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FTIR-PCA analysis as an initial analysis to distinguish the origin of skin and leather

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ABSTRACT

Leather products are parts of daily fashion in Indonesia, such as bags, shoes, jackets, and gloves. Adulteration of raw materials for leather products can occur if there are no labels on these products. Various methods such as PCR, GC-MS, HPLC, and FTIR have been carried out to distinguish the origin of leather products. The FTIR method is known as an easy and inexpensive method to use. The objective of this study was to evaluate the capability of FTIR spectroscopy and Principle Component Analysis (PCA) for lipid identification and initial analysis to distinguish the original materials on leather products. Lipid extracts obtained from the various skin were scanned using an FTIR spectrophotometer at 4000–450 cm^{-1}. It resulted in spectral differences in several wavenumbers (3000-2800 cm^{-1} and 1200-1000 cm^{-1}). The same result is also found in lipid spectra from leather product extraction. The FTIR spectroscopy and PCA can differentiate pigskin and goatskin through specific peaks in infrared spectra. This can be used as an initial analysis on determining the existence of skin adulteration in leather products. This study is prospective to be continued by chemometrics as quantitative analysis.

Keywords: FTIR spectroscopy, goatskin, leather products, pigskin, PCA analysis.

INTRODUCTION

The tanning and leather industry never stops innovating to meet the needs of consumers in line with the development of fashion and automotive. The Indonesian Ministry of Industry explained that there was an increase in the trend of exports of leather goods in 2016. An increase in the trend of footwear exports for daily use was 10.26%, field engineering shoes/industrial use was 9.54%, and goods from leather and artificial leather for personal use by 6.36%. Domestically, the industry growth of leather, leather goods, and footwear increased by 18.78%. An increase in the product information did not accompany these increases. The information for the customer about the authentication of the origin of materials on leather products is limited. Determining the origin of product material is one of the main issues in the industrial sector, not only for producers but also for consumers (Erwanto *et al.*, 2016). The detection of the original material of the products is necessary for consumer protection as well as for various reasons, such as religious reasons. For Muslim and Jewish communities, the use of pork is prohibited by their religion. Recently, leather product manufacturers in some countries choose to use pork skins as a substitute for other skins, because of their low cost and easy access (Aida *et al.*, 2007). The identification of the origin of the skin on the leather products is important for the customer, and it needs to be proven scientifically. Identification of origin material on the product has often been made on food products. Detection of rat meat in beef sausage (Pebriana *et al.*, 2017), porcine contamination in Dendeng (Maryam *et al.*, 2016), and lard adulteration in Rambak crackers (Erwanto *et al.*, 2016) were analyzed by various methods. Fourier-Transform Infrared (FTIR) spectroscopy has been known as one method to identify the origin of material based on the lipid profile. According to Muttaqien *et al*. (2016), this method that was combined with chemometrics, such as PCA, is easy, fast, and inexpensive. Research on identifying the origin of material on the skin has never been studied. This research was aimed to develop the utilization of FTIR spectroscopy combined with PCA as an initial analysis to distinguish skin materials.

MATERIALS AND METHODS

Lipid Extraction

Lipid extraction using the Soxhlet method was performed according to AOAC (2012). Pigskin, goatskin, pigskin leather, and goatskin leather were obtained from the traditional market and leather distributors. 50 g of samples in filter paper were placed into the Soxhlet apparatus (Iwaki SOXH-SET, Indonesia) and added 250 mL of n-hexane as an extracting solvent. The extraction was conducted for 8 h at 70 °C (±50 cycles). Anhydrous sodium sulfate is added into the lipid extract, mixed, filtered, and evaporated until the solvent was completely removed. The resulting lipid fraction was then used for FTIR spectral measurements.

FTIR Spectral Measurements

Extracted lipids were located in attenuated total reflectance (ATR) crystal at 25 **°C**. The spectrum was obtained in the wavenumbers region of 4000-450 cm^{-1} using an FTIR spectrophotometer (Perkin-Elmer, Singapore).

Data Analysis

The spectrum from FTIR spectral measurement results was analyzed descriptively by Principal Component Analysis (PCA) using The Unscrambler X 10.4 (CAMO Software AS).

RESULTS AND DISCUSSION

Lipid Extraction

Raw skin and leather have been extracted by the Soxhlet method and using n-hexane as solvent. N-hexane is suitable for use in the extraction of fat on the skin. It caused n-hexane is non-polar, however fat which is also non-polar, and n-hexane is quickly evaporated because it has a low boiling point of 69 °C (Erwanto *et al.*, 2016). The extraction of fat from all samples produced yellowish and thick oil, but specifically in goatskin fat produces oil that is quickly frozen at room temperature, while others are not.

FTIR Analysis

The FTIR spectra of lipid obtained from skin and leather samples have similar profiles. Figure 1 shows lipid spectra of pigskin, goatskin, pigskin leather, and goatskin leather lipid. Infrared spectra are read at 4000-450 cm^{-1}, which is the middle region. Many molecules have a strong absorbance in the middle infrared region. Many types of samples including liquids, gases, powders, polymers, solids, semisolids, organic, inorganic, biological substances, pure substances, and mixtures can be measured in the middle region

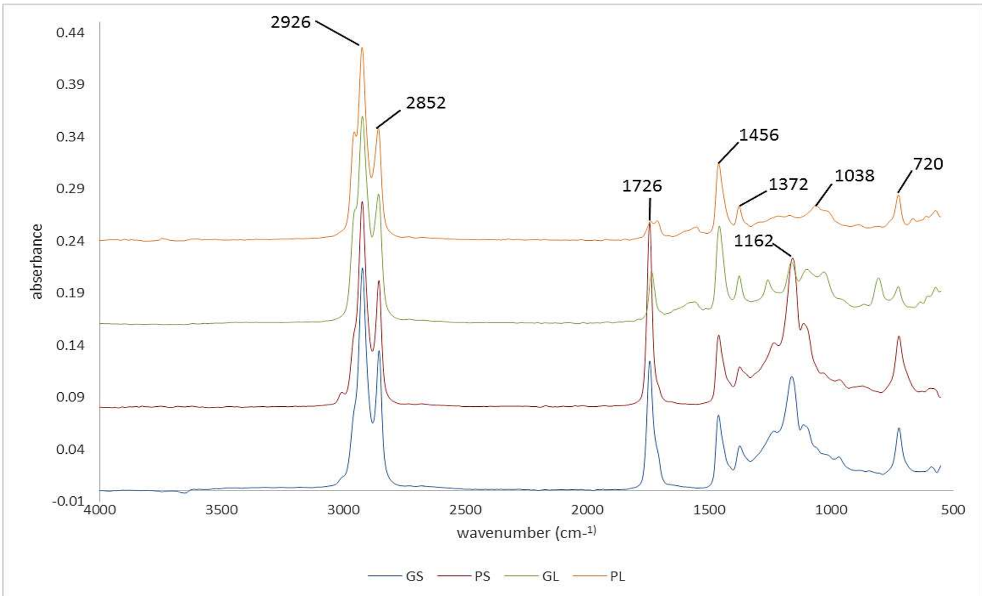

Figure 1. FTIR spectra of skin and leather samples.

Table 1. The wavenumbers of FTIR spectra of skin and leather lipid samples and the corresponding functional groups' vibration.

Wavenumber (cm^{-1})	Type of bending and vibration
3000-2840	C-H stretching
1750-1735	C=O stretching (ester)
1740-1720	C=O stretching
1465-1450	C-H bending
1390-1380	C-H bending
1260-1234	C-O stretching (ester)
1202-1124	C-O stretching
808-716	C-H bending

(Rohman *et al.*, 2017).

The compilation of wavenumbers from each peak in the FTIR spectrum of the skin and leather samples and the related functional group vibrations are shown in Table 1. Basically, functional groups of skin and leather almost similar, but there is a bit of difference in peak intensities at around 1200 and 3000 cm^{-1}. The skin samples at around 1200-1000 cm^{-1} there is a peak while the leather samples are not. It was suspected that due to the existence of natural fat in the skin. Degreasing is a process for decreasing the natural fat in raw skin during tanning (Covington, 2009). Pig and goat lipid samples (skin and leather) also almost similar but at around 3000-2800 cm^{-1} and 1200-100 cm^{-1} there are slightly different peak intensities. Therefore, optimization of FTIR spectra by selecting the wavenumbers region and spectral treatment was carried out to differentiate between pig and goat (Riyanta *et al.*, 2020).

Principal Component Analysis

Principal Component Analysis (PCA) is an analysis that is often used to be applied to find differences in samples that have close similarities based on absorbance values (Riyanta *et al.*, 2020). Figure 2 shows two loading plots from spectra at wavenumber 3000-2800 cm^{-1} (A) and 1200-100 cm^{-1} (B). Based on loading plots, the samples spread in a different area. Loading plot A can separate the sample into two areas, the upper area consists of pigskin leather (PL) and goatskin leather (GL), while the bottom area consists of pigskin (PS) and goatskin (GS), although the distance between each sample is far. Loading plot B shows a better sample distribution by separating the sample into three areas. Pig and goat samples (skin and leather) are in different areas. Even

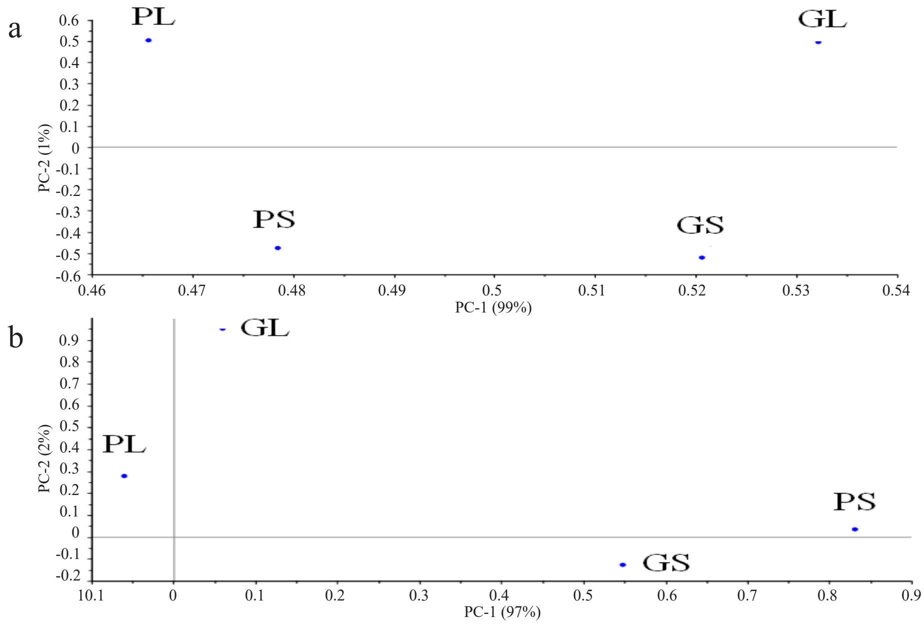

Figure 2. The loading plot of PCA for the classification of pigskin (PS), goatskin (GS), pigskin leather (PL), goatskin leather (GL) at wavenumber 3000-2800 cm^{-1} (a) and 1200-100 cm^{-1} (b).

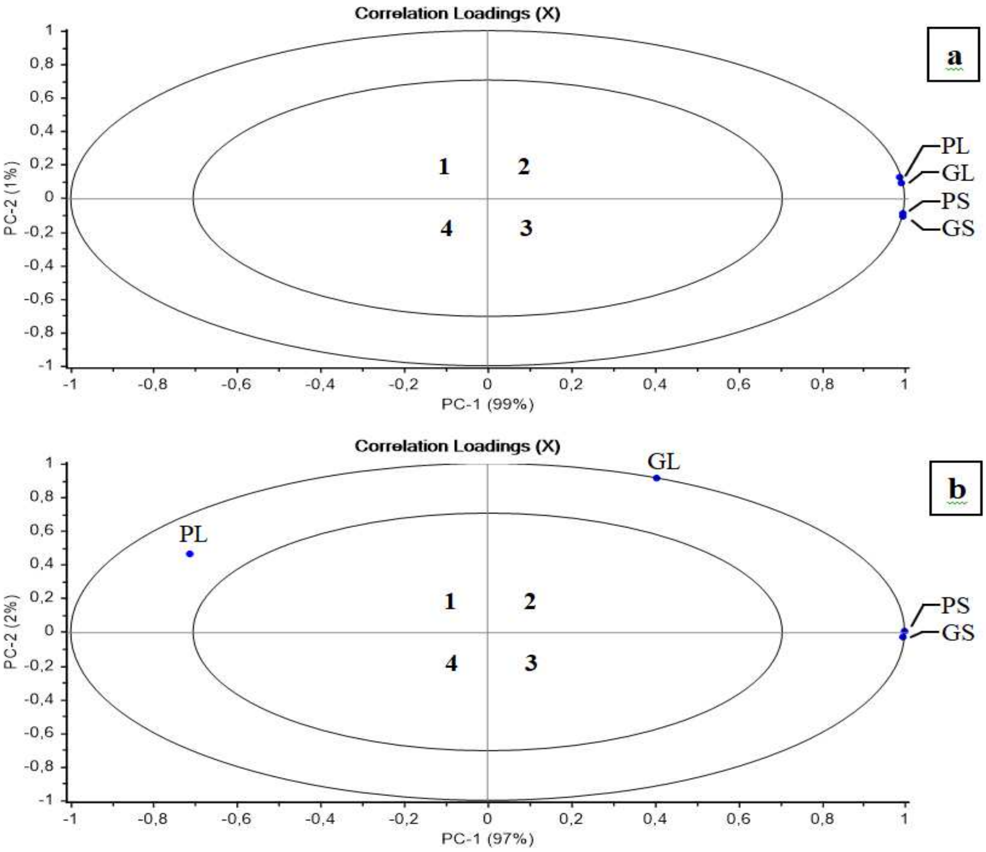

Figure 3. The correlation plot from samples in range 3000-2800 cm^{-1} (a) and 1200-100 cm^{-1} (b).

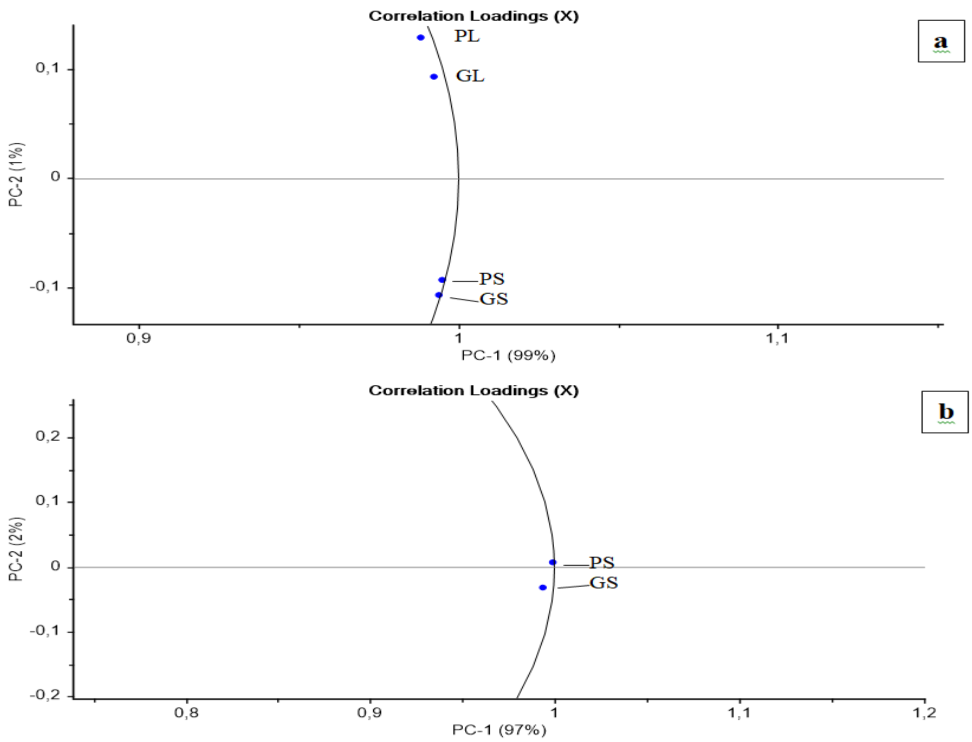

Figure 4. Enlargement of correlation plot (region 2&3) from samples in range 3000-2800 cm^{-1} (a) and 1200-100 cm^{-1} (b).

though PL and GS are in the same area, they are on a long-distance. These states are supported with a correlation plot in Figures 3 and 4. Correlation plot A shows the correlation among the samples at wavenumber 3000-2800 cm^{-1}, while B shows at 1200-100 cm^{-1}. Based on the correlation plot, the wavenumber at 3000-2800 cm^{-1} separated samples closer, than the wavenumber at 1200-100 cm^{-1}. Correlation plot B can well separate pigskin and goatskin leather however pigskin and goatskin show a closer position to each other. Even though, magnification showed these samples (PS and GS) separated with a line between two areas. Classification in the wavenumber range at 1200-100 cm^{-1} corresponds to results Erwanto *et al.* (2016), Muttaqien *et al.* (2016), and Rohman *et al.*, (2017), which can distinguish between lard and other species of fat, such as beef or buffalo fat.

CONCLUSIONS

The use of FTIR Spectroscopy method and analysis by PCA can be applied and developed to initial analysis for distinguishing and classifying the origin skin (pigskin and goatskin) in leather products (pigskin and goatskin leather). Analysis results using PCA from spectra samples in wavenumber at 1200-1000 cm^{-1} showed separated samples better than wavenumber at 3000-2800 cm^{-1}.

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