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${17}$O-Excess Measurements of Water Without Fluorination Using Optical Spectroscopy

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The parameter ^{17}O-excess (defined as ln(δ^{17}O +1)-0.528(ln(δ^{18}O)+1)) offers significant promise for improving our understanding of fractionation processes in the hydrologic cycle. Unlike the conventional δ^{18}O, δD and deuterium excess, ^{17}O-excess is only very weakly influenced by temperature-dependent equilibrium processes. This means that it offers a more precise means to isolate the influence of diffusive processes, such as evapotranspiration, evaporation the ocean surface, the kinetic effects during the formation of ice in clouds under conditions of supersaturation. The measurement of ^{17}O-excess is usually done by conversion of water to O$_2$by fluorination, followed by analysis with dual inlet mass spectrometry. This method is both labor- and consumables-intensive and is subject to uncertainty due to fractionation during fluorination and O$_2$collection. Here, we report on a new method for measuring ^{17}O-excess using cavity ring-down spectroscopy (CRDS). We use two separate lasers in tandem to access the isolated optical absorptions associated with $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, and HD^{16}O. High data acquisition rates result in 1 σ precision of better than 0.3‰ for ^{17}O excess at measurement rates $>$1 Hz. Closed loop control of temperature, pressure, and laser wavelength minimized drift allows precision of $<$0.01‰ for ^{17}O excess using data averaging over $\sim 10^3$ s. Coupling of a continuous flow water vaporization system to the CRDS instrument permits the measurement of ^{17}O-excess on small water samples.