The 7th International Conference on Science and Applied Science (ICSAS 2022)

Monday, 31 October 2022
Universitas Sebelas Maret, Central Java, Indonesia

Background

The **ICSAS 2022** conference is aimed to bring together scholars, leading researchers and experts from diverse backgrounds and applications areas in Science. Special emphasis is placed on promoting interaction between the science theoretical, experimental, and Education Sciences, engineering so that a high level exchange in new and emerging areas within Mathematics, Chemistry, Physics, and Biology, all areas of sciences and applied mathematics and sciences is achieved.

Topics of Interest

1. Physics
2. Mathematics
3. Chemistry
4. Biology
5. Educational Physics
6. Educational Mathematics
7. Educational Chemistry
8. Educational Biology
9. Natural Science Education
10. Materials Engineering
11. Chemical Engineering
12. Civil Engineering

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Distinguishing of Leather Garment Raw Materials Using FTIR Spectroscopy Coupled to Chemometric Analysis

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Abstract. Leather jacket is the most popular fashion clothes made of garment leather. Garment leather generally derived from cattle, goat, sheep or pig skin. Muslim countries, including Indonesia, prohibit (haram) the products that derived from pig materials. If there are no labels on these products the costumers unable to find out the raw materials in leather products. Several techniques such as HPLC, PCR, GC-MS, electronic nose, and FTIR spectrophotometers have been carried out to distinguish the raw materials. The FTIR method is regarded as being affordable and simple to utilize. This study aims to evaluate the FTIR method coupled to chemometrics to distinguish the raw materials in leather garment. Lipid extracts derived from the various raw skin and leather garment were scanned using an FTIR spectrophotometer at 4000–450 cm^{-1}. There is the differentiation of spectral in two range of wavenumbers (3000-2800 cm^{-1} and 1200-1000 cm^{-1}). The FTIR spectroscopy coupled to chemometrics can distinguish pig skin, sheep skin, pig garment and sheep garment through specific peaks in infrared spectra. This can be used as an initial analysis on determining the existence of skin adulteration in leather garment.

INTRODUCTION

The tanning and leather industries are continuously developing to fulfil customers' requirements in tandem with the evolution of the fashion industries. The Indonesian Ministry of Industry noted that the export trend for leather items increased in 2019. The export trend of footwear for daily use increased by 10.26%, footwear for field engineering/industrial use was up by 9.54 %, and exports of leather and synthetic leather items for personal use increased by 6.3%. On the other hand, the leather, leather products, and footwear business expanded domestically by 18.78% [1]. These business rises did not coincide with an increase in the product information. Limited information is provided to customers on the authentication of the provenance of materials on leather items. Determining the origin of product materials is one of the most important challenges in the industrial sector, both for manufacturers and customers [2]. Identifying the product's original substance is required for consumer protection and other reasons, such as religious ones. For Muslim and Jewish groups, the consumption of pork or daily products containing lard is forbidden.

Recently, leather product makers in certain countries have chosen to utilize pig skins as a substitute for other skins because of their low cost and simple access [3]. The identification of the origin of the skin on leather items is essential to the consumer and must be scientifically demonstrated. It is common practice to identify the origin of the elements in food goods. Various approaches were used to examine the detection of pig in sausage [4], rat meat in beef sausage [5], porcine contamination in Dendeng [6], lard adulteration in Rambak crackers [7], and pig element in leather products [3].

FTIR spectroscopy has been recognized as a technique for determining the provenance of a substance based on its lipid profile. It is one of the analytical techniques used to determine the original material of its products due to its fingerprinting capacity. According Muttaqien et al. [8], this approach that combines chemometrics with Partial Least Square (PLS) and Principal Component Analysis (PCA) is simple, economical, and quick. This study sought to develop the use of FTIR spectroscopy in conjunction with chemometrics analysis as a preliminary analysis for distinguishing materials of the skin and its product, such as a garment.

MATERIALS AND METHODS

Lipid extraction

Lipid extraction using the Soxhlet method was performed according to AOAC [9]. Pigskin, sheepskin, pig garment, and sheep garment are obtained from the traditional market and leather distributors. A-50.0 g of samples was wrapped with filter paper and placed into the Soxhlet apparatus (Iwaki.SOXH-SET, Indonesia). A-250 mL of n-hexane was used as an extracting solvent. The extraction was performed for 8 h at 70 °C (±50 cycles). The lipid extract was added with anhydrous sodium sulfate, mixed, filtered by filter paper, and then evaporated until the solvent was completely removed. The resulting lipid fraction is then used for FTIR spectral measurements.

FTIR spectral measurements

The lipids obtained by lipid extraction were placed in attenuated total reflectance (ATR) crystal at ambient temperature (25°C). The spectrum was acquired in the wavenumbers region of 4000-550 cm^{-1} using an FTIR spectrophotometer (Perkin-Elmer, Singapore).

Data analysis

The spectrum from FTIR spectral measurement results was analyzed Chemometrically by Partial Least Square (PLS) to measure calibration and validation of the samples, and Principal Component Analysis (PCA) to classify the samples using The Unscrambler X 10.4 (CAMO Software AS).

RESULTS AND DISCUSSION

FTIR Analysis

Pig skin, sheep skin, pig leather garment, and sheep leather garment lipid spectra are shown in Figure 1. FTIR was read at the middle region of infrared spectra, 4000-550 cm^{-1}. A large number of molecules strongly absorb middle infrared radiation. The middle region may be used to measure a wide variety of samples, including liquids, gases, powders, polymers, solids, semisolids, organic, inorganic, biological substances, pure substances, and mixes [10].

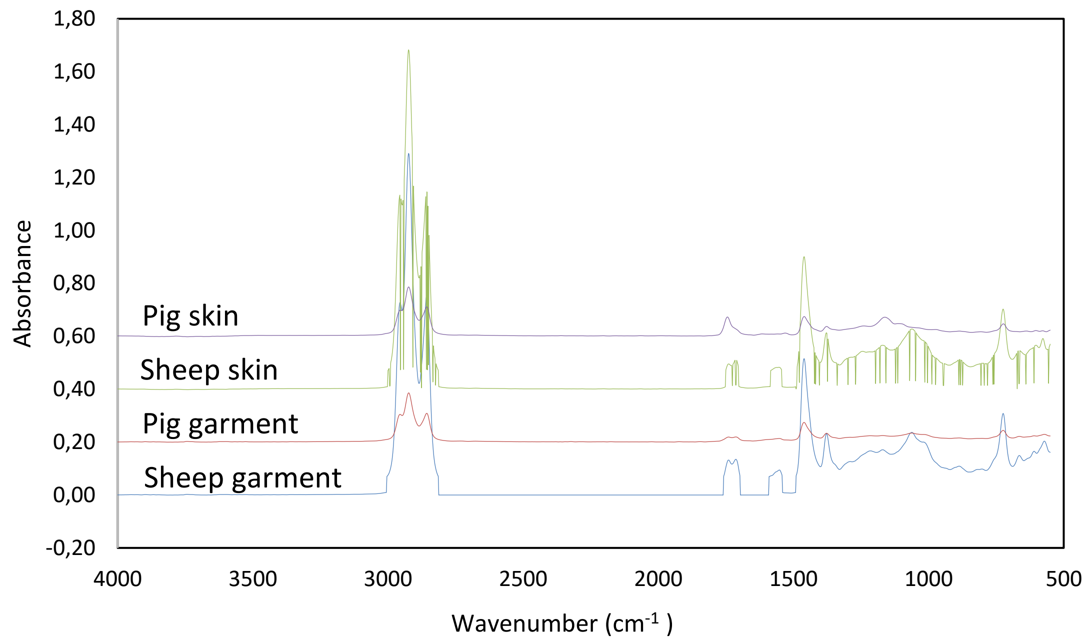

FIGURE 1. FTIR spectra of lipid fraction extracted from pig skin, sheep skin, pig garment, and sheep garment at mid infrared region (4000–550 cm^{-1}).

In Figure 1, the wavenumbers from each peak in the FTIR spectrum of the skin and leather samples are compiled, along with the associated functional group vibrations. However, there is a slight variation in peak intensities at around 1200-1000 and 3000-2800 cm-1. Those functional groups of skin and leather are essentially comparable. In those wavenumbers, there are peaks in the sheep skin and sheep garment samples but not in the sheep skin and sheep garment samples. They are the same discovery as Erwanto et al.[11], which was successfully used for quantification and classification of lard in skin crackers at wavenumber regions of 1200–1000 cm^{-1}.

Moreover, in those spectrums, there is a difference in peak between the skin (pig and sheep) and leather garment (pig and sheep). There is a degreasing process in the tanning process, which converts skin to leather. Degreasing can reduce the natural fat skin [12], so it can make different characteristics of fat in skin and leather (garment). Therefore, the distinction between pig and sheep might be the focus of FTIR spectrum optimization in terms of wavenumber area selection and spectral treatment to distinguish the origin material.

Calibration and Validation Samples Using Partial Least Square

PLS multivariate calibration was used to perform sample calibration and validation. To identify the best wavenumber that provides a good correlation between the actual value of fat and the anticipated value of FTIR, a number of wavenumbers were optimized. In this study, we obtain two wavenumber ranges, those are 3000-2800 cm^{-1} and 1200-1000 cm^{-1}. In the initial calibration and validation, pig and sheep skin were mixed 10-100% of pig skin, and 100% of sheep skin. They are shown in Figure 2. From FTIR spectra, they analyzed using Partial Least Square.

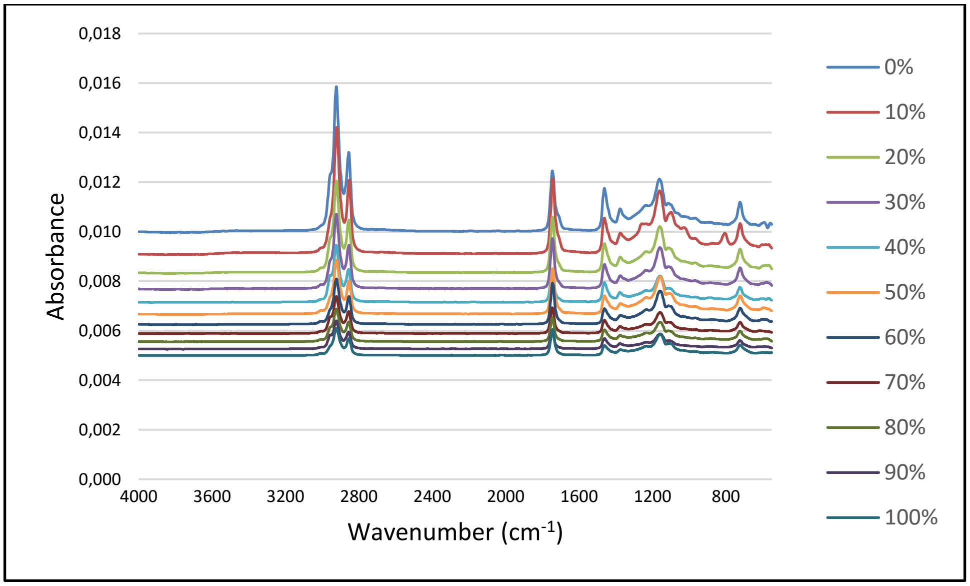

FIGURE 2. FTIR Spectra of lipid derived from pig-sheep skin with gradual concentration (0-100% pig skin) at the middle area of wavenumber (4000-550 cm^{-1})

The calibration and validation results are shown in Figures 3 (wavenumber 3000-2800 cm^{-1}) and 4 (wavenumber 1200-1000 cm^{-1}). Based on the results, the coefficient determination (R^2) of wavenumber 1200-1000 cm^{-1} is 0,983. It means that the calibration models can describe accuracy of 98.3%. That is better than R2 of wavenumber 3000-2800 cm^{-1} (0,968). The more linear the relationship between the independent variable and the dependent variable, the closer R^2 is to 1[13].

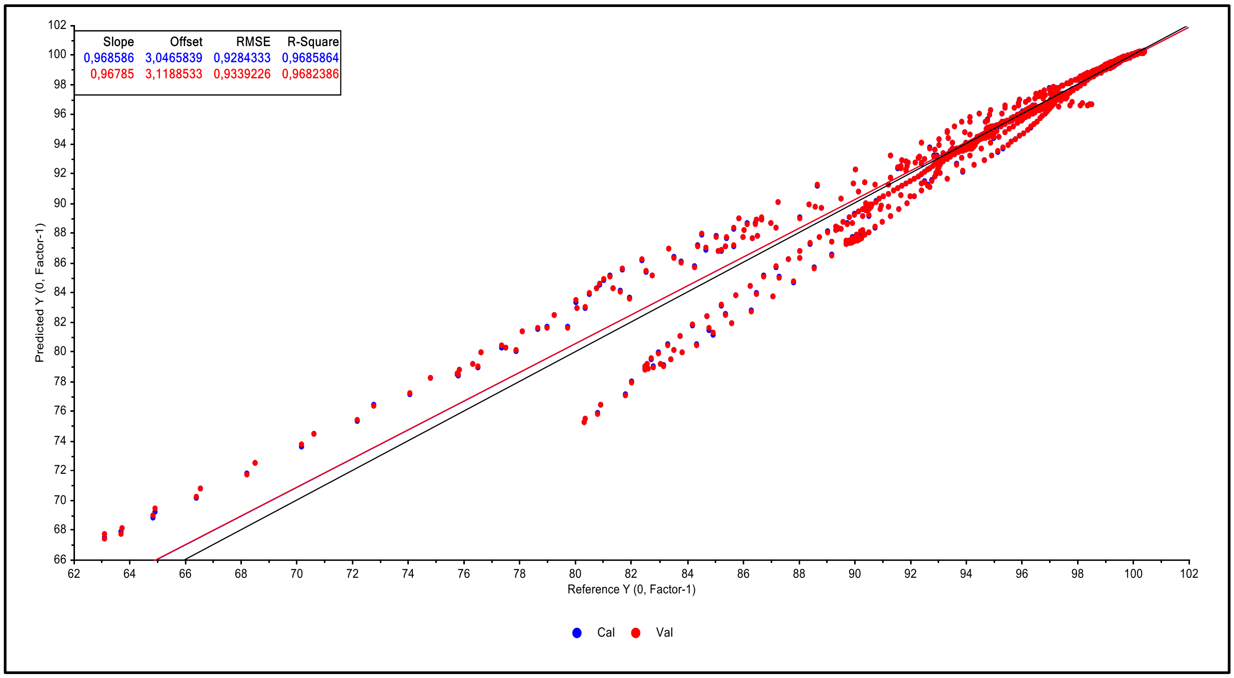

FIGURE 3. The relationship between the measured value of lard (x-axis) and the predicted value of the FTIR (y-axis), which was obtained from pig skin at wavenumbers of 3000-2800 cm^{-1}.

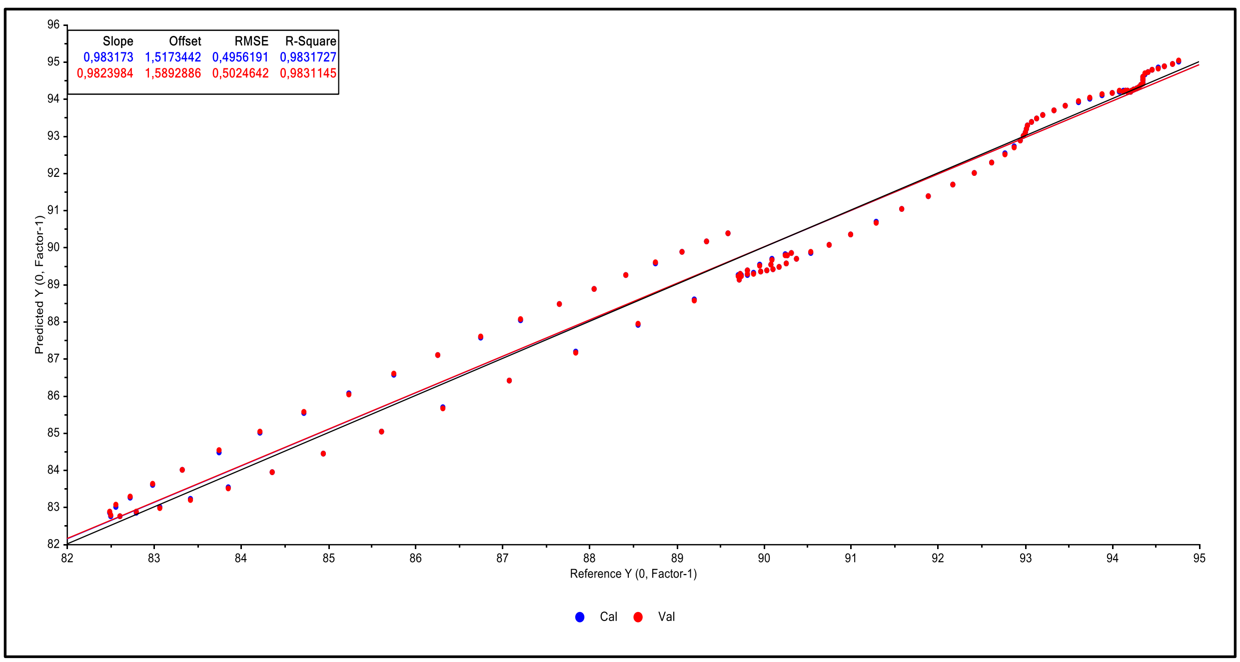

FIGURE 4. The relationship between the measured value of lard (x-axis) and the predicted value of the FTIR (y-axis), which was obtained from pig skin at wavenumbers of 1200-1000 cm^{-1}.

Classification of Samples Using Principal Component Analysis

The methodology known as principal component analysis (PCA) is frequently used to distinguish between samples with a high degree of similarity based on absorbance values over the whole mid-infrared spectrum (4000-550 cm^{-1}). One unsupervised pattern recognition method that is frequently used to categorize samples is PCA [13]. Two score plots from spectra at wavenumbers 3000-2800 cm-1 and 1200-100 cm^{-1} are shown in Figure 5 and 6 consecutively. The distribution of the samples was determined via score plots.

The PCA results of samples from FTIR Spectra at wavenumber 1200-1000 cm^{-1} were separated more precisely than spectra at wavenumber 3000-2800 cm^{-1}. Figure 6 shows that 4 samples (PS, SS, PG, and SG) were distributed on 4 regions, while the others are on 2 regions (Figure 5). According to the findings of Erwanto et al.[7], [8], and Rohman et al.[10], classification in the wavenumber range at 1200-100 cm^{-1} correlates to results that may discriminate between lard and other species fat, such as sheep fat.

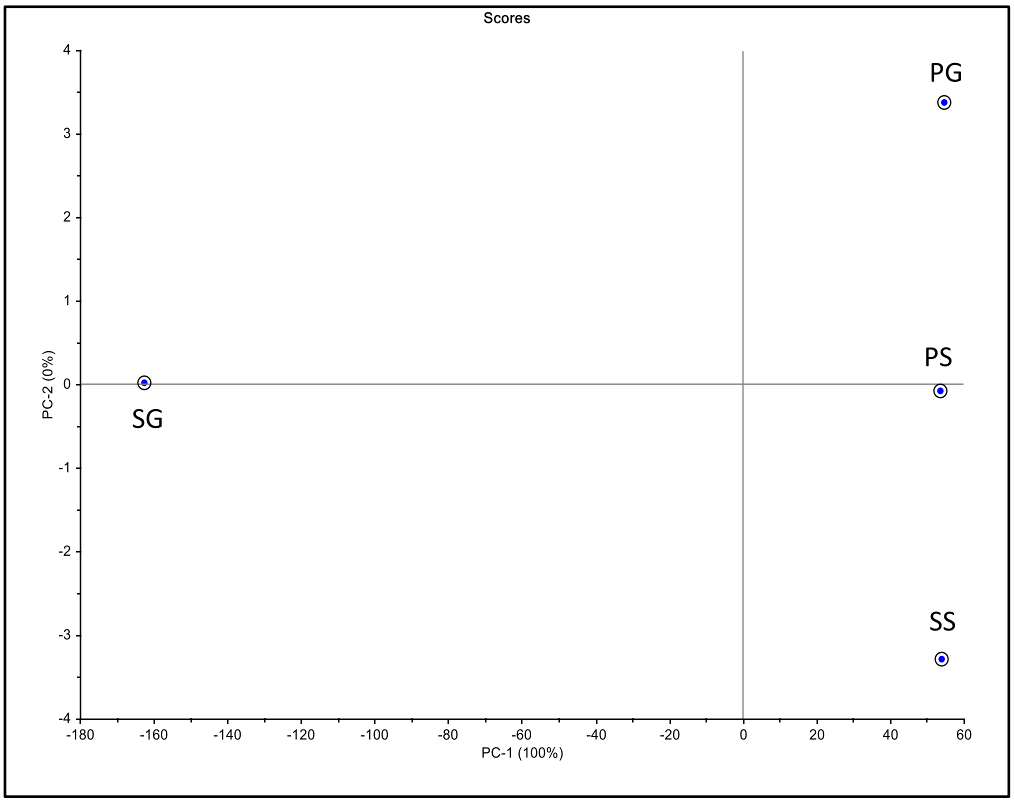

FIGURE 5. The Score plot of first principal components (PC1) and second principal components (PC2) of pig skin (PS), sheep skin (SS), pig garment (PG), and sheep garment (SG) at wavenumber 3000-2800 cm^{-1}.

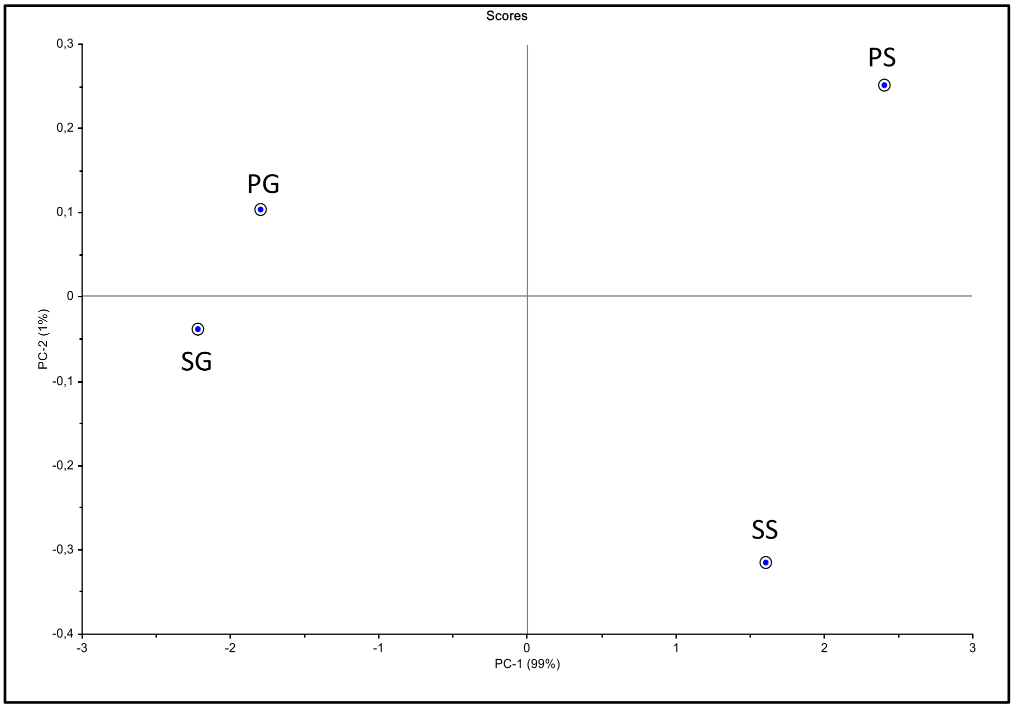

FIGURE 6. The Score plot of first principal components (PC1) and second principal components (PC2) of pig skin (PS), sheep skin (SS), pig garment (PG), and sheep garment (SG) at wavenumber 1200-1000 cm^{-1}.

CONCLUSIONS

To do an initial analysis for distinguish the origin skin (sheep and pig skin) in leather garment, the FTIR Spectroscopy and coupled with chemometrics can be used. PLS and PCA analysis results on spectra data indicated separated samples performed better than wavenumber at 1200-1000 cm^{-1}.

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