

## New procedure of CO<sub>2</sub> extraction for radiocarbon analysis of DIC in water samples: assessments of isotopic fractionation and radiocarbon background

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Carbon isotope of DIC in waters is a useful indicator for investigation of anthropogenic CO<sub>2</sub> budgets. On radiocarbon (<sup>14</sup>C) analysis of DIC in water samples, effective and simple carbon extraction is required. A bubbling procedure known as the WOCE method is the most widely used for seawater preparation, but it is difficult to be adapted to water samples having wide range of DIC concentration, such as groundwater and hot-spring water. Moreover, it is not easy for new entrant laboratories to introduce an extraction system having bubbling and circulation of carrier gas. We need to develop an easier extraction method in order to obtain precise radiocarbon data of DIC more easily and widely. Therefore, we established a new procedure of CO<sub>2</sub> extraction applicable to various kinds of water samples.

The required specifications for new procedure are as follows: (1) Changeable water amount of 1 mL to 250 mL injected to the system, depending on the various DIC concentration (0.5-100 mM) of the water samples in order to extract from terrestrial waters as well as seawater. (2) No use of carrier gas. This is important because there is a capacity limitation of using of gas cylinder with high pressure by law. (3) Simple procedure and compact system (easy and cheap). (4) Short time needed for experiment and interval (quick). (5) The high yield of CO<sub>2</sub> extraction.

The new procedure was improved based on the headspace method. A large size of reaction flask (100-500 mL) was used in the new system. Step 1: Enter magnet stirrer and phosphoric acid into the reaction flask. Step 2: Set joint with septum (pierceable chlorobutyl rubber for Labco Standard Extainer® caps) by O-ring fitting to the reaction flask. Step 3: Evacuate inside air after connection to the vacuum line. Close valve and disconnect from the vacuum line. Step 4: Water is injected through the needle by vacuum suction as same as headspace method. Water amount is computed using weights before and after water injection. The maximum limit of water sample amount is approximate half volume of reaction flask (water amount: 50-250 mL). Step 5: CO<sub>2</sub> is released to the headspace of the reaction flask. Step 6: CO<sub>2</sub> and water vapor in the headspace of reaction flask are introduced by expanding to vacuum line due to pressure gradient, instead of using carrier gas, and then trapped at cryogenic traps. The direct connection of reaction flask and cryogenic traps of vacuum line is not allowed, because the ice clog the tube of traps. Because this procedure can suppress the water intrusion to the vacuum system, the evacuation between treatments became shorter.

The cycle of gas expanding and trap was repeated 3-5 times, in order to obtain high CO<sub>2</sub> yield, and they reached to be ca. 97-98%. The yield increased as the number of iterations increased: 54-73% at single cycle, 85-92% at double ones, 93-97% at triple ones, and 96-100% at quadruple ones. Time required for the CO<sub>2</sub> extraction was shortened to 30 minutes for one water sample (quadruple cycles) by the new system. The stable carbon isotopic values were shifted positively along increases of CO<sub>2</sub> yield, but <sup>14</sup>C concentration showed identical values. We considered that <sup>14</sup>C concentration was too low to detect isotopic fractionation during the extraction processes. We would like to retry experiments using waters having relatively high <sup>14</sup>C concentration, and clarify the relationship between CO<sub>2</sub> yield and carbon isotopic compositions of extracted CO<sub>2</sub>. The background of carbon contamination seemed to be negligible though more discussion about radiocarbon background is needed. We would like to discuss

what kind of sample is suitable to assess.