



Measurement of Isotopic CO₂ in Dissolved Inorganic Carbons of Water Samples from Various Origins Using Wavelength-Scanned Cavity Ring-Down Spectrophotometer

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Given the growing need to monitor the containment efficiency of CO₂ sequestration storage sites through the use of field-deployable instruments, we report here on the novel employment of a small footprint Wavelength-Scanned Cavity Ring-Down Spectrometer (WS-CRDS) for the measurement of the isotopic CO₂ signature of dissolved inorganic carbon (DIC). The above system is interfaced to an online aqueous sample treatment device in which 10% H₃PO₄ solution is bubbled through exetainer vials containing water samples to liberate gaseous CO₂ from dissolved inorganics. The WS-CRDS instrument is used to measure the isotopic carbon signature of the liberated CO₂, which can then be used to trace the carbonates back to their point of origin. In a first phase, a manual process was employed in which DIC containing samples were acidified and the evolved CO₂ was collected inside gas pillows. The gas pillows were then connected to the inlet of the isotopic WS-CRDS instrument for carbon ratio measurement. In a second phase, the acidification process was partially automated through the use of a software-controlled sample preparation system directly connected to the gas inlet of the isotopic WS-CRDS instrument via manual one three-way and one 2-position four-port valving system. A measurement precision of the isotopic ratio of less than 1 permil was achieved in minutes of measurement time. Such precision readily distinguishes the isotopic carbon signatures from three DIC samples collected from various sites in Northern California and presents a rugged and inexpensive analytical instrumentation alternative to the traditional use of methods based on the more complex isotope ratio mass spectrometry technique.