Certified Research and Development Need - CRDN

Refractive Index of Seawater

The SCOR/IAPSO Working Group 127 on "Thermodynamics and Equation of State of Seawater", WG127, has examined the published work available for the determination of the refractive index of seawater under the conditions appearing in the ocean and adjacent seas.

The information and devices available are not sufficient to permit:

(a) The construction of a comprehensive and accurate 'optical equation of state' of seawater over the entire ranges of interest in oceanographic research, providing the density of standard seawater as a function of temperature, pressure, refractive index and wavelength.

(b) The description of the impact of important regional composition anomalies of seawater on its refractive index as compared to that of standard seawater over the entire ranges of interest

(c) The technological development of long-term stable, fast, high-resolution optical in-situ sensors attached to instruments for use by sea-going oceanography, applicable over the entire ranges of natural conditions

Although encouraging this work, WG127 is not able to provide financial support. The WG127 contact can provide any further development information and will liaise between research and development groups. This CRDN is intended to support project applications of these groups at funding authorities.

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Thermodynamics and Equation of State of Seawater

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Background

The next important progress in observing and modelling the thermodynamic properties of the seas will come from the appropriate consideration of natural or anthropogenic chemical composition anomalies of seawater (Millero et al. 2007). For this purpose, at least one additional independent variable beyond conductivity, temperature and pressure must be measured and evaluated in oceanographic observations, stored in data bases and implemented in numerical models. The resolution of this parameter achieved by measuring instruments/sensors must be comparable to those of temperature and salinity in terms of its impact on density.

The density anomalies to be regularly detected and resolved are estimated as given in Table 1.

Table 1: Density anomalies observed in different regions

Region	Anomaly ppm	Source
North Pacific	15	Brewer & Bradshaw (1975)
Coastal waters	40 - 60	Connors & Kester (1974)
Red Sea	35	Poisson et al. (1981)
Indian Ocean	6	Poisson et al. (1981)
Baltic Sea	120	Millero & Kremling (1976)
in general	50	Fofonoff (1985)

The refractive index of seawater is the currently most promising parameter to be measured for this purpose. The resolution achieved with prototype instruments, the accuracy of related experimental data and the feasibility of constructing in-situ optical field sensors support this approach. The refractive index can recognise the presence of non-dissociated dissolved species like organic silicate which do not influence the conductivity of seawater.

The regular use of optical sensors attached to conventional CTD instruments can reveal the spatial and temporal variability of composition anomalies, as e.g. observed in the Baltic Sea by occasional studies on the decadal time scale.

Although the measuring principle is known for more than a century, and its usability has been demonstrated several times, the construction of practically applicable instruments has suffered in the past from various technological difficulties. Up to now, no robust sensor for sea-going oceanography has yet become available for general use.

The Range of Properties Required

Experimental data, theoretical descriptions and the applicability of in-situ sensors should cover the ranges of naturally occuring oceanic conditions, –2 to 40℃ in temperature, 0 to 40 in practical salinity, 0 to 100 MPa in pressure.

The resolution of refractive index measurements as well as the corresponding uncertainties of theoretical formulas are required to be 1 ppm at atmospheric pressure, and 3 ppm at high pressures, corresponding to 4 ppm and 10 ppm in density, respectively. The response time of the optical sensor should be comparable to the response time of high-precision temperature sensors, its desired long-term stability is several months, in particular for applications in automatic observational systems. Synchronous measurement at several optical wavelengths in the visible range is considered as helpful.

Previous Work and Current Studies

The functioning of the physical principle and of sensor prototypes was reported by many authors (Miyake 1939, Seaver 1987, Mahrt and Waldmann 1990, Seaver at al. 1997, Esteban and Cruz-Navarrete 1999, Waldmann 1999, Alford et al. 2006). None the less, practically working ‘optical CTD’ instruments sufficiently stable for regular field applications are still not available today.

An accurate ‘optical equation of state’ of pure water is already available (IAPWS 1997), consistent with the thermodynamic formulation IAPWS-95 for fluid water. Related investigations on seawater should preferably be conducted relative to pure water.

An ‘optical equation of state’ is available for seawater as an empirical refractive index formula with 27 coefficients for wavelengths 500 to 700 nm, temperatures 0 to 30 °C, practical salinities 0 to 40, and pressures 0 to 110 MPa (Millard and Seaver 1990). Its uncertainty ranges from 0.4 ppm for pure water at 1 atm to the insufficiently accurate figure of 80 ppm for seawater at high pressures. Its consistency e.g. with the ITS-90 temperature scale or the latest pure-water standard (IAPWS 1997) requires verification. The equations of Matthäus (1974) and of Quan and Fry (1995) are valid for atmospheric pressure only. The latter is valid between 0 and 30 °C, 0 and 35 salinity, 400 and 700 nm wavelength, with an uncertainty of 15 ppm.

Theoretical or experimental studies on the refractive index of seawater with anomalous composition are almost completely missing (Heydweiller 1913, Fajans and Joos 1924, Frenkel 1955, Leyendekkers and Hunter 1976).

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