

REEVALUATION OF ISOTOPIC SCALE FOR CO₂ IN NIES AND ITS RELATION WITH INTER-COMPARISON WORKS

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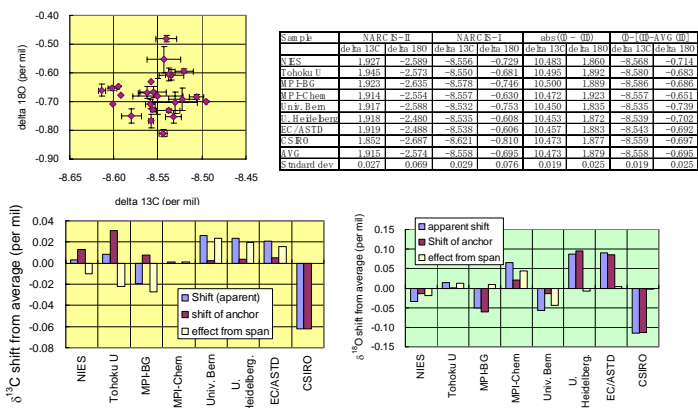
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ABSTRACT

To establish isotope scale for CO₂, we need to study many analytical steps, such as working standard, calculation scheme, N₂O correction and extraction process. In this revision of the scale, we will not change isotope anchor value (such as NARCIS-I) but will change N₂O correction factors. Through some inter-comparison works for CO₂ isotope analysis for several years, we found key points which we can include in revised isotope scale (NIES2009iso).

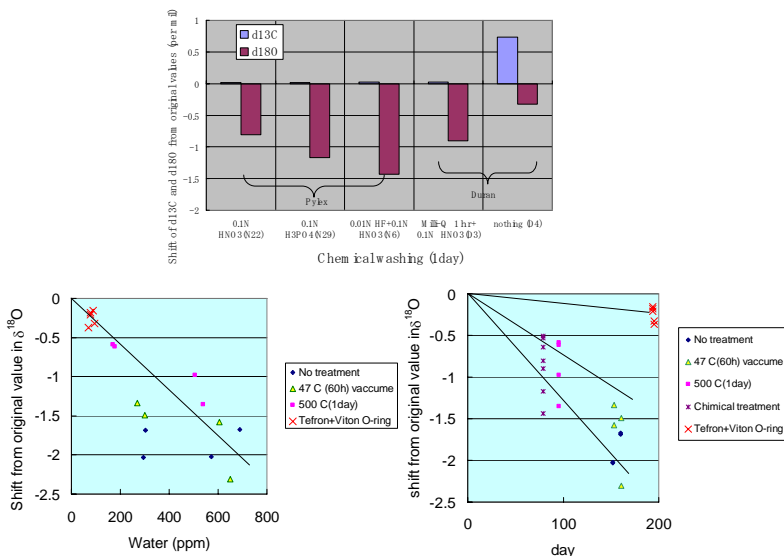
NBS19 and NARCIS scale in NIES;

Because NARCIS-II has a similar isotope ratio to NBS-19-CO₂, we can check an anchor point for isotope analysis, comparing with other laboratories. However, due to cross contamination effect in mass spectrometer, determination of isotope values for working standards (such as NARCIS-I) may include small uncertainty. In NIES, air sample is analyzed against working standards, which have similar isotope values to air CO₂ such as NARCIS-I. Therefore, NIES isotope scale for air analysis is almost based on the same scale as NARCIS-I rather than NARCIS-II.



Sample extraction effect and sample preserving property;

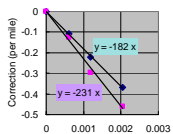
We found that the extraction by NIES glass vacuum line have little effect on isotope values. On the other hand oxygen isotope ratio in the sample was found to be modified by contact with water in a glass bottle during preservation. We tried several chemical treatments and heating of the glass bottles, but they did not affect strongly to it. Although this modification effect in $\delta^{18}O$ is about -0.3 per mil/month, it is difficult to include the effect into the scale, because it must differ according to the bottle properties.



N₂O correction;

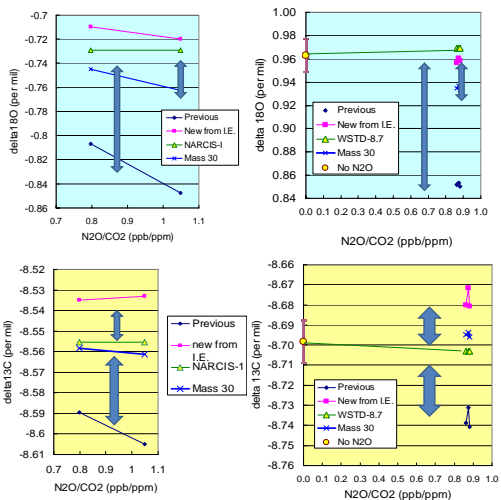
Although NIES has two kinds of N₂O correction factors, which were experimentally determined (previous) and estimated from ionization efficiency (new), these factors were found to be too low and too high respectively. Using mass 30 method and dilution experiment with N₂O containing zero air, we determined revised N₂O correction factors (NIES2009iso). These change of factors had a large effect (above 0.02 per mil) to the final values of isotope ratios.

const.	Previous	new	NIES2009iso	mass 30
delta 13C	-0.182	-0.250	-0.223	-0.223
delta 18O	-0.235	-0.357	-0.355	-0.318

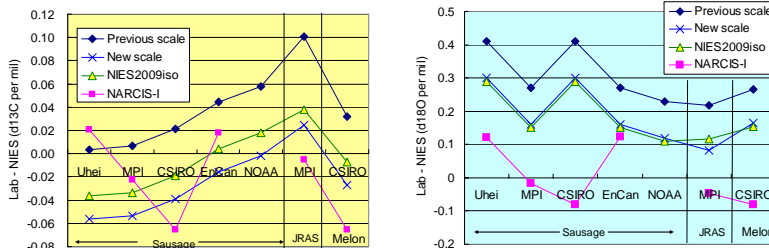


Experimentally determined (previous factors)

Sausage inter-comparison showed isotope value dependency in d18O. difference. Two institutions showed different characteristics.



NARCIS-I and WSTD-8.7 were diluted with zero air and N₂O containing air.



If we compare NIES2009iso scale to the previous inter-comparison, d13C differences between NIES and MPI, and NIES-En Canada in Sausage were became consistent with the differences in pure CO₂ (NARCIS-I). In the case of CSIRO, Sausage and Melon showed similar difference. Relation between MPI-NIES using JRAS (NBS19 like) was different from the result of Sausage.

Results of delta 18O still showed a relatively large difference (e.g. 0.2 per mil) between NIES and other labs. This difference may be partly related to the problem of preserving property in the glass bottle. Melon used stainless steel container with a metal valve (keeping dry condition) and showed relative smaller difference than the case of Sausage. This may suggest the effect of the glass bottle used. We recently changed O-ring from Viton to double O-ring of Teflon and Viton to minimize modification effect in the glass bottles.

*Previous factor case gave 0.04 per mil and 0.1 per mil lower values in d13C and d18O.
 *A new factors gave 0.02 per mil and 0 per mil higher values in d13C and d18O.
 *Mass 30 method gave reasonable value in d13C but 0.02 per mil lower value in d18O.
 *NIES2009iso takes factor from average factor from mass 30. Because the factor for d18 by mass 30 gave 0.03 per mil lower value, we take we took theoretical value.

Reference
 Brand WA, Hunag L, Mukai H, Chivulescu A., Richer JM., Rothe M., Rapid Communication Mass Spectrom, 23, 915-926, 2009
 Assonov SS. and Brenninkmeijer CAM., Rapid Communications Mass Spectrom., 20, 1809-1819, 2006.