Atmos. Chem. Phys. Discuss., 5, S4392–S4394, 2005
www.atmos-chem-phys.org/acpd/5/S4392/
European Geosciences Union

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 #1

Received and published: 11 December 2005

General comments:

The paper by Blaine et al. addresses and solves an important issue in high-precision analysis of the major components of air, namely, thermal fractionation at the sample intake. Recently, the relevance of this well-known problem became more obvious by the introduction of continuous mass-spectrometric Ar/N_2 measurements in the lab of the authors. However, as pointed out by Blaine et al., the same problem is of relevance for on-going flask sampling programs and measurements of the O_2 abundance, even though the manifestation of this problem is less apparent in the latter two cases due to higher flow rates and higher signal-to-noise ratios, respectively. The authors demonstrate that thermal fractionation at the inlet can be eliminated by using an as-

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

EGU

pired air-shield that minimizes radiative heating and cooling effects at the inlet.

The authors are to be commended for describing this problem and its solution in a succinct and exceptionally clear manner. The findings are supported by adequate figures and photographs. The paper is very well written, adequate in length and presents data and interpretation in a concise and straightforward way. Indeed, the paper is most pleasing to read. I have very few comments and requests for corrections (see below), which should be addressed in the final ACP manuscript, but otherwise recommend prompt publication of this important paper.

Specific comments:

p. 11900, l. 21: In the half-sentence following equation 1, delete "multiplied by 10^6", since δ(Ar/N_2) is not multiplied by 10^6, only the unit is changed to "per meg", just as a length of 1 m equals 100 cm. This means that the length is not multiplied by 100, just the numeral in front of the unit. δ values are dimensionless, so if the δ value is multiplied by 10^6, then it's numerical value increases by this factor. However, what is intended (generally) is not to change the dimensionless value, but to introduce some sort of "pseudo-dimension", e.g. per meg. So, one could only say that δ(Ar/N_2) is multiplied by "10^6 per meg" (which is identical to 1). Otherwise its numerical value would change.

p. 11900, l. 22: Please give a reference for the composition of air, on which these calculations are based. I've tried to verify the calculations with the air composition given in the Handbook of Chemistry and Physics, 80th Edition, which gives the following molar fractions for N_2 and Ar in dry air, respectively: 0.78084 and 0.00934. However, I obtain different results than given in the paper: A 1 mol increase of Ar in 10^6 mol air (with a corresponding decrease of the number of other air molecules, without changing their relative proportions, e.g., the O_2/N_2 ratio, and without changing the total number of 10^6) gives a 108.1 per meg increase of δ(Ar/N_2). A 1 mol increase of N_2 in 10^6 mol air with a corresponding decrease of the other constituents gives a -5.8 per meg change in δ(Ar/N_2). I do obtain the same numerical changes as the authors, but I have

ACPD

5, S4392–S4394, 2005

to assume that the *total* number of air molecules changes as well, i.e., increases to 100001 molecules, in contradiction to the phrasing in the paper. Please correct these numbers or change the phrasing.

p. 11901, l. 15: Please reference the following paper: Sturm, P., M. Leuenberger, F. L. Valentino, B. Lehmann, and B. Ihly (2005), Measurements of CO_2, its stable isotopes, O_2/N_2, and ^{222}Rn at Bern, Switzerland, Atmos. Chem. Phys. Discuss., 5, 8473-8506. Their findings on thermal Ar/N_2 fractionation should be discussed in the context of the present paper.

p. 11902, l. 5: Again, cite Sturm et al. (2005) here.

p. 11902, l. 15: Please change to "in order to reduce the water vapor pressure", since even at $-80°$C, some gaseous water will still be present.

Technical Corrections:

p. 11902, l. 12: Correct spelling of "diaphragm".

p. 11902, l. 13: Replace "ft" by metric units.

p. 11903, l. 10: Please change to "m/s" or "meters per second", not a mixture of both.

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