Detection of Lard on Face Mask Using a Combination of FTIR Spectroscopy and Chemometric Methods

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Abstract: Halal cosmetic products cover all aspects of the production process, including the starting raw materials, handling, processing, storage, distribution, transportation, and delivery to consumers. For this reason, detection of lard on the facemask products is very important to ensure the halalness of the cosmetic products used. The purpose of this study was to analyze the lard on the face mask samples containing olive oil which the products did not have a permit from The Indonesian Drug and Food Control (BPOM) by using Fourier Transform Infrared (FTIR) Spectroscopy combined with chemometric. The code of samples is LTL, QN, NR, MDG, and HCN. The control of the research is lard and olive oil. The data from the FTIR spectrum is combined with a Principal Component Analysis (PCA) analysis of chemometrics. The combination is quite effective and accurate for analyzing the mixture of oils in face mask samples. The MDG sample shows the presence of the C=C cis functional group in the wave region of 1664.74 cm-1. On the wavenumber area of 1546.17 cm-1, it indicates the presence of a C=C aromatic functional group. The wavenumber region on 1065.70 cm-1 indicates the presence of a C-O functional group (ester, CA). Based on the pattern of the spectrum related to the wavenumber area that appears in lard, the MDG sample is suspected to contain lard. By the PCA chemometric graph, the MDG and lard samples are located in the same quadrant. The research shows that the MDG sample contains lard that this not written on the packaging label.

Keywords: FTIR, PCA, cosmetics, halal, lard, olive.

1. Introduction

From the Muslim perspective, it is important to know the raw materials, ingredients, and the making process of the raw materials or the final product of cosmetics. Accordance to Islamic law, Muslims are only allowed to consume and use halal products, then they avoid haram products [1].

This has been stated in Surah al-Baqarah verse 168 [2]:

ٰٓأَيُّهَا ٱلنَّاسُ كُلُوا۟ مِمَّا فِى ٱلْأَرْضِ حَلَٰلًا طَيِّبًا وَلَا تَتَّبِعُوا۟ خُطُوَٰتِ ٱلشَّيْطَٰنِ ۚ إِنَّهُۥ لَكُمْ عَدُوٌّ مُّبِينٌ

Translation:
O humanity! Eat from what is lawful and good on the earth and do not follow Satan's footsteps. He is truly your sworn enemy.

The development of the halal lifestyle has occurred in various parts of the world, especially in Muslim-populated countries. The halal concept is now appreciated because it is considered to be a healthier and cleaner product based on facts and research. The application of a halal lifestyle requires caution because partially cosmetics on the market are not yet labeled. Based on Islamic law, not only halal but also tayyib or good and safe. On Indonesian Ulama Council (MUI) regulation No. 26 of 2013, it is stated that the use of cosmetics for decorative purposes is legal by the condition that the materials used are halal and holy. It is intended for purposes that are permitted by sharia and do not harm others.

Most of the cosmetics and other personal care products are made by non-Muslim manufacturers and they come from non-Muslim countries which can lead to differences of opinion about the halalness of the ingredients. Many cosmetics contain alcohol as a humectant, emollient, or cleansing agent that carries ingredients into the skin. Similarly, some fatty acids and gelatin used in products such as moisturizers, shampoos, face masks, and lipsticks come from pigs. Muslim scientists are concerned that many international brands use enzymes extracted from pork or alcohol. For Muslim customers, concerns about the method of making cosmetics are one of the reasons for looking for halal cosmetic products [3].

Facial care products that are often used are face masks to increase the firmness of skin tone. The ingredients in the product are expected to treat skin, provide moisture, stimulate new skin cells, remove dirt and horn cells that are attached to the skin, normalize skin from acne disorders, remove dark spots and excess fat on the skin, prevent and reduce wrinkles, and improve blood circulation. Face masks containing olive oil have many benefits because this fruit is rich in vitamin E. To get rid of acne scars, olive oil needs a long time but it is much safer than chemical-based products on the market [4].

Pure oil and blended oil are difficult to distinguish. It becomes a challenge to detect genuine oil from pig contaminants that becomes the concern of several researchers today. The FTIR method is an identification method that is fast, simple, easy, and relatively inexpensive. Even direct sample tests can be carried out without going through the difficult chemistry preparation stage [5]. The characterization analysis is quite fast, has good inaccuracy, and is relatively sensitive. In the FTIR analysis procedure, the sample is exposed to infrared radiation. The radiation has an impact on the atomic vibrations of a molecule in the sample resulting in the absorption and/or transmission of certain energies. This makes FTIR useful for determining the specific molecular vibrations contained in the sample [6].

An FTIR spectrophotometer has been developed to detect and characterize edible oils and lard. IR spectra were recorded and bands originating from lard caused by vibrations in the fingerprint region allowed to make groupings of edible oil and lard [7]. Furthermore, the FTIR spectra of lard and beef oil are basically similar to the FTIR spectra of other oils and fats. Basically, oils and fats are composed of triglycerides (fatty acid esters and glycerol) which differ in terms of the type of constituent fatty acids, fatty acid sequences, and degrees of fatty acid saturation. For this reason, identification of lard in animal fat or in other vegetable oils is often difficult. However, due to its ability as a fingerprint technique which means that no two oils or fats have the same number of peaks or intensities, FTIR spectroscopy is a promising technique for the analysis of lard and other fats [6].

Chemometrics is the application of mathematical procedures to process, evaluate and interpret large amounts of data. The combined technique of spectroscopy and chemometrics has been widely used in the development of halal analytical methods [4]. There are several types of chemometrics used in the analysis, which can be grouped into chemometrics related to spectral processing techniques, clustering, and linking between vibrational spectra. The use of either PCA or PLS chemometric techniques is used to reduce the amount of data when there is a correlation between data[4].

Based on the development of the existing FTIR and chemometric spectroscopy methods, this study was directed to the analysis of the presence of pork oil in cosmetic face mask products containing olive oil. The samples are distributed in the online marketplace and are not licensed by the Indonesian Drug and Food Control Agency (BPOM).

2. Methods

2.1 Chemicals and Instrument

Chloroform, aquadest, acetone, face mask samples containing olive oil on the label, FTIR Spectroscopy, vacuum rotary evaporator, olive oil, and lard derivative samples.

2.2 Oil Extraction from Face Mask Samples

A total of 10 grams of the liquid mask sample was added with 1 ml of concentrated HCl and 9 ml of aquadest then it was shaken vigorously. The filtrate was multiple extracted by using chloroform on a separating funnel. The extract was put into a round bottom flask for evaporation by a rotary evaporator at 40o C. The thick extract was put into a vial and chloroform was added to a volume of 25 ml. Then, the obtained oil was analyzed using an FTIR Spectroscopy.

2.3 Extraction of pork oil with the oven method

The lard tissue samples were washed and sliced into small pieces. The sample was put in a beaker and heated in an oven at 75ºC for 6 hours until the fat tissue melted. The liquid fat was separated in a separatory funnel and purified with n-hexane. Then, the filtrate was filtered using filter paper which has been added with sodium sulfate. The results of the filtering become samples of pork oil as the control.

2.4 Functional group analysis using the FTIR Spectroscopy method

Face mask chloroform extract, olive oil, and lard were prepared for mixing with KBr. FTIR Spectroscopy analyzes were made in triplicate at a frequency of 4000-650 cm-1. After each measurement, the plate was cleaned with acetone until no oil sample was left behind, then dried it using a tissue.

2.5 Data Analysis

The spectrum from FTIR spectroscopy is based on the absorption of infrared electromagnetic radiation in the form of transmittance and absorbance spectra data. Spectra that show positive results are indicated when there is C-H absorption in the 3050-2800 cm-1 wave area. The resultant spectra were then processed using a chemometric analysis program by software of MINITAB 16.

3. Result and Discussion

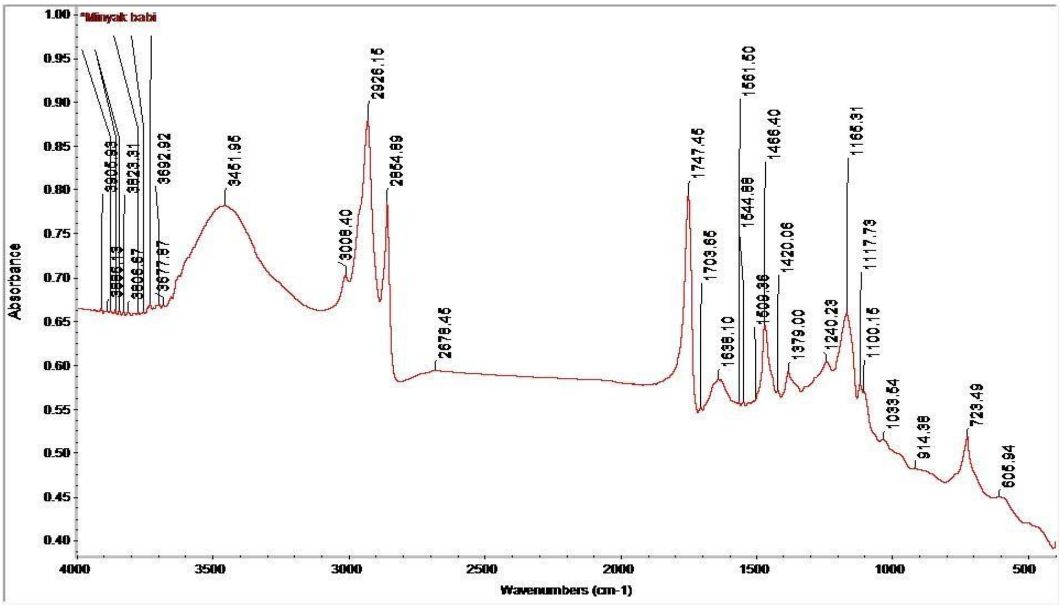

Figure 1. FTIR Spectroscopy Spectrum of Lard

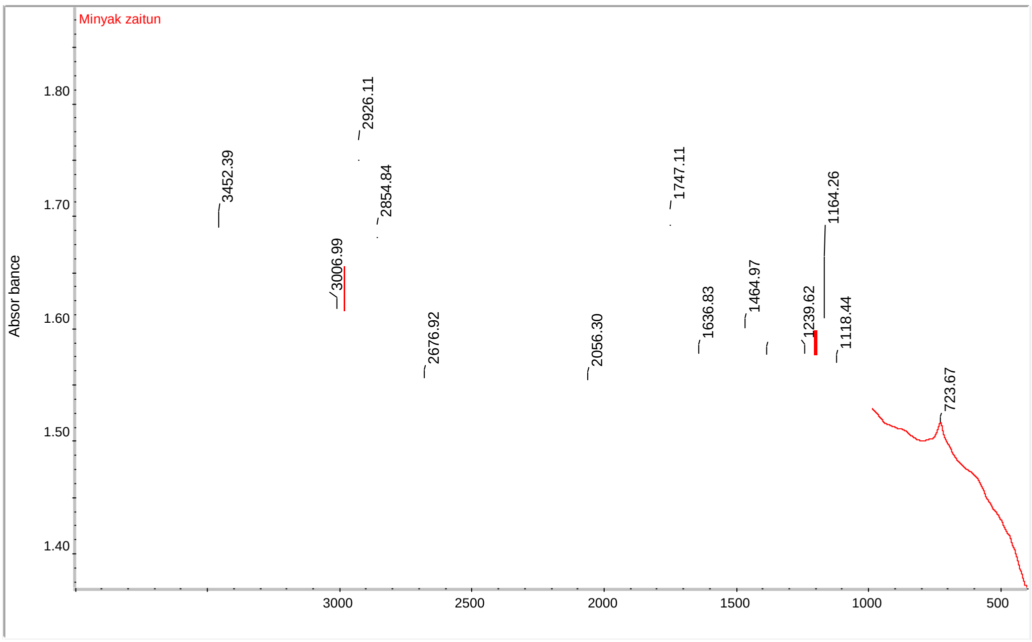

Figure 2. FTIR Spectroscopy Spectrum of Olive Oil

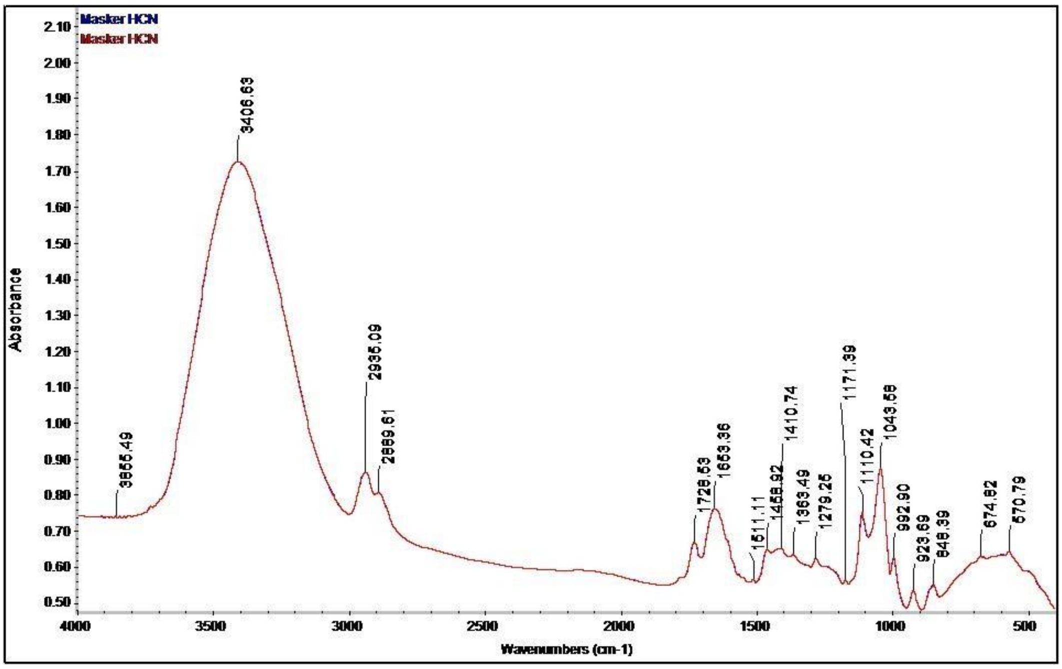

Figure 3. FTIR Spectroscopy Spectrum of HCN Sample

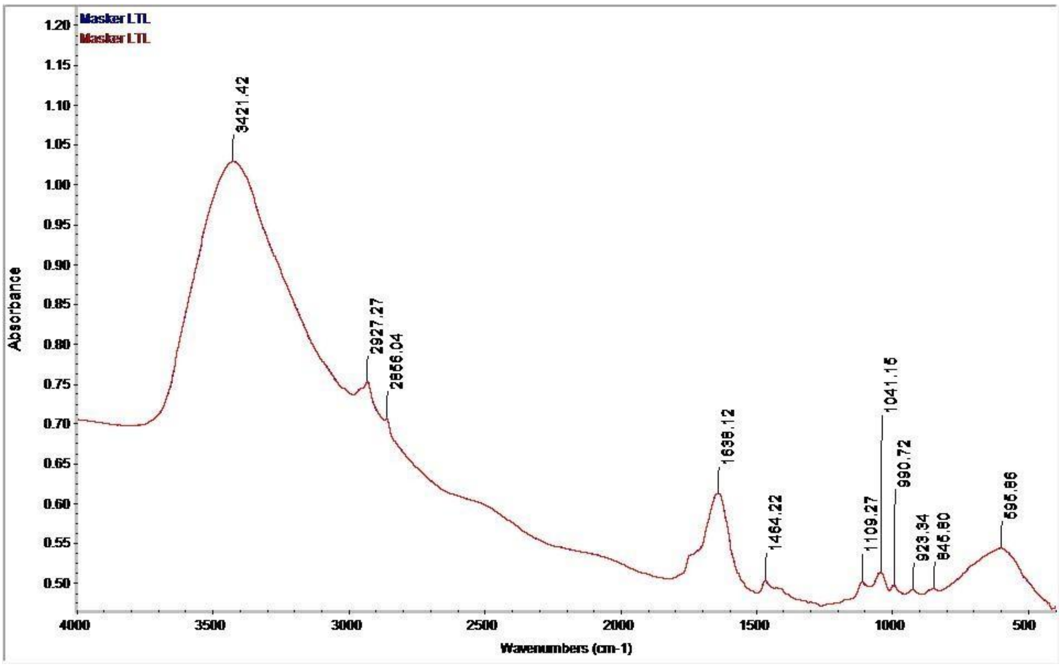

Figure 4. FTIR Spectroscopy Spectrum of LTL Sample

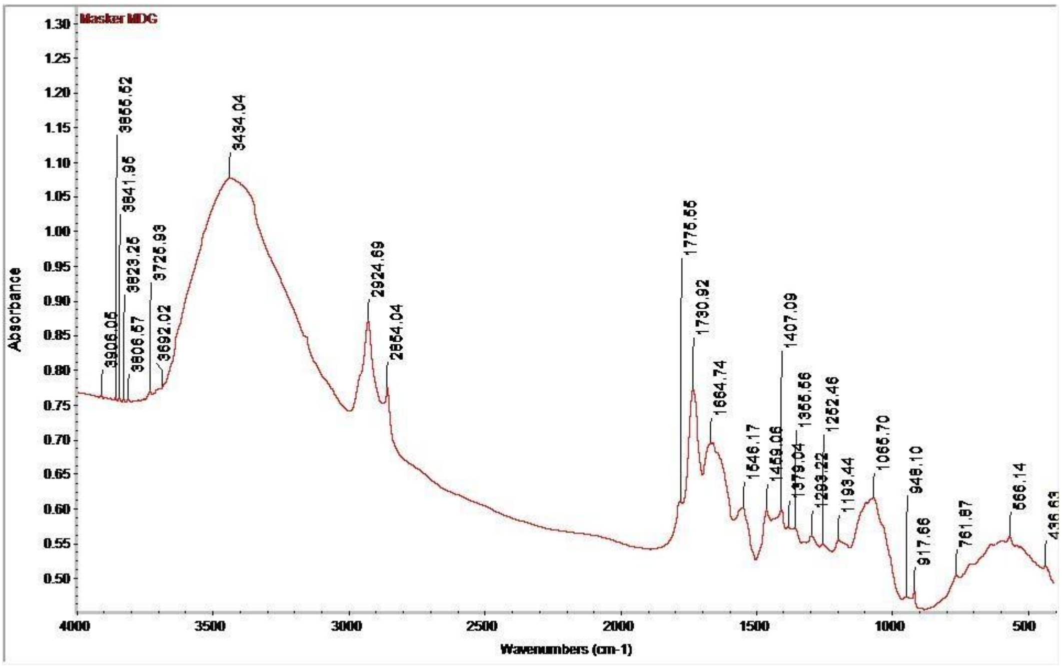

Figure 5. FTIR Spectroscopy Spectrum of MDG Sample

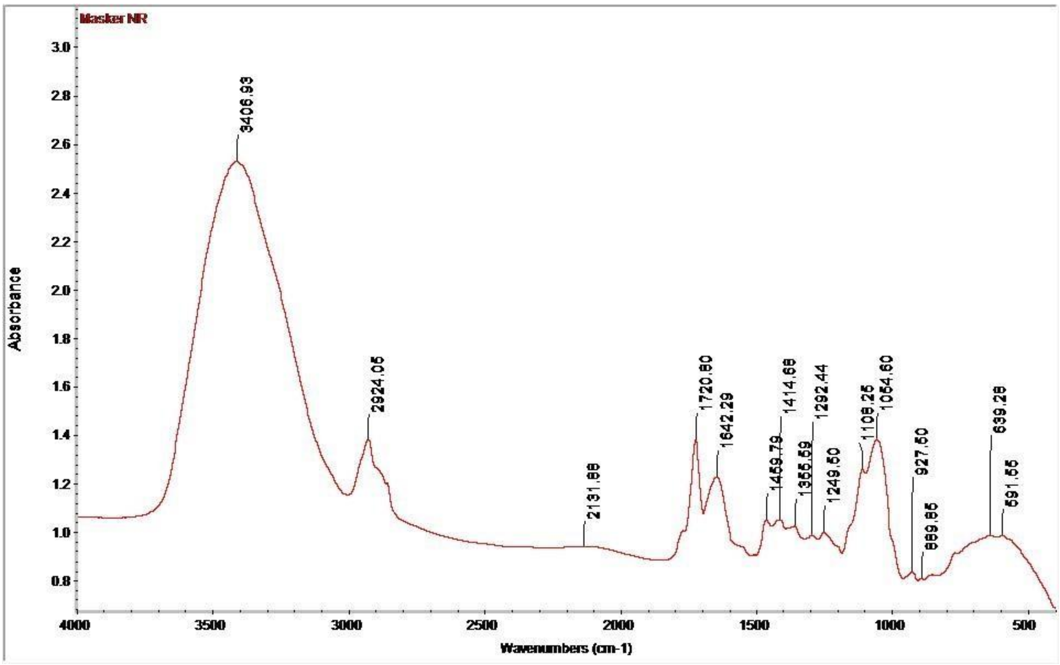

Figure 6. FTIR Spectroscopy Spectrum of NR Sample

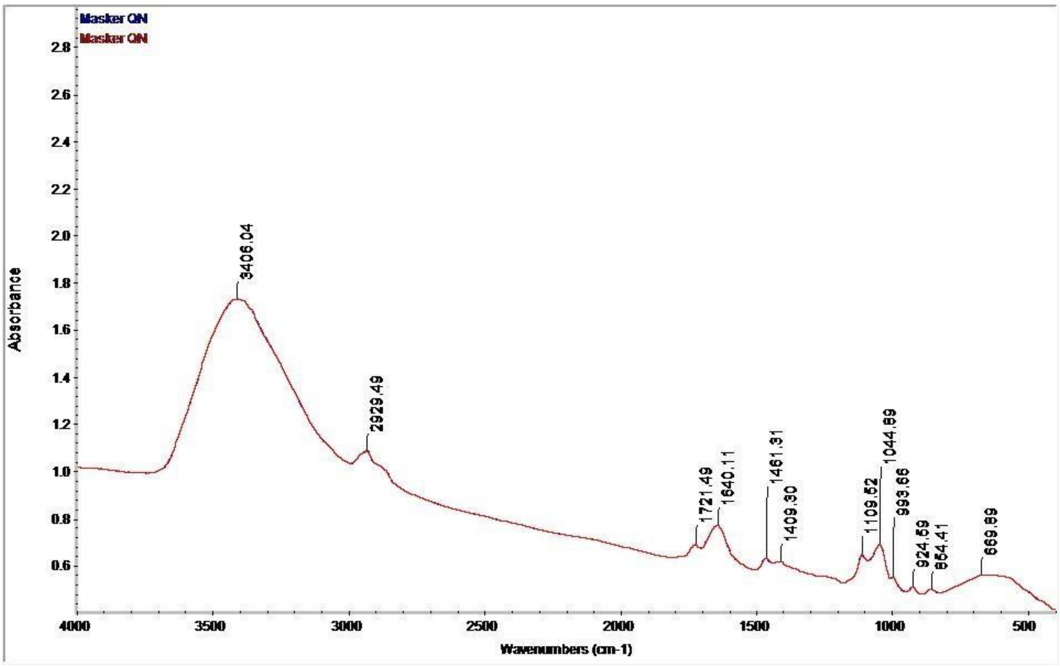

Figure 7. FTIR Spectroscopy Spectrum of QN Sample

Table 1. Data Analysis of Function Groups Related to the Wavenumber

No	Wavenumber (cm^{-1})							Function Group
	Sample Code					Lard	Olive Oil	
	LTL	QN	MDG	NR	HCN			
1	3421,42	3406,04	3434.04	3406.93	3406,63	3451,95	3452,39	O-H (alcohol)
2	-	-	-		-	3008,40	3006,99	=C-H (Cis-)
3	2927,27	2929,46	2924,69	2924.05	2936,63	2926,15	2926,15	C-H (CH_2)
4	2866,04	-	2854,04	2131,88	2889,61	2854,89	2854,84	C-H (CH_2)
5	-	1721,49	1775,55	-	-	1747,45	1747,45	C=O (ester)
6	-	-	1730,92	1720.80	1728,53	1703,65	-	C=O (CA)
7	1638,12	1640,11	1664,74	1642,29	1653,36	1638,10	1636,83	C=C (Cis-)

In this study, extraction of oil was carried out from five samples of face masks containing olive oil. The samples were obtained from an online marketplace that does not have a distribution license from the Indonesian Drug and Food Control Agency (BPOM). In addition, oil was extracted from lard tissue to be used as a positive control. In procedures, olive oil was also used as a comparison. Samples, lard, and olive oil were analyzed using FTIR spectroscopy after being pre-prepared with KBr.

The results of the spectrum analysis of pork and olive oil showed almost the same spectrum pattern because the main components in both oils were triglycerides. The difference can be seen in the high or low absorption in each spectrum pattern. In the pork fat spectrum, there is a peak in the wavenumber region of 1703.65 cm-1 which is the stretching vibration of the carboxylic acid (CA) group of the carbonyl group (C=O) [4].

In the lard spectrum, the peak at wavenumber 1561.5 cm-1 is the absorption of the C=C double bond vibration. This absorption does not appear on the olive oil spectrum because it is only found in animal oils. In the lard spectrum, the peak at 1420.06 cm-1 is the C-H group of cis olefin. That peak indicates the content of unsaturated fats, especially linoleic acid, which contributes to the high absorbance value in the C-H region of the stretching vibration of the cis double bond. In the lard sample, the content of polyunsaturated fatty acids (PUFAs) such as linoleic acid and linolenic acid was much higher than monounsaturated fatty acids [8].

Lard has a bending vibration of CH2 at a wavenumber of 914 cm-1, while olive oil has no pattern in the wavenumber in that area. At the 1033.53 cm-1 wave, it shows the presence of C=O bonds in the ester. It can be concluded that the difference of peak between lard and olive oil is 1700 cm-1; 1561.50 cm-1; 1544.88 cm-1; 1033.54 cm-1; and 914.38 cm-1. The lard spectrum generally shows absorption (C-O) in the wavenumber region of 1000-1300 cm-1, O-H bending vibrations in the 1300-1440 region, carbonyl bonds (C=O) in the 1680-1750 cm-1 region, and C-H bonds in the area of 1000-1300 cm-1 and area between 2853-2962 cm-1 [3]. In another study, it was stated that the lard spectrum of FTIR showed the spectrum had a carbon group (C=O). This is due to the strong bond with sharp intensity in the 1745 cm-1 wavenumber. The presence of absorption at a wavenumber of 1462 cm-1 indicates the bending vibration of the C-H group of methylene (CH2) [9].

The results of the FTIR spectrum of the five face mask samples showed differences in the FTIR spectrum. The LTL face mask sample did not show any similarity in the spectrum pattern in the wavenumber region of 2678.79-2363.84 cm-1. The LTL mask has a relatively higher peak when compared to lard. The sample does not have a wavenumber of 1703.65 cm-1; 1561.50 cm-1; 1420.06 cm-1;1033.54 cm-1; and 914.38 cm-1 which are characteristic of pork fat spectrum. Based on the spectrum profile, the LTL face mask sample did not show any pork oil content.

The QN sample does not show any similarities in the spectrum pattern at wavenumbers 1561.50 cm-1 and 1703.65 cm-1. The sample does not have a spectrum pattern of 1703.65 cm-1 and 1561.50 cm-1 which are characteristic of the lard spectrum. This shows that the QN face mask sample was not detected to contain pork oil.

The MDG sample shows the presence of the C=C cis functional group in the wave region of 1664.74 cm-1. On the wavenumber area of 1546.17 cm-1, it indicates the presence of a C=C aromatic functional group. The wavenumber region on 1065.70 cm-1 indicates the presence of a C-O functional group (ester, CA). Based on the pattern of the spectrum related to the wavenumber area that appears in lard, the MDG sample is suspected to contain lard.

The NR sample has a similar wavenumber in the area of 1703.61 cm-1; 1420.06 cm-1; and 1033.54 cm-1 to the spectrum of lard. However, this sample does not show the aromatic C=C functional group which is characteristic of the lard at a wavenumber of 1561.50 cm-1. Based on this spectrum, the NR face mask samples did not show the presence of pork oil.

The HCN sample has a similar wavenumber in the area of 1703.61 cm-1; 1420.06 cm-1; and 1420.06 cm-1 relating to the lard spectrum, but the sample does not show the C-O functional group which is a characteristic of the lard at wavenumber 1032.54 cm-1. It shows that the HCN does not contain lard on the ingredients.

Some absorbance values from the FTIR spectrum were processed using the PCA method. Eleven selected points are absorbed in the regions at 2922-965 cm-1 because it can be seen that there are significant differences in the absorbance of lard and olive oil in that region. The results of the chemometric by PCA analysis in the form of a score plot can be seen in Figure 8. The figure shows that there are four quadrants that can differentiate standard lard from 0%-100%. Each standard lard from 0%-100% is grouped at different distances from each other. The distance between samples shows the similarity between samples. The farther the distance, the less similarity between the samples. From the figure, it can be seen that the samples with 0% and 100% lard content were separated by different quadrants and were quite far apart. This means that each of the samples has characteristics that can be distinguished from one another.

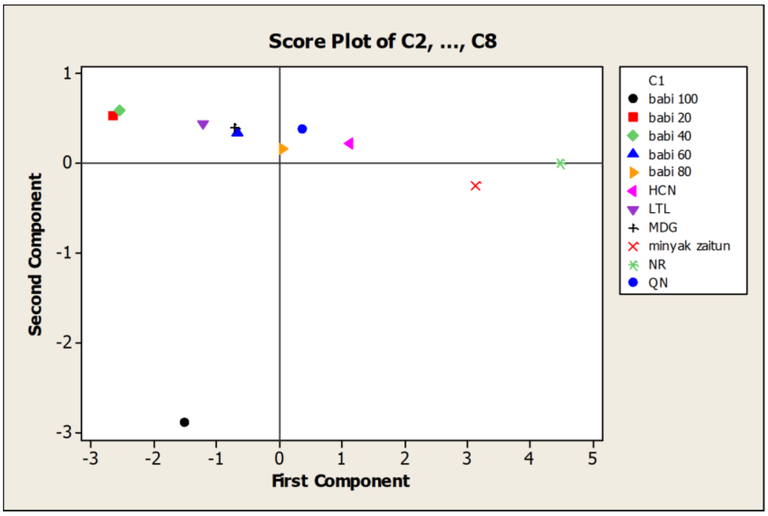

Figure 8. PCA Graph by Chemometric Analysis

Figure 8. shows the relative similarity between the objects of observation. The score plot graph provides the greatest contribution or influence by looking at the distance between the sample points and the lard point. The closer the distance between the sample point and the lard standard, the greater the possibility of a mixture of lard in the sample. On the PCA chemometric graph, the MDG and lard samples are located in the same quadrant. This shows that the MDG sample contains lard which is not written on the packaging label.

4. Conclusion

Based on the research that has been done, a combination of Fourier Transform Infrared (FTIR) Spectroscopy and Principal Component Analysis (PCA) by chemometric methods can qualitatively detect the presence of lard in a face mask sample containing olive oil. Furthermore, the research on the detection of lard from face mask samples by FTIR Spectroscopic and chemometric method shows that the product with the code number MDG contains lard without notice in the composition on the product label.

Conflicting Interest

All authors declare no conflict of interest.

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