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Characterization of the Optical Properties of Heavy Metal Ions Using Surface Plasmon Resonance Technique

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Abstract

The aim of this research is to characterize the optical properties of heavy metal ions (Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) using surface plasmon resonance (SPR) technique. Glass cover slips, used as substrates were coated with a 50 nm gold film using sputter coater. The measurement was carried out at room temperature using Kretchmann SPR technique. When the air medium outside the gold film is changed to heavy metal ions solution, the resonance angle shifted to the higher value for all samples of heavy metal ions solution. By our developed fitting program (using Matlab software), the experimental SPR curves were fitted to obtain the refractive index of Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions solution with different concentrations. Both the real and imaginary part of refractive index of the heavy metal ions solution increased with the concentration. The results give the basic idea such that the SPR technique could be used as an alternative optical sensor for detecting heavy metal ions in solution.

Keywords: Surface Plasmon Resonance, Optical Properties, Heavy Metal Ions

1. Introduction

Heavy metals are natural components of the Earth's crust. It mainly includes the transition metal in periodic table. As trace elements, heavy metals such as copper and zinc, are essential to maintain the metabolism of the human body. Copper is an essential component of several metalloenzymes, which plays a major role in the formation and repair of extracellular matrix, and catalyzes a key reaction in energy metabolism [1,2]. Zinc involves in a wide variety of metabolic processes, supports a healthy immune system, and is important for normal growth during pregnancy, childhood and adolescence [3]. However, they can be poisoning at higher concentration. Heavy metals are dangerous because of the potential for bioaccumulation, which means increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Some of heavy metals are dangerous to health or to the environment (e.g. mercury, lead), some may cause corrosion (e.g. zinc, lead) and some are harmful in other ways. Mercury poisoning causes loss of myelinated nerve fibers, autonomic dysfunction and abnormal central nervous system cell division [4]. Over doses of copper can cause anemia, liver and kidney damage, nausea, vomiting, abdominal pain, and gastrointestinal distress [5]. Acute zinc toxicity in humans causes severe irritation to the gastrointestinal, as well as fever, chest pain, chills, cough, dyspnea, nausea, muscles soreness, fatigue and leukocytosis. Lead poisoning may cause severe damage in brain, kidney, liver, central nervous system, cardiovascular system, immune system, or even death [6-8].

Surface plasmon resonance (SPR) spectroscopy is a surface-sensitive technique that has been used to characterize the thickness and refraction index of dielectric medium at noble metal (gold) surface. For the last decade, surface plasmon resonance sensors have been extensively studied. SPR technique has emerged as a powerful technique for a variety of chemical and biological sensor applications. The first chemical sensing based on SPR technique was reported by Liedberg *et al.* (1983) [9]. SPR is an optical process in which light satisfying a resonance condition excites a charge-density wave propagating along the interface between a metal and dielectric material by monochromatic and p-polarized light beam. The intensity of the reflected light is reduced at a specific incident angle producing a sharp shadow (called surface plasmon resonance) due to the resonance energy occurs between the incident beam and surface plasmon wave [10]. SPR is regarded as a simple optical technique for surface and interfacial studies and shows the great potential for investigating biomolecules [11]. SPR has been used to study the refractive index of liquid measurement [12,13], pesticide detection [14] and SPR also can be regarded as a significant tool for analyzing saccharides where saccharides solution commonly has a high refractive index [15]. Optical properties of chlorine and commercial carbonated drinks using SPR techniques also had been reported from our laboratory by Yusmawati *et al.* (2007) [16,17].

In this paper, we investigate the optical properties of mercury, copper, lead and zinc ions solution with different concentration using SPR techniques. The real and imaginary parts of refractive index of all the heavy metal ions with different concentration were determined. These results are important in our ongoing research on multilayer SPR optical sensor for heavy metal ions.

2. Theoretical Background

The SPR is a charge-density oscillation that exists at the interface of two media with dielectric of opposite signs, *i.e.* a metal and a dielectric. The interaction between a light wave and a surface plasmon in the attenuated total reflection method can be described using the Fresnel theory [18,19]. In this study, we used Kretchmann configuration where the metal layer (gold film) is sandwiched between prism and dielectric layer (heavy metal ion sample). For this system, the reflection coefficient R, which depends on thickness d, can be expressed as [20]

$$R = \left|r_{012}\right|^2 = \left|\frac{r_{01} + r_{12}\exp\left(2ik_1 d\right)}{1 + r_{01}r_{12}\exp\left(2ik_1 d\right)}\right|^2 \tag{1}$$

$$k_j = \sqrt{\varepsilon_j\left(\frac{2\pi}{\lambda}\right)^2 - k_x^2} \tag{2}$$

where r_{01} and r_{12} are the reflection coefficient of prism-gold and the reflection coefficient of gold-heavy metal ion sample, respectively. The k_x is the propagation constant of the evanescent wave, which is given by the following equation:

$$k_x = \frac{2\pi}{\lambda} n_p \sin\theta_1 \tag{3}$$

The excitation of surface plasmons occurs when the wave vector of evanescent wave exactly matches with that of the surface plasmons of similar frequency. The resonance condition for surface plsmon resonance, which depends on the refractive index of gold and the sample, as follow:

$$n_p \sin\theta_R = \sqrt{\frac{n_1^2 n_2^2}{n_1^2 + n_2^2}} \tag{4}$$

where n_p, n_1 and n_2 are the resonance angle, refractive index of the prism, gold layer and sample, respectively. The refractive index of the sample is [21]:

$$n_2 = \sqrt{\frac{n_1^2 n_p^2 \sin^2\theta_R}{n_1^2 - n_p^2 \sin^2\theta_R}} \tag{5}$$

Hence to perform calculation of refractive index of sample, a simulation and automatic fitting program had been developed using Matlab based on the theory as explained above.

3. Experimental

Prism with refractive index, $n = 1.7786$ at 632.8 nm and the substrate, glass cover slips 24 × 24 mm with thickness 0.13 - 0.16 mm were purchased from Menzel-Glaser. The glass cover slips were cleaned using acetone to clean off the dirt or remove fingerprint marks laid on the surface of glass slides. Then gold layer were deposited using SC7640 Sputter Coater.

Mercury, copper, lead and zinc ion AAS standard solutions (Merck, Germany) with a concentration of 1000 ppm were diluted accordingly to produce Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} solution with concentrations 0.5, 1, 5, 10, 30, 50, 70, 100, 500 and 700 ppm.

The coated glass cover slip was attached to the prism using index matching liquid. A cell was constructed to hold and supply the heavy metal ions solution to the glass cover slip with gold film, as shown in **Figure 1** (based on Kretchmann configuration). An open-ended cylindrical brass cavity with an O-ring seal was attached to the glass cover slip that was attached to the prism. The heavy metal solution was filled into the hollow formed so that the laser light irradiated solution. The prism and the cell were mounted on a rotating plate to control the angle of the incident light.

The SPR measurement had been carried out by measuring the reflected He-Ne laser beam (632.8 nm, 5 mW) as a function of incident angle. The optical set up consists of a He-Ne laser, an optical stage driven by a stepper motor with a resolution of 0.001˚ (Newport MM 3000), a light attenuator, a polarizer and an optical chopper (SR 540). The reflected beam was detected by a sensitive photodiode and then processed by the lock-in-amplifier (SR 530). The experimental setup for SPR measurement that we used is schematically shown in **Figure 2**.

4. Results and Discussion

Prior to measurement, a preliminary SPR test was carried out for gold film in contact with deionized water. By fitting the experimental data to the Fresnel equation

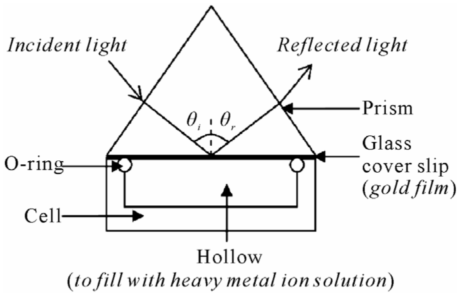


Figure 1. Structure of the cell for SPR measurement.

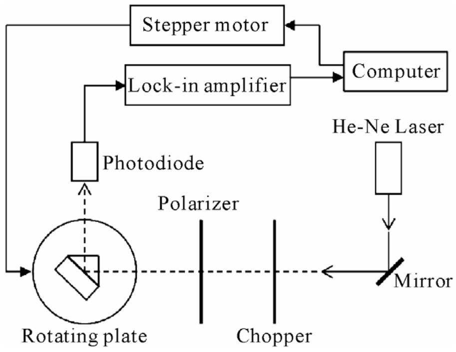


Figure 2. Experimental setups for angle scan surface plasmon resonance technique.

[18,19] using our self developed fitting program (matrix method), the refractive index of deionized water was obtained. **Figure 3** shows that the fitting line is in good agreement with the experimental data as compared to the theoretical result for deionized water. The value of refractive index for this fitting line is 1.3317, and the resonance angle was obtained as 55.043°.

The fitting result for refractive index of deionized water, *i.e.* 1.3317, shows a good agreement with other published values as reported by Weast *et al.* (1978), Webb *et al.* (1989) and Ma *et al.* (2000) [22-24]. Thus, it shows that the SPR measurement can be used to determine the optical properties of the liquid sample.

Then the SPR experiment was carried out for Hg^{2+} solutions (concentration range between 0.5 to 1000 ppm), which was injected one after another into the cell to contact with the gold film. It was observed that the resonance angles determined were 55.071°, 55.350°, 55.467°, 55.601° for Hg^{2+} at concentrations of 100, 500, 700 and 1000 ppm, respectively. The resonance angles remain unchanged (same as deionized water) for the concentrations less than 100 ppm. The SPR curves were shown in **Figure 4**. The values of real and imaginary parts of refractive index for Hg^{2+} solutions obtained by fitting were notified and tabulated in **Table 1**.

Similarly, the above processes were applied to other heavy metal ions solutions, Cu^{2+}, Pb^{2+} and Zn^{2+}. The resonance angles obtained were 55.071°, 55.267°, 55.378°, 55.490° for Cu^{2+} at concentrations of 100, 500, 700 and 1000 ppm, respectively. For Pb^{2+}, we determined that the resonance angles were 55.071°, 55.326°, 55.431°, 55.569° at concentrations of 100, 500, 700 and 1000 ppm, respectively. While for Zn^{2+}, the resonance angles obtained were 55.071°, 55.278°, 55.388°, 55.501° at concentrations of 100, 500, 700 and 1000 ppm, respectively. Also, same as Hg^{2+}, the resonance angles, for all Cu^{2+}, Pb^{2+} and Zn^{2+} with concentrations less than 100 ppm, were same as deionized water, *i.e.* 55.043°. The SPR curves for Cu^{2+}, Pb^{2+}, Zn^{2+} were shown in **Figures 5-7**, respectively.

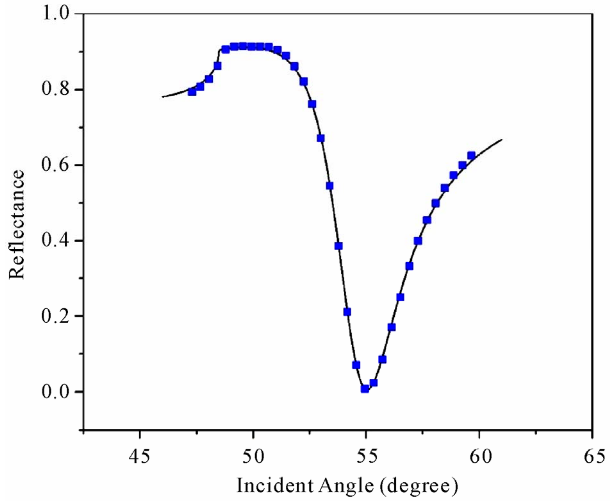
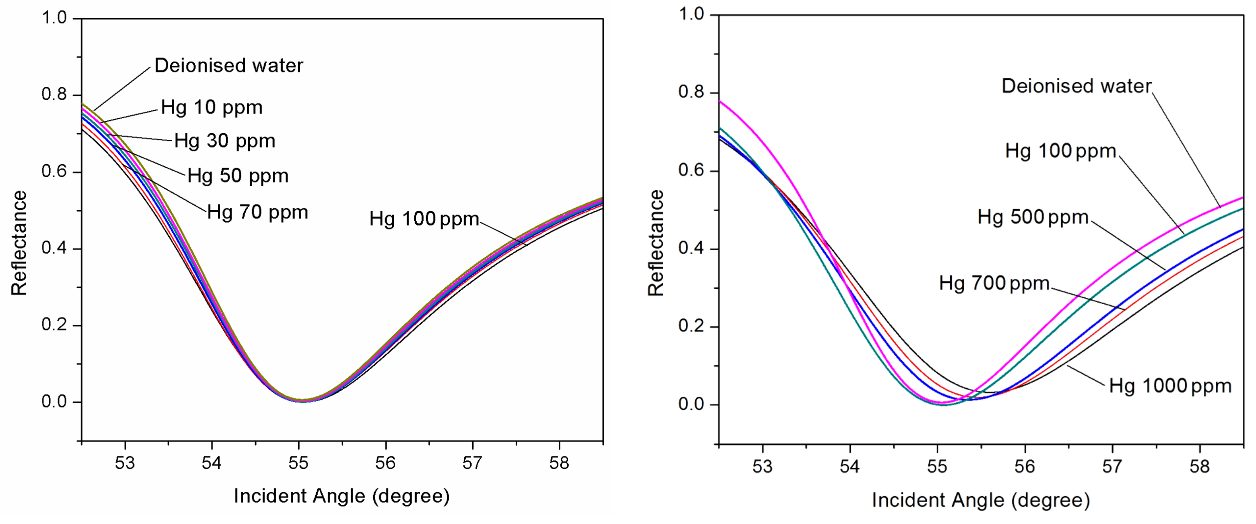


Figure 3. Fitting experimental data to theoretical data for gold layer in contact with deionized water. The solid line represents the theoretical curve.

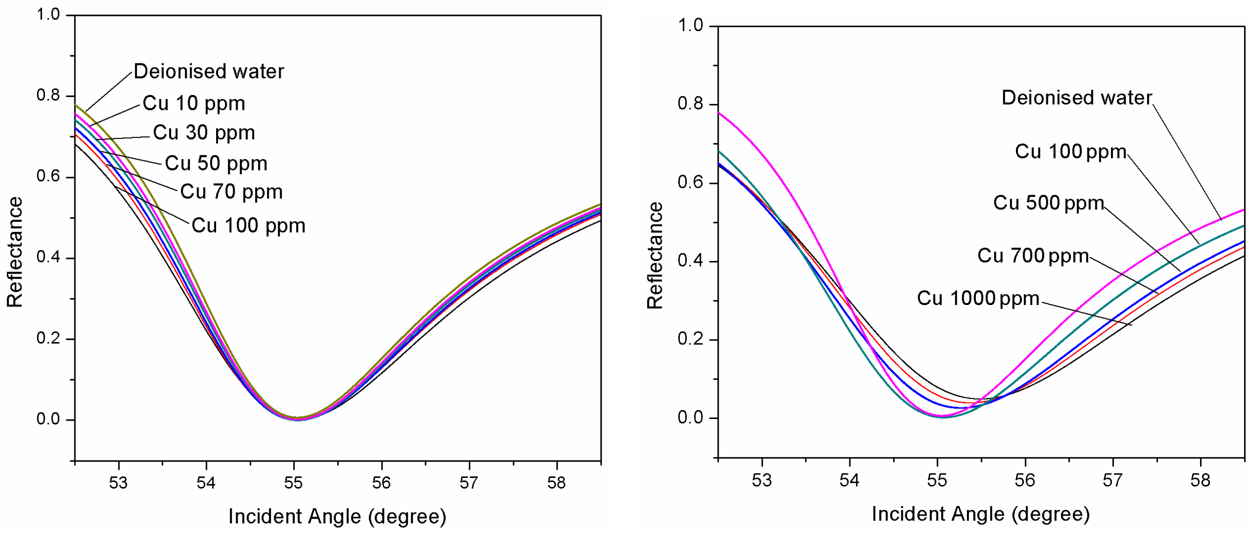
Table 1. The real and imaginary part of refractive index for different concentration of mercury ion solutions from fitting.

Concentration of Hg (ppm)	Real Part of Refractive Index, *n* (±0.0005)	Imaginary Part of Refractive Index, *k* (±0.0002)
0.5	1.3317	0.0002
1	1.3317	0.0002
5	1.3317	0.0003
10	1.3317	0.0005
30	1.3318	0.0010
50	1.3318	0.0014
70	1.3318	0.0021
100	1.3321	0.0029
500	1.3359	0.0061
700	1.3374	0.0071
1000	1.3392	0.0089



(a) (b)

Figure 4. Optical reflectance as a function of incident angle for mercury ion solutions with concentration: (a) 10 - 100 ppm, and (b) 100 - 1000 ppm.



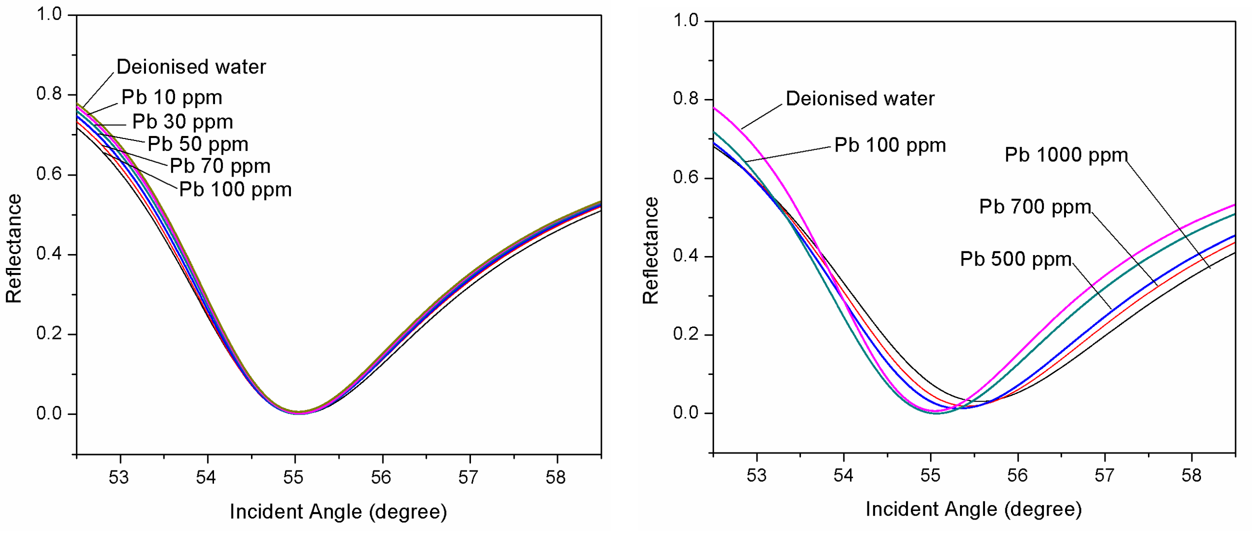
(a) (b)

Figure 5. Optical reflectance as a function of incident angle for copper ion solutions with concentration: (a) 10 - 100 ppm, and (b) 100 - 1000 ppm.

The real and imaginary parts of refractive index for Cu^{2+}, Pb^{2+} and Zn^{2+} solutions obtained by fitting were determined and tabulated in **Tables 2-4**, respectively.

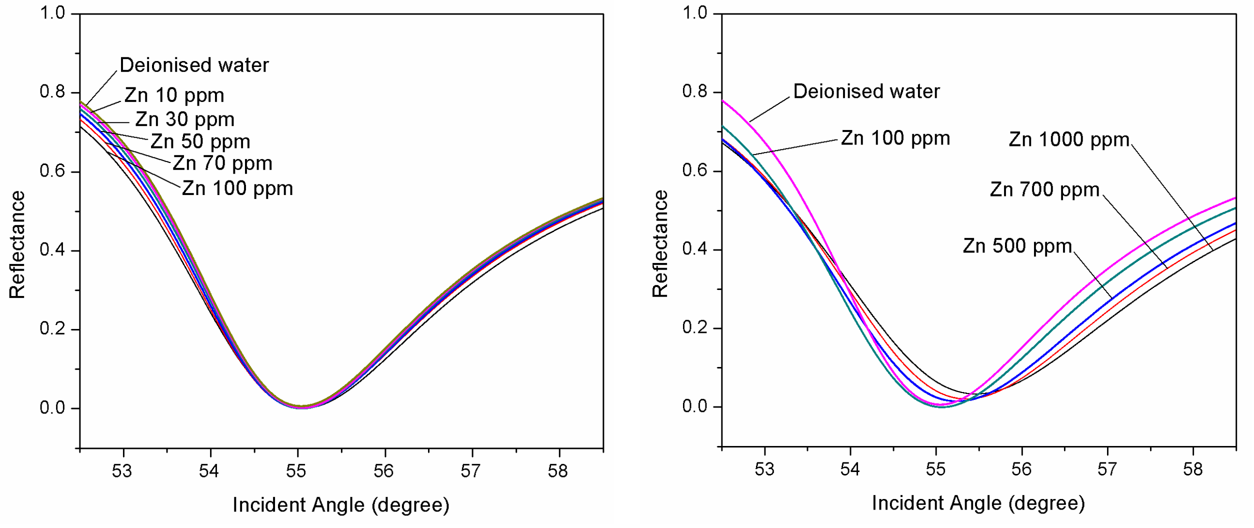
All the results of fitting were summarized in **Figures 8(a)** and **(b)**, which shows the real and imaginary parts of refractive index for all four heavy metal ions, respectively. From the figures, we found that both of the real and imaginary parts of refractive index for all heavy metal ions generally increase with the increase of heavy metal ions concentration. However, the real part of refractive index for all heavy metal ions below 100 ppm does not show the significant change. Also, we found that the real part of refractive index is almost similar for Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, while the value of the imaginary part of refractive index for Cu^{2+} is slightly higher than that of Hg^{2+}, Pb^{2+} and Zn^{2+}. We believe that the blue colour of Cu^{2+} compared to colourless Hg^{2+}, Pb^{2+} and Zn^{2+} increase the absorption and hence the value of imaginary part of refractive index.

The results also show that the SPR curves shift to the right as the concentration of heavy metal ions increases (for concentration 100 ppm and above). This trend was found in all four heavy metal ions. The increase in resonance angle with concentration is mainly due to the in-



(a) (b)

Figure 6. Optical reflectance as a function of incident angle for lead ion solutions with concentration: (a) 10 - 100 ppm, and (b) 100 - 1000.



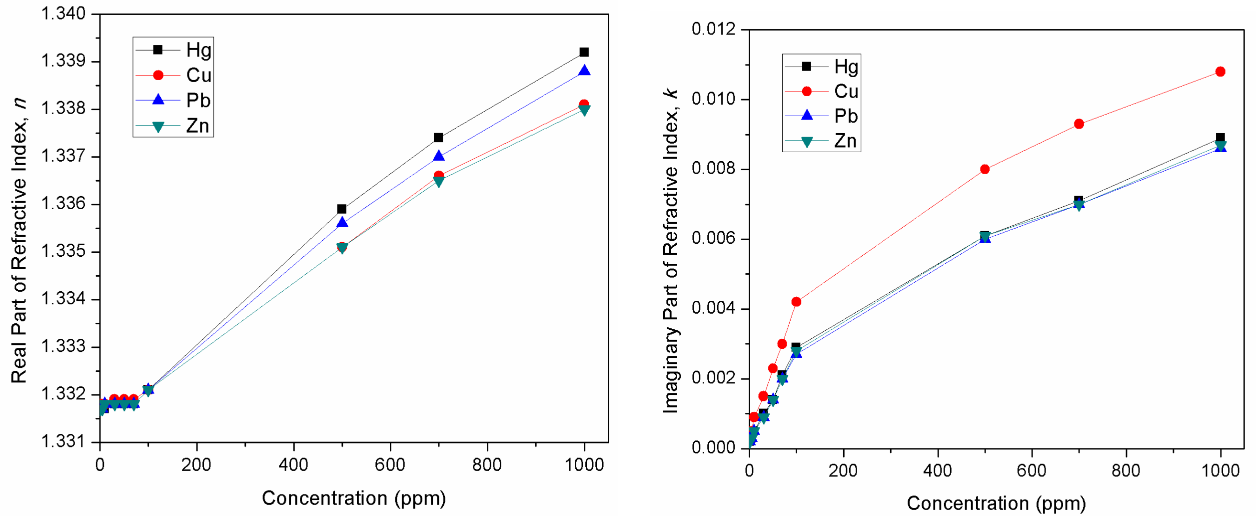
(a) (b)

Figure 7. Optical reflectance as a function of incident angle for zinc ion solutions with concentration: (a) 10 - 100 ppm, and (b) 100 - 1000 ppm.

crement number of ions absorbed to the metal surface. There is a slight difference for the shift of resonance angle among different heavy metal ions. This may due to the small difference of the size of these ions based on periodic table. The SPR curves are almost similar for deionized water and solution with concentration below 100 ppm. This research results are very important such that we can use these information (real and imaginary parts of refractive index) to further increase the sensitivity of SPR technique as an alternative optical sensor for heavy metal ions by coating an active layer onto the gold film. This activity is ongoing in our laboratory.

5. Conclusions

In this work, the optical properties of heavy metal ions solution have been obtained using surface plasmon resonance technique. Both the real and imaginary part of refractive index of the heavy metal ions solution increased with the heavy metal ions concentration. The resonance angle shifted to higher values to the right with the increasing of the concentration of heavy metal ions,



(a) (b)

Figure 8. (a) The real part of refractive index, *n*, as a function of Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} concentration. (b) The imaginary part of refractive index, *k*, as a function of Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} concentration.

Table 2. The real and imaginary part of refractive index for different concentration of copper ion solutions from fitting.

Concentration of Cu (ppm)	Real Part of Refractive Index, *n* (±0.0005)	Imaginary Part of Refractive Index, *k* (±0.0002)
0.5	1.3318	0.0003
1	1.3318	0.0003
5	1.3318	0.0005
10	1.3318	0.0009
30	1.3319	0.0015
50	1.3319	0.0023
70	1.3319	0.0030
100	1.3321	0.0042
500	1.3351	0.0080
700	1.3366	0.0093
1000	1.3381	0.0108

Table 3. The real and imaginary part of refractive index for different concentration of lead ion solutions from fitting.

Concentration of Pb (ppm)	Real Part of Refractive Index, *n* (±0.0005)	Imaginary Part of Refractive Index, *k* (±0.0002)
0.5	1.3317	0.0002
1	1.3317	0.0002
5	1.3317	0.0003
10	1.3318	0.0005
30	1.3318	0.0009
50	1.3318	0.0014
70	1.3318	0.0020
100	1.3321	0.0027
500	1.3356	0.0060
700	1.3370	0.0070
1000	1.3388	0.0086

for concentration 100 ppm and above. In this range of concentration, the shift of resonance angle increases linearly with concentration for all Hg^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} solution. This study also gives us the basic idea such that the SPR technique could be used as an alternative optical sensor for detecting heavy metal ions in solution. The real and imaginary part of refractive index for heavy metal ions that obtained from fitting (single layer) in this study gives us the important information required to further increase the sensitivity of SPR optical sensor in future research. We suggested that it can be carried out by introducing an active layer on the gold film (multilayer SPR sensor).

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Table 4. The real and imaginary part of refractive index for different concentration of zinc ion solutions from fitting.

Concentration of Zn (ppm)	Real Part of Refractive Index, *n* (±0.0005)	Imaginary Part of Refractive Index, *k* (±0.0002)
0.5	1.3317	0.0002
1	1.3317	0.0002
5	1.3317	0.0003
10	1.3318	0.0005
30	1.3318	0.0009
50	1.3318	0.0014
70	1.3318	0.0020
100	1.3321	0.0028
500	1.3351	0.0061
700	1.3365	0.0070
1000	1.3380	0.0087

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