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Application of cavity ring-down spectroscopy for *in situ*, real-time measurements of properties of oceanographic interest in the surface ocean

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In situ, real-time measurements of chemical properties, e.g., dissolved CO_2 and its carbon isotopic compositions, dissolved inorganic carbon, water isotopes, etc., are highly desired for understanding various physical and biogeochemical processes in the surface ocean. Due to its high sensitivity, stability and portability, cavity ring-down spectroscopy (CRDS) has been increasingly used as a core technique for shipboard systems that automatically measure properties of oceanographic interest at high spatial-temporal resolution. These systems typically require front-end components that convert the sample into a continuous gas flow that can be continuously sampled by the CRDS. Here, we review the progress in the development of CRDS-based systems for shipboard, high-frequency measurements of various properties in the surface ocean, including pCO_2, $\delta^{13}C\text{-}CO_2$, pCH_4, $\delta^{13}C\text{-}CH_4$, and water isotopes. In most systems, gas extraction devices are keys to the sample preparation units that are coupled with the CRDS analyzers. In our present work, we summarize the major gas extraction techniques used in these methods (e.g. the showerhead-type equilibration, the bubbling equilibration, the high-porosity membrane contactor extraction, the expanded polytetrafluoroethylene-based extraction, etc.), present examples how these techniques are coupled with CRDS analyzers, and evaluate the major factors that determine the overall performance (precision, accuracy, response time, etc.) of the systems. Based on the working principles and field data generated by these systems, we were able to identify the major factors that affect the system performance, including the efficiency (completeness) of gas extraction, magnitude and stability of isotopic fractionation during the gas extraction, internal volume of the system (e.g., the volume of the equilibration chamber and that of the CRDS cavity) and the carrier gas flow rate. Finally, we make recommendations, for each type of system, the optimal configuration of the CRDS analyzer specifications (e.g., inlet gas flow rate, dynamic range, etc.) and the front-end properties (volume, carrier gas flow rate, etc.) to maximize the performance of the systems.