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Detection of Vegetable Oil Variance Using Surface Plasmon Resonance (SPR) Technique

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Abstract. The difference between coconut oil, corn oil, olive oil, and palm oil has been detected using surface plasmon resonance (SPR) technique. This is a new method in material characterization that can be used to identify vegetable oil variance. The SPR curve was measured by SPR system consisting of optical instruments, mechanical instruments, Main UNIT, and user interface (computer). He-Ne laser beam of wavelength 633 nm was used as light source, while gold (Au) thin film evaporated on half cylinder prism was used as the base so that surface plasmon polariton (SPP) waves propagate at the interface. Tween-80 and PEG-400 are used as surfactant and co-surfactant to make water-oil emulsion from each sample. The sample was prepared with the ratio of oil: surfactant: co-surfactant as 1:2:1 and then stirred on the water to make emulsions. The angle shift was measured by the change of SPR angle from prism/Au/air system to prism/Au/water-oil emulsion. The different SPR angle of each sample has been detected in the various number of spray, a method that was used for depositing the emulsion. From this work, we conclude that the saturated fatty acid component was the most significant component that changes the refractive index in the vegetable oil in water emulsion that can be used to characterize the vegetable oil variance.

Keywords. HE-Ne laser, SPR, and vegetable oil.

1. Introduction
Vegetable oils are important materials for home cooking and food industry. The composition of contained fatty acid makes the difference of vegetable oil. Some fatty acids are essential for growth and in metabolism so we must get them from the diet. Unsaturated fatty acid is good for heart-healthy because it can reduce blood pressure and tend to promote inflammation, while saturated fat increases heart disease risk and blood pressure [1]. We have to know the difference between vegetable oil variance because it will affect our healthy life.

Several works have been reported for characterizing vegetable oil such as electronic nose [2], gas chromatography [3], Fourier transform infrared [4], and digital image and pattern recognition techniques [5]. However, most of the methods are highly-sophisticated and expensive. In a developing country like Indonesia, we need a low cost and simple method for characterizing material such as surface plasmon resonance (SPR) technique. Although this method was less accurate than the other methods, SPR technique offers a simple, rapid and accurate tool for distinguished vegetable oil variance.
SPR technique has a high sensitivity and fast response due to the refractive index changes at the sensor interface. The penetration depth or decay length explains the sensitivity at the interface of the evanescent field. Only changes of the dielectric properties in the vicinity of the interface between the dielectric and metal will affect the evanescent field. This extreme sensitivity to the surrounding dielectric media makes the SPR technique is an extraordinarily useful tool for characterizing materials in different fields [6]. In this work, we aim to distinguish vegetable oil variance using homemade SPR system.

2. Materials and methods

2.1. Material and reagents
Olive oil, corn oil, palm oil, and coconut oil were purchased from the local store Mirota Kampus. Polyethylene glycol 400/PEG 400 (HO(C_2H_4O)_nH, Merck) was purchased from Laboratorium Penelitian dan Pengujian Terpadu (LPPT) UGM. Polyoxyethylene 20 sorbitan monooleate which is also known as Tween 80 (C_{64}H_{124}O_{26} with the molecular weight of 1,310 g·mol⁻¹) was purchased from Gudang Kimia Jogja Chemical Shop. Au (99 %, Antam) was obtained from Laboratorium Fisika Material UGM. Double distilled water was purchased from Progo Chemical Shop.

2.2. Sample preparation
Vegetable oil in water emulsion was prepared by mixing the vegetable oil (1 mL), Tween 80 (2 mL), and PEG 400 (1 mL). Tween 80 was a hydrophilic nonionic surfactant and used as an emulsifier. PEG 400 was a cosolvent/cosurfactant which makes the stability of emulsion by wedging themselves between surfactants molecules. The ratio of oil: surfactant: cosurfactant is 1:2:1 so that a self-micro-emulsifying performance was successfully obtained [7]. The next process to make an emulsion was dissolving and stirring all of them with 40 mL of double distilled water.

Pure gold (Au 99 %) with mass 20 mg was evaporated on the surface of the half cylinder prism using Vacuum Evaporator System JEE 4X EM 300023144 RA JEOL-Technic Co. Ltd, Japan to make a gold thin film called Prism/Au/Air system. This system was characterized by SPR technique to get the SPR Curve or Attenuated Total Reflection (ATR) Curve as the base curve to distinguish the vegetable oil and get the SPR Angle. After sprayed with the emulsion, the system was called Prism/Au/Vegetable oil-Water emulsion/Air system and the SPR Angle shifted to the higher number.

2.3. Sample characterization
This sample was characterized by Fourier Transform Infra-Red (FTIR) and SPR technique. FTIR transmission characterization was used to obtain the contained functional groups. All samples were made under two conditions (i) pure vegetable oil and (ii) vegetable oil in water emulsion. Both samples were analyzed with FTIR spectrophotometer 8201PC Shimadzu either in Laboratorium Kimia Organik dan Biokimia UGM (pure vegetable oil) and Laboratorium Politeknik ATK Yogyakarta (vegetable oil in water emulsion).

In the SPR characterization, the emulsion was deposited onto the surface of Au thin film using spray method. The SPR system consists of optical instruments, mechanical instruments, main UNIT, and user interface (computer). Optical instruments in this system are a He-Ne laser beam of wavelength 633 nm, a beam splitter, a half cylinder prism, and a pair of a light detector. The mechanical system was used to rotate both prism and detector. Main UNIT and user interface were used to control this measurement. SPR device set-up is shown in Figure 1.

The light from the laser was passed through a polarizer to get the p-polarized or a transverse magnetic (TM) light mode and then divided into two parts with the same wavelength and intensity by the beam splitter. The intensity of first p-polarized light was measured by the detector as the reference laser intensity. Meanwhile, the second light was reflected by the prism towards the second detector to get the reflected light intensity. The reflectivity was obtained by dividing the reflected light and the
first light intensity. In this experiment, we varied the angle by rotating the prism and the second detector (angle scanning).

![Figure 1. SPR device set-up](image)

3. Results and discussion

3.1. FTIR Analysis

We know that every vegetable oil differs in composition, length and unsaturated degree of the fatty acid as well as their position in the chain. The double bond is considered as unsaturated fatty acid, while the single bond is considered as saturated bond. The fatty acid composition of each sample is shown in Table 1.

| Fatty Acid Component   | Corn Oil | Palm Oil | Coconut Oil | Olive Oil |
|------------------------|----------|----------|-------------|-----------|
| Saturated              | 16%      | 48%      | 90%         | 12%       |
| Caprylic 8:0           | -        | -        | 8%          | -         |
| Capric 10:0            | -        | -        | 7%          | -         |
| Lauric 12:0            | -        | -        | 48%         | -         |
| Myristic 14:0          | -        | -        | 16%         | -         |
| Palmitic 16:0          | 13%      | 44%      | 9%          | 10%       |
| Stearic 18:0           | 3%       | 4%       | 2%          | 2%        |
| Unsaturated            | 84%      | 50%      | 9%          | 86%       |
| Oleic 18:1 n-9         | 31%      | 40%      | 7%          | 78%       |
| Linoleic 18:2 n-6      | 52%      | 10%      | 2%          | 7%        |
| Linolenic 18:3 n-3     | 1%       | -        | -           | 1%        |
| Other                  | -        | 2%       | 1%          | 2%        |

The symbol for an acid includes the total number of carbons and double bonds, followed by the location of the first double bond counting from the methyl end of the chain. From that table, we know that both corn oil and olive are high in unsaturated fatty acid. The difference is that corn oil is dominant in polyunsaturated fatty acid (linoleic acid), while olive oil is dominant in monounsaturated fatty acid (oleic acid). Meanwhile, coconut oil is high in saturated fatty acid, while palm contains both saturated and unsaturated fatty acids is mostly in the same percentage.

Figure 2 (a) shows the FTIR transmission spectra of pure vegetable oil samples. The triglyceride is dominant in the spectra. The major peaks that represent triglyceride functional groups could be observed around 2924.09 cm\(^{-1}\) (C–H stretching (asymmetry)), 2854.65 cm\(^{-1}\) (C–H stretching (symmetry)), 1743.65 cm\(^{-1}\) (C=O stretching), 1458.18 cm\(^{-1}\) (C–H bending (scissoring)), 1165 cm\(^{-1}\) (C–O stretching and C–H bending), and 725.23 cm\(^{-1}\) (C–H bending (rocking)). There was a very weak peak at 1651.07 cm\(^{-1}\) (Olive Oil, Corn Oil, and Palm Oil) and 1612.49 cm\(^{-1}\) (Coconut Oil) in IR spectra, which was C=O stretching. In the other hand, the C–C bond was found at 1226.73 cm\(^{-1}\) (Coconut Oil) and 1234.44 cm\(^{-1}\) (Olive Oil, Corn Oil, and Palm Oil). These show that all of the samples have both saturated and unsaturated fatty acid components. This means FTIR show the same result of all samples (it can’t detect the difference in the samples).
Figure 2.b shows the FTIR transmission spectra of vegetable oil in water emulsions. There was a dominant peak at 3313.98 cm\(^{-1}\) in the IR spectra that represent the water and PEG 400 (both have O–H bond), while the peaks of triglyceride functional groups of vegetable oil decreased. The other dominant peak was a C=C bond at 1637.30 cm\(^{-1}\). From the FTIR spectra of pure vegetable oil, we found that the peak of the C=C bond was very weak. The increasing intensity of this C=C bond at the IR spectra of water in oil emulsion represents the Tween 80.

![Figure 2. FTIR spectra of (a) pure vegetable oils and (b) vegetable oil in water emulsions](image)

### 3.2. SPR analysis

Figure 3 shows the ATR curve of vegetable oil in water emulsion. The dotted line shows the ATR curve of Prism/Au/Air system functioned as the base curve or the reference curve, while the full line shows the ATR curve of Prism/Au/Vegetable oil/Air system in multiple numbers of spray from 10x to 50x number of sprays. The shifts of ATR curve show the characteristic of each vegetable oil in water emulsion. That is caused by the increase of the refractive index at the sensor surface. The value of the refractive index increment depends on the structure of the analyte molecules [9], hence the angle shift of each sample is different. The number of shifts in SPR angle and minimum reflectance is described in Table 2 and Table 3.

![Figures](image)
Figure 3. The ATR curve of (a) coconut oil in water emulsion, (b) corn oil in water emulsion, (c) palm oil in water emulsion, and (d) olive oil in water emulsion.

Table 2. The SPR angle shift (°) of the vegetable oil variance

| Number of Sprays | Coconut Oil | Corn Oil | Palm Oil | Olive Oil |
|------------------|-------------|----------|----------|-----------|
| 10x              | 0           | 0.06     | 0.04     | 0         |
| 20x              | 0.11        | 0.06     | 0.16     | 0         |
| 30x              | 0.46        | 0.06     | 0.16     | 0         |
| 40x              | 0.52        | 0.06     | 0.16     | 0.03      |
| 50x              | 0.58        | 0.17     | 0.16     | 0.06      |

Table 3. The Increasing of minimum reflectance of the vegetable oil variance

| Number of Sprays | Coconut Oil | Corn Oil | Palm Oil | Olive Oil |
|------------------|-------------|----------|----------|-----------|
| 10x              | 0.23        | 0.01     | 0.07     | 0.01      |
| 20x              | 0.36        | 0.05     | 0.14     | 0.02      |
| 30x              | 0.41        | 0.13     | 0.17     | 0.02      |
| 40x              | 0.44        | 0.14     | 0.18     | 0.05      |
| 50x              | 0.45        | 0.17     | 0.19     | 0.08      |

From Table 2 and Table 3, we find that both of the SPR angle and the minimum reflectance are shifted to a higher number when the number of sprays is increased, but the amount of each sample was different. Coconut oil in water emulsion shows the biggest shift both in the SPR angle and the increase of minimum reflectance, while olive oil in water emulsion shows the smallest shift. According to the fatty acid composition in Table 1, coconut oil contained 90% saturated fatty acid while olive oil contained 12% fatty acid. Coconut oil containing the highest fatty acid component shows the biggest shift both in the SPR angle shift and the minimum reflectance. In the other hand, olive oil containing the lowest fatty acid shows the smallest shift both in the SPR angle shift and the minimum reflectance. The SPR angle of corn oil and palm oil have the similar result after sprayed to the Au thin film. Nevertheless, palm oil containing 48% saturated fatty acid shows the bigger minimum reflectance shift than corn oil which contains 16% saturated fatty acid.

The other result, the SPR sensor is able to quantitatively describe the interaction of oleic acid molecules on gold thin film by detecting localized small refractive index shifts [10]. The change in the
amount of free fatty acids sensed by SPR correlated well with the acid value of the AOCS official method when refined vegetable oils and pressed and non-refined vegetable oils are measured. These support our result that fatty acid component, especially the saturated fatty acid, is the most significant components that change the refractive index of the vegetable oil in water emulsion. The SPR technique can distinguish coconut oil, corn oil, palm oil, and olive oil by detecting the changes of the refractive index at the sensor interface.

4. Conclusions
We have successfully identified differences between coconut oil, corn oil, olive oil, and palm oil that have been detected using SPR technique. The difference in the ATR curve of vegetable oil in water emulsion was dominantly caused by the saturated fatty acid composition of each sample. This confirms the new method for characterizing materials, especially in identifying vegetable oil variance which could be further developed in the near future.

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