

Adulterated Powdered White Pepper Products by Tapioca Flour Sold in Indonesian's Online Market Investigated by Simple FTIR Analytical Method

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Abstract Powdered pepper is very susceptible to be adulterated by flour. Adulteration of online-marketed powdered pepper product by tapioca flour was investigated by employing the FTIR technique. Powdered pepper products sold in five online market of Indonesia were surveyed then the FTIR spectra of some pepper products representing different pepper product categories were examined. By using the linear correlation between the concentration of powdered pepper and the normalized absorbance intensity of FTIR then the relative purity of powdered pepper products was determined. Result showed that out of 15 pepper products, 3 powdered pepper products (sample C, D and M) were confirmed being added by other ingredients, however, they cannot be classified being adulterated since their label says that they contain ingredients other than pepper. One product (sample K) in the category of powdered pepper products having brand and their label says that it is made of ground pepper was suspected being adulterated in which its relative purity was 67.3%. Based on this result, FTIR can be used as a fast and reliable analytical method to detect adulteration of powdered pepper product by tapioca flour.

Keywords: food adulteration, powdered pepper, tapioca flour, detection method, FTIR

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1. Introduction

Globalization opens opportunity to supply food products globally. Despite of the big opportunity of global food trading, new challenges arise that food products are vulnerable to be adulterated along the food trading chains. Food adulteration is defined as an illegal effort made to achieve a greater amount of food for profit. Adulterants can be chemicals that should not exist legally or something that consumer do not want [1]. Recently, food adulteration cases have increased significantly which mostly dominated by economical motifs [2]. Some adulterated food products may cause potential health problems, consumer distrust, and provide illegal profits for delinquent food supplier [3]. Therefore, food adulteration becomes a global threat that should be vanished.

Indonesia is known as the largest pepper-producing and exporting country in the world. It produced 87,029 tons and 87,934 tons in 2017 and 2018, respectively. The most common varieties of pepper produced in Indonesia are

Lampung black pepper and Muntok white pepper [4]. They are quite popular due to their superior aroma and taste qualities. Among them, white pepper shows higher demand for export market [5]. Moreover, the demand of ground white pepper increases significantly in online and offline markets which might be due to its practical use as ready-to-use condiment. Since ground pepper products have a high economical value commodity, therefore, it is potential to be a target of food adulteration [2].

Ground black and white pepper have been reported as subject of food adulteration. Papaya seed and wild pepper berries are commons adulterants of ground black pepper [6,7]. Moreover, low price material such as rice powder has also been reported as adulterant of white pepper powder [8]. Starch has also been identified as adulterant of ground pepper products [9,10]. Lima, Batista [11] reported that cassava starch is the most common adulterant of powdered pepper products. This is due to it has low price and neutral sensory parameters i.e., colour, smell, and flavour, thus, it blends well with pepper powder. In the case of powdered pepper products sold in the Indonesian online market, there are no reports on the use of cassava

flour as adulterant yet. Therefore, it is necessary to investigate the possibility on the use of cassava flour as adulterant of ground pepper products sold in the Indonesian online market.

A common technique that can be used to detect food adulteration is Fourier Transform Infra-red spectroscopy (FTIR) method. FTIR analysis requires only a small amount of sample, no sample preparation is needed, it doesn't use hazardous reagents. Moreover, FTIR analysis is also quite rapid and costless [12]. In the case of adulteration of pepper products, it has been used to detect the presence of husk, chili, and papaya seed powder in black pepper [3,8,11]. Moreover, the data of FTIR analysis can be processed by many statistical tools such as multivariate data or partial least square analysis to predict the level of adulteration [13]. The use of simple regression analysis in prediction of ground pepper purity is helpful for ground pepper users to decide the status of the product rapidly.

This study aims to investigate the presence of cassava flour as adulterant in ground white pepper products sold in the Indonesian online market by using simple FTIR analytical method.

2. Material and Methods

2.1. Materials

White peppercorn and tapioca flour were obtained from local market in Subang, West Java, Indonesia. Some selected products of powdered white pepper were purchased from Tokopedia online market.

2.2. Market Survey of Powdered White Pepper Products

A survey was conducted to determine the number of powdered white pepper product sold in the Indonesians most popular online market in 2019 [14] which are Tokopedia, Shopee, Lazada, Blibli and Jdid. The region of survey was limited to West Java Province. Fifteen (15) powdered pepper products were selected from four (4) categories of powdered pepper products, as seen in Table 1.

Table 1. The studied pepper products from Tokopedia online market

Category	Code
Powdered pepper products having brand and their label says that it contains ingredients other than pepper	M
	D
	C
	G
Powdered pepper products having brand and their label says that it is made of 100% ground pepper	L
	J
	I
	H
	A
Powdered pepper products having brand and their label says that it is made of ground pepper	K
	F
	E
	B
Powdered pepper products without brand and composition	N (No brand packaged in bottle)
	O (No brand packaged in plastic sheet)

2.3. Preparation of Standard of Powdered White Pepper

Standard of powdered white pepper was prepared according to Lohumi, Lee [10] with some modifications. White peppercorn was powdered then it was weighed and mixed with tapioca flour to reach certain percentages (100%, 99%, 98%, 97%, 96%, 95%, 92.5%, 90%, and 85%).

2.4. FTIR Analysis and Data Processing

FTIR *Spectrometer* ALPHA II (Bruker instrument, Billerica, MA-USA) was employed to assess the FTIR spectra of all samples. Reading was taken three times for each sample. Data of FTIR spectra were processed according to Goodacre, Timmins [15]. All data were normalized by using Origin Pro Software 2016. The height of a peak was measure from the peak baseline A standard curve was built by correlating the normalized absorbance intensity of selected peaks with the powdered pepper concentration. The relative purity of powdered pepper sample was calculated based on the simple linear regression equation of the standard curve.

3. Results and Discussion

3.1. Powdered White Pepper Products in Indonesians the Most Popular Online Market

Table 2 reports the number of powdered white pepper products offered in the most popular online markets in Indonesia. It shows that Tokopedia is the most used online market to sell the powdered white pepper products. The percentage of powdered white pepper products can be found from this market reaches 53% of the total online market. According to Cuponation.co.id [14], Tokopedia is also the most popular online market of Indonesia in 2019. Table 2 also reveals that jd.id gains the lowest number of sellers of powdered white pepper product seller. Result of this survey was taken as a basis to study the powdered white pepper products sold in Tokopedia as samples of this study.

Table 2. Powdered pepper products in online market of Indonesia*

Popular online market in Indonesia	Number of powdered pepper products	Percentage [%]
Tokopedia	7,028	53
Shopee	1,000	8
Lazada	4,605	35
Blibli	628	5
Jdid	20	0
Total	13,281	100

3.2. FTIR Spectra of Standard of Ground White Pepper and Tapioca Flour and Selection of Characteristic Peaks of Powdered Pepper

The FTIR spectra of powdered white pepper standard at some concentrations including 100%, 92.5 % and, 85%

and tapioca flour are presented in Figure 1. It can be seen that the number of peaks appear on the FTIR spectra of powdered white pepper is higher than those of tapioca flour. The peaks are located at wavenumber of 804, 831, 846, 848, 928, 944, 1134, 1193, 1251, 1350, 1366, 1434, 1446, 1463, 1492, 1512, 1584, 1613 and 1633 cm^{-1} (Figure 1). In this study, piperin which is the major active compound of pepper was selected to determine the quality of pepper product. Five functional groups of piperin including C-N aliphatic amines, C-O stretch ethers, C-N stretch aromatic amines, C-C stretch in ring aromatics, and C=C stretch alkenes [16,17] (Figure 2) appeared as peaks at wavenumber of 1134, 1193, 1251, 1492 and 1633 cm^{-1} , respectively (Figure 1). Wilde, Haughey [18] reported that these peaks are the finger print in pepper identification. Therefore, these peaks were used as identity key to differentiate the peaks come from the functional group of

starch. The correlation between the intensity of these peaks with the ratio of pepper and cassava flour was further analysed to determine the purity of the pepper products.

Table 3 summarized the linear correlation between the concentration of powdered pepper as X-axis in (w/w) % and the normalized absorbance intensity of FTIR as Y-axis in arbitrary unit. The correlation was selected from the peaks at some wavenumbers which are the fingerprint of functional group of piperin. Result shows that the concentration of powdered pepper is highly correlated with the normalized absorbance intensity at all selected wavenumbers exhibited as indicated by the correlation coefficient (R^2) were greater than 0.95. FTIR technique with high correlation coefficient is recommended in determining the quantify of adulterant [18,20]. This result implies the selected wavenumbers can be used in determination the quality of the pepper.

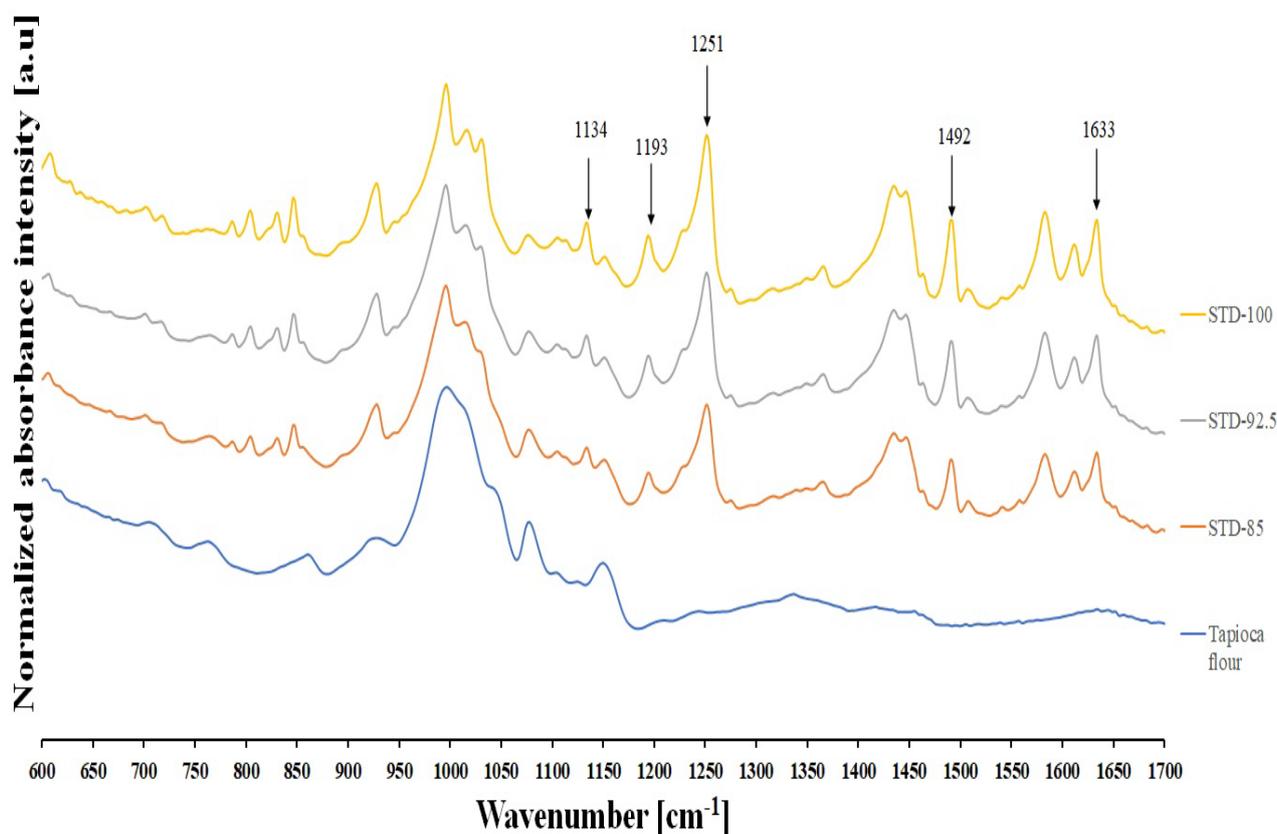


Figure 1. FTIR spectra of standard ground pepper 100% (STD-100), 92.5% (STD-92.5), 85% (STD-85) and tapioca flour

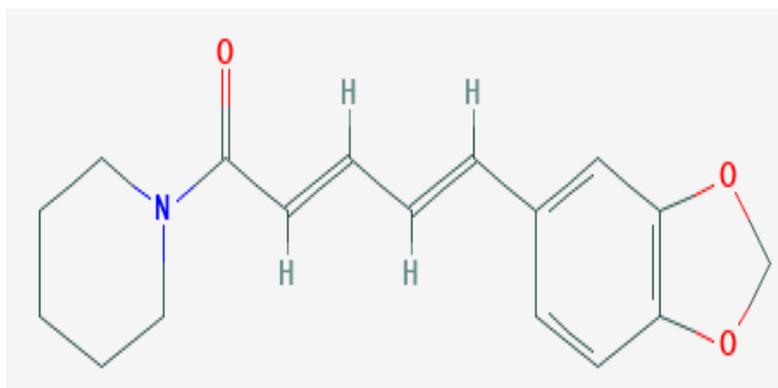


Figure 2. Chemical structure of piperin [19]

Table 3. Linear correlation between concentration of powdered pepper (X) and normalized absorbance intensity (Y) of FTIR spectra at certain wavenumber

Wavenumber [cm ⁻¹]	Linear regression equation	Regression correlation coefficient (R ²)
1134	$y = 0.5365x - 38.088$	0.9688
1193	$y = 0.4488x - 26.278$	0.9902
1251	$y = 1.5434x - 93.881$	0.9673
1492	$y = 0.7635x - 45.1$	0.9797
1633	$y = 0.7812x - 46.591$	0.9783

3.3. FTIR Spectra of Powdered Pepper Products

The FTIR spectra of powdered pepper products in different categories are presented in Figure 3, Figure 4, Figure 5, and Figure 6. Figure 3 showed that the FTIR spectra of sample C, D and M exhibits weakly three out of five characteristic peaks of piperine which are peaks at wavenumber of 1251, 1492 and 1633 cm⁻¹. This result suggested that the piperine content in these samples is quite low. Therefore, it is consistent with their label that says it contains ingredients other than pepper. The C, D and M products contain green bean flour, mix of corn and rice flour, and soy bean flour, respectively.

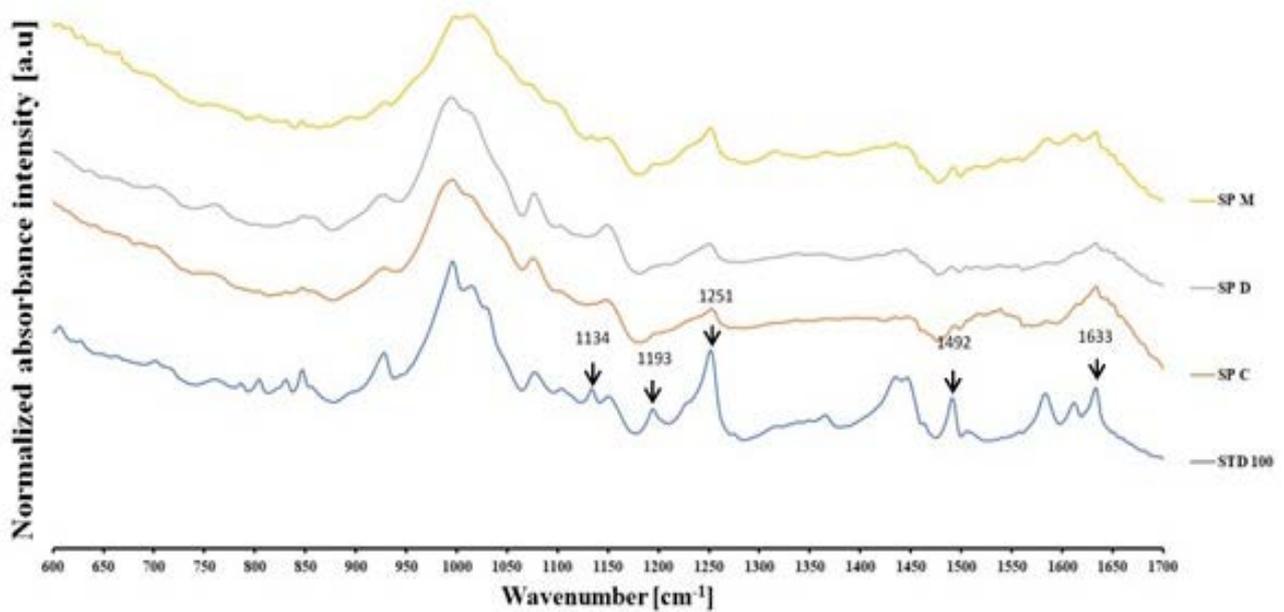


Figure 3. FTIR spectra of powdered pepper products having brand and their label says that it contains ingredients other than pepper (M, D, and C), and standard ground pepper (STD-100)

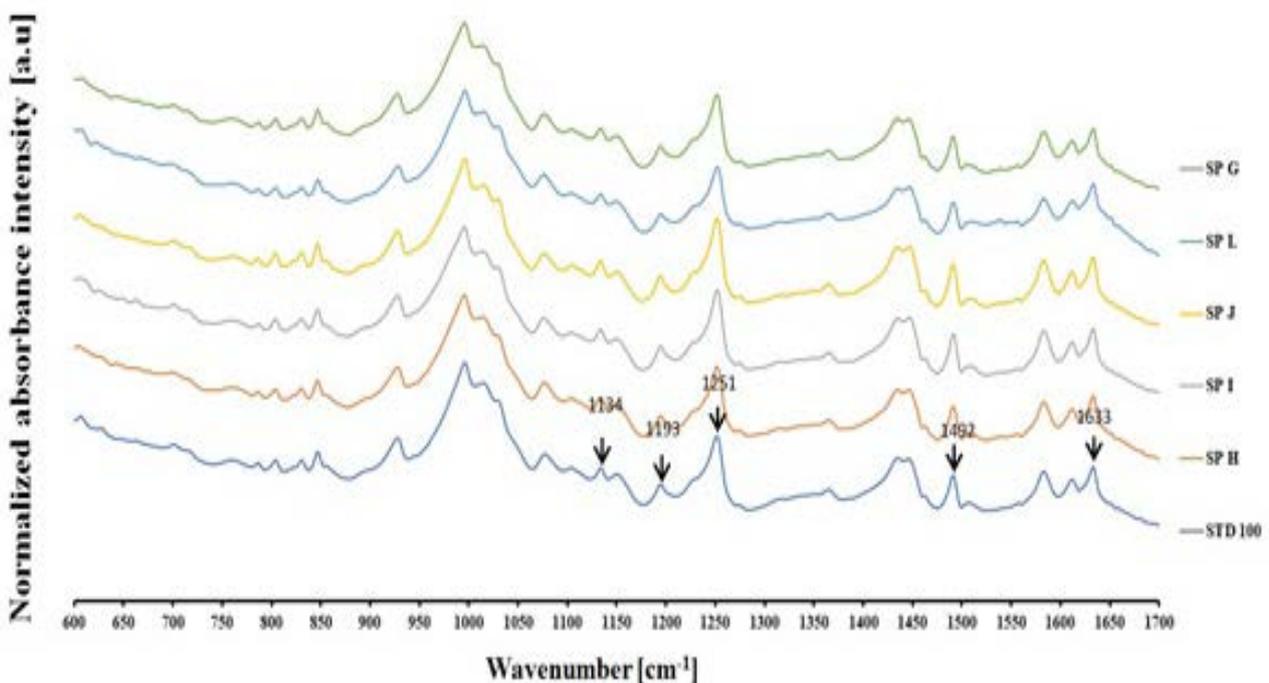


Figure 4. FTIR spectra of powdered pepper products having brand and their label says that it is made of 100% ground pepper (G, L, J, I, and H), and standard ground pepper (STD-100)

The FTIR spectra of all samples (H, I, J, L, and G) in Figure 4 exhibited the five characteristic peaks of piperine with intensity relatively similar to the standard. It indicated that all pepper products under this category are relatively pure as their label says that it is made of 100% ground pepper. Therefore, it can be concluded that these products are free from adulteration.

The FTIR spectra of pepper products in the category of

having brand and their label says that it is made of ground pepper are presented in Figure 5. Among these FTIR spectra, the FTIR spectra of sample K exhibited the lowest intensity of five characteristic peaks of piperine. Based on this result, it can be indicated that sample K contains ingredients other than ground pepper. In other word that since the label of products says it is made of ground pepper, therefore, the sample K might be adulterated by foreign ingredients.

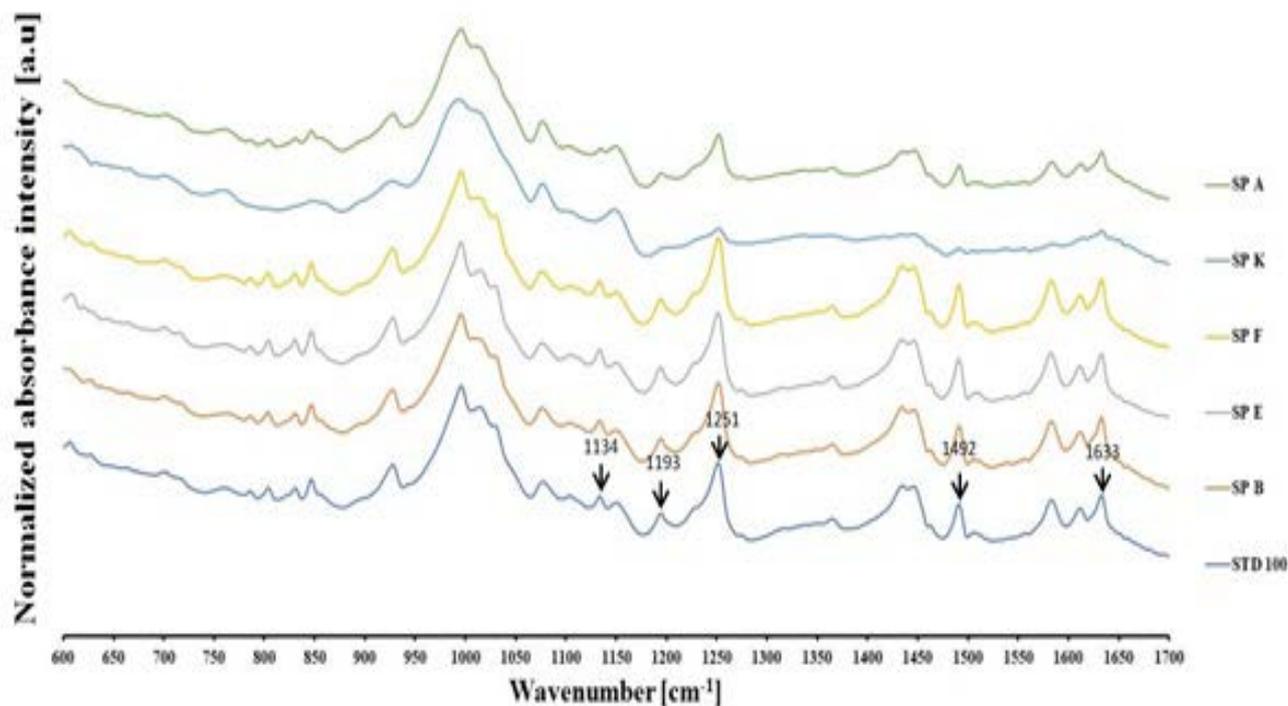


Figure 5. FTIR spectra of powdered pepper products having brand and their label says that it is made of ground pepper (A, K, F, E, and B), and standard ground pepper (STD-100)

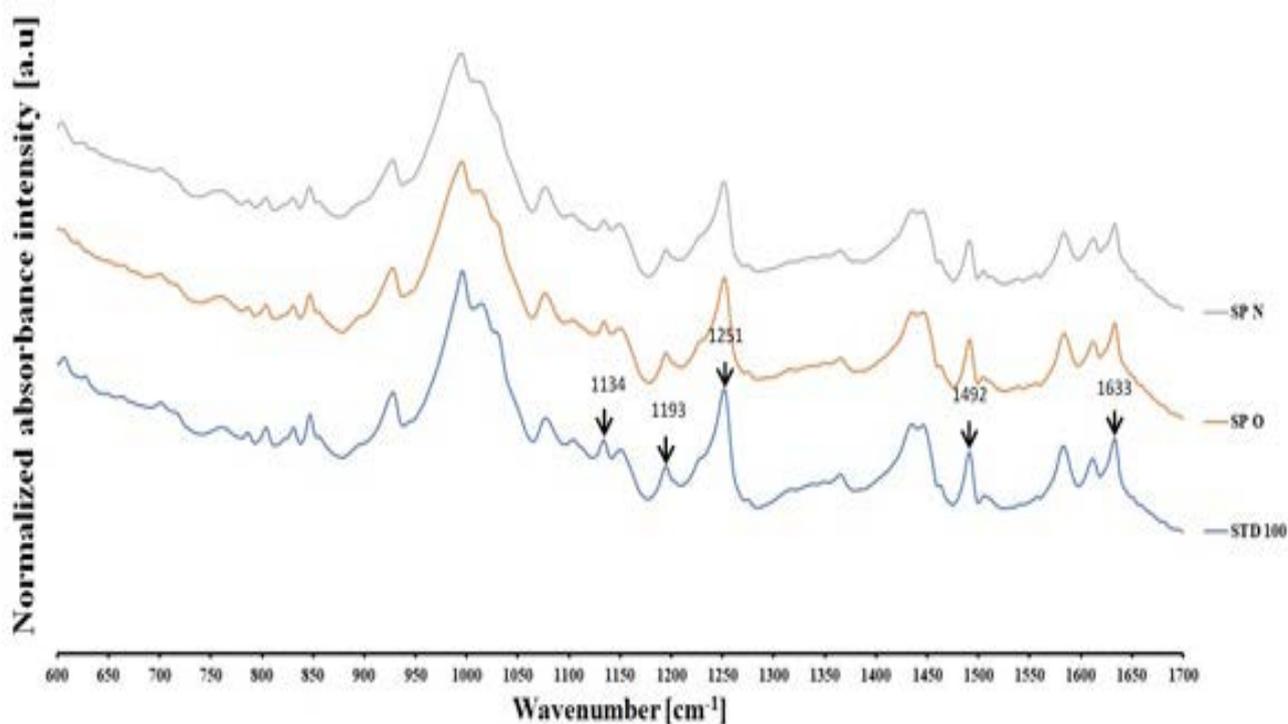


Figure 6. FTIR spectra of powdered pepper products without brand and composition (no brand packaged in bottle (N), and no brand packaged in plastic sheet (O)), and standard ground pepper (STD-100)

Figure 6 presents the FTIR spectra of pepper products under category without brand and composition (sample O and N). It can be seen that all spectra exhibit the five characteristic peaks of piperine with intensity quite similar to the standard. This result suggested that adulteration was not observed in the pepper products of this category. The result also implies that even though the pepper product does not have brand or label, it doesn't mean that the quality of the product is low. A fast and reliable analytical method such as FTIR is required to assure the quality of pepper product sold in the online market.

3.4. Relative Purity of Powdered Pepper Products from Tokopedia Online Market

Table 4 summarized the quality of some pepper products sold in Tokopedia online market determined by FTIR technique. It's should be noted that the quality of the pepper products was calculated based on the intensity of the five characteristic peaks of piperine in the FTIR spectra of sample and standard. In this study, the standard was prepared from ground white peppercorn in which the

piperine content is unknown. Therefore, the purity of sample is defined as relative purity to the powdered pepper standard used in this study.

In the category of powdered pepper products having brand and their label says that it contains ingredients other than pepper, the pepper product of D showed the lowest relative purity of 69.1%, meanwhile the highest was the pepper product of M with relative purity of 71.4%. The powdered pepper products having brand and their label says that it is made of 100% ground pepper exhibited the highest relative purity compared to the pepper products from other categories. The product of J reached relative purity of 89.8, while the product of L showed relative purity of 82.3%. The pepper product of K showed relative purity of 67.3%. This product was suspected being adulterated since its label says that it is made of ground pepper. In the category of powdered pepper products without brand and composition, the pepper product of N and O showed relatively high purity of 79.2 and 81.6%, respectively. According to Kar, Tudu [21] adulterant found in pepper product can reach up to 30% (w/w).

Table 4. Relative purity of powdered pepper products from Tokopedia online market from certain categories calculated based on FTIR data from some selected wavenumbers

Category	Code	Relative purity based on some selected wavenumber					
		1134	1193	1251	1492	1630	Avg± stdev*
Powdered pepper products having brand and their label says that it contains ingredients other than pepper	M	74.4	70.4	71.3	68.8	72.0	71.4±2.0
	D	71.8	65.9	67.3	64.0	65.6	66.9±3.0
	C	72.1	66.6	67.5	69.0	70.1	69.1±2.1
Powdered pepper products having brand and their label says that it is made of 100% ground pepper	G	83.3	84.6	86.3	83.7	85.2	84.6±1.2
	L	81.9	82.0	82.4	82.3	82.9	82.3±0.4
	J	88.3	89.4	90.9	89.9	90.8	89.8±1.1
	I	85.2	88.3	88.7	88.4	88.7	87.8±1.5
	H	83.2	83.8	85.4	83.8	85.0	84.2±0.9
Powdered pepper products having brand and their label says that it is made of ground pepper	A	76.7	75.5	76.5	74.0	75.4	75.6±1.1
	K	73.1	66.6	67.4	63.7	65.5	67.3±3.6
	F	87.1	88.5	90.3	89.4	90.0	89.1±1.3
	E	89.1	89.2	89.2	87.9	88.3	88.7±0.6
Powdered pepper products without brand and composition	B	85.4	85.5	87.9	87.2	88.3	86.9±1.3
	N	77.5	79.9	80.9	78.0	79.8	79.2±1.4
	O	79.3	82.4	83.4	81.5	81.7	81.6±1.5

*average ± standard deviation.

4. Conclusions

Tokopedia was the biggest online market of Indonesia for powdered pepper product. The characteristic peaks of piperine appeared at wavenumber of 1134, 1193, 1251, 1492 and 1633 cm^{-1} can be utilized in determining the purity of powdered pepper product. Based on the linear correlation between the concentration of powdered pepper and the normalized absorbance intensity of FTIR, it can be concluded that the pepper product of K was suspected being adulterated with relative purity of 67.3%. The FTIR method can be employed as a fast and reliable tool to determine the quality of pepper product sold in the online market.

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Authors' Contributions

Contributions of each author are listed below:

Achmat Sarifudin: funding acquisition, methodology, validation, writing and editing.

Enny Sholichah: methodology, validation, review and editing.

Woro Setiaboma: methodology, data curation.
 Riyanti Ekafitri: supervision, review and editing.
 Nok Afifah: project administration, review and editing.
 Lia Ratnawati: data curation
 Eko Ari Pudiyanto: data curation, writing and editing.
 Nana Sutisna Achyadi: supervision.

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