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Determining salinity using a multimode fiber optic surface plasmon resonance dip-probe

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Abstract

For the first time a fiber optic surface plasmon resonance sensor with demonstrated accuracy and precision of less than 200 ppm salinity is presented for calibration across a range of temperatures and salinities. Also shown is the potential for the sensor system to reach precisions of 10 ppm or less. Calibration models are constructed for 28–48‰ salinity and a method for translating the calibration models to account for varying temperatures between 0 and 25 °C are demonstrated. The long-term susceptibility of the fiber optic sensor to fouling and drift is discussed.

Keywords: Hydrothermal vents; Practical salinity scale; Refractive index; Ocean density; Fiber optic sensors

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1. Introduction

1.1. Why measure salinity with refractive index sensors?

Density (salinity), temperature and pressure (depth) are the fundamental parameters for the seawater equation of state, which is essential to climate models [1]. Because seawater is an aqueous solution of dissolved salts, salinity is the standard measurement used to determine the density of ocean water [2]. Prior to 1967, the standard method of determining salinity was through titration of chloride-dominated seawater against silver nitrate, with an accuracy of 30 ppm [2]. Conductivity was touted as a possible salinometric technique, but it was not standardized until 1967 when conductometric sensors attained a precision and accuracy exceeding that of the chemical technique [3]. The conductivity–salinity scale was further revised in 1978 to account for the advent of portable conductivity-temperature-depth (CTD) sensors used in field monitoring with high-precision/accuracy bench-top thermosalinographs [3,4]. This practical salinity scale of 1978 (PSS 78), further recognized by UNESCO in 1980, is now so universal in the oceanographic determination of density that salinity is used almost synonymously for density in references [1,5]. The accuracy of PSS 78 is 1 ppm, with a precision of <1 ppm [4]. It should be noted PSS 78 uses “Practical Salinity Units” or PSU, as the measurement is based on a ratio of standard seawater to the sample and is therefore inherently unitless. For this paper, salinity will be reported in either ‰ or ppm KCl, the former of which is essentially the same as PSU.

Conductivity cannot account for species that may add to seawater’s density but do not measurably conduct electricity and is compositionally dependent due to heterovalency [5]. When conductivity was being standardized in the 1960s, the use of refractive index (RI) to determine salinity was suggested [6]. However, the precision and accuracy of conductometric sensors developed faster than refractometric sensors, the former of which were also made portable more easily. Recently, meticulous statistical treatment of

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salinity–density data sets has shown that RI correlates to density 80% better than conductivity [7]. Interferometric refractometers can achieve sub-1 ppm accuracy, but are inherently bench-top devices that require strict temperature control in their surrounding environment to at least ±0.1 °C [6]. Thus, refractometric determination of seawater density tends to be limited to exacting studies where sample-capture is acceptable. Climatological research depends on density information to track global ocean circulation, an application for which 10–100 ppm is an acceptable sensitivity [8,9]. Therefore, a refractometric sensor that can attain a sub-100 ppm sensitivity while being robust enough for field deployment would find itself useful in salinity/densitometry.

1.2. State of the art in fiber optic refractive sensors for oceanography

Chemical oceanography has become increasingly attracted to the use of fiber optic based sensors [10]. The flexible nature of fiber optics, combined with their relatively low fabrication cost, makes them attractive to any field where in situ remote sensing is desirable. A fiber optic system can also miniaturize many table-top optical systems, bringing the possibility of in situ refractometry to the ocean. Several groups have attained accuracies between 1000 and mid-100 ppm using various fiber optic systems [11–13]. The best sensitivity reported is that by Zhao et al., with precision of ±300 ppm using a miniaturized differential refractometer [14–16]. Zhao et al. estimate their spectral resolution gives a sensitivity of 12 ppm. Their design requires a saline standard and a prism in the sensor head, so the potential to miniaturize the sensor is limited.

Surface plasmon resonance (SPR) is another technique that measures RI changes, and has been successfully used with fiber optics in environmental systems in recent years [17–23]. SPR spectroscopy can be employed to determine RI when light in a waveguide is attenuated following excitation of a surface plasmon on a thin metallic film deposited on the waveguide. In the case of a fiber optic waveguide, there need be no prisms or moving parts in the sensor tip. Therefore, such sensors can be <200 μm diameter at the tip and inexpensive. At a minimum, such a sensor could be mated next to a traditional conductivity/temperature (CTD) probe for in situ ocean salinity monitoring and the two sensors used in concert to better characterize the density of seawater.

Three groups have used FO-SPR to measure salinity; however, none of these three studies calibrated the sensors across a range of temperatures. Grunwald and Holst have attained a sensitivity of 1000 ppm using a multimode fiber with a tapered tip [24,25]. Liu et al., using a multimode fiber, report an RI sensitivity of 8.9×10^{-5} RIU and claim this corresponds to a salinity sensitivity of 10 ppm [25]. However, based on the accepted values for RI change with salinity of $\sim 3 \times 10^{-7}$ RIU/ppm, [6,27] the sensitivity of Liu et al.'s sensor is closer to 450 ppm. Lastly, Esteban et al., using a single mode system report a sensitivity of 100 ppm, as their SPR data tracked with conductivity probe good to 100 ppm [20].

1.3. Our relationship to the state of the art

In order for an SPR salinity probe to be useful in the field, its performance must be demonstrated both over a range of salinities and temperatures. The RI of seawater changes monotonically from 0‰ to 42‰ and monotonically from −1 to 32 °C at typical ocean salinities. However, a sensor is unlikely to encounter this full range of salinities and temperatures in a given deployment. The fiber optic system under development here is envisioned for two particular applications. First is the stationary deployment near deep-sea hydrothermal vents where the goal is to monitor the diffusion of vent fluid. In these applications, thermal equilibrium is rapidly achieved, but fluid mixing and diffusion is spatially varied with predominant currents. The second application is drop sensing where the probe would rapidly collect data while descending to the ocean floor. Here the probe will possibly encounter thermoclines and haloclines. Laboratory experiments chosen to test this sensor have been designed to present a significantly greater range of salinities than would be expected in most applications and a comparable range of temperatures that would be encountered for a given field experiment. This paper shows the fiber optic based SPR dip-probe (FO-SPR) can achieve salinity predictions of <200 ppm with a precision of at least 100 ppm over several temperatures and salinities of marine relevance. This result is in the same range as the isothermal 100 ppm reported by Esteban et al. [20]. Both data sets relied on conductivity probes with sensitivities of 100 ppm at best. Thus, it is believed that with better calibration, these small and inexpensive FO-SPR sensors could achieve sensitivities of <100 ppm, rendering them useful to field studies of the ocean.

Our laboratory has demonstrated the ability to make reproducible flat-polished tip FO-SPR sensors for use in aqueous systems [19,28,29]. Sensing tips are constructed from 400 μm core optical fibers, and are typically less than 5 cm in length. Connection to a light source and spectrometer is achieved with fiber optic "jumpers," thus the sensor apparatus can be easily multiplexed and adapted for remote use. Studies with aqueous sucrose have shown correlating the λ_{SPR} with bulk RI or analyte concentration are sensitive and robust enough for quantitative applications [29]. Previous studies in our laboratory suggested a prediction of salinity over of <1000 ppm several temperatures was attainable with this sensor [29]. The current study improved on the experimental design by collecting conductivity and temperature data simultaneously with the SPR spectra in temperature controlled solutions of aqueous KCl. A limit of determination based on observed prediction errors of at least 200 ppm and a precision of <100 ppm is attainable with these FO-SPR sensors. The potential to deliver accuracy and precision of <100 ppm is foreseeable with a more powerful, less portable, spectrometer and CCD camera.