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In situ salinity measurements in seawater with a fibre-optic probe

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Abstract
We have successfully proved the feasibility of an optical salinity meter for marine applications in a two-week measurement campaign, carried out for the realization of *in situ* salinity measurements in seawater. An optical instrument (optode), in which the main element is a fibre-optic refractive-index sensor based on surface plasmon resonance (SPR), has been developed for that purpose, and has been especially designed to be able to operate in realistic conditions. The performance of the optode has been evaluated on an oceanographic ship in the Baltic Sea, close to the Vistula estuarine area. The obtained results (in different tests, such as depth-profiling, towing and stationary measurements) show good correlation with the data provided by a commercial probe. Although the device is currently a part of a more complex measuring platform and uses an axial spectrograph as detector, the output power measurement used and the simplicity of its conception allow us to conceive a closed, extremely compact set-up which can be in principle commercially competitive with existing sensors.

Keywords: fibre-optics sensors, salinity measurement, surface plasmon resonance

1. Introduction

One of the most important parameters in marine research is salinity because of its great significance in marine environment monitoring, seasonal climatic prediction, fishing and many industrial fields, including offshore oil exploration. Salinity is also commonly used to measure the density of the ocean water due to the fact that seawater is an aqueous solution of dissolved salts. What is more, salinity is used almost synonymously for density in oceanographic references concerning density determination.

Salinity is usually measured by determining electrical conductivity [1, 2]. Normally, these measurements are carried out in conjunction with depth and temperature ones by means of a so-called CTD sonde (CTD stands for conductivity, temperature, depth). In this way, the measures of salinity are based on the mobility of ions in seawater, which means that the obtained values can depend on the type of salt which is dissolved in water. Since they are inherently electrical measurements, they can also be affected by any kind of electrical interference. In addition, conductivity does not take into account other species that can vary the seawater density but do not conduct electricity.

These problems could be avoided with the use of optical techniques for the determination and monitoring of salinity. Optical methods are non-invasive, and most of them can

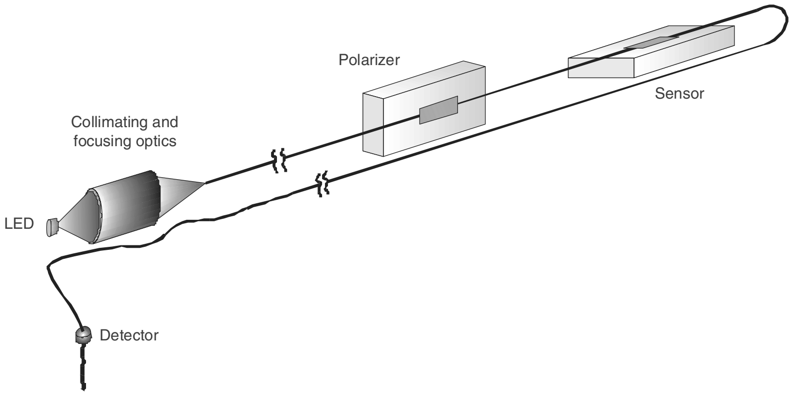

Figure 1. Scheme of the optical components of the optode.

provide responses independent of the specific distribution of salts in the water. Among the optical technologies, optical fibre sensors have demonstrated their suitability as environmental monitoring tools, and many configurations have been applied to the measurement and control of a number of parameters of environmental interest such as chemical and biological components [3, 4]. Optical fibre sensors are immune to electromagnetic interference, present high sensitivity, have small size, are safe in hazardous environments and provide accessibility to difficult places. Because of these good characteristics, the interest in developing salinity fibre-optics sensors has increased in the past few years. Some of them, based on refractive index measures, have been recently presented [5–8] although all of them have only been tested in the laboratory.

The authors proved the suitability of using SPR-based refractometry for salinity measurements in a laboratory arrangement consisting of a side-polished fibre with a double-layer deposited on it [5]. The physical basis of the measurement was the resonant coupling of the light guided by the single-mode fibre with the surface plasma waves supported by the deposited planar structure for a given refractive index of the outer medium, which produces the attenuation of the optical power transmitted by the fibre, which is the measured parameter.

Refractometric methods are less sensitive if sample capture is feasible but in climatological research they show an acceptable sensitivity to determine density. The dependence of the refractive index of seawater on salinity is a well-known fact extensively referenced in the literature [9–14]. Temperature and pressure also have some influence on it, so these parameters must be taken into account when refractometric measurements are performed.

The use of fibre optic sensors in the marine environment has been very limited. However Pereira *et al* [15], who have tested an *in situ* system made by a specially designed optical fibre cable to measure water temperature in the Mira Channel of Ría de Aveiro (Portugal), are preparing future salinity measurements in the extremity of the optical cable.

In this work we demonstrate the suitability of SPR-based refractometer devices for this use as *in situ* real-time controllers of the degree of salinity. We present the optical instrument developed for that purpose (optode), whose performance has been evaluated during a measurement campaign on an oceanographic ship in the Baltic Sea, showing good correlation with the results provided by a commercial CTD sonde (ref: FSI model IMCTD-MBP-D). This optode has been developed as part of a monitoring platform to determine the presence of pollutants in seawater, in the framework of a European research project (MISPEC, multi-parametric *in situ* spectroscopic measuring system for coastal monitoring, EVK3-CT2000-00045).

2. Instrument configuration

The salinity optode is included in the concept of an all optical probe based on a multi-channel axial optical fibre spectrograph. This multi-channel platform is designed to be connected to several optodes, namely the salinity optode (SO), a dissolved oxygen (DO) optode and a surface-enhanced Raman scattering (SERS) optode [16, 17], each one with its own light source but with the same light detector, an axial spectrograph.

A complete schematic view of the optical set-up for the salinity optode used in the measurement campaign is shown in figure 1.

The light source used in the salinity channel is a commercial LED (Hitachi HE8404SG, peak wavelength 807 nm), which is a very stable and reliable source when we are working in a power-output sensing scheme. The selection of this LED source also means unpolarized light, so control of the polarization of the incident light is required for the enhancement of the SPR phenomenon.

The salinity optode includes two SPR-based devices, namely, the sensor mentioned in the introduction and an *in-line* polarizer. The concept of the sensor is described in [5], and we have deposited an aluminium layer 8 nm thick and a titanium dioxide layer 60 nm thick, which are values well adjusted to the range of refractive indices of seawater at the wavelength we are using [18]. The polarizer is also based on the deposition of layers on a side-polished fibre, but in this case the upper layer is substituted by a thick layer of a high refractive index [19]. If the polarizer is placed at 90° with respect to the sensor, only the component of the field which is parallel to the layers of the polarizer (and thus perpendicular to the ones of the sensor) is incident, obtaining an effective coupling between the guided light through the fibre and the surface plasma modes. In this way, we assure a stable response of the system

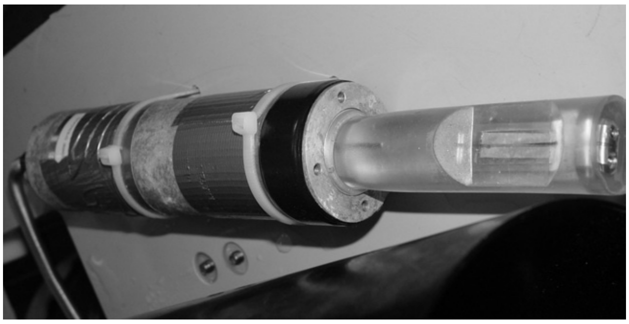

Figure 2. Photograph of the optode used for the measurements. Only the sensing layer is exposed to water.

while working with an unpolarized source and it represents some advantages with respect to the final measurement noise since we will polarize the light near the transducer. The design of the optode keeps a certain degree of freedom to slightly rotate one of the elements from this nominal orthogonal position until the highest signal is obtained, because some imperfections in the polishing usually appear. The fibre between polarizer and sensor is straight to prevent any change in the polarization plane.

The spectrograph is composed by a dispersive element made with a *grism* (grating plus prism) coupled to a CCD matrix which gives an image of the LED light profile after crossing the sensing head. The emission and detection set-ups are housed in a separate underwater container called the core instrument (CI) and a flexible connection between the CI and the optode is achieved by an 80 cm pressure hose. The numerical data are then recovered after transmission over a several hundred metres long cable. A mere pixels integration over the signal wavelength range is then provided on a PC giving in real time a plot of the underwater salinity evolution. Data are also stored to be post-processed in order to make temperature and pressure compensations. Although this is a complex set-up, since only output power measurements are required for our salinity measurements, a further replacement of the spectrograph by a simple photodiode would lead us to a very simple, compact and portable set-up, proper characteristics for *in situ* measurements.

For field measurements we need the complete instrument to be watertight. The optode requirements have been fulfilled by an original design carried out by the authors in collaboration with IFREMER (Institut Français de Recherche pour l'Explotation de la Mer). As can be seen in figure 2, aluminium pressure housing has been manufactured to isolate the polarizer head from any external interference and to protect it. The sensing head is encased in a resin (Araldite$^{\text{TM}}$ 2020). With this configuration, we obtain a complete watertight instrument, while ensuring the sealing of the fibres, suitable for salinity measurements since the sensing head is conveniently exposed to the water flow under continuous pressure condition up to 30 bars.

3. Experimental results

3.1. Preliminary tests

The sensor performance has been extensively tested in the laboratory (using a commercial HP power meter, for intensity measures) to determine its response to refractive index variations. The high linearity of the output signal was shown in [5]. The sensitivity attained was 100 ppm, which represents a sensitivity of $\sim 3 \times 10^{-5}$ RIU, considering the relation between refractive index and salinity of $\sim 3 \times 10^{-7}$ RIU/ppm [18]. Some other tests have been carried out. The cross-sensitivity to other components was studied. For instance, concentrations of 150 ppm of humic acid or 1‰ of glycerol produce no significant variations of the response. These concentrations are much higher than expected in seawater, so we can conclude that the cross-sensitivity to them or other components is not a problem with our system. Also, we studied the temporal degradation of the system. The devices showed no degradation in the laboratory for months and, in field measurements, after 72 h of continuous functioning with the device immersed in water, a simple jet of fresh water is enough to clean the sensor. The above characteristics are very useful for *in situ* measurements and the results obtained in [5] showed that the calibration of the sensor to the refractive index is sufficient to permit salinity-degree measurements.

After the characterization of the sensor in the laboratory, a complete set of calibration measurements with the core instrument of the MISPEC project were carried out at the IFREMER facilities in Brest (France) in order to evaluate the influence on the optode as a whole of the parameters which can affect the refractive index of seawater, namely pressure and temperature, when it is used in realistic conditions. It should be mentioned that it is not usual to carry out pressure calibrations on such sensors, but they are very important in this case because it would allow us to check both the suitability and the influence of the housing. A first calibration of the optode with real seawater coming from the Atlantic Ocean at Brest (standard salinity around 35‰, and decreasing the salinity value with a freshwater solution) shows the same qualitative performance as the isolated sensor. Moreover, the behaviour of the optode with temperature and pressure showed a nonlinear drift of the received signal for each salinity value of the sample, although in both cases the signal decreases as the corresponding parameter increases. Due to this nonlinear drift, the influence of the temperature is clearly stronger than the influence of the pressure in the range between 15 and 25 °C, but in the range corresponding to the Baltic seawater (usually less than about 13 °C) does not seem to be so significant (see figure 3).

3.2. Field tests

We have tested the instrument in real, *in situ* measurements, during a two-week measuring campaign on the *Oceania* oceanographic ship owned by the Institute of Oceanology of the Polish Academy of Sciences (IO-PAS, Sopot, Poland) as a part of the MISPEC project. The tests were performed in the Baltic Sea, near the Vistula estuary at the Gulf of Gdańsk (Poland). In figure 4 the complete area is shown, as well as the locations where the measurements shown in this paper were performed. Three different kinds of tests were carried out: stationary, towing and depth profile.

For these field measurements, the instrument was settled on the towed frame (MTV: MISPEC Towed Vehicle, developed by the Marine Technology and Optical Institutes of the

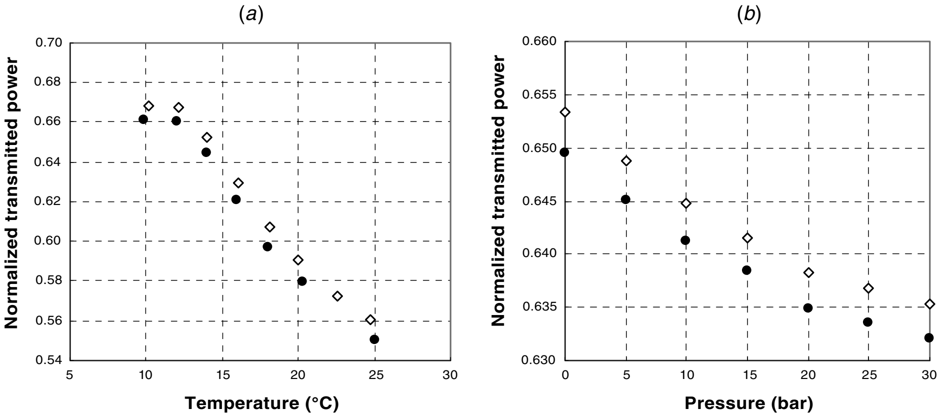

Figure 3. Response of the instrument at the IFREMER facilities. (a) Response to temperature variations at constant salinity. The solid circles correspond to $S = 6.8$ psu and the squares correspond to $S = 24.6$ psu. (b) Response to pressure variations at constant salinity. The solid circles correspond to $S = 22.9$ psu and the squares correspond to $S = 15.7$ psu ('psu' stands for 'practical salinity units' and is equivalent to 'per thousand').

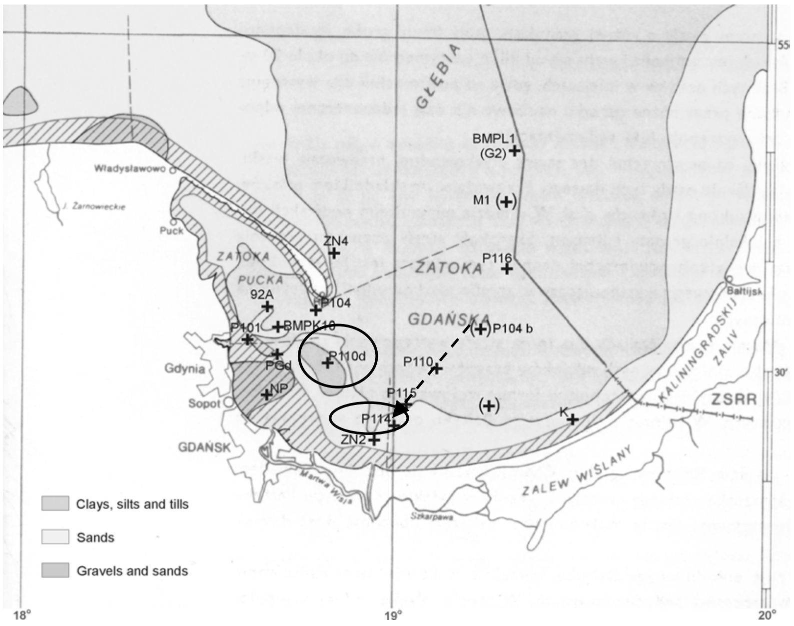

Figure 4. Map of the Gulf of Gdańsk. The points where the reported tests were made are marked. Circles show both stationary and depth-profile measurements, and the dashed line shows the path of the towed experiment.

Technical University of Berlin, Germany) shown in figure 5, where the location of the sensors in the platform appears. Slightly different positions of the sensing points for both CTD and SO sensors are clearly seen, which can explain some differences in both measurements. This frame can be stabilized at a convenient depth at a speed up to 4 knots.

The results of the salinity optode are compared with those provided by a commercial CTD in order to validate them. The sampling rate of this CTD is around 1.76 Hz, so the values obtained have been re-sampled to permit the comparison. We have used the data provided by the CTD to calculate the refractive index of seawater with the algorithm of [18]. We will compare it with the curves showing the response of our optode in terms of normalized transmitted power ('normalized' in this context means 'with respect to the power transmitted with the optode in air'). We are mainly interested in the correlation of this signal with that provided by the CTD.

A first kind of test was performed by towing the instrument between the two station points P104 and P114 (see figure 4). A series of measurements were continuously taken over 2:30 hours with a sampling rate of around 0.06 Hz and an integration time of the signal in the detector of 400 ms. The results are shown in figure 6, where the thick solid line corresponds to the SO results and the values provided by the CTD probe are represented by a thin dashed line for comparison. We can see that the signal obtained with the SO sensor follows perfectly almost in real time all the variations detected by the CTD probe. Due to the difference in the sampling rate, the signal obtained by means of the optical instrument seems to be affected by a low-pass filter when compared with the conventional conductivity sensor.

Stationary measurements were performed at the point P114 marked in figure 4, which corresponds to the thermocline of the Vistula estuary. The sampling rate and integration

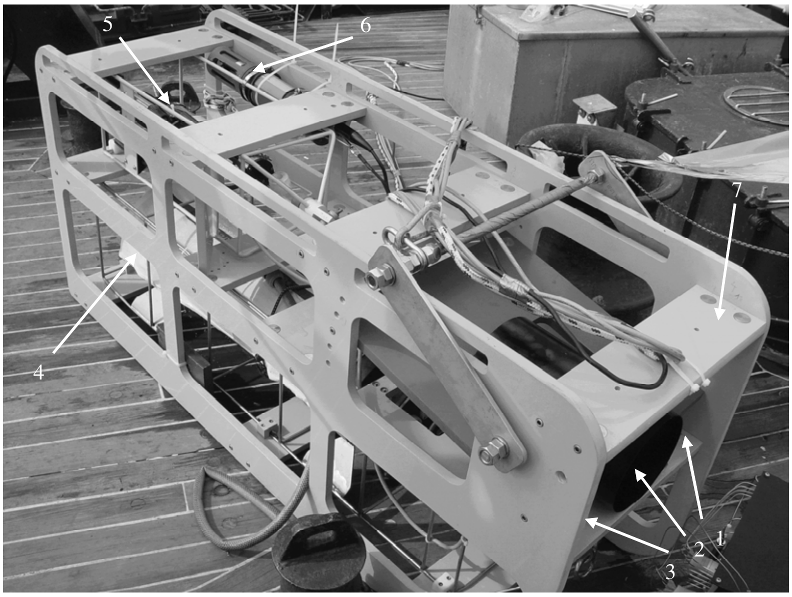

Figure 5. Scheme of the underwater MISPEC system. (1) SO, (2) SERS, (3) DO, (4) CI, (5) CTD, (6) commercial sensor for measurements of pH, dissolved oxygen and turbidity, (7) robust frame.

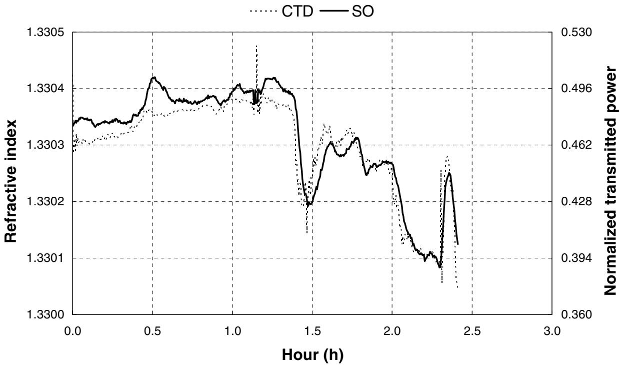

Figure 6. Results obtained in the tow experiment from point P104b to P114. Solid line corresponds to the values provided by the optical instrument and dashed line corresponds to the CTD measurements.

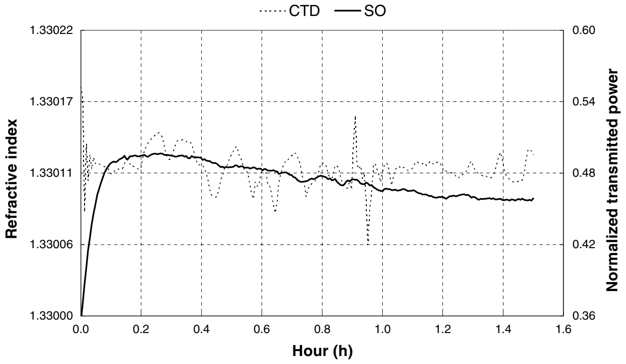

Figure 7. Stationary measurements at point P114. The solid line corresponds to the response of the optical instrument while the dashed line represents the data provided by the CTD probe.

time are the same as in the previous case. Now the complete instrument was immersed to a depth of 5 m for about 90 min. The results obtained are shown in figure 7 (solid line) in comparison to the ones provided by the commercial CTD (dashed line). We can also see good correlation between the two signals: the SO sensor follows quite well the variations detected by the CTD. A drift can be observed in the output signal from the optical instrument which could be due to a thermal drift of around 1 °C in the complete measurement and also to a little pressure fluctuation. The slightly different measurement point, as well, may be important in a zone such as an estuary where different currents of water are mixed. Such behaviour could be corrected with a more effective algorithm for the conversion to salinity from refractive index measurement coming from a more exhaustive calibration of the sensor with respect to temperature and pressure.

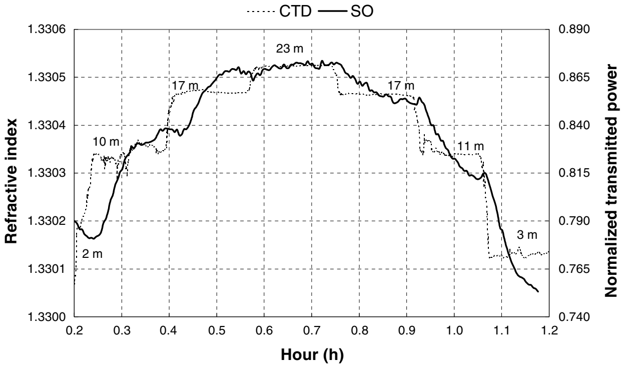

Figure 8. Depth-profile test at point P110d. The solid line is the optical instrument signal and the dashed line is the CTD one.

Finally, a third kind of test, depth profile, was carried out. The procedure consists in the immersion of the complete instrument in several steps at the same location of the given marked point, with continuous acquisition of the signal coming out the instrument. In figure 8, the result of a test performed at point P110d of figure 4 is shown. In this case, a depth profile from 2 to 23 m was carried out in steps of 7 m, both with increasing and decreasing depth. The sampling rate of the optical instrument and the CTD was the same as in the above cases, but the acquisition time was increased to 500 ms for a complete time of about 1 h. We see again that the agreement is good enough. In this test, as can be seen from figure 8, there exists a slower response of the optical instrument with respect to conductivity measurements. This feature could be due to the process of immersion which can produce some turbulence near the sensing surface, which would represent the mixing of seawater of different layers with different salinity values and to the positions of the two sensors on the MTV which are not identical depending on the towing direction. Also, it is very important to take into account that our instrument measures in a continuous mode while the CTD measures in a sampled mode, i.e., it is turned off and on between measurements.

4. Conclusions

We have demonstrated for the first time the operativity of these fibre-optic sensors for measuring salinity in real conditions, not only in laboratory but in realistic situations, and therefore the suitability of using SPR-based refractometry in real measurements for monitoring purposes in marine tests.

We have shown an ‘all in fibre’ sensing instrument based on optical techniques, which minimizes the optical loses over the complete light path, and shows high mechanical stability when it is used in harsh environments. The long term stability has been proven during the complete measurements campaign in the Baltic Sea, namely two weeks into a series of more than 2 h with a little maintenance, namely a light cleaning with freshwater after each test. In this sense, the optode has proven its robustness in addition to the feature of compactness.

The optode performance has been tested in three different measurement scenarios such as depth profile, stationary measurements and towing experiments. All results obtained with the optical instrument are in good agreement with those provided by a commercial CTD probe. The correlation is high enough and only some minor deviations between the signals occur due to the pressure and temperature influence on the optode and to the different point of test in both instruments (since the location of sensors in CTD and SO are non-coincident, the measurements performed by both instruments can be affected by the highly variable environment that the test area is). These are very promising results because these tests have been the first ones carried out with the equipment still in the experimental phase.

The feasible implementation with a photodiode as detector would make the instrument autonomous, and will improve the simplicity and compactness of the arrangement, making it suitable for use in commercial devices.

Acknowledgments

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