

Surface Plasmon Resonance Based Sensing of Aqueous Solutions Using Spectral Interferometry

J. LUŇÁČEK^{a,b,*}, P. HLUBINA^{a,b}, D. CIPRIAN^{a,b}, M. DULIAKOVÁ^a AND M. LUŇÁČKOVÁ^c

^aDepartment of Physics, VŠB — Technical University of Ostrava,
17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic

^bRegional Materials Science and Technology Centre, VŠB — Technical University of Ostrava,
17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic

^cDepartment of Mathematics and Descriptive Geometry, VŠB — Technical University of Ostrava,
17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic

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This paper deals with a polarimetric setup to measure the refractive index change of aqueous solutions. The experimental method is based on the surface plasmon resonance effect in the Kretschmann configuration combined with spectral interferometry. In order to retrieve surface plasmon resonance-induced differential phase change, a windowed Fourier transform was adopted to extract the phases from two spectral interferograms, one corresponding to the reference material (air) and the second to the analyte (NaCl aqueous solution). The shift of phase curve is related to the analyte refractive index change. The refractive index of the NaCl aqueous solutions (0, 2 and 5 percent) was measured by the Abbe refractometer at a wavelength of 589.3 nm and compared with theoretical one, calculated by the Lorentz–Lorenz equation. An excellent agreement between the values was confirmed. The resonance wavelengths as extremes of the surface plasmon resonance-induced differential phase changes retrieved from spectral interference signals were compared with the resonance wavelengths determined from spectral reflectance measurements. A good agreement between the values was confirmed.

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1. Introduction

Sensors based on the surface plasmon resonance (SPR) effect have been demonstrated for numerous applications, especially in biology, chemistry and physics, over the past several decades [1–3]. Surface plasmons are electromagnetic excitations propagating along the boundary between a suitable lossy medium with sufficiently high density of free electrons, usually metal, and dielectric material. These waves can be excited only by a *p*-polarized incident wave and not *s*-polarized one. Their electromagnetic fields decay exponentially in the direction perpendicular to the boundary [4]. If a special resonance condition is fulfilled (SPR), maximum power of the incident wave can be coupled to the surface plasma oscillations and the power carried by reflected wave drops down. The SPR condition is sensitive to the change of the refractive index of the surrounding medium (analyte). This mechanism can be used to sense the change of properties of the surrounding medium (usually liquid or gas) via the change of its refractive index, observing the shift of the spectral reflectance minimum. Frequently used SPR sensing structures are based on silver or gold layers, because these metals exhibit sufficient conditions mentioned above for the effective excitation of surface plasmons. Gold offers better chemical stability, on the other hand silver is more sensitive [4].

In order to extract useful information from SPR systems, a number of various schemes and detection techniques have been supposed. Spectral reflectance and

spectral phase change measurements rank among often used techniques in the last year [5, 6]. There are several techniques, based on the fringe analysis in the spatial, temporal and spectral domain, which are able to retrieve the phase changes caused by the SPR effect according to experimental conditions [1, 3, 5].

Recently, we proposed an SPR sensing setup based on spectral phase change and spectral reflectance measurements using the Kretschmann SPR sensor prism with spectral interference fringes generated in a polarimetric configuration employing a white light source and a birefringent crystal [7]. This experimental configuration was tested for water as an analyte and air as a reference material.

Present paper deals with spectral phase change and spectral reflectance measurements of the NaCl aqueous solutions in the same experimental configuration. Further, the refractive index of the NaCl aqueous solutions is determined at a wavelength of 589.3 nm. First, the refractive index is measured by the Abbe refractometer and second, it is calculated by the Lorentz–Lorenz equation [8]. Finally, discrepancies between experimental spectral curves and theoretical ones are shortly discussed.

2. Theoretical background

The refractive index of analyte $n_a(\lambda)$, in our case NaCl aqueous solutions, was calculated by the Lorentz–Lorenz equation [8]:

$$n_a^2(\lambda) = \frac{2 \left\{ \left[\frac{1}{\rho_{\text{NaCl}}} \left(\frac{n_{\text{NaCl}}^2 - 1}{n_{\text{NaCl}}^2 + 2} \right) \right] w_{\text{NaCl}} \rho_a + \left[\frac{1}{\rho_{\text{H}_2\text{O}}} \left(\frac{n_{\text{H}_2\text{O}}^2 - 1}{n_{\text{H}_2\text{O}}^2 + 2} \right) \right] w_{\text{H}_2\text{O}} \rho_a \right\} + 1}{1 - \left\{ \left[\frac{1}{\rho_{\text{NaCl}}} \left(\frac{n_{\text{NaCl}}^2 - 1}{n_{\text{NaCl}}^2 + 2} \right) \right] w_{\text{NaCl}} \rho_a + \left[\frac{1}{\rho_{\text{H}_2\text{O}}} \left(\frac{n_{\text{H}_2\text{O}}^2 - 1}{n_{\text{H}_2\text{O}}^2 + 2} \right) \right] w_{\text{H}_2\text{O}} \rho_a \right\}}, \quad (1)$$

where ρ_{NaCl} , $\rho_{\text{H}_2\text{O}}$, n_{NaCl} , $n_{\text{H}_2\text{O}}$, w_{NaCl} , and $w_{\text{H}_2\text{O}}$ are density, refractive index and mass fraction of NaCl and water, respectively. The refractive indices n_{NaCl} and $n_{\text{H}_2\text{O}}$ were calculated according to the well-known Sellmeier formula [9]. Density of the NaCl aqueous solutions ρ_a can be determined as

$$\rho_a = p_1 w_{\text{NaCl}}^3 + p_2 w_{\text{NaCl}}^2 + p_3 w_{\text{NaCl}} + p_4, \quad (2)$$

where $p_{1,2,3,4}$ are the polynomial coefficients of the interpolation and w_{NaCl} are mass fractions of NaCl solutions.

The SPR effect was analyzed by standard Fresnel equations [8]. We remind only the basic ideas; the spectral complex reflection coefficients for both p - and s -polarized components can be expressed as

$$r_{p,s}(\lambda) = \sqrt{R_{p,s}(\lambda)} \exp(i\delta_{p,s}(\lambda)), \quad (3)$$

where $R_{p,s}(\lambda)$ and $\delta_{p,s}(\lambda)$ are the spectral reflectance and the spectral phase for both polarizations, respectively. When the resonance condition is fulfilled, we are able to find the dip position for a certain wavelength which corresponds to the minimum of the spectral reflectance ratio $R_p(\lambda)/R_s(\lambda)$ and to the maximum of the spectral phase difference change $\Phi(\lambda) = \Delta_{\text{analyte}}(\lambda) - \Delta_{\text{reference}}(\lambda)$. The position of the dip and the phase shift, respectively, is very sensitive to the analyte refractive index variations.

We processed the spectral interferogram recorded by a spectrometer which stores the useful phase information. The spectral signal $S(\lambda)$ can be expressed as

$$S(\lambda) = V(\lambda) \cos(\Delta(\lambda) + \delta_{\text{noise}}(\lambda)), \quad (4)$$

where $V(\lambda)$ is the spectral visibility term related to $R_p(\lambda)$ and $R_s(\lambda)$; $\delta_{\text{noise}}(\lambda)$ is effectively eliminated by mutual subtraction of the phase terms in Eq. (4). The spectral phase difference $\Delta(\lambda) = \delta_p(\lambda) - \delta_s(\lambda)$ is retrieved from the spectral signal $S(\lambda)$ by a windowed Fourier transform (WFT) method [10].

3. Experimental setup and measurement methods

The refractive index of the NaCl aqueous solutions and water was measured by the well-known Abbe refractometer at a wavelength of 589.3 nm. This apparatus is able to measure the refractive index with uncertainty ± 0.0001 .

The experimental setup with the Kretschmann SPR structure with special cell for liquid samples used for the measurement of the spectral reflectance ratio $R_p(\lambda)/R_s(\lambda)$ and the spectral phase difference $\Delta(\lambda)$ was presented in a previous paper [7]. Setup comprises a white-light source (halogen lamp HL-2000, Ocean Optics), an optical fiber, a collimating lens, a crystal of birefringent quartz of thickness 4 mm, the Glan-Taylor calcite polarizer and analyzer (Thorlabs), SF10 Kretschmann SPR sensor prism with Au film of 44 nm

nominal thickness, a microscope objective, micropositioners and a read optical fiber. The output spectral interference signals affected by the SPR are recorded by spectrometer USB4000 (Ocean Optics, spectral range from 350 to 1000 nm) controlled by a PC. Its spectral resolution is limited by a Gaussian response function. The incident angle was approximately 60° (see Fig. 1).

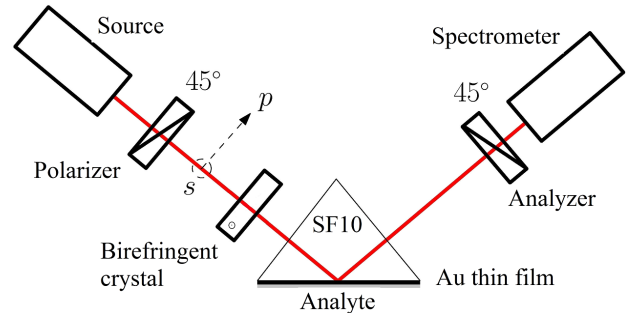


Fig. 1. Experimental setup of the SPR sensing system with a polarimetric configuration and a birefringent crystal.

The reflectance ratio $R_p(\lambda)/R_s(\lambda)$ measurement consists of three steps [5]. First, with the source blocked, the background spectrum $I_{\text{bkg}}(\lambda)$ is measured; second, with the analyzer oriented perpendicularly to the plane of the incidence, the reflection spectrum $I_s(\lambda)$ for s -polarization is measured; and third, with the analyzer oriented parallel to the plane of the incidence, the reflection spectrum $I_p(\lambda)$ for p -polarization is measured. The reflectance ratio $R_p(\lambda)/R_s(\lambda)$ is given as

$$R_p(\lambda)/R_s(\lambda) = \frac{I_p(\lambda) - I_{\text{bkg}}(\lambda)}{I_s(\lambda) - I_{\text{bkg}}(\lambda)}. \quad (5)$$

On the other hand, recording of the spectral interferograms, from which we retrieved the spectral phase, consist of only one step. The analyzer was oriented 45° to the optical axis of a birefringent quartz crystal and the interference of p - and s -polarized waves was resolved.

4. Results and discussion

The validity of the Lorentz–Lorenz equation as the model computation of the refractive index for the binary mixture of miscible liquids was verified for the NaCl aqueous solutions (see Fig. 2). Solutions with 0, 2 and 5 percent of NaCl were measured by the Abbe refractometer at a wavelength of 589.3 nm and compared with theoretical ones, calculated by the Lorentz–Lorenz model, Eq. (1). An excellent agreement between the values was confirmed as can be seen in Table I. The experimental and calculated values are different at the fifth decimal place.

TABLE I

Experimental and theoretical refractive indices of the NaCl solutions ($\lambda = 589.3$ nm).

solution (analyte)	refractive index	
	(Abbe refr.)	(Lorentz-Lorenz eqn.)
NaCl 0%	1.3328	1.33283
NaCl 2%	1.3363	1.33628
NaCl 5%	1.3415	1.34152

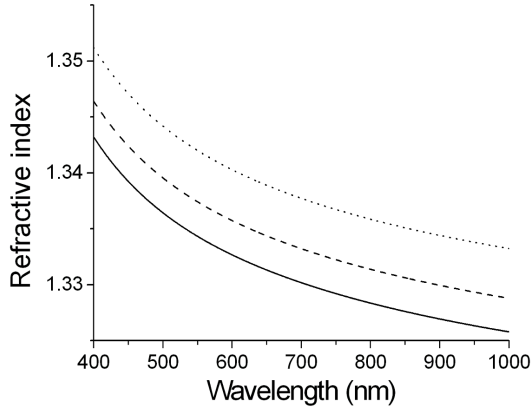


Fig. 2. Spectral dependence of the refractive index of NaCl solutions (NaCl 0% — solid line, NaCl 2% — dashed line, NaCl 5% — dotted line) calculated according to the Lorentz-Lorenz model.

The measurements of the spectral reflectance ratio $R_p(\lambda)/R_s(\lambda)$ and the spectral phase difference $\Phi(\lambda)$ were performed for three NaCl aqueous solutions with 0, 2 and 5 percent of NaCl. Figure 3 shows the measured reflectance ratio $R_p(\lambda)/R_s(\lambda)$ for NaCl solution with 5 percent NaCl. The SPR effect is demonstrated clearly via dip position, to which the resonance wavelength $\lambda_{\text{res_exp}} = 682.7$ nm corresponds. The spectral interferograms recorded for air as a reference material and for the same NaCl solution are shown in Fig. 4. The corresponding spectral interference signals $S(\lambda)$ were determined according to Eq. (4) and processed by the WFT to retrieve the SPR induced differential phase change $\Phi(\lambda)$:

$$\Phi(\lambda) = \Delta_{\text{NaCl}}(\lambda) - \Delta_{\text{air}}(\lambda). \quad (6)$$

The resonance wavelength can be obtained from the spectral difference phase change using the differentiation, and it is $\lambda_{\text{res_exp}} = 681.7$ nm, as can be seen from Fig. 5. Comparison between both values of the resonance wavelength shows an excellent agreement. The difference of these values is 1 nm. The measurement results of the spectral reflectance ratio $R_p(\lambda)/R_s(\lambda)$ and the spectral phase difference change $\Phi(\lambda)$ for three NaCl aqueous solutions (0, 2 and 5 percent of NaCl) are presented in Figs. 6 and 7. The differences of both values are 1.8 nm for water and 0.9 nm for NaCl 2%. We can see that the dip positions are shifted with increasing mass fraction of NaCl to longer wavelengths. Subsequently, we can assign the measured resonance wavelength to the refrac-

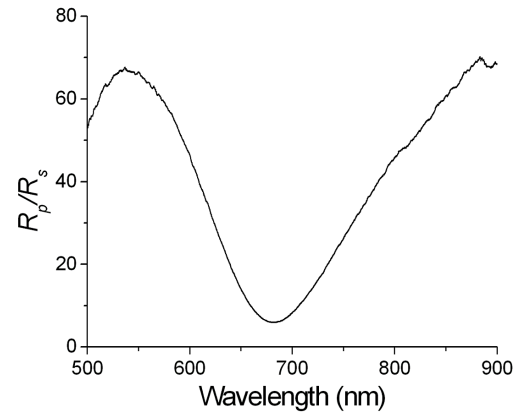


Fig. 3. Measured reflectance ratio $R_p(\lambda)/R_s(\lambda)$ as a function of the wavelength for the solution NaCl 5%.

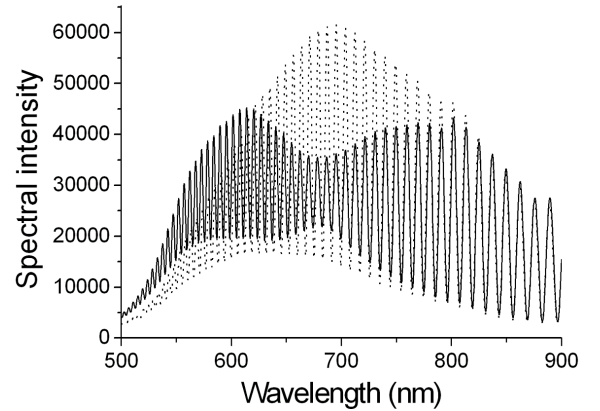


Fig. 4. Measured spectral interferograms for the solution NaCl 5% (solid) and air (dotted).

tive index of the NaCl solution calculated according to Lorentz-Lorenz model, Eq. (1). It seems that the dependences are approximately linear (see Fig. 8). Of course, this idea must be supported by following experiments with other concentrations.

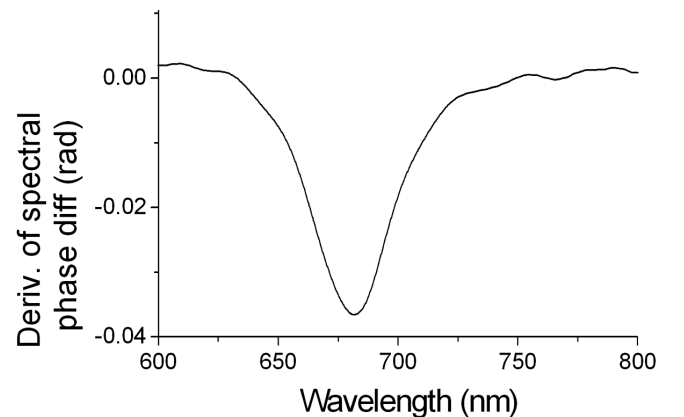


Fig. 5. Derivative of the measured spectral phase difference for the solution NaCl 5%.

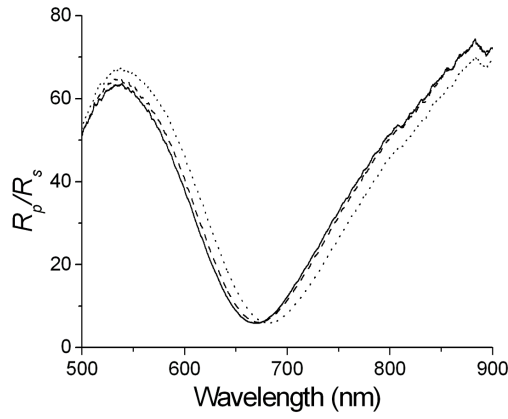


Fig. 6. Measured reflectance ratio $R_p(\lambda)/R_s(\lambda)$ as a function of the wavelength for NaCl solutions (NaCl 0% — solid line, NaCl 2% — dashed line, NaCl 5% — dotted line).

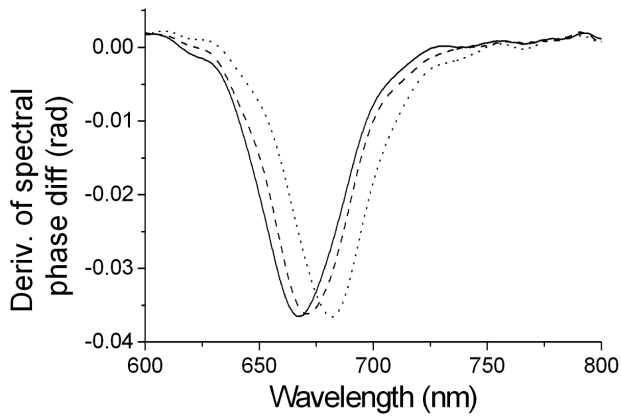


Fig. 7. Derivative of the measured spectral phase difference as a function of the wavelength for NaCl solutions (NaCl 0% — solid line, NaCl 2% — dashed line, NaCl 5% — dotted line).

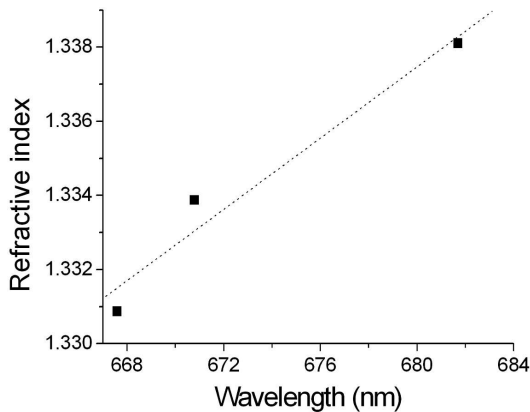


Fig. 8. Refractive index calculated according to the Lorentz-Lorenz model as a function of the resonance wavelength obtained from derivative of the measured spectral phase difference (dotted line indicates linear regression).

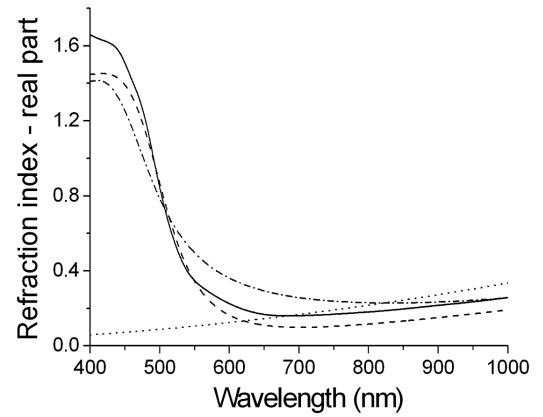


Fig. 9. Real part of the refractive index as a function of the wavelength according to models and experimental data (solid line).

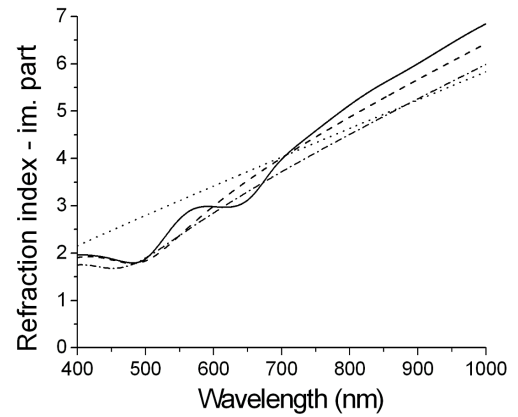


Fig. 10. Imaginary part of the refractive index as a function of the wavelength according to models and experimental data (solid line).

We would like to compare the experimental spectral dependences of $R_p(\lambda)/R_s(\lambda) = f(\lambda)$ and $\Phi(\lambda) = f(\lambda)$ for NaCl solutions with the theoretical ones, as we presented in a previous paper for water [7], but there are discrepancies among them. At present, we are not able to explain it. This contradiction can probably be caused by several reasons. Primarily, in our Kretschmann SPR configuration optical dispersion of all materials is assumed. It seems that the major problem could be connected with a suitable model for the complex refractive index of Au thin film. We tried to calculate it by three models [8, 11, 12] and compared it with the experimental compilation data from [13] as can be seen in Figs. 9 and 10. It is obvious that the elementary Drude model [8] (dotted line) is impossible to use for wavelengths smaller than 600 nm. Nevertheless, neither model corresponds exactly (dashed line according to [11] and dash-dotted line according to [12]) to the experimental curve (solid line) according to [13]. Considering high sensitivity of the SPR structure to the refractive index change these

discrepancies can be principal. Moreover, further problems can be related to experiments, namely to thickness and cleanness of the Au thin film, which can affect the experimental curves. These problems will be the topic of our subsequent research.

4. Conclusion

In this paper we tested the prism SPR sensor based on white-light spectral interferometry. The Kretschmann configuration of SF10 glass prism coated with Au thin film was utilized for sensing NaCl aqueous solutions with 0, 2 and 5 percent of NaCl. We used two experimental methods to determine the resonance wavelength: measurement of the spectral reflectance ratio $R_p(\lambda)/R_s(\lambda)$ and the spectral phase difference $\Phi(\lambda)$. We demonstrated that the value of the resonance wavelength is sensitive to the refractive index change of the NaCl solution and it is approximately linear. Refractive index of the NaCl solutions is calculated according to the Lorentz–Lorenz model. Validity of the Lorentz–Lorenz model is verified by measurement with the Abbe refractometer. Finally, some problems, which can cause discrepancies between experimental and theoretical spectral dependences for $R_p(\lambda)/R_s(\lambda) = f(\lambda)$ and $\Phi(\lambda) = f(\lambda)$, are discussed.

Acknowledgments

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