# Underway surface water sample collection system for dissolved gases and triple isotopic composition of dissolved oxygen

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A continuous underway-sampling system is developed for the collection of oceanic water samples for the study of dissolved gas ($N_2$, $O_2$, Ar, etc.) ratios and triple oxygen isotope composition. At present, the majority of oceanic gas analysis is performed using discrete samples involving collection of dissolved gas samples in the vacuum flask, leaving 50% of the flask volume as headspace, and equilibrate water and headspace in the sampling flasks for 24h for extraction of dissolved gases. This approach becomes very labor intensive when high-frequency measurements are required to fully resolve the spatial and temporal variability in gas concentrations and/or isotopic composition. In our new method, about 50-70 ml of the surface sample is passed through the hollow fiber membrane that has high permeability only for dissolved gases. Outside of the fiber membrane is evacuated so that dissolved gases are extracted to vacuum phase, then these are collected on the molecular sieve at liquid nitrogen temperature. A constant flow rate (less than 3ml/min) is the key controlling factor to obtain satisfied gas recovery. The increase in flow rate from that of 3ml/min results in fractionation of oxygen isotopes. A series of laboratory tests using this technique on air-saturated distilled water confirmed the $\delta^{17}O$ and $\delta^{18}O$ isotopic fractionation between air and water at 22° C resulting in 0.385±0.03 and 0.703±0.01 per mil respectively and $O_2$/Ar ratio of ~1% in accordance with the previous results based on equilibration method. It takes about 20 minutes for one sample and requires no vacuum bottles for collection of samples. Study of triple oxygen isotopes and gas ratios using this underway sampling technique would be helpful in understanding spatial and temporal variations in the plankton metabolic rates (gross, net community production and respiration rates) in the mixed layer.