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Simultaneous measurement of CO_2 concentration and isotopic ratios in gas samples using IRMS

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Isotopic methods are indispensable tools for studies on atmosphere-biosphere exchanges of CO_2 and environmental monitoring such as CO_2 leakage detection from subsurface carbon storages. CO_2 concentration is an important variable in interpreting isotopic composition of CO_2 especially in atmospheric applications (e.g., 'Keeling plot'). Optical methods such as CRDS (Cavity Ring Down Spectroscopy) are gaining attention recently because of its capability to simultaneously measure CO_2 concentration and isotopic ratios with a short measurement interval (up to 1 sec.). On the other hand, IRMS (Isotope Ratio Mass Spectrometer) has been used only for isotopic measurements.

In this study, we propose a method to measure CO_2 concentration from gas samples along with isotopic ratios using conventional IRMS system. The system consists of Delta V Plus IRMS interfaced with GasBench II (Thermo Scientific, Germany). 12-mL vials with open top screw cap and rubber septum were used for both gas sampling and analysis. For isotopic analysis, gases in the vials were transferred into GasBench II by He carrier flow and CO_2 was trapped by a single cryotrap (-180 ℃) after passing a water trap (Mg(ClO4)2). Upon release of the cryotrap, liberated CO_2 was separated from N2O using gas chromatography column inside the GasBench II and introduced online into the IRMS. Isotopic ratios were measured for the masses of 44, 45 and 46, and the peak intensity (mV of mass 44 and peak area) was recorded for the concentration calculation.

For the determination of CO_2 concentration, a calibration curve relating the peak intensity with molar concentration of CO_2 was constructed. By dissolving $NaHCO_3$ in de-ionized water, solutions containing 0.05, 0.1, 0.25 and 0.5 μmol of inorganic carbon were prepared in 12 mL vials. Phosphoric acid was injected through rubber septum of the vials to acidify the solution and released CO_2 was analyzed for the isotopic ratios and the corresponding peak intensity was recorded using the same procedure with gas samples. The peak area (Vs) linearly correlated with the molar concentration of inorganic carbon ($r2 > 0.99$) with sufficient stability, thereby enabling the determination of CO_2 concentration in gas samples. The calibrated range of CO_2 concentration corresponds to $200 \sim 1000$ ppm of atmospheric pCO_2. Accuracy of the method is continuously being improved by analyzing standard gas samples with known concentration and isotopic ratios. This method provides a simple, cost-effective technique that can be applied for various studies based on the isotopic composition and concentration of CO_2.