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An autonomous spectrophotometric system for high resolution measurement of seawater pH

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The increase in carbon dioxide (CO_2) concentration in the ocean is a growing concern and is undergoing considerable research. A comprehensive monitoring of the carbonate system in seawater is essential to understand ocean acidification and modification to oceanic carbon transport and the ocean's atmospheric CO_2 uptake. Providing calibration and drift-free measurements, spectrophotometric detection of pH, with the monitoring of one of the other "major" carbonate variables (pCO_2, total alkalnity, dissolved inorganic carbon) allows the determination of the entire carbonate system speciation with the uncertainty required to detect long-term oceanic acidification. Stability, reliability and robustness are the critical features when in-situ long-term deployment is required. We have developed a method that makes use of a high-resolution low noise miniature spectrophotometer and a combined low power LED source, an optimal absorbance detection is achieved in a custom designed bubble-free cuvette with a sample volume of 6 ml, limiting indicator perturbations within the on-line precision of the instrument, currently evaluated at 0,0005 pH units and achieving the adequate uncertainty for systematic shifts evaluation. The system operates unattended with a sampling frequency up to 2 samples per minute and the actual temperature of the sample is monitored, not controlled, thus reducing power consumption. With its portability, the system is ideally suitable for both underway operation on ships of opportunity and for discrete sample analysis in remote research campaigns.