Research of measurement errors caused by salt solution temperature drift in surface plasmon resonance sensors

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Influence of temperature on measurement of surface plasmon resonance (SPR) sensor was investigated. Samples with various concentrations of NaCl were tested at different temperatures. It was shown that if the affection of temperature could be neglected, measurement precision of salt solution was 0.028 wt.-%. But measurement error of salinity caused by temperature was 0.53 wt.-% in average when the temperature drift was 1 °C. To reduce the error, a double-cell SPR sensor with salt solution and distilled water flowing respectively and at the same temperature was implemented.

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In recent years, there have been large efforts on the research of sensors based on the surface plasmon resonance (SPR) phenomenon[1]. SPR sensors have advantages such as flexibility, low cost, small size, and possible use in remote sensing. The principle of SPR sensors is the fact that surface plasmon wave (SPW), which can be excited in the interface between a metal film and medium, is extremely sensitive to tiny change in the refractive index (RI) of medium. But RI of medium (sample) is a function of its concentration and temperature, and changes in order of $10^{-4}/°\mathrm{C}$[2], so measurement result would be affected by temperature[3]. This study is very important to measure seawater salinity quickly and accurately in oceanography, ocean environment monitoring, ocean fishery, and aquatic breed.

SPR sensors have been developed into three types, prism-coupled[4], integrated optical waveguides-coupled[5], and optical fiber-coupled[6] sensors. In the study of Gentleman *et al.*[3], probes were made of 3M silica fiber. The distal end was epoxied into a connector for coupling to a bifurcated fiber optic jumper conducting light from the source to the probe and back to the detector. In this research, the prism-coupled Kretschmann configuration was utilized and the prism made of K9 glass was employed as substrate. The Ag 50-nm-thick film was deposited on one side of the prism by radio frequency (RF) magnetron sputtering. A film thickness monitor (FTM) was used to control the thickness of the film during deposition. Two flowing cells were built on the Ag film, one served as sample solution, and the other as distilled water. The SPR system consisted of light source, monochromator, polarizer, focusing lens, light power meter, and other devices[7].

A 5-member set of NaCl solution with salinity between 1.7340 and 7.7150 wt.-% incremented by about 1.50 wt.-% was created. Each sample was made of 100-ml distilled water and different concentration NaCl. The electrical balance used above was accurate to 1×10^{-4} g, and an Abbé refractometer and SPR system were employed to measure the RI and resonance wavelengths of all samples at various temperatures.

The relation between RI of sample and temperature is shown in Fig. 1. It is clearly demonstrated that RI decreases as temperature increasing. Figure 2 indicates that the changing rate of RI (R) is greater in higher salinity sample with the same temperature drift of 1 °C. Between 0 and 25 °C, R of sample with 7.7150 wt.-% reaches $1.09 \times 10^{-4}/°\mathrm{C}$ in average.

The difference of resonance wavelength, $\Delta\lambda = \lambda_{\mathrm{SPR}} - \lambda_{\mathrm{SPR0}}$, is used to describe the salinity of sample, where λ_{SPR} and λ_{SPR0} are resonance wavelengths of sample and distilled water, respectively. As salinity changes from 1.7340 to 7.7150 wt.-%, RI difference Δn and resonance wavelength difference $\Delta\lambda$ are 1.23×10^{-2} and 20.9 nm,

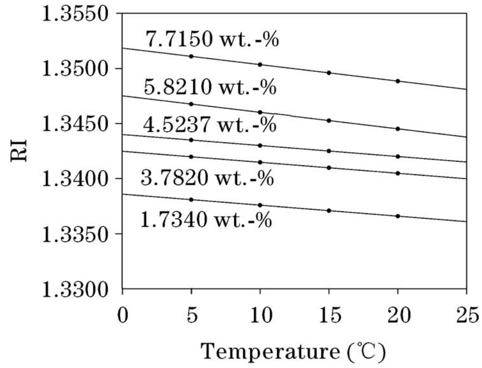

Fig. 1. RI of samples at various temperatures.

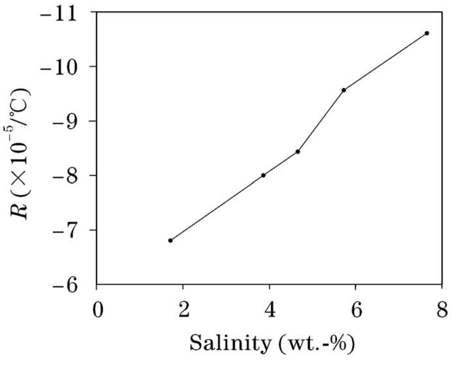

Fig. 2. Changing rate of RI (R) versus salinity.

respectively, so the sensitivity of the SPR system is 5.87×10^{-4} nm^{-1}. The precision of the monochromator used in the system is 0.1 nm, so resolutions of RI and salinity in experiment are 5.87×10^{-5} and 0.028 wt.-%, respectively.

However, Figs. 1 and 2 imply also that the influence of temperature on RI of samples cannot be neglected. RI is a function of salinity and temperature, when temperature $0 < T < 25$ °C and salinity $0 < s < 7.7150$ wt.-%, based on experimental data, it can be described as

$$n\left(s,T\right) = n_0 + \sum_{i=1}^{\infty} A_i s^i - (BT - Cts), \tag{1}$$

where n_0 is RI of distilled water at $T = 0$ °C, A_i is a constant for certain i, $B = 5.84 \times 10^{-5}/°\mathrm{C}$, $C = 6.27 \times 10^{-4}/(\mathrm{s}\cdot°\mathrm{C})$.

Equation (1) means that the influence by temperature fluctuation is composed of two parts, one (B) corresponds to distilled water property, it makes RI incline, and the other (Cs) is related to the salinity making RI increase with temperature.

The relation between resonance wavelength of sample and temperature is given in Fig. 3. $\Delta\lambda$ becomes smaller as temperature increasing. Figure 4 shows that measurement error affected by temperature is in order of 10^{-3}, i.e. 0.1 wt.-%, greater than resolution of salinity (0.028 wt.-%), and it becomes larger in sample with higher salinity. In the sample with salinity of 5.8210 wt.-%, it reaches 0.53 wt.-%.

It is worthy noting that in our experiment, two flowing cells were kept in the same temperature, so that measurement error by temperature could be reduced in the part of B. The precision of the SPR system is in order of 10^{-4}. This may be explained as follows.

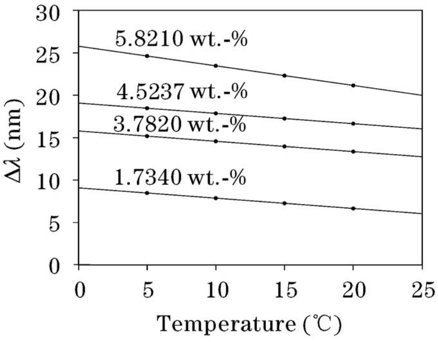

Fig. 3. $\Delta\lambda$ of various samples between 0 and 25 °C.

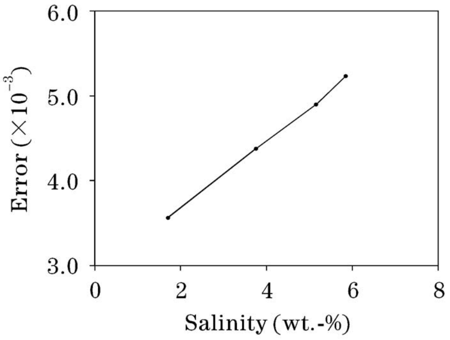

Fig. 4. Relation between measurement error and salinity.

As $\Delta\lambda$ is used to indicate the salinity, it can be expressed as

$$\Delta\lambda = 2\pi\sqrt{\varepsilon_{\mathrm{g}}}\sin\alpha\left[\frac{1}{k_{\mathrm{sp}}\left(s,T\right)} - \frac{1}{k_{\mathrm{sp}}\left(0,T\right)}\right], \tag{2}$$

$$\vec{k}_{\mathrm{sp}}\left(s,T\right) = \vec{k}_0\sqrt{\frac{\varepsilon_{\mathrm{m}}\cdot n^2\left(s,T\right)}{\varepsilon_{\mathrm{m}} + n^2\left(s,T\right)}},$$

$$\vec{k}_{\mathrm{sp}}\left(0,T\right) = \vec{k}_0\sqrt{\frac{\varepsilon_{\mathrm{m}}\cdot n^2\left(0,T\right)}{\varepsilon_{\mathrm{m}} + n^2\left(0,T\right)}},$$

where ε_{g} and $\vec{k}_{\mathrm{sp}}$ are permittivity of prism and wave vector of SPW, respectively, $\vec{k}_0$ is the wave vector of incident light in vacuum, and ε_{m} is permittivity of the metal film.

For distilled water, its RI is given as

$$n\left(0,T\right) = n_0 - BT, \tag{3}$$

so that

$$\Delta n = n\left(s,T\right) - n\left(0,T\right) = \sum_{i=1}^{\infty} A_i s^i - CTs. \tag{4}$$

Equations (2) and (4) mean that the part caused by B can be reduced with $\Delta\lambda$, but the other by C cannot be eliminated completely.

In summary, measurement error caused by temperature in SPR aqueous system has been investigated. This SPR sensor with double flowing cells could reduce the measurement error in an order. For making SPR system more applicable and improving its precision further, compensation of temperature should be fully considered.

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