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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An improved inlet for precisely measuring the atmospheric Ar/N_2 ratio" *by* T. W. Blaine et al.

Anonymous Referee #2

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General comments:

The technically oriented paper addresses a long standing problem of sampling air with the aim to quantify the constituents at the per meg (= 10^-6) level. This is a particular requirement for the O2 and Ar content of atmospheric samples which normally are internally expressed as deviations of the O2/N2 or Ar/N2 ratios from a reference air kept in the laboratory. The high precision required arises from the variations related to the globally changing atmosphere mostly related to anthropogenic activities. O2/N2 is measured in order to complement the rise of CO2. O2 is decreasing as the CO2 level is raised, albeit with a different slope owing to the differing sources and sinks of the two gases. In particular, the amount of CO2 dissolved in the world oceans

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exceeds the atmospheric content by a factor of roughly 50 whereas the situation is reversed for O2. From the observed quantitative relation, the partitioning of the CO2 sink levels between ocean and land can be examined. Ar/N2 is measured to study effects of outgassing in reaction to changing conditions of the oceans, in particular the increase in sea surface temperature. The measurement of the quantity is even more challenging than O2/N2 because of the smaller amount of Ar in the atmosphere, the small variations observable, and the relatively large mass difference between N2 and Ar. A particular recurring experimental problem has been related to fractionation effects at the inlet of the sampling device. The use of T-junctions in the inlet line for instance has been a constant source of error and therefore is considered non-appropriate. The major cause behind the problem has often been suspected to be thermal diffusion effects, either from cooling effects in the gas streams or from temperature differences between the gas phase and the sampling orifice / tubing.

The paper by Blaine and Keeling offers an elegant experimental solution by employing an aspirated solar shield inlet designed originally for precise air temperature measurements. The design strictly avoids temperature differences between the sampled air and the inlet orifice placed into the original position of the temperature sensor. The authors have studied Ar/N2 ratios as a function of wind speed and of solar radiation, the latter by observing diurnal cycle of Ar/N2 with and without the inlet design simultaneously. The results clearly demonstrate the problematic role of radiative heating by the sun and corresponding cooling during the night. The remaining average Ar/N2 diurnal cycle over the period of a whole year exhibits a residual swing of only ś 0.4 per meg, whereas the difference between the aspirated and shielded inlet versus the open inlet can be as large as 80 per meg.

Specific comments: The paper is considered appropriate for ACP, the use of an aspirated inlet line with solar shield for this application is new and the experiments have been conducted with great care and are presented in a clear and logical way. Related work has been taken into account and is properly acknowledged.

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5, S4095–S4097, 2005

Technical corrections:

Page 2, line 6: Ěunits. An increaseĚ Page 3, line 1: Ěratios in air are difficultĚ

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11899, 2005.