Three-Layer Optical Sensor "Prism–Metal–Water Suspension of Inclusions" Based on Surface Plasmon Resonance

A.D. Suprun, L.V. Shmeleva

Faculty of Physics, Taras Shevchenko National University of Kyiv

Corresponding author: lshmel@univ.kiev.ua

An optical scheme of the Krechman type is considered, in which the receptor layer and the analyte layer do not exist separately, but represent a single receptor-analyte layer in the form of an aqueous suspension of micro-inclusions.

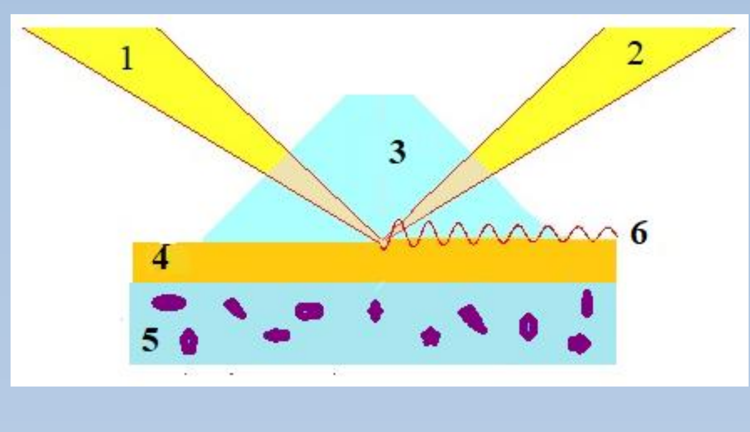

Fig. 1. Scheme of the sensor for the Krechman configuration: 1 – excitation light; 2 – reflected light; 3 – dielectric prism with a high refractive index; 4 – metal nanolayer (here gold nanolayer); 5 – dielectric (here, an aqueous suspension of molecular inclusions); 6 – surface plasmon.

The presence of micro-inclusions forms the effective dielectric constant of the suspension, different from the dielectric constant of the components (water and inclusions). Surface plasmon resonance (SPR) consists in the possibility of determining the resonance wavelength and resonance angle of incidence from the minimum of the reflection coefficient and depending on the sign of the effective permittivity of the suspension.

The paper investigated the effect of two factors on the effective dielectric constant: the concentration of inclusions in the aqueous suspension and their dielectric constant.

1. Effective dielectric constant ε of an aqueous suspension with inclusions from nucleic of acid molecules

For the sensor effect to occur at the metal-dielectric interface in the form of surface plasmon resonance (SPR), the dielectric must have a positive real part of the effective permittivity. The minimum light reflection coefficient at a certain wavelength and a certain angle of incidence provides a resonant effect. Therefore, it makes sense to investigate the effective dielectric constant of the suspension for its non-negativity.

The effective dielectric constant ε of a one-component aqueous suspension [1, 2] (all molecular structures are the same or of the same type in view of their dielectric properties) is determined by the formula

$$\varepsilon = \varepsilon_0 + 3\varepsilon_0 \frac{f_1 \frac{\varepsilon_1 - \varepsilon_0}{\varepsilon_1 + 2\varepsilon_0}}{1 - f_1 \frac{\varepsilon_1 - \varepsilon_0}{\varepsilon_1 + 2\varepsilon_0}}. \quad (1)$$

Here ε_0 is the dielectric constant of water; ε_1 is the dielectric constant of molecular structures (inclusions to an aqueous suspension), and f_1 is their partial volume fraction (hereinafter, concentration), which is determined by the ratio:

$$f_1 = \frac{V_1}{V_0 + V_1}, \quad (2)$$

where V_1 is the partial volume of nucleic molecular inclusions in the suspension, and V_0 is the partial volume of water in the suspension

Next, expression (1) will be used in a more compact form:

$$\varepsilon = \varepsilon_0 \frac{\varepsilon_1 + 2\varepsilon_0 + 2f_1(\varepsilon_1 - \varepsilon_0)}{\varepsilon_1 + 2\varepsilon_0 - f_1(\varepsilon_1 - \varepsilon_0)}. \quad (3)$$

2. Influence of the concentration of inclusions on the effective dielectric constant of the suspension

We analyze the influence of the concentration of inclusions f_1 on the effective dielectric constant ε with fixed parameters: ε_0 and ε_1.

The dielectric constant of water ε_0 can be estimated using the known dependence [3] of the refractive index of water $n(\lambda, t)$ on the wavelength λ and temperature t:

$$n(\lambda, t) = A(t) + \frac{B(t)}{\lambda^2} + \frac{C(t)}{\lambda^4} + \frac{D(t)}{\lambda^6}, \quad (4)$$

where:

$A(t) = 1.3208 - 1.2325 \cdot 10^{-5}\, t - 1.8674 \cdot 10^{-6}\, t^2 + 5.0233 \cdot 10^{-9}\, t^3$;

$B(t) = 5208.2413 - 0.5179\, t - 2.284 \cdot 10^{-2}\, t^2 + 6.9608 \cdot 10^{-5}\, t^3$;

$C(t) = -2.5551 \cdot 10^{8} - 18341.336\, t - 917.2319\, t^2 + 2.7729\, t^3$;

$D(t) = 9.3495 + 1.7855 \cdot 10^{-3}\, t + 3.6733 \cdot 10^{-5}\, t^2 - 1.2932 \cdot 10^{-7}\, t^3$.

According to [3], the dependence (4) is applicable in the temperature range $0°C \le t \le 100°C$ i in the wavelength range $300\ \text{nm} \le \lambda \le 1000$ nm, and all numerical coefficients in the definitions of factors $A(t), B(t), C(t)$ and $D(t)$ have such dimensions that ensure the dimensionlessness of each term in (4). The wavelength in (4) has the dimension of nanometers.

Under the conditions: $t = 20°C$ and $\lambda = 589$ nm (the latter corresponds to the doublet D-line of sodium in the yellow part of the spectrum), the refractive index of water n is 1.333, and, accordingly, the dielectric constant $\varepsilon_0 \equiv n^2$ is 1.777. In the visible range, the dielectric constant ε_0 can vary from 1.756 to 1.807. The deviation is ~2% from 1.777 and for some inclusions can compete with the difference $\varepsilon_1 - \varepsilon_0$

The value of dielectric constant ε_1 without taking into account that the refractive index is complex is, for example, for nucleic acids [4] $\varepsilon_1 = 2.34$ $(n_1 = 1.53)$, for proteins [5] $\varepsilon_1 = 1.89$ $(n_1 = 1.375)$, for erythrocytes, at different stages of liver cirrhosis, taking into account the thickness of the studied samples, varies within $2.22 \le \varepsilon_1 \le 2.53$ $(1.49 \le n_1 \le 1.59)$.

The results of calculations of the effective dependence of the dielectric constant ε on the concentration of inclusions f_1 for the above values of the parameter ε_0 and a selection of values of the parameter ε_1 are shown in Fig. 1.

Dependencies for the extreme values of the optical range: $\varepsilon_0 = 1.756$ and $\varepsilon_0 = 1.807$, qualitatively do not differ from those shown in Fig. 1.

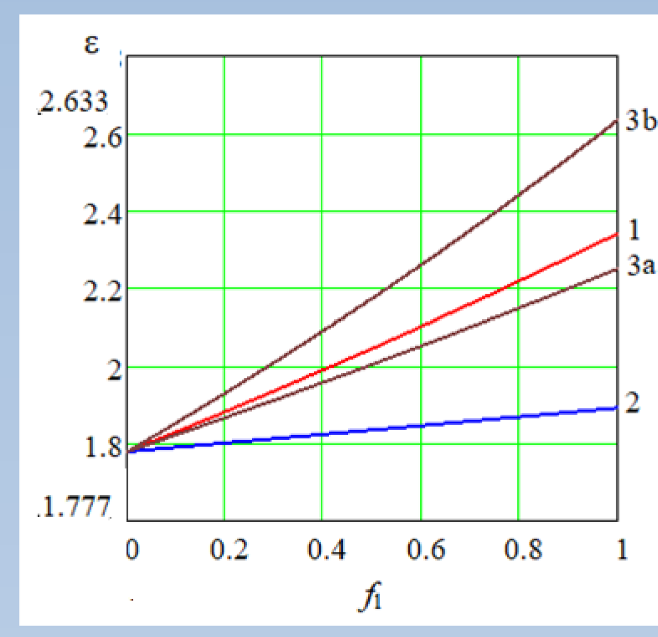

Fig. 1. Dependence of the effective dielectric constant ε of the analyte in the form of an aqueous suspension of molecular structures on their concentration f_1 for different values of the dielectric constant ε_1 of molecular structures (inclusions) in an aqueous suspension. Dependency 1 corresponds to the value of $\varepsilon_1 = 2.34$ for nucleic acids, dependence 2 corresponds to the value of $\varepsilon_1 = 1.89$ for proteins, and dependencies 3a, 3b relate to the values of $\varepsilon_1 = 2.22$, $\varepsilon_1 = 2.53$, respectively, for erythrocytes at different stages of liver cirrhosis, taking into account the thickness of the studied samples(the figure shows the two extreme values of the range).

Analogous dependences for the extreme values of the optical range: : $\varepsilon_0 = 1.756$ and $\varepsilon_0 = 1.807$, qualitatively do not differ from those shown in Fig. 1. This means that the variation of the dielectric constant of water ε_0 within the optical range does not affect the sign (positive) of the effective dielectric constant ε at a temperature of $t = 20°C$, and this, in turn, means the presence of SPR under the considered conditions.

From the graphs in Figure 1, it can also be seen that the dependence $\varepsilon(f_1)$ is so sensitive to the dielectric constant ε_1 of molecular inclusions in an aqueous suspension that one can ask questions about the analysis of not only the mutual influence of ε and f_1, but also about the determination of the type of substance of molecular inclusions in an aqueous suspension by creating appropriate databases, or comparing calculations according to formula (3) and corresponding experimental measurements.

3. The influence of the dielectric constant of inclusions ε_1 on the effective dielectric constant ε of an aqueous suspension

Figure 1 shows the results for the entire formally permissible concentration range f_1 from 0 to 1. According to (2), the value $f_1 = 0$ means the absence of inclusions in the aqueous suspension, and the value $f_1 = 1$, on the contrary, the absence of water. For physical reasons, to describe the aqueous suspension of inclusions, consider the range $f_1 < 0.5$, since at $f_1 > 0.5$ the part of inclusions will exceed the part of water.

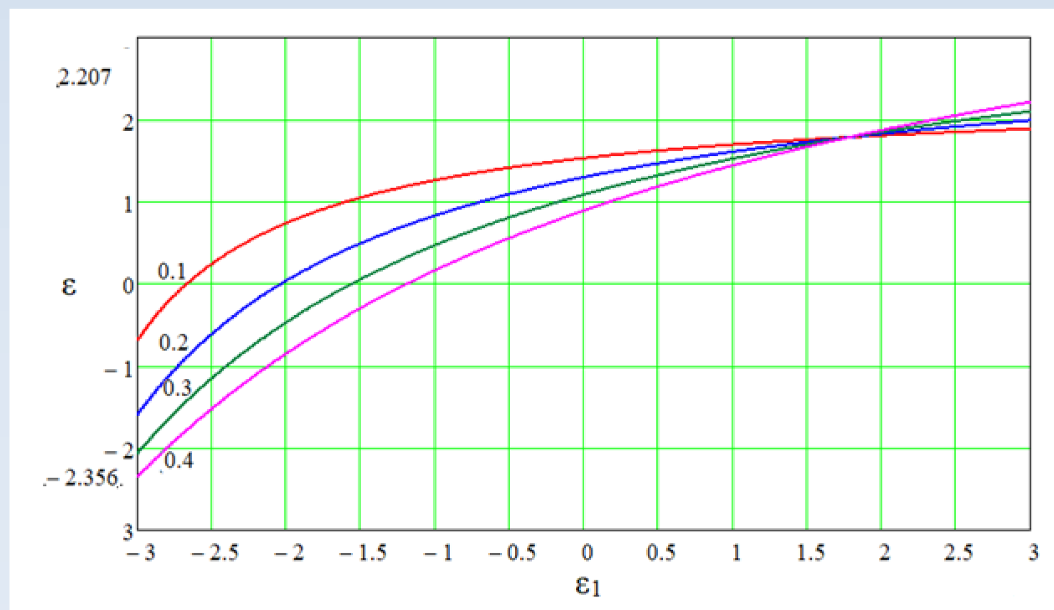

Fig. 2. Dependence of the effective dielectric constant ε of the analyte in the form of an aqueous suspension of molecular structures on the value of the dielectric constant of these structures ε_1 for four values of their concentration $f_1 = \{0.1;\ 0.2;\ 0.3;\ 0.4\}$.

Figure 2 shows the real part of the dielectric constant ε_1 in the range of values $-3 < \varepsilon_1 \le 2.5$, which completely covers and exceeds the real values of the complex dielectric constant of inclusions for nucleic and protein molecular structures. The figure shows that for inclusions in the form of nucleic and protein molecular structures $(-1 < \varepsilon_1 \le 2.5)$ at any concentration f_1 $f_1 = \{0.1;\ 0.2;\ 0.3;\ 0.4\}$ the dielectric constant satisfies the condition $\varepsilon > 0$. This means that the effective dielectric constant ε of the mixture in this range $(-1 < \varepsilon_1 \le 2.5)$ can only be positive and surface plasmon resonance (SPR) will exist under any of the considered conditions for suspensions with protein and nucleotide inclusions.

Figure 2 also shows the situation when the dielectric constant of inclusions ε_1 is less than -1. It can be seen that for inclusions in which $-3 \le \varepsilon_1 \le -1$, the effective dielectric constant of the suspension ε can take the value $\varepsilon < 0$ and the SPR disappears. The effect of its disappearance-appearance can be interesting, for example, in the analysis of metallization of DNA due to its interaction with ions [6].

Conclusions

The article discusses the scheme of an optical sensor on a SPR, in which the receptor layer and the analyte layer are a single receptor-analyte layer. This layer is an aqueous suspension of micro-inclusions, where the dielectric constant of the suspension is different from the dielectric constant of the components (water and inclusions). Shown:

-- For inclusions with a dielectric constant ε_1 in the range of 1.89 – 2.53 (typical for protein and nucleic molecular fragments without consideration the complexity), the effective dielectric constant cannot be negative for any concentration.

-- For protein and nucleic inclusions (with accounting the complexity), the effective dielectric constant of the suspension can only be positive, and SPR is guaranteed to be realized at concentrations of 10% - 40%.

-- Negative values of the effective permittivity of the suspension can be realized when (Re $\varepsilon_1 < -1$) and can be interesting in the study of DNA metallization.

References

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