# 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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**SCOR/IAPSO Working Group 127 on**
**Thermodynamics and Equation of State of Seawater**

**at its Meeting 6th - 11th May 2007 in Reggio/Calabria, Italy**

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## Refractive Index of Seawater

### 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).

**References:**


Alford, M.A., D.W. Gerdt, C.M. Adkins (2006): An Ocean Refractometer: Resolving millimeter-scale turbulent density fluctuations via the refractive index. J. Atmos. Ocean. Technol. 23, 121-137

Brewer, P.G., and A. Bradshaw (1975): The effect of the non-ideal composition of sea water on salinity and density. Journal of Marine Research 33, 157-175

Connors, D.N. and D.R. Kester (1974): Effect of major ion variations in the marine environment on the specific gravity – conductivity – chlorinity – salinity relation. Marine Chemistry 2, 301-314

Esteban, O. and M. Cruz-Navarrete (1999): Measurement of the degree of salinity of water with a fiber-optic sensor, Applied Optics, 38, 5267-5271

Fajans, K. and Joos,G. (1924): Molrefraktion von Ionen und Molekülen im Lichte der Atomstruktur. Zeitschrift für Physik 23, 1-46

Fofonoff, N.P. (1985): Physical Properties of Seawater: A New Salinity Scale and Equation of State for Seawater. Journal of Geophysical Research 90, 3333-3342

Frenkel, J. (1955): Kinetic Theory of Liquids. Dover Publications, Inc. New York

Heydweiller, A. (1913): Über physikalische Eigenschaften von Lösungen in ihrem Zusammenhang. IV.Refraktion, Dispersion und Dissoziation von Salzen im Wasser. Annalen der Physik, 4. Folge, 41, 499-542

IAPWS (1997): Release on the Refractive Index of Ordinary Water Substance as a Function of Wavelength, Temperature and Pressure. The International Association for the Properties of Water and Steam, Erlangen, Germany 1997.
Internet: **http://www.iapws.org/relguide/rindex.pdf**

Leyendekkers, J.V., Hunter, R.J. (1976): The Tamman-tait-Gibson model for aqueous electrolyte solutions. Application to the refractive index. J. Phys. Chem. 81, 1657-1663

Mahrt, K.-H. and Waldmann, H.C. (1990): Extrinsic Fiber Optical Point Refractometer for Top to Bottom Optical Density Profiling in the Ocean with $10^{-6}$ Precision. Conf. Proc. Oceanology International 90, Brighton, March 1990

Matthäus, W. (1974): Empirische Gleichungen für den Brechungsindex des Meerwassers. Beiträge zur Meereskunde 33, 73-78

Millard, R.C., and G. Seaver (1990): An index of refraction algorithm for seawater over temperature, pressure, salinity, and wavelength. Deep-Sea Research 37, 1909-1926

Millero, F.J., Feistel, R., Wright, D.G., McDougall, T.J. (2007): The Standard Composition of Seawater: The Definition of a Reference Salinity Scale. Deep-Sea Reseach, submitted

Millero, F.J, and K. Kremling (1976): The densities of Baltic Sea waters. Deep-Sea Research 23, 1129-1138

Miyake, Y. (1939): Chemical Studies of the Western Pacific Ocean. IV. The Refractive Index of Sea Water. Publ. Chem. Soc. Jap. 14, 239-242

Poisson, A., J. Lebel and C. Brunet (1981): The densities of western Indian Ocean, Red Sea and eastern Mediterranean surface waters. Deep-Sea Research 28A, 1161-1172

Quan, X. and E.S. Fry (1995): Empirical equation for the index of refraction of seawater. Applied Optics 34, 3477-3480

Seaver, G. (1987): The optical determination of temperature, pressure, salinity and density in physical oceanography. Marine Technology Society Journal 21, 69-79

Seaver, G. A., V. L. Vlasov and A. G. Kostianoy (1997): Laboratory calibration in distilled water and seawater of a multichannel interferometer-refractometer, J. Atmos. Oceanic Tech., 14, 267-277

Waldmann, C. (1999): The Optical Refractometer Project OPRA: Further Development of an in situ going Optical Density measuring Sensor, OCEANS‘ 99, Seattle, 13-16 September 1999

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