CO₂ Reference Gas Prepared in NIES for Intercomparison of Isotope Analysis

H. Mukai and H. Iwami

National Institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba, Ibaraki 305-0053, Japan; 81-298-50-2536; Fax: 81-298-50-2569; E-Mail: lmukaih@nies.go.jp

There are several difficulties in determining precise isotopic ratios of CO₂ in the atmosphere. First, there is no gaseous CO₂ standard that has a precise isotope value (e.g., precision <0.01 per mil) relative to VPDB-CO₂. Recently, the U.S. National Institute of Standards and Technology (NIST) supplied three CO₂ reference materials for isotope analysis. These RMs are very useful to check measurement values and the cross contamination effect in mass spectrometers. However, there are uncertainties in the certified values (over 0.03 per mil for δ¹³C and 0.1 per mil for δ¹⁸O, although these uncertainties may decrease in the future) and, unfortunately, they do not span ambient oxygen isotope ratios for atmospheric CO₂ (about 0 per mil). In such circumstances, NIES decided to make a reference sample for atmospheric CO₂ especially for intercomparison in the CO₂ community. For easy handling, each CO₂ sample was sealed in a 6 mm diameter glass tube. CO₂ was produced from reagent carbonate and the carbon isotope ratio was adjusted to -8.5 per mil. The oxygen isotope ratio of about 0 per mil was obtained by using an equilibrium process with seawater. About 3 L of CO₂ were prepared and about 2 mL of CO₂ were sealed in each glass tube to obtain over 1000 samples. This reference CO₂, called NIES Atmospheric CO₂ Isotope ratio Standard (NACIS), is now being distributed for intercomparison. After the cross contamination effect in isotope analysis by MAT 252 was studied by using NIST RMs, NBS19, and NBS18, an isotope ratio of NACIS was tentatively determined at -8.57 and -0.70 for δ¹³C and δ¹⁸O respectively.

Second, the isotopic fractionation of CO₂ in the extraction process from air samples was studied by using NACIS. An air standard was used frequently to ensure traceability of measured values. In this study, the NACIS reference gas was diluted by CO₂ free air to produce an ambient level concentration. This reference air was used to check the extraction process. Several trials showed good agreement in determination of δ¹³C, but slight deviation (about 0.05 per mil) was sometimes observed in δ¹⁸O analyses. This reference air sample was more useful to assess the extraction process than use of real air.