Designing A Low-Cost Surface Plasmon Resonance (SPR) Instrument For Monitoring Degradation Of Milk Quality

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Abstract. A design of a low-cost SPR instrument has been made to monitor the degradation of milk quality. The cost-production of the SPR instruments is much more economical, namely around IDR 10,000,000 where the price of commercial SPR instruments such as nanoSPR6 is $ 9,950. The main components of the instrument are consist of an Arduino Uno microcontroller, red laser, polarizer, stepper motor, prism, gold chip, and a cell phone camera. The light detection system of the instruments is using image processing that utilizes recorded data from the cell phone camera programmed with python software. The sample in this research used is pasteurized milk. The measurement results obtained from the SPR instruments are compared with nanoSPR6. The sensorgram result from the monitoring of pasteurized milk using both SPR instruments for 12 hours and nanoSPR6 for 4 hours has experienced a decrease in light intensity. The light intensity had decreased up to 8 hours from the time of observation and remained flat for the next 4 hours. This decreased intensity states that there is a shift in the angle dip during the monitoring process. This explanation is supported by track mode measurement data by nanoSPR6 that run for 2 hours, showing a change in the angle dip from 67.34º to 67.6º. The increase in angle dip during the monitoring process is because of increasement in the dielectric constant and the density of the milk during the process of quality degradation. In addition, it is also suspected to be due to the appearance of fatty deposits in milk which results in an increase in the milk refractive index. The change of the milk refractive index within 2 hours is 0.0023 obtained by a fitting process using the Winspall software.

1. Introduction

Surface Plasmon Resonance (SPR) technology is widely used in various fields, one of which is in the medical field. SPR is a very sensitive method based on the detection of changes in the refractive index on the surface of thin gold films [2]. The sensitivity of the SPR instrument is mostly in the range of $\Delta n \approx 10^{-5}$ or 1 pg/mm² from protein material [6]. Because of its high measurement sensitivity and highly sophisticated technology, the price of commercial SPR is very expensive. For example the price of nanoSPR6 with dimensions 215x130x100 mm reaches $ 9,950 (https://nanospr.com/nanospr6-dual-channel-electrochemical-surface-plasmon-resonance-spectrometer/). The high price of commercial SPR becomes a problem for researchers, therefore researchers study to make SPR at an economical price. The SPR method can be carried out for various studies such as determining the concentration of solution, detecting a substance in solution, including monitoring changes in the degradation of solution quality. One solution that can be monitored of it’s quality degradation is milk.
Milk is one of the most consumed nutritious by the people. Because of its high nutritional content, milk is an good medium for microorganisms to grow. Abubakar and others (2000) stated that there are microbes such as bacteria, molds and yeast that will have a great chance to grow because microbes also need food ingredients in their growth. Microbial growth is the cause of quality degradation in milk. So far, studies on regradation milk quality have been carried out using biological and chemical methods by looking at bacterial activity, discoloration, chemical reactions, changes in odor, changes in pH. But in physics it can certainly be done a study of the decline in milk quality. Some specifications of physical quantities of milk that can be observed are density, pH, conductivity and refractive index that can be observed using SPR. The occurrence of physical changes is indicated by changes in the values of the quantities mentioned.

In this study I will examine the design of SPR instruments in a laboratory and economical scale. Cost-production in making instruments is not more than Rp. 10,000,000. The SPR instrument is used to monitor the decrease in milk quality in real time. The measurement results will be displayed in the form of graphs of SPR curves and sensograms that are processed using Python.

2. Experiment

2.1 SPR Instrument

The SPR instrument consists of a laser with a wavelength of 620 nm, a NEMA stepper motor with a Gear Box 1: 100, a motor driver, a set of instruments made of acrylic, a prism with a refractive index of 1.562, a glass with a refractive index of 1.61 thin gold with a refractive index of 0.183 + i3.3, Arduino microcontroller, computer and a mobile phone. The SPR instrument that has been made is shown in Figure 1.

![Figure 1](image-url)

Figure 1. (1) Power Supply; (2) Mobile; (3) Stepper motor driver; (4) Screen; (5) Arduino Uno Microcontroller; (6) Stepper motor; (7) Gold chips, and (8) Laptops.

The experimental scheme of the SPR instrument is shown in Figure 2. The experimental scheme explained that the data is collected by Arduino Uno microcontroller. It controls the stepper motor to set the coming angle of laser light. The light on the laser will pass through the polarisator and forward to a set of containers consisting of prisms and gold chips. The laser light will penetrate the prism and be passed on to a thin layer of gold. The light reflected by layer of gold will be passed to the prism and after that it captured by the screen. The light on the screen will be recorded by the cellphone. The recording data will be processed using python software.
2.2 Sample Preparation
The samples used in this study were distilled water and pasteurized milk. All pasteurized milk which is used has 3 days to the expiration date as shown in Table 1.

| Pasteurized milk | Date of opened from packaging | Expired date |
|------------------|-------------------------------|--------------|
| Sample #1        | 22 July 2018                  | 25 July 2018 |
| Sample #2        | 23 July 2018                  | 26 July 2018 |
| Sample #3        | 27 July 2018                  | 30 July 2018 |

Pasteurized milk is stored in a cup after it has been purchased from the trader, then opened and poured into a measuring cup for approximately 15 minutes until the temperature is as same as the room temperature. After that measurements were taken on the sample.

2.3 Data of Experiment
In this study, measurement data will be made using SPR instruments that have been made and also from nanoSPR6 as a comparison. The measurement results are graphs of the SPR curve and also the sensogram where the samples used are air, aquades and pasteurized milk.

3. Result and Discussion
The results obtained in making the SPR curve from the air medium and from the sample medium are shown in Figure 3.

From Figure 3.a obtained dip from the measurement results using nanoSPR6 for medium air at an angle of 42.42° while Figure 3.b shows the measurement results of the SPR instrument obtained dip at an angle of 36.69°. The error rate from the measurement results from the SPR instrument is 13.507%. Measurement using nanoSPR6 for distilled water samples obtained dip at an angle of 62.14°, it shown in Figure 3.c while from the measurement using SPR instrument obtained dip at an angle of 57.2°, it shown in Figure 3.d. The error rate from the measurement results from the SPR instrument is 7.3577%. For the results of sample #1 (pasteurized milk), the dip obtained from measurement using nanoSPR6 was at an angle of 67.31, it shown in Figure 3.e while Figure 3.f shows the results of measurement using SPR instrument for sample #2 (pasteurized milk) obtained dip at an angle of 62.5°. The error value of the measurement result is 7.146%. SPR curve from measurement results using SPR instruments is not very good, there are repetitive dips and unstable pixel value readings. This is because the laser is not
stable enough. In addition there are differences in the refractive index of the prism, matching oil and glass used during the experiment.

Figure 3. The results of the SPR curve measurement. (a) nanoSPR6 with air medium, (b) SPR instruments with air medium, (c) nanoSPR6 with water medium, (d) SPR instruments with air medium, (e) nanoSPR6 with sample#1, and (f) Instruments SPR with sample#2

To estimate the change in value from the refractive index of milk for 2 hours, it can be done by obtaining the refractive index value of milk at the beginning of the observation and the refractive index of milk after 2 hours of observation. The refractive index is obtained through the process of data fitting.
using winspall software. The processed data is obtained from the measurement results of the SPR curve using nanospr6 as shown in Figure 4.

**Figure 4.** Track mode measurement results. (a) Beginning of observation, and (b) After 2 hours of observation

From Figure 4.a the dip at the beginning of the measurement is at an angle of $67.31^\circ$ while the dip after 2 hours of observation is at an angle of $67.5^\circ$ shown in Figure 4.b. The SPR curve in Figure 4 is processed using image processing to be converted into text which is then fitted using winspall from the text data by entering the thickness data and the refractive index of each layer. Figure 5 shows the results of winspall fitting.

**Figure 5.** The fitting results of data use winspall. (a) Initial observation data, and (b) Data after 2 hours of observation.

The results of fitting in Figure 5.a show that the refractive index of pasteurized milk for the initial observation is 1.267 while the results of fitting for the refractive index of milk after 2 hours are 1.2693 as shown in Figure 5.b. Changes in the refractive index of milk for 2 hours of observation were 0.0023.

Measurement in making a sensogram is done by placing the laser at a certain angle and then reading the intensity of the reflectance light on the screen in real time. Samples are dropped over gold chips and allowed to interact with the air during the monitoring process. Measurements using nanoSPR6 were carried out for 3 hours 40 minutes for sample # 3. The measurement results in the form of a sensogram graph are shown in Figure 6.a While measurements using SPR instruments for 12 hours for sample # 2 with a laser are at an angle of $60^\circ$. Figure 6.b is a sensogram graph obtained from the measurement results using the SPR instrument.
Figure 6 (a) Sensogram of nanoSPR6 measurement results for 3 hours 40 minutes, (b) Sensogram measurement results of SPR instruments for 12 hours.

From Figure 6, we can see that the results of the sensogram both from measurements using nanoSPR6 and also the SPR instruments, intensity of light is decrease. The measurement results using nanoSPR6 decreased from 974.31 ru to 943.94 ru for 225 minutes. While the measurement results using SPR instrumentation show that the decrease in light intensity up to 30731 (8.53 hours) of 195 pixel value is up to 161 pixel value and looks flat at 30731 seconds to 43011 (11.94 hours). The addition of the refractive index in the milk is because during the process of decreasing the quality of the milk the density of the milk is increased due to the growth of microorganisms. Liu et al. (2008) states that if the density of a medium increases then the refractive index will increase. Teleken et al. (2011) have conducted a study of modeling microbial growth in milk where the modeling results state that the density of medium milk increases exponentially due to the growth of the microbes. Microbes in the milk include Bacillus cereus, Pseudomonas, and Listeria monocytogenes. The addition of the milk refractive index is also thought to be due to the release of free fatty acids caused by the clotting process resulting from interference with the thin membrane of fat lumps [4]. The disturbance in the thin membrane is due to Bacillus cereus. As explained by Rahimah, (2011) that the cause of milk clots due to Bacillus cereus will break down P-lipids in the granular membrane of fat so that fat coalesces and separates to the surface. Fat index in milk is higher than the refractive index of milk. Like the measurement of milk fat that has been done by Michalski et al. (2001) where the measurement results obtained a fat refractive index in milk of 1.46. Because the refractive index of fat in milk is higher than the refractive index of milk (1.3440 - 1.3485), then when fat clots the refractive index of milk increases. The intensity at 30731 seconds was saturated because the sample had dried so that it was suspected that there was no change in density and the refractive index.

4. Conclusion
The design of an SPR instrument at an economical price to monitor the degredation in milk quality has been successfully made. The instrument was able to make measurements to make the SPR curve and the sensogram used for monitoring the degredation in milk quality. The data acquisition system uses python. Based on the results and discussion, the change in dip angle for 2 hours on the SPR curve occurs at 0.19° with a change in the refractive index 0.0026 obtained from the fitting using winspall. Changes in the refractive index are due to changes in density and dielectric constant in the milk. Monitoring the decrease in milk quality from the measurement results of the sensogram found that there was a decrease in the intensity of light up to 30731 seconds.
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