

Spec pH at the push of a button

Hugh Doyle¹ and Christina McGraw^{1,2}

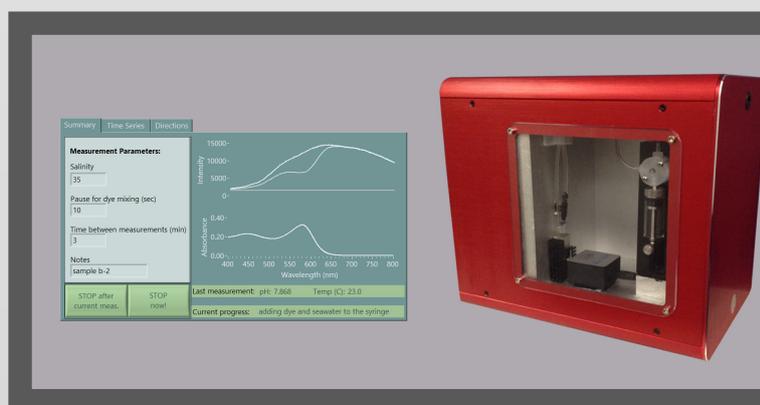
¹ Institute for Marine and Antarctic Studies, University of Tasmania, hugh.doyle@csiro.au

² School of Science and Technology, University of New England, cmcgraw@une.edu.au

Automated spectrophotometric systems allow rapid and precise measurement of seawater pH. However, such systems are difficult to build and expensive. Here, we present a fully automated system with a **rugged construction, reliability, and exceptional precision** that makes it ideally suited for ocean acidification studies in the laboratory or field.

The system: Automated fluid handling, including sampling and dye mixing, is achieved with a high-precision syringe pump (Tricontinent, C3000) integrated with an optical flow cell and Ocean Optics spectrometer (STS-Vis). An **intuitive user interface** was designed to simplify the measurement and minimise operator error.

Standardisation: The system was standardised using **tris buffer solutions and purified meta-cresol purple dye**, which were obtained from the laboratories of Professors Andrew Dickson and Robert Byrne, respectively. Measured values were standardised to the assigned pH of the tris buffer solutions (N=28, 4 bottles, batch 27). In the future, an instrument-specific calibration will be developed by obtaining apparent molar absorptivity ratios and dissociation constant over a range of temperatures.



Assessment: pH measurements were made on Oceanic CO₂ CRMs (N = 54, 3 bottles, batch 130). The measured pH was compared with the pH calculated from the certified values of A_T and C_T using the dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987):
 $\Delta\text{pH}_{T, 297.2 \text{ K}} (\text{measured} - \text{calculated}) = -0.003 \pm 0.001$
The excellent agreement and low standard deviation suggests the system can be used reliably for the calculation of carbon system parameters.

The system was taken on a 2016 hydrographic cruise to the Southern Ocean (RV Investigator). The **precision (± 0.001)** and oceanographic consistency of the pH profile highlights the capabilities of the system.

