

Measurement of the concentration of a solution with surface plasmon resonance heterodyne interferometry

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Abstract. A linearly polarized light beam is incident on the boundary surface between the thin metal film of a surface plasmon resonance (SPR) apparatus and the tested solution. If the incident angle is very near to the resonant angle, then the phase difference between *p*- and *s*-polarizations of the reflected light is changed with the concentration of the solution. The phase difference can be measured accurately by heterodyne interferometry. Based on these effects, a method for measuring the concentration of a solution is presented. Because the reflected light is measured, only a small quantity of the solution is required. In addition, the method has the advantages of both common-path interferometry and heterodyne interferometry. © 2003 Society of Photo-Optical Instrumentation Engineers. [DOI: 10.1117/1.1577115]

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1 Introduction

Concentration measurements are often operated in chemical,^{1,2} biochemical,³ and biomedical³ analysis processes. To make the processes smooth, it is necessary to develop an easy and simple method for measuring the concentration of a solution in real time. Several optical methods⁴⁻⁷ have been presented for measuring the concentration of a solution. Almost all of them measure the intensity variation of the transmitted light. The method using the surface plasmon resonance effect was also proposed,⁷ but it also measures the intensity variation of the reflected light. However, the stability of light source, the scattering light, the internal reflection, and other factors influence the accuracy of the measurement. On the other hand, an optical polarized heterodyne polarimeter³ was proposed by measuring the phase variation of the transmitted light. But because it measured the transmitted light, it is necessary to know the optical path length of the solution in advance and the optical setup becomes more complicated. Moreover, the quantity of the test solution should be more than a threshold amount to make the measurand detectable.

To overcome these drawbacks, we propose an improved method for measuring the concentration of a solution by using surface plasmon resonance (SPR) heterodyne interferometry. A linearly polarized light passes through the glass material and the thin metal film coated on this glass material, as shown in Fig. 1. Then, it is incident on the boundary surface between the thin metal film and a test solution. If the incident angle is very near to the resonant angle, the surface plasmons can be excited.^{7,8} The surface plasmons are the longitudinal electron density fluctuations excited on the boundary surface and are accompanied by an evanescent electromagnetic field at the boundary surface emitted from the thin metal film to the solution. Conse-

quently, the phase difference between the *s*- and the *p*-polarizations of the light reflected at the boundary surface between the thin metal film and the solution is changed with the refractive index of the solution. Its refractive index is related to the concentration. The phase difference can be accurately measured using heterodyne interferometry. From the data of the phase difference, the concentration of the test solution can be estimated. Because the light reflected from the test solution is measured, only a small quantity of solution is required. In addition, the method has the advantages of both common-path interferometry and heterodyne interferometry.

2 Principle

2.1 Phase Difference of Reflected Light

A linearly polarized light beam enters one surface of the SPR apparatus, as shown in Fig. 1. This apparatus has a Krestschmann configuration⁹ and is an isosceles right-angle prism with a thin metal film of thickness d_2 deposited on the hypotenuse surface. This linearly polarized light beam is incident at an angle θ on the hypotenuse surface. For convenience, the numbers 1, 2, and 3 are labels in Fig. 1 to represent the media of glass (prism), metal (film), and the test solution. Their refractive indices are n_1 , n_2 , and n_3 , respectively. If θ is very near to the resonant angle θ_{sp} , then surface plasmons are excited. Thus, the reflection coefficient can be expressed as⁷

$$r_q = \frac{r_{12}^q + r_{23}^q \exp(i2k_z d_2)}{1 + r_{12}^q r_{23}^q \exp(i2k_z d_2)} = |r_q| \exp(i\phi_q) \quad q = p, s, \quad (1)$$

where r_{ab}^p and r_{ab}^s are the Fresnel reflection coefficients of

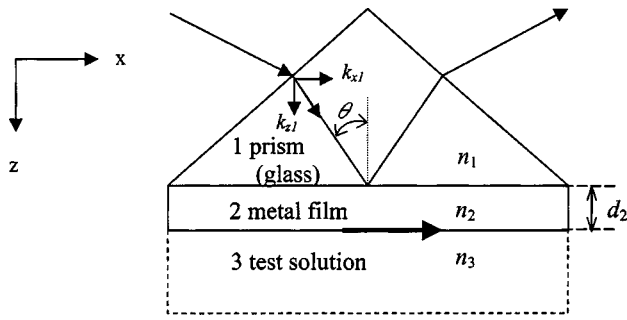


Fig. 1 Reflection in an SPR apparatus.

p- and *s*-polarizations as the light beam propagates from medium *a* to medium *b*, and k_{za} is the component of the wave vector in medium *a* along the *z* direction. They can be written as

$$r_{ab}^p = \frac{n_b^2 k_{za} - n_a^2 k_{zb}}{n_b^2 k_{za} + n_a^2 k_{zb}} \quad a, b = 1, 2, 3, \quad (2a)$$

$$r_{ab}^s = \frac{k_{za} - k_{zb}}{k_{za} + k_{zb}}, \quad (2b)$$

and

$$k_{za} = \mathbf{k}_0 (n_a^2 - n_1^2 \sin^2 \theta)^{1/2}, \quad (2c)$$

respectively, where \mathbf{k}_0 is the free-space wave vector. Then the phase difference variations ϕ between *p*- and *s*-polarization components is given as

$$\phi = \phi_p - \phi_s. \quad (3)$$

It is obvious from Eqs. (1) to (3) that the phase difference ϕ is strongly dependent on n_3 . In general, the refractive index n_3 of a solution relates to its concentration^{5,7,10} *c*. If the relation curve of the phase difference ϕ versus the concentration *c* is specified, then the concentration *c* can be estimated with the measurement of the phase difference ϕ .

2.2 Phase Difference Measurements with Heterodyne Interferometry

A schematic diagram of the optical arrangement of our method, which is based on Chiu et al.'s¹¹ considerations, was designed and is shown in Fig. 2. A linearly polarized light passes through a half-wave plate H and its polarization plane is at α with respect to the horizontal axis. Then it passes through an electro-optic modulator EO, and is incident on the boundary surface between an SPR apparatus and a test solution. The incident angle θ to the boundary surface is very near to the resonant angle θ_{sp} of the SPR apparatus. The reflected light passes through an analyzer AN with the transmission axis at 45 deg to the horizontal axis and it is detected by a photodetector D. The fast axis of EO is in the horizontal direction, and a sawtooth voltage signal with angular frequency ω and amplitude $V_{\lambda/2}$, the half-voltage of EO, is applied to EO. Consequently, the intensity measured by D can be derived as¹¹

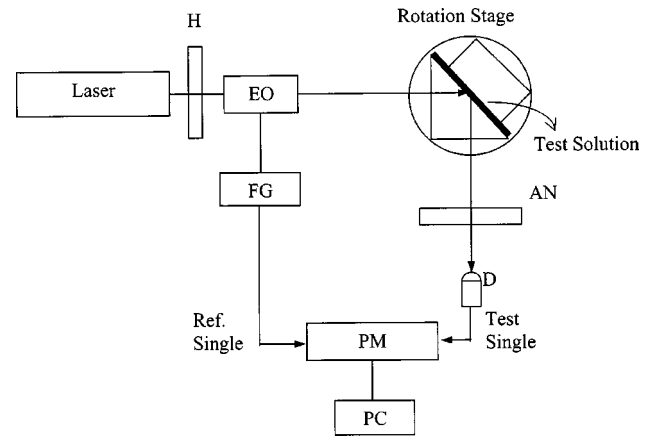


Fig. 2 Schematic diagram for measuring the phase difference of the reflected light: H, half-wave plate; EO, electro-optic modulator; FG, function generator; PM, phase meter; AN, analyzer; D, detector; PC, personal computer.

$$I_t = |E_r|^2 = \frac{1}{4} [r_p^2 \cos^2 \alpha + r_s^2 \sin^2 \alpha + 2r_p r_s \cos \alpha \sin \alpha \cos(\omega t + \phi)], \quad (4)$$

and I_t is the test signal. On the other hand, the electrical signal generated by the function generator FG is filtered and becomes the reference signal. It has the form as

$$I_r = \frac{1}{2} [1 + \cos(\omega t)]. \quad (5)$$

Both of these two sinusoidal signals are sent to a phase meter PM, hence ϕ can be measured accurately. By substituting the data of ϕ into the specified relation curve of phase difference ϕ versus concentration *c*, the associated concentration can be estimated.

3 Experiments and Results

To demonstrate the feasibility of this method, saltwater, glucose solution, acetone, and ethanol were tested at room temperature, 20°C. An SPR apparatus consisting of a BK7 prism and a thin gold film of thickness 35 nm was used. A He-Ne laser with wavelength 632.8 nm and an electro-optic modulator (Mode 4002, New Focus, Inc.) with a half-wave voltage of 125 V were used in these tests. The frequency of the sawtooth signal applied to the EO modulator was 1 kHz. The refractive indices of a BK7 prism and a thin gold film were measured with an ellipsometer (Model eta, Stag Inc.) and they are 1.5151 and $0.1973 + i3.5631$ at wavelength 632.8 nm, respectively. A high-resolution rotation stage (Model URM 80, Newport) with angular resolution 0.001 deg was used to mount the SPR apparatus and the test solution. The azimuth angle α of the half-wave plate H was 10 deg with respect to the horizontal axis. A phase meter with angular resolution 0.01 deg was used to measure the phase difference. A personal computer was used to record and analyze the data. First, we estimated the resonant angle for each solution of concentration 5 mg/ml by measuring the critical minimum reflectance.^{6,7} They are 71.1, 71.09, 71.04, and 71.03 deg for saltwater, glucose

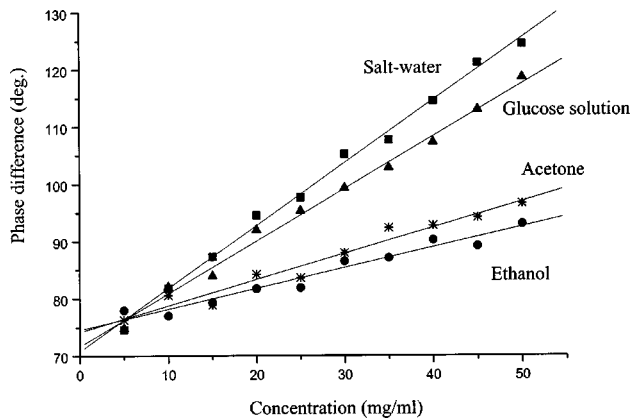


Fig. 3 Measurement data and the fitting curves of phase difference at different concentrations.

solution, acetone, and ethanol, respectively. Then we set the incident angles to be 71.1, 71.09, 71.04, and 71.03 deg for these four test solutions in our experiments, respectively. Although they did not exactly equal the associated resonant angles for the concentrations of the test solutions, they were still very near to the associated resonant angles. The measured results and their fitting curves are shown in Fig. 3. In this figure, the symbols \blacksquare , \blacktriangle , $*$, and \bullet represent the measurement data of saltwater, glucose solution, acetone, and ethanol, respectively. It is seen that the four fitting curves are nearly straight lines with different slopes. Hence this method can be realized if the relation curve of phase difference ϕ versus concentration c for another test solution is specified in advance, then the concentration c can be estimated from the measurement of ϕ .

4 Discussion

Because θ is very near to the resonance angle θ_{sp} , the reflection coefficient r_p is very small. A half-wave plate H is located before the EO so as to increase the component of p -polarization of the incident light. Consequently, the contrast of the test signal is enhanced. In our experiments, the angle between its fast axis and the horizontal axis is set to 10 deg, the contrast of the test signal is about 0.88.

The slopes of the fitting curves for saltwater, glucose solution, acetone, and ethanol in Fig. 3 are 1.092, 0.917, 0.474, and 0.364 deg ml/mg, respectively. Considering the second-harmonic error, the polarization-mixing errors, and the angular resolution of the phase meter, the total phase difference errors $\Delta\phi$ can be decreased to 0.03 deg in our experiments.¹² Substituting these data and the slope of each fitting curve into the equation

$$\Delta\phi = s\Delta c, \quad (6)$$

the error Δc of the concentration can be calculated. They are 2.75×10^{-2} , 3.27×10^{-2} , 6.33×10^{-2} , and 8.24×10^{-2} mg/ml for saltwater, glucose solution, and ethanol, respectively.

Substituting the measured results into Eqs. (1) to (3), the relation curves of the concentration resolution and the reflection coefficient r_p for saltwater and ethanol can be depicted as shown in Fig. 4. From Fig. 4, it is obvious that

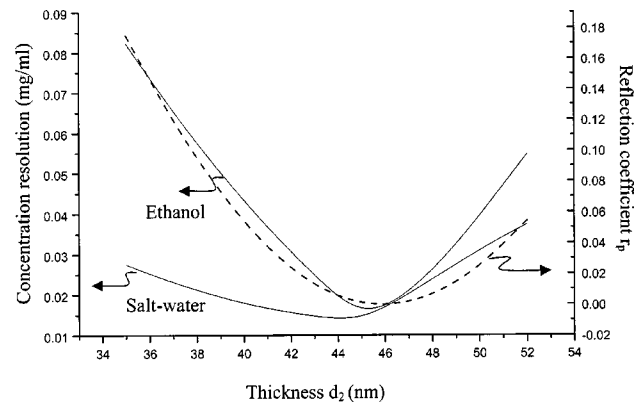


Fig. 4 Relation curves of concentration resolution and reflection coefficient r_p versus thickness d_2 . Note that the reflection curves for saltwater and ethanol are almost identical and superimpose each other.

high resolution may be obtained as $d_2 \approx 45$ nm, but its associated r_p is too low and its associated test signal cannot be detected. To comprise these conditions, the condition $d_2 = 35$ nm is chosen in our experiments.

The resonant angle varies slightly with the concentration of a test solution. In our experiments, the concentration of each test solution was varied from 5 to 50 mg/ml. Thus, the resonant angle for saltwater, glucose solution, acetone, and ethanol, changes from 71.1 to 72.08, 71.09 to 71.9, 71.04 to 71.46, and 71.03 to 71.35 deg, respectively. In the experiment, we fixed the incident angle to be the resonant angle of 5 mg/ml solution for convenience, that is, 71.1, 71.09, 71.04, and 71.03 deg for saltwater, glucose, acetone, and ethanol, respectively. Hence the fitting curves in Fig. 3 are suitable only for these four tested solutions with the concentration is in the range between 5 and 50 mg/ml. If the relation curve of the phase difference ϕ versus the concentration c for another solution is specified in advance, then its concentration c can be estimated from the measurement of ϕ under the specified range. In addition, this method is suitable only for a solution with a refractive index smaller than that of the prism.

5 Conclusion

An optical method for measuring the concentration of a solution was presented based on the surface plasmon resonance effect and heterodyne interferometry. It was experimentally confirmed that under our experimental conditions, it is convenient to obtain the concentration of a solution such as saltwater, glucose solution, acetone, and ethanol. Their resolutions are about 2.75×10^{-2} , 3.27×10^{-2} , 6.33×10^{-2} , and 8.24×10^{-2} mg/ml, respectively. Only a small quantity of solution is required for the measurements. In addition, the method has the advantages of both common-path interferometry and heterodyne interferometry, such as high stability, high resolution, and easy operation.

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