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RESEARCH ON WATER QUALITY TESTS BASED ON OPTICAL WAVEGUIDE SURFACE PLASMON RESONANCE TECHNOLOGY

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The water quality testing principle by surface plasmon resonance (SPR) is introduced. Using the scanning mode angular spectral testing and the CCD angular spectral testing, a kind of high-resolution, wide-range, and portable optical waveguide SPR angular spectral testing system is studied, the method of improving the testing accuracy is discussed, and a long-life surface plasmon optical waveguide transducer is also proposed. Utilizing the SPR testing system, we contrastively tack some test for several sorts of solution, the results presented that significant differences of SPR peaks observed in different sorts of liquid, which indicated the effectiveness of SPR technology used in water quality testing and analysis.

Keywords: Surface plasmon resonance; optical waveguide; angular spectral; water quality analysis.

1. Introduction

Surface plasmon resonance (SPR) effect is used to make transducers and develop non-invasive monitoring test instruments in fields of water quality analysis, biology, biochemistry, and environment protection. It has been developed toward the design and production of commercial instruments in recent years.[1] Optical waveguide SPR technology monitoring instruments is used to examine and analyze water quality. It is not only of the unique advantage for completely non-invasive and pollution-free tests, but also able to carry out the dynamic processes for real-time monitoring reactions.[2] For SPR-based methods for testing and analyzing water quality, there are wavelength-modulated, phase-modulated, and angle-modulated methods, etc. In addition, for structures, there are planar waveguide, fiber optic waveguide, probe, etc.[3–5] Each testing system of different structures has its own advantages and disadvantages. In this article, a portable angular spectral SPR water quality analysis system with planar optical waveguides and line array CCD as an optical signal acquisition unit is studied, which has broad scope of spectrum detecting, high resolution, and free of point-by-point scanning. That is to say, SPR tested curves can be observed directly. Through the tests for water quality solution of several different compositions, this structure has a relatively high liquid concentration testing resolution and a very good stability.

2. The Detecting Principle and the Set Up of SPR

2.1. *Principles*

SPR is a sort of waveguide effects. SPR optical waveguide is composed of four kinds of media: glass prisms (to generate total internal reflections),

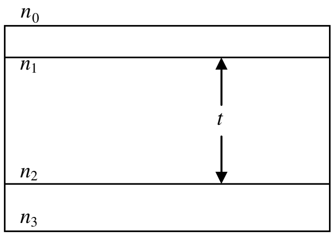

Fig. 1. SPR optical waveguide schema.

metallic films coated on prism surface, samples to be tested, and air, as shown in Fig. 1. The physical process of the testing can be described briefly as follows: the total internal reflection of incident light on glass surface generates evanescent wave, which excites the free electron on metal surface and makes it to be plasma when it satisfies certain conditions. The frequency and wave number of surface plasmon and evanescent wave would be equal when its angle of incidence or wavelength of incident light is of a certain appropriate value. Meanwhile, it sets up resonance, incident light energy is absorbed, reflecting light energy declines, and, to the minimum value, resonance peak appears. If the refractive index of sample on metal surface changes, the position of resonance peak would change correspondingly. Establishing a corresponding relationship between refractive index and the position of resonance peak, the sample's refractive index can be measured according to calibration of resonance peak's change in position.[6] Changing the wavelength of incident light with the angle of incidence fixed, or changing the angle of incidence with the fixed wavelength of selected light source, from both of which, a resonance peak curve can be obtained. In this article, a test method of changing the angle of incidence with fixed wavelength, namely the test of SPR angular spectrum, is provided. Given the permittivity of SPR optical waveguides ε_1, ε_2, ε_3, and ε_0, respectively, and magnetic permeability μ_1, μ_2, μ_3, and μ_0, respectively, the condition of generating SPR must be $\varepsilon_3 > \varepsilon_0$, and the incident light must be polarized light, the vibration direction of electric field vector, and the light incident plane are in plumb, namely TM wave. The evidence for this conclusion is given below.[7]

Given a plane wave incidenting on an interface between metallic film and the sample media, we have:

$$n_0 \sin\alpha_0 = n_1 \sin\alpha_1 \tag{1}$$

when incident light is reflected and refracted on the interface of two media.

Generally, n_3 is a complex number; therefore, Eq. (1) can be transformed into:

$$n_0 \sin\alpha_0 = (n_3' - i\mu_3)\sin\alpha_3. \tag{2}$$

In Eq. (2), n_0 and n_3 are complex refractive index of two different media, respectively. α_0 and α_3 are angles of incidence and refraction, respectively. Considering only dielectric layers of samples and air, according to boundary conditions, light-intensity reflection coefficient is calculated as:

$$r_p = \frac{n_0\cos\alpha_3 - n_3\cos\alpha_0}{n_0\cos\alpha_3 + n_3\cos\alpha_0}. \tag{3}$$

In addition, when total reflection occurs, with light-wave phase difference introduced by thickness (denoted as t) of metal film added

$$\delta = \frac{2\pi}{\lambda} n_3 t \cos\alpha_3. \tag{4}$$

Light-intensity reflection coefficient is changed to:

$$R_p = \frac{(\beta_1-\beta_3)^2\cos^2\delta_2 + \left(\frac{\beta_2\beta_3}{\beta-\beta_1}\right)^2\sin^2\delta_1}{(\beta_1+\beta_3)^2\cos^2\delta_1 + \left(\frac{\beta_2\beta_3}{\beta+\beta_1}\right)^2\sin^2\delta_1}. \tag{5}$$

In Eq. (5), $\beta = n/\cos\alpha$. When film thickness t and wavelength λ are fixed, it can be concluded from the equation above that energy reflection coefficient is determined by refractive index and the angle of incidence. In practical tests, the refractive index is usually fixed. Therefore, as long as the angle of incidence is changed, which makes plasma wave vector to be equal to evanescent wave vector, the SPR can occur.

2.2. *Descriptions for detecting system*

The measurement system is made up of optical system, control system, and data-processing system. Figure 3 shows the structure of practical SPR measurement device.

Here, the key part to ensure the stability of the detection system is SPR optical waveguide. We optimize the design of waveguide with the optimal design concept. In fact, to get the optimal optical waveguide is to optimize the thickness of metal film. For the water solution with its refractive index in some region, we can get sharp SPR curve. The film thickness is optimal, and the detect resolution is the highest, too. The metal film is the key part of SPR

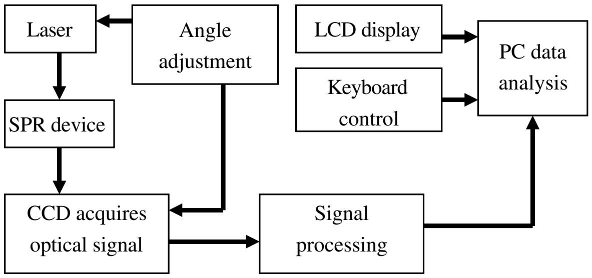

Fig. 2. Test system of SPR schema.

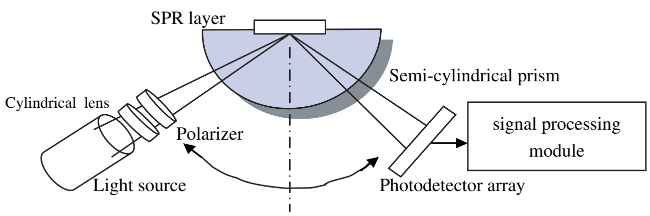

Fig. 3. Structure of SPR angular spectrum test device.

sensor test system, and the stability of the detection system depends on the material of metal film, then the resolution depends on the film thickness. If we use gold film as the surface waveguide, it will be very stable and the SPR phenomenon will appear easily, but is costly; therefore, the silver becomes our choice; the silver is cheap and can be easily obtained. As long as we treat it appropriately, good SPR curve can also appear and it is also very stable. From Eq. (5), when the wavelength is determined, for a certain incident angle, the reflective index will depend on the refractive index of specimen and the thickness of waveguide film. Through some experiment, we know that SPR phenomenon appears when the film thickness changes from 40 to 100 nm, but the sharpness degrees differ a lot, which impacts the sensitivity and resolution greatly. The experiment shows that when wavelength is 670 nm, we can get the optimal curve with the film of 55 nm thick. In addition, the SPR curve of alcohol and water are also obtained, it seems that the two curves are sharp when the film is 55 nm thick that makes the curve resolution higher than others; therefore, it can be concluded that for the water solution with some refractive index region, the optimal film thickness exists when other parameter is invariable.

Generally, scanning method can be used to test angular spectrum, that is to say, the light source and receiver rotate synchronously, as the light source rotates receiver rotates symmetrically, until the detective light intensity reaches the minimum. In addition, the incident angle is the SPR resonant angle. However, what is described above needs to measure lots of angles to derive the resonant one, which is inefficient and prone to mechanical error. As a result, we design a type of SPR angular spectrum-testing system with high precision and wide range, the optical part of which is made up of LD, collimating lens, cylindrical lens, polarizer, SPR optical film, and photoelectric detection array, as shown in Fig. 3. After collimated and expanded, the laser beam is condensed onto the waveguide metal film of SPR device with the light-cone angle about 6–8°. The light LD emits is a Gaussian beam, only part of the light energy reflected from the SPR layer can be detected by line column optoelectronic devices, and the utilization ratio of light energy is too low, which makes it difficult to increase the resolution, then in order to improve the system testing resolution, a cylindrical lens is inserted between the light source and SPR layer, which compresses the light spot in the detect array direction, and a semi-cylindrical lens is used to achieve SPR total internal reflection. When the compressed beam is condensed into the center of semi-cylindrical lens, SPR waveguide reflects all the light onto the photo detector array, which decreases the light energy loss and improves the resolution of SPR spectrum. Besides the polarizer is used to meet the requirements to generate the SPR spectrum, that is to say, the optical field generating SPR spectrum must be TEM mode.

Generally, the refractive index of water solution lies between 1.2 and 1.4, from Fresnel equation, the beam incident angle used to generate the SPR spectrum is between 74° and 65° (refer to the normal that is perpendicular to the incident plane). Though detector array can achieve wide detect region, but since the light-cone angle is only about 6° after condensed, if the incident angle is fixed at some degrees, the refractive index of water solution corresponding to the resonant angle will be limited in a small region and if the refractive index of different solution changes in a too large range, the resonant spectrum will exceed the region of the detector array, then the testing cannot be accomplished. As a result, we design a fine-tuned scanning angular spectrum testing device in order to help catch the SPR resonant angle and expand the testing region. The fine-tune part is shown in Fig. 4. In Fig. 4, O denotes the fulcrum position at which the adjusting mechanism is fixed, OA denotes the light source position with the minimum incident angle, and OB

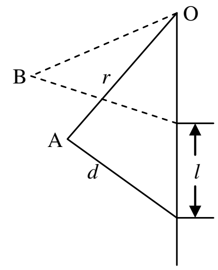

Fig. 4. Adjustment schema.

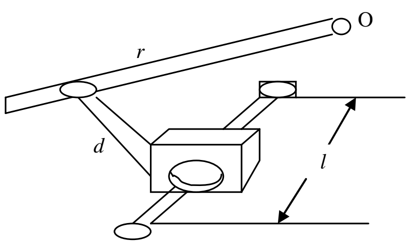

Fig. 5. Mechanical adjustment diagram.

the light source position with the maximum adjusting angle; the angle can be changed from 45° to 75°, correspondingly, the adjusting rod stroke can be determined as described below:

$$l = \sqrt{d^2 - r^2 + \sqrt{2}rd} - \sqrt{\frac{d^2 - r^2 + \sqrt{2}rd(\sqrt{3}-1)}{2}}. \tag{6}$$

If the refractive index of the testing material is approximately 1.333 (close to that of water), the light incident angle can be set to about 60°. In addition, if the refractive index deviates from this value largely, what is only needed to do is fine-tune the light source incident angle appropriately. Of course, in the fine-tuning process, the SPR spectrum detector array and incident beam will still rotate synchronously and symmetrically. Besides, in order to ensure the consistency of the testing result, after the incident angle is changed, the position the beam condenses at in the semi-cylindrical lens will not change.

Moreover, a relative position tagging method is used to tag the position of testing spectrum, that is to say, only if the SPR relative resonant angular spectrum is tagged, we can obtain the concentration of the water solution.

3. Test Results

Based on the above analysis, the dielectric constant and refractive index are changing while the test concentration is changing. Owing to Eq. (5),

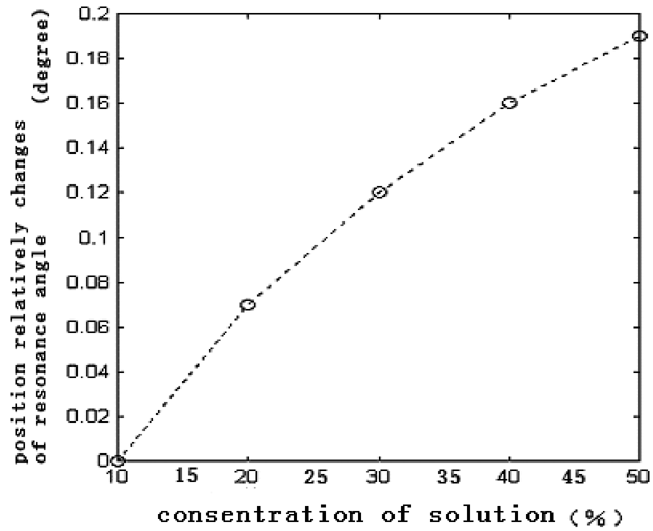

Fig. 6. Relation between the concentration of solution and resonant angle.

resonant angular position and the changes of relative position vary with concentration. According to the experimental results,[4] angular spectrum and the refractive index are linear, which is shown in Fig. 6. Therefore, changing the parameters of sample solution concentration can get different SPR angle spectrum curves. The SPR angular spectrum tester that are designed by us is used to measure several kinds of liquids, and the resonance curve that is using the oscilloscope observation is shown in Fig. 7. As shown in Fig. 7, comparing the resonant angle of tap water with the SPR resonant angle of alcohol solution, there is relative right offset, which reflects the difference between the two refractive indices; and the rest of the liquid SPR resonant angle also have some differences with each other, which reflects differences in the refractive index of different liquids. Figures 7(a) and 7(b) show the SPR relative angular spectrum of a group of pure water and tap water and Figs. 7(c)–7(e) display the SPR relative spectrum of different alcohol concentrations. Thus, while the concentration is changed differently in the same solution, the relative SPR angular spectrum is also different. Figures 7(f)–7(h) show SPR relative angular spectrum of the different concentrations of beverages, the curves show the differences between their SPR angular spectrum.

4. Conclusions

The devices for testing and analyzing SPR water quality introduced in this article are able to test solutions of different substances or solutions of the

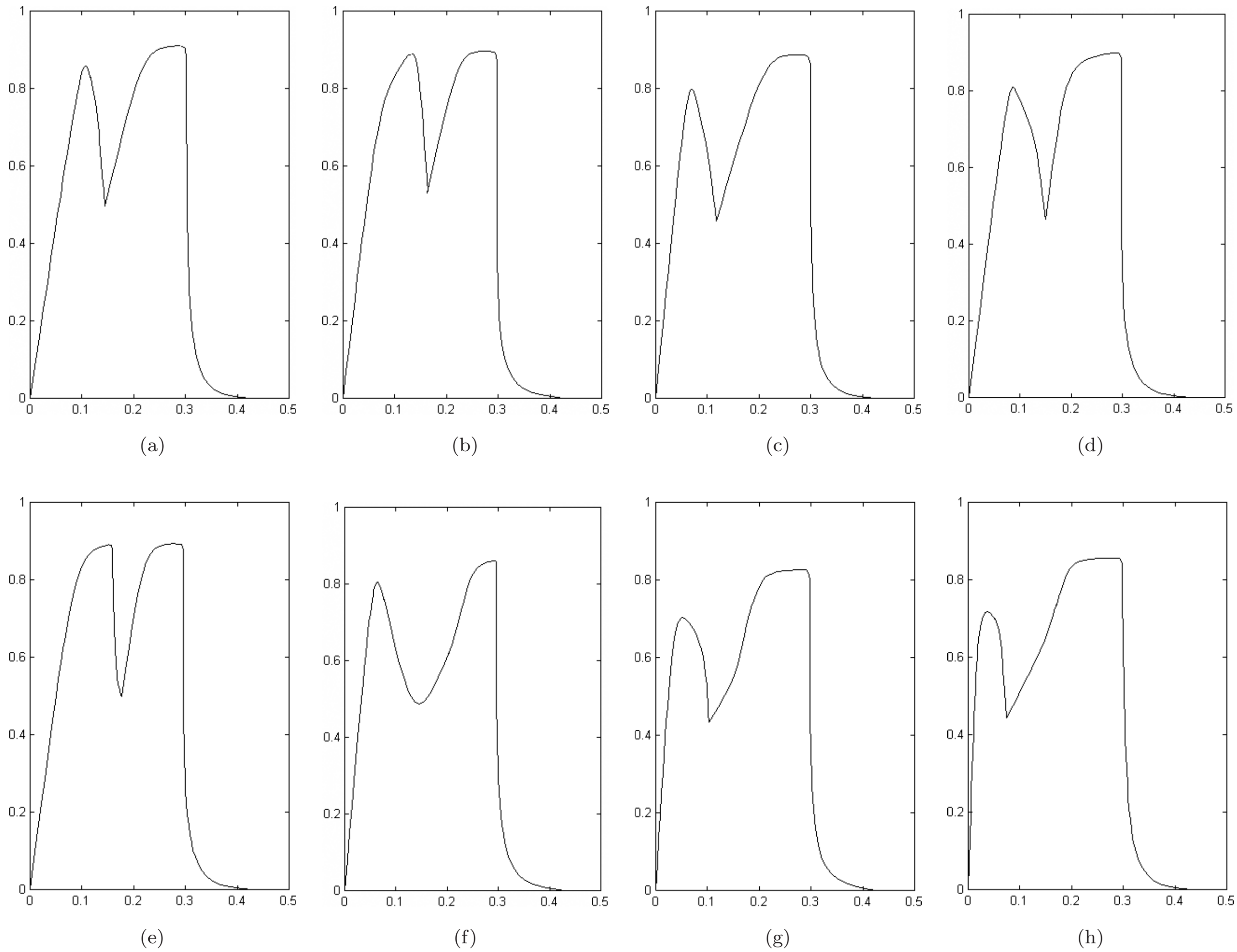

Fig. 7. The test results to different liquid solutions. (a) Pure water, (b) tap water, (c) 5% alcohol solution, (d) 10% alcohol solution, (e) 15% alcohol solution, (f) 100% nutrient solution, (g) 60% nutrient solution (including air bubbles), and (h) 40% nutrient solution. In Fig. 7, the horizontal axis is normalized intensity of light and the vertical axis shows relative positions tested by CCD.

same substances but in different concentration, with resolution meeting the required accuracy of inspection departments. However, it is quite a job to use SPR to test and analyze the solutions of complex compositions, and therefore reduces the efficiency of testing. In this case, it would be more effective to do SPR tests with multi-channel optical waveguides or microfluidic system.[8]

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