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Atmospheric Measurement Techniques Discussions

Interactive comment on "Ozone sonde cell current measurements and implications for observations of near-zero ozone concentrations in the tropical upper troposphere" *by* H. Vömel and K. Diaz

Anonymous Referee #3

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The paper presents a new analysis of the background current of the ECC sondes used for ozone profiling. The issue is important for the accuracy of ozone profiles, in particular in the tropical troposphere, where ozone conentrations are low, and has been subject to many discussions. The analysis is based on laboratory measurements and the results are used for a reanalysis of ozone soundings made over the equatorial pacific during the CEPEX campaign (Kley et al., 1996). The major outcome of the experiments is that the so-called background current of the ECC sondes results from the treatment with high ozone concentrations. It is demonstrated that this current is not a universal constant but decreases in time.

The data presented are as such convincing, although one might argue that a larger ensemble of sondes should have been investigated in order to improve the statistical basis. Therefore, some caution might be appropriate before changing the routine operation of ECC soundings. Nevertheless, the findings themselves support earlier findings about the chemistry involved.

General Comments: I fully agree with anonymous referee 1, that the best explanation of the experimental results presented in figures 2-4 is a memory effect due to slow reactions in the oxidation of iodide by ozone in the solution. I would argue further that the results suggest that the overall stoichiometry of the reaction is approximately 1.1 (instead of 1, as normally assumed in ECC analysis). I disagree with the argumentation of the authors on the higher deviations after long exposure times. The effect seems to be almost proportional to the ozone concentration in the sample gas. The results in Figure should thus be plotted and analysed in terms of relative deviation (i.e. stoichiometry).

In order to prove or disprove the influence of exposure time, the experiments need to be repeated. Rather than terminating the individual runs at the highest concentration they should be continued with smaller concentrations of O3. This should give a clear answer if a change in stoichiometry as a function of O3 or an effect of a slowly concentrating solution is the cause for the slight increase in the ECC equilibrium response to a given O3 concentration.

To me, the conclusion of the paper is that the ECC chemistry has a fast and a slow component which leads, in equilibrium, to a stoichiometry of about 1.1. Therefore, the reanalysis of the CEPEX soundings, albeit intriguing in providing a much more homogeneous picture, should be made using an appropriate memory function, as detailed by referee 1, and including the appropriate stoichiometry. While it is clear that the approach suggested by the authors (with the modifications suggested above and by referee 1) is a clear improvement above the use of a constant background current, it should be pointed out more clearly that it still awaits in-situ validation before imple-

mented in the ozone sounding network.

The authors fall short in putting the findings into perspective. There has been a long discussion in the literature on the stoichiometry of the O3-iodide chemistry as a function of pH. The results for neutral solutions as used in the ECC range from slightly under 1.0 to as much as 1.5 (e.g., Dietz et al., 1973 and references therein). See also the comment by Stuebi, who found a stoichiometry of 0.98 in contradiction to the results of the authors. Therefore, the conclusions may be not as universal as the authors suggest and need to be verified in intercomparison experiments involving, e.g., the JOSIE community before one could try to adopt it for general use.

I noted that some of the soundings plotted in Figure 5a appear as almost linear functions in the semilogarithmic diagram. They are still seen in Fig. 5b. I couldn't identify such soundings in the original publication by Kley et al. This needs to be addressed or corrected if due to erratic data. It would be easier if a linear ozone scale would be used in Figure 5.

R.N. Dietz et al., Analytical Chemistry, 45, 402, 1973 D. Kley et al., Science, 274, 230-233, 1996

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3153, 2009.