchez, R. A., Salazar, R., Luna-Bárcenas, J. G., & Mendoza-Galván, A. (2018). FTIR spectroscopy studies on the spontaneous neutralization of chitosan acetate films by moisture conditioning. *Vibrational Spectroscopy*, *94*, 1–6.

Pauli, E. D., Barbieri, F., Garcia, P. S., Madeira, T. B., Junior, V. R. A., Scarminio, I. S., da Camara, C. A. P., & Nixdorf, S. L. (2014). Detection of ground roasted coffee adulteration with roasted soybean and wheat. *Food Research International*, *61*, 112–119.

Rose, C., & Smith, M. D. (2002). Mathstatica: mathematical statistics with mathematica. *Compstat: Proceedings in Computational Statistics*, 437–442.

Toci, A. T., Farah, A., Pezza, H. R., & Pezza, L. (2016). Coffee adulteration: More than two decades of research. *Critical Reviews in Analytical Chemistry*, *46*(2), 83–92.

Wang, J., Jun, S., Bittenbender, H. C., Gautz, L., & Li, Q. X. (2009). Fourier transform infrared spectroscopy for Kona coffee authentication. *Journal of Food Science*, *74*(5), C385–C391.