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# Reducing measurement uncertainty of instruments based on the phenomenon of surface Plasmon resonance

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**Abstract:** Considered in this paper are mechanisms of temperature influence on the results of optical measurements based on the surface Plasmon resonance phenomenon. It has been ascertained that the error of measurement results is related with the temperature influence on the refraction index of substances under study as well as on elements of optical setup in measuring equipment. The authors have experimentally demonstrated the influence of thermal stabilization of measuring equipment on dispersion of results obtained in optical measurements.

**Keywords:** Error of Measurement Results, Thermal Stabilization, Surface Plasmon Resonance

## 1. Introduction

Optical measurements based on the phenomenon of surface Plasmon resonance (SPR) are widely used in chemical and biological analyses that are found on registration of molecular adsorption in gas-like and liquid media [1-2]. Diagnostic devices that operate using the SPR phenomenon possess high sensitivity to low concentrations of studied substances, which enables to use them as precise analytical tools in laboratory investigations performed in food, chemical and pharmaceutical industry, agriculture, medicine and ecology. At the same time, up to date the temperature influence on accuracy and stability in operation of SPR sensor appliance is investigated insufficiently. As known, change in temperature causes changes in optical parameters of the medium under study, which is able to introduce some errors into results of measurements.

The analysis of literature sources [3-7] showed that enhancement of measurement accuracy as well as reliability and efficiency of devices can be provided by temperature stabilization of the measuring cell. It means that doing so we stabilize the temperature of studied liquid or gas medium placed above the sensitive element of the analytical device operating as based on the SPR phenomenon. When carrying out these measurements, one of the problems is to provide an allowable error for the measured value. The error value of measurement results is essentially influenced by temperature oscillations both of the investigated object (liquid or gas) and all the measuring equipment. It is related with temperature changes in ambient medium, heating the measuring equipment, and in some cases with chemical processes in the studied substances, when the heat energy can be evolved or absorbed. During measurements, this error can change as a consequence of the difference in temperature at the beginning of measurements and after their completion. It follows from the mentioned above that it is necessary to determine the reasons for temperature errors in optical measurements based on SPR and investigate experimentally the influence of thermal stabilization that provides reducing these errors when performing measurements in various media.

## 2. Theoretical Backgrounds

### *2.1. Temperature Influence on the Sensitivity*

The temperature influence on the sensitivity of SPR-sensors results in some error of measurement data, which is caused by temperature changes in the refraction index of the studied substance and in optical scheme of the measuring device during the measurement process. The value of this error depends on the temperature gradient in the course of measurements and temperature coefficients of the refraction indexes. Therefore, it is pertinent to study the temperature influence on the main system elements, namely: water, glass, source of exciting light and metal layer where Plasmon is excited.

SPR can be optically excited if the wave vector of the incident light with angular frequency has a surface-parallel component equal to the wave vector of the surface Plasmon (SP) waves. However, the SP waves cannot be excited by a light directly incident from air onto the interface because energy and momentum conservation cannot be satisfied simultaneously in the frequency range of their dispersion curves. This problem is solved using a dispersive medium (i.e., prism, gratings, etc.) that can enable. Then can be satisfied by varying the angle of incidence of the light. The incident angle at which the SPR occurs is always higher than that of the total internal reflection for the prism and the bulk medium that form interfaces with the metal. Two basic configurations that use prisms for photon–SP coupling are the Otto and Kretschmann configurations [8], [9]. In the Otto configuration, the sample to be sensed is limited with the air gap between the metal and prism. On the other hand, in the Kretschmann configuration, the sensing layer is located between the metal layer and air so that the sample is not limited to a very small volume. Therefore, it is more suitable for sensing applications.

The excitation of the SPR is understood by observing the reflected light spectrum obtained either by "angular interrogation" or "wavelength interrogation." In the angular interrogation approach, λ of the incident light is kept constant and $\theta$ is varied. At a specific $\theta$, the incident light is absorbed due to the SPR excitation, resulting in a sharp dip in the reflected light spectrum. This spectrum is characterized by three parameters: resonance angle $\theta_{min}$, half width at half maximum $\Delta\theta$, and the reflection minimum $R_{min}$ (Fig. 1). In the wavelength λ interrogation approach, wavelength of the incident light is varied while the incidence angle is kept constant. At $\lambda = \lambda_{min}$, resonance condition is achieved and this is understood with a dip in SPR spectrum. In this approach, parameters which are used to characterize the spectrum are resonance angle $\lambda_{min}$, half width ($\Delta\lambda$), and reflection minimum $R_{min}$. SPR sensors generally use the following detection approaches: 1) measurement of resonant angle shift; 2) measurement of resonant wavelength shift; and 3) measurement of change in light intensity.

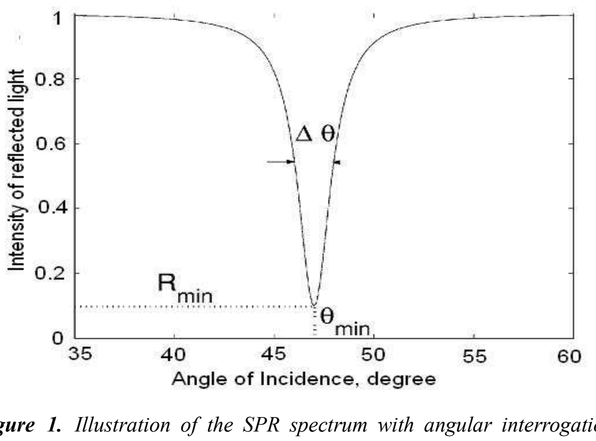


***Figure 1.*** *Illustration of the SPR spectrum with angular interrogation approach.* $\theta_{min}$ *: SP resonance coupling angle.* $\Delta\theta$*: SP half width.* $R_{min}$*: intensity of the reflected light in the resonance condition.*

Since the extreme sensitivity of SPR phenomenon relies on the collective oscillation of free electrons at the metal surfaces, any physical factor that can cause variations in the refractive in dices and thicknesses of materials forming the SPR configuration will generate significant changes in the Plasmon dispersion relations and, hence, in the SPR spectrum. Among these factors, temperature has shown to have deteriorating effects on the SPR spectrum resulting in decrease in the sensitivity of the SPR sensors. Temperature effects show themselves as the changes in the thickness and refractive index of the layers in the SPR geometry. Several schemes have been presented which can compensate these temperature effects on the SPR sensor.

### *2.2. Temperature Dependence of Refractive Index of Glass*

Used in SPR-sensors are the following glass elements: prisms, dividers and substrates. Change in temperature of these optical elements as a consequence of temperature changes in ambient medium causes changes in their optical characteristics, in particular, of their refraction index. Dependences of the glass refraction index on temperature for four wavelengths of laser radiation exciting SPR are shown in Fig. 2. The temperature coefficient of the glass refraction index is equal to $1\cdot 10^{-5}$ $1/^{0}C$ from literature source [10].

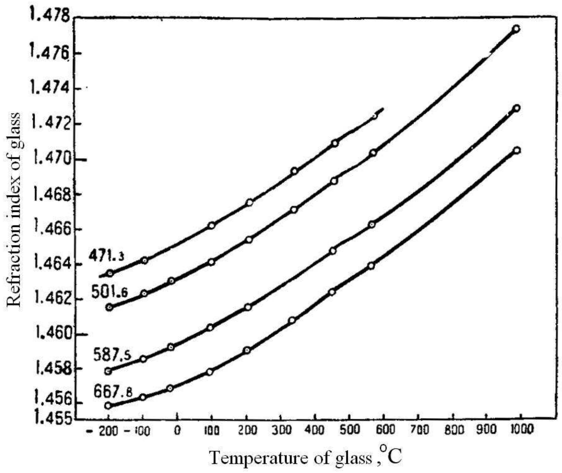


***Figure 2.*** *Temperature dependences of the glass refraction index for four wavelengths of laser radiation [10].*

### *2.3. Temperature Influence on a Source of Exciting Light*

Temperature influence on a source of exciting light depends on the type of source and its operation conditions. In SPR-sensors, predominantly low power (3 – 10 mW) semiconductor injection lasers are used as these sources. Generation of radiation in these lasers is possible under conditions that the current through the *pn*-junction exceeds the threshold one. When the temperature is increased, the threshold current is increased, too, which causes decreasing the radiation intensity. If the current through the *pn*-junction becomes lower than the threshold one, generation of radiation disappears. Also, the temperature influences stability of the wavelength. Changes in the laser wavelength cause an undesirable shift of the SPR-curve minimum. In the case of injection lasers, the gradient of the wavelength shift is (0.12…0.15) nm/K from literature source [11].

### *2.4. Temperature Dependence of Metal Film Properties*

It is known that the properties of the metal film significantly affect the SPR mechanism. An up-to-date survey of literature and our studies have shown that these effects on a two-interface system can be listed as follows [12]–[15]:

1) An increase in the imaginary part ($\varepsilon_1''$) of the dielectric permittivity ($\varepsilon_1 = \varepsilon_1' + j\,\varepsilon_1''$) of the metal film introduces higher damping and causes significant broadening the SPR curve shift $\Delta\theta$ to higher angle values. Effect on $\theta_{min}$ is very small.

2) When $|\varepsilon_1'|$ is increased, the obvious effect is the shift of $\theta_{min}$ to higher values and increase in $\Delta\theta$.

3) SPR can be observed for metal thickness < λ/8. When the thickness increases, the reflectivity minimum of the SPR curve becomes shallower, and it is no longer observed once the thickness exceeds λ/8. When the thickness is decreased, there is a slight change in $\theta_{min}$, however, $\Delta\theta$ is significantly affected due to the larger radiation damping by light emission into the prism. Surface Plasmon wave vector can be linked to the SPR spectrum parameters as:

$$\mathrm{Re}\lfloor k_{spw}\rfloor = k_{inc} n_0 \sin(\theta_{sp}) \qquad \mathrm{Im}\lfloor k_{spw}\rfloor = k_{inc} n_0 (\Delta\theta)\cos(\theta_{sp}) \tag{1}$$

If surface Plasmon waves reach the prism, they transform into a plane wave leading to a back-coupled radiation. The destructive interference of the back-coupled light with the incident light at the prism–metal boundary will transform the energy of the incident light into heat. The effect of the refractive index ($n_1 = n_{r1} + jn_{i1}$) of the metal film on our model must be analyzed in detail, because it is well known that the thermal changes affect this parameter significantly. To carry out this analysis, we use the Drude model:

$$\varepsilon = (n_r + jn_i)^2 = 1 - \frac{\omega_p^2}{\omega(\omega + j\omega_c)} \tag{2}$$

Where ε, $n_r$, and $n_i$ are the dielectric permittivity and the real and imaginary parts of the refractive index of the metal, respectively, ω is the angular frequency of the electromagnetic wave, and $\omega_p$ and $\omega_c = \omega_{cp} + \omega_{ce}$ represent the Plasmon frequency and collision frequency of electrons in metal, respectively. The plasma frequency can be found using the following expression (3).

$$\omega_p = \sqrt{\frac{4\pi N e^2}{m^*}} \tag{3}$$

Where, $N$ and $m^*$ are the density and effective mass of the electrons, respectively. Both of these parameters are temperature dependent, however, the relatively very small temperature dependence of $m^*$ can be neglected. Hence, $\omega_p$ at a given temperature $T$ can be calculated using the expression (4).

$$\omega_p(T) = \omega_p(T_0)[1 + 3\gamma(T - T_0)]^{-1/2} \tag{4}$$

Where, $\omega_p(T_0)$ is the plasma frequency at a reference temperature $T_0$. Here, the temperature dependence of $N$, which is defined as $N(T) = N(T_0)[1+3\gamma(T - T0)]^{-1}$, is exploited [16]. The contributions of phonon-electron and electron–electron scattering on $\omega_c$ are described as follows [17]–[19]:

$$\omega_{cp} = \omega_0\left[\frac{2}{5} + \frac{4T^5}{\theta_D^5}\int_0^{\theta_D/T}\frac{z^4}{e^z - 1}dz\right] \tag{5}$$

$$\omega_{ce} = \frac{\pi^3\Gamma\Delta}{12\hbar E_F}\left[(k_B T)^2 + (\hbar\omega/2\pi)^2\right]. \tag{6}$$

Value $\omega_0$ in (6) is a constant, and care should be taken to calculate its value. In order to determine the value of $\omega_0$, we solve the equations:

$$n_r^2 - n_i^2 = 1 - \frac{\omega_p^2}{\omega^2 + \omega_c^2} \qquad 2n_r n_i = \frac{\omega_c\omega_p^2}{\omega(\omega^2 + \omega_c^2)} \tag{7}$$

Simultaneously for $\omega_p$ and for $\omega_c$ the reported experimentally obtained refractive index value for a gold metal film. At room temperature ($T$ = 300 K) and with an incident light of the wavelength λ = 650 nm, a gold film with the thickness 50 nm has $n_r = 0.1795$ and $n_i = 3.6245$, and a silver film has $n_r$ = 0.14 and $n_i$ = 4.02 from literature sources [20]–[22]. In Table 1, the values given in parentheses are for silver, and the parameters for which there is no parentheses, the value is the same for silver and gold.

***Table 1.*** *List of parameter values used in the calculation of temperature effects on metals*

| Symbol | Meaning | Value | Unit |
|---|---|---|---|
| Γ | Fermi-surface average ofscattering probability | 0.55 | |
| γ | Thermal linear expansion coeficient | 14.2 (19) | $10^{-6}$ K$^{-1}$ |
| Δ | Fractional Umklapp scattering | 0.77 (0.73) | |
| $\theta_D$ | Debye temperature | 185 (220) | K |
| $E_F$ | Fermi Energy | 5.51 (5.48) | eV |
| ħ | Planck’s constant | 1.0546 | $10^{-34}$ Js |
| $k_B$ | Boltzmann constant | 1.38062 | $10^{-23}$ JK$^{-1}$ |
| μ | Poisson’s number | 0.42 (0.32) | |

Temperature effect can be summarized as $dn_{r1}/dT \approx 3.408 \times 10^{-4}$ K$^{-1}$ and $dn_{i1}/dT \approx -1.381 \times 10^{-4}$ K$^{-1}$ for the gold film, and $dn_{r1}/dT \approx 3.559 \times 10^{-4}$ K$^{-1}$ and $dn_{i1}/dT \approx$

$-1.770 \times 10^{-4}$ $K^{-1}$ for the silver film. Temperature dependence of the film thickness can be modeled using $d = d_0 [1 + \gamma' (T - T_0)]$ with the corrected thermal expansion coefficient $\gamma'$, which is given as:

$$\gamma' = \gamma (1 + \mu)/(1 - \mu) \quad (8)$$

Where $\mu$ is Poisson's number of the film material [23]. This corrected coefficient is used instead of the linear expansion coefficient due to the expansion of the film only in the normal direction. For a gold (silver) thin film, a change in 1000 K will cause a change of ~ $0.0348d_0$ (~ $0.0348d_0$) in its thickness.

In this geometry, the SP wave is excited at the boundary of the metal film and the environment (bulk medium). Then the SP wave vector can be written as:

$$k_{spw} = k_{inc}\left[\frac{\varepsilon_1\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right]^{1/2} = k_{inc}\left[\frac{\varepsilon_{1r}\varepsilon_3}{\varepsilon_{1r}+\varepsilon_3}\right]^{1/2} + jk_{inc}\frac{\varepsilon_{1i}}{2\varepsilon_{1r}^2}\left[\frac{\varepsilon_{1r}\varepsilon_3}{\varepsilon_{1r}+\varepsilon_3}\right]^{3/2} \quad (9)$$

Where we have assumed $\varepsilon_1 = \varepsilon_{1r} + j\varepsilon_{1i}$ with the small damping approximation of $\varepsilon_{1i} << |\varepsilon_{1r}|$. For simplicity, we assume that the bulk medium has a real refractive index with $\varepsilon_3 = n_3^2$. Using (1) in (9) and taking the derivative with respect to temperature, we arrive at the following equation, which explicitly shows the dependence of the resonance angle $\theta_{min}$ on temperature:

$$\frac{d\theta_{\min}}{dT} = \frac{\left[\varepsilon_{1r}\left(n_0^2-\varepsilon_3\right)+n_0^2\varepsilon_3\right]^{-1/2}}{2\left(\varepsilon_{1r}+\varepsilon_3\right)\sqrt{\varepsilon_{1r}\varepsilon_3}}\left[\varepsilon_3^2\frac{\partial\varepsilon_{1r}}{\partial T}+\varepsilon_{1r}^2\frac{\partial\varepsilon_3}{\partial T}\right] \quad (10)$$

The temperature dependence of the full-width of the SPR spectrum can be found in the same way; however, it is too lengthy to give here. It is found that $d\Delta\theta/dT$ is a function of the form:

$f(n_0, \varepsilon_{1r}, \varepsilon_3, \theta_{min})\partial\varepsilon_3/\partial T + g(n_0, \varepsilon_{1r}, \varepsilon_{1i}, \varepsilon_3, \theta_{min})\partial\varepsilon_{1r}/\partial T + h(n_0, \varepsilon_{1r}, \varepsilon_3, \theta_{min})\partial\varepsilon_{1i}/\partial T.$

*f, g, h* – functions depend on properties of material optical system.

As it is clearly seen in these equations, the SPR spectrum is a function of the refraction indices of the metal film and the environment together with the film thickness, which are all temperature dependent. Therefore, any change in the SPR curve can be attributed to the changes both in the film and the environment; we cannot discriminate and resolve their effects. As it was pointed out in the previous section, the refraction index of environment can be altered not only by the thermal changes but by contamination, changes in the concentration, and changes in pressure, as well. This constitutes a serious drawback in two-interface SPR sensing schemes. For the sake of simplicity in the numerical simulations, we will neglect the effects of contamination and concentration changes and assume that all changes in the refractive indices and thickness are caused by thermal changes. These results clearly show that changes in the refractive index of the environment strongly affect the sensitivity of SPR phenomenon.

# 3. Experimental

In V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, performed for many years are experimental investigations of applied aspects for designing biosensors based on SPR. One of the designed models is the spectrometer "Plasmon-6" (Fig. 3) suitable for operation in labs of biochemical and biophysical profiles. Within the frameworks of these investigations, developed and manufactured was the thermostat that enables to keep the set temperature with rather high stability. Offered after performed investigations was thermostating not only of the studied object but also of all the measuring equipment including boxes with the studied substances. This approach enabled to minimize the temperature error in measurement results and, in addition, temperature loading the measuring equipment, which prolongs its functioning term.


***Figure 3.*** *Appearance of the SPR spectrometer Plasmon-6.*

The spectrometer Plasmon-6 was placed into the thermostat operation chamber where a constant temperature was kept, values of which could be set within the range +10 up to +40°C with the step 0.1°C. The volume of this chamber was close to 13 liters, which allowed us to place there not only spectrometer but micro-pump and containers with studied substances. To connect the spectrometer with power and control cables, we provided the thermostat case with special packed openings. Experiments aimed at temperature influence on results of measurements were performed in the Multiple mode of Plasmon-6.

As a result of measurements in the Multiple mode, we took the intensity of light reflected from the sensitive element for the angle of incidence corresponding to the minimum of SPR-curves. It means that in this mode we followed the shift of the angle corresponding to the minimum of SPR-curves ΔΘ. The chamber was filled with air, the temperature of which was stabilized at the level +19°C. It was 1°C above the room temperature. As a sensitive element, we used glass plates with a deposited gold layer of 50-nm thickness. The sensogram obtained in these experiments is shown in Fig 4.

Depicted in Fig. 4 are the results of measurements for gas-like medium. In these figures, the abscissa corresponds to the time of observation in minutes, while the ordinate corresponds to the position of the SPR-curve minimum in degrees. At the very beginning, the spectrometer was placed outside the thermostat, air passed through the cell of the volume 30 μl, and we measured the shift of the SPR-curve minimum for 95 min at the room temperature (+18°C). After that, the spectrometer was placed into the thermostat, and measurements were repeated for 85 min at the stabilized temperature +19°C. The measured values of the reflected light intensity were recorded using the special program.

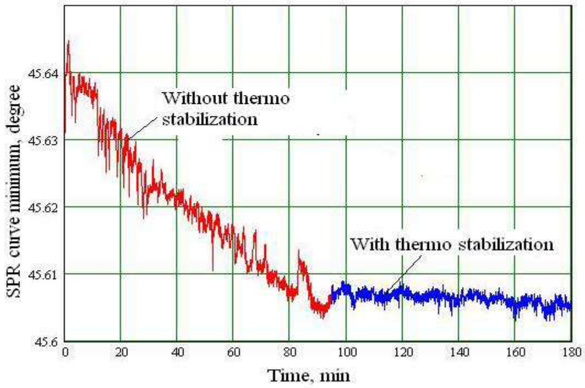


***Figure 4.*** *Temperature drift of the SPR-curve minimum when the cell is filled with air.*

## 4. Conclusions

Thus, it is ascertained in this work that thermal stabilization of the measuring equipment based on the SPR phenomenon decreases the temperature error caused by the temperature shift of the SPR-curve minimum by 5 times, which is very important when studying the kinetics of chemical and biological processes.

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