Geophysical Research Abstracts, Vol. 8, 05162, 2006
SRef-ID:

On the N_2O correction used for mass-spectrometric analysis of atmospheric CO_2

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To obtain accurate values of δ13C (CO_2) and δ18O (CO_2) by CO_2 mass-spectrometry, the raw isotope data must be corrected for the N_2O contribution. The key parameter, i.e. the N_2O relative ionisation efficiency, E(N_2O), cannot be determined by direct measurements of pure gas. Instead, present publications suggest determining the effective E(N_2O) by analyses of CO_2-N_2O mixtures of known isotope composition and mixing proportions. Based on our experiments we propose a new N2O-correction. In this case, independent E(N_2O) determinations are not required, and in fact, its effective value may be determined by the proposed algorithm. The formalism and physical meaning of this correction are considered and results of various critical tests are presented. Based on our experiments we demonstrate that parameters determined with our MAT 252 are rather stable so that the proposed corrections would result an inaccuracy of the N_2O/CO_2 determination of only $\sim$1%. Presently, based on our test runs, the inaccuracy is up to 2.5% of the correction magnitude. For tropospheric CO_2 where N2O-correction of δ13C (CO_2) and δ18O (CO_2) amounts to $\sim$0.22 and $\sim$0.33 per mile respectively, this would give an inaccuracy of $\sim$0.005 and $\sim$0.008 per mile respectively. The proposed algorithm may be valuable for samples where separate N_2O determinations by GC are not available, as well as for testing E(N_2O) and the "traditional" N_2O-correction based on mass balance calculations.