Quality control of flask sample data using Ar/N_2 measurements

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Long-term atmospheric observations of greenhouse gases provide key information for the understanding of their budgets. Since spatiotemporal background concentration gradients of these long-lived trace gases are very small, measurements have to be made with high accuracy. One component in maintaining the accuracy of observation networks has been flask sampling programs where the air samples are then analysed in laboratories. This also allows the measurement of additional parameters of these samples.

The MPI-BGC operates flask sampling programs at 11 stations. Pressurized samples are generally collected in triplicate. At some of the stations logistic challenges have repeatedly caused big delays in shipment of samples to the laboratory. The length of storage times prior to analysis can affect the sample's integrity due to micro leaks in the container seals, causing individual samples to exhibit large deviations in their composition from their siblings. The underlying process is described as Knudsen diffusion that results in a mass fractionation of the escaping relative to the remaining gas. This is manifested in an enriched Ar/N_2 ratio that generally has very little atmospheric variability. The correlation of the effect on different trace gases relative to the bias in the Ar/N_2 ratio can be theoretically derived based on Graham's Law. We compare this theoretical relationship with the observed patterns of flask samples that have been affected by leaks.

The results show a very good correlation of O_2/N_2 deviation relative to Ar/N_2 that allows correcting O_2/N_2 measurements for fractionation effects with concurrent Ar/N_2 measurements, assuming a station-specific time invariant Ar/N_2 ratio. The correlation of the deviations of most of the species analysed relative to the Ar/N_2 deviation also reveals the theoretically expected relationship (CO_2, CH_4, N_2O), yet with too much scatter to be used for a correction. Nevertheless, bounds on the permissible Ar/N_2 ratio can be defined within which the introduced fractionation error for the corresponding other species remains within the WMO accuracy target. This Ar/N_2 ratio indicator then can be used to flag invalid or suspicious data to avoid a systematic bias of the trace gas mixing ratios.