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Interactive comment on "Calibration of atmospheric hydrogen measurements" *by* A. Jordan and B. Steinberg

A. Jordan and B. Steinberg

ajordan@bgc-jena.mpg.de

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RC: "P. 4934, L. 25: 'Stable reference standards' are one way to ensure accurate measurements but not the only approach; perhaps 'reproducible standards' is better."

AC: We feel that the term "reproducible" stresses the consistent "re-production" of standards but leaves out the period between re-production cycles. Standards that are generated with a reproducible method but stored in a container which influences the composition over time will lead to inaccurate measurements. We think that the third condition listed of "accurate assignment" of these stable standards implies that the standards are reproducible and would tend to leave the text as it is:

"Three conditions are required for the accurate determination of hydrogen in air: A precise analytical method, stable reference standards and an accurate assignment of H_2 mixing ratios to these standards."

RC: "P.4935, L. 22: Why was peak height chosen to quantify the peak rather than area?

Does it make a difference which approach is used?"

AC: The chromatographic peak of the GC-HgO reduction detector is always tailing and the baseline generally has some noise (more detailed work performed by S. Hammer from University of Heidelberg identified the UV lamps that are used in these analysers as primary source for this noise). This limits the reproducibility of determining the peak integration borders. The reproducibility of the peak height is less influenced by this setting of the end of the peak integration than the reproducibility of the peak area. Thus, peak height results in more precise analytical measurements and was therefore chosen as quantitative measure for the signal.

RC: "P. 4936, L. 5-7: I suggest the authors revise ': : : made relative to a set of standard

gases: : :'? by replacing 'set' with the number of standards."

AC: "Measurements of atmospheric hydrogen are made relative to a set of standard gases in high pressure cylinders." is meant as a general statement describing the common approach and intended to introduce the procedure to prepare these standard gases. We suggest to move this sentence as it is to the preceding page as first sentence of the second paragraph (l. 24). The first sentence of section 2.2 would then read: "These standard gases are natural air samples.."

The number of standards that were used to define the MPI implementation of the CSIRO94 scale has been extended over time. This is partly reflected by the different production dates of the standards used at MPI-BGC that are given in Table 1. Starting in 2003 three such standards were used, in 2004 four more standards were added to this number, in 2005 and 2006 each one new standard were added and since 2007 the same set of 13 standards is in use – with some of the old standards having been replaced with new preparations.

RC: “P.4937. What is the point of the 13 air mixtures discussed in section 2.2 and Table 1?”

AC: These 13 air mixtures form the final set of standards relative to which the measurements of atmospheric hydrogen are made in our laboratory. The point of their use is

a) prior to 2009: to serve as calibration standards with preliminary assignments

b) during the preparation period of the 53 reference gases (end of 2008): to document the stability of the detector response over the full range of mixing ratios throughout the production period of the 53 reference gases (see p. 4940 l.13) and

c) since 2009: to fix the scale from the 53 single mixtures to this very set of 13 standards discussed in section (p. 4948, l.8-9).

RC: “Do the 53 reference gases listed in Table 2 define the new scale?”

AC: Yes, these 53 reference gases specified in Table 2 have been prepared such that their H_2 mixing ratios can be derived in a metrologically traceable way. Except for the gas with the lowest H_2 mixing ratio they have defined the new scale. These 53 mixtures themselves were not kept as their long-term stability was questionable. The 13 standards in well-tested cylinders described in Table 1 now constitute this scale (see comment above).

RC: “It is not clear why the comparison with CSIRO in Table 1 is presented before the MPI standards are discussed. This might be moved to after Section 2.3.”

AC: The comparison between MPI and CSIRO is mentioned in Section 3.1. In Table 1 the mixing ratio that was initially assigned to the standards and used throughout the experimental period of the study is specified in the Table 1 “CSIRO94” column. These

numbers were derived from one standard linked to the CSIRO94 scale in the described way (section 2.2, p. 4936, l.18-23) but are no numbers provided directly by CSIRO. The numbers in Table 1 column “MPI-2009” are derived from 52 of the 53 standards prepared using the procedure outlined in Section 2.3. The difference in the numbers of the two columns reflects both a scale difference as well as a difference resulting from the different response function descriptions (polynomial and exponential).

RC: “In the summary it is stated that 13 standards make up the new scale. Are these the same as those in Table 1?”

AC: Yes. We will add the reference to Table 1 on p. 4948 to make this clear.

RC: “Does the scale include the Luxfer 50 L Al tank?”

AC: Yes it does (see Table 1: Tank code = Lux-3502361; see footnote a). This standard received a special electropolishing treatment in 2000 and has been in use for 6 years without any sign of drift of its H2 mixing ratio relative to other standards.

RC: “P. 4941, L. 1-2: The mean offset between two data sets over time may not show drift. The authors should fit the data vs. time and determine the change and uncertainty.”

AC: We will follow this suggestion and add a respective figure. The figure does not show a significant trend in the CSIRO-MPI offset (<= 0.5 ppb/5 yr). The offset corresponds to the scale change offset (17 ppb).

RC: “P. 4941, L. 15-30, P. 4942, L. 1-13; Figure 4: Some additional detail and discussion would benefit this section. 1) Are the US N265 tanks 265 L.? Is the difference in stability between the 150 and 265 Luxfer tanks due to size or treatment?”

AC: N265 is the product code for one type of cylinders. They are of a volume of 46 L with a maximum pressure of 153 bar. We do not see any explanation why the size could make this qualitative difference. It appears more likely to result from a difference in the production.

RC: “They appear as stable as the steel tanks. The caption for Figure 4 says these are Luxfer Al tanks purchased from the Conwin Carbonic Co. Were they treated in any way?”

AC: No details on the proprietary procedures were obtained upon our request from the company. No difference in treatment was made between these and other cylinders before filling at our institute.

RC: “2) What kind of steel cylinders were tested? Were they all from the same manufacturer? Were they the same size, steel or stainless steel, treated or not?”

AC: Steel cylinders tested include normal steel, tempering steel and different alloys of stainless steel cylinders (316Ti, 316L, 304L, 34CrMo4), in various sizes (3, 20, 27, 34, 50 L) from five manufacturers. The different cylinder types also underwent different passivation procedures (pickling, electropolishing or mechanical surface finishing). As all tested steel cylinders were keeping H_2 mixing ratios stable it suggests that there is no major influence from the production procedures and steel alloying additions but that there rather is a qualitative advantage of steel compared to aluminium for keeping H_2 mixing ratios stable.

RC: “3) Did the cylinders all hold the same type of valve?”

Most cylinders were equipped with brass diaphragm packless valves (D200 type, Rotarex, Luxembourg): this includes all Luxfer cylinders (first four columns in Figure 4) and some of the cylinders summarized in the last two columns of Figure 4 (“alu div” and steel). Thus, the same type of valve was mounted on cylinders that exhibited a growth of H_2 and on those that kept H_2 mixing ratios stable. Different valves were mounted on the various steel cylinders including the above mentioned brass valves, the same valve type in stainless steel and other valves of various origins. Irrespective of the valve type none of the standards contained in these cylinders exhibited a drift in H_2 mixing ratios. While an additional contribution of some inappropriate valves cannot be excluded the substantial effect is rather attributed to the cylinders.

RC: “If the cylinders that were found to drift were refilled did they still show increasing H2 over time?”

AC: Some of the standards with drifts displayed in Figure 4 are replacement fillings after other standard gases had already been stored in the cylinder. We do have only very few cylinders that have been refilled and monitored for a sufficiently long period of time for both fillings. In these few examples the cylinder influence was maintained, i.e. H_2 levels were growing in the new filling if the standard that had been in the same cylinder before had shown a drift or they were stable when H_2 in the previous standard had been stable.

RC: “P. 4943, L. 26: Is the first time the H2 generator mentioned previously? If the generator was used for the preparation of the ‘primary’ standards it should be mentioned on page 4939.”

AC: The hydrogen generator is mentioned and specified on P 4938 L.17.

RC: “P. 4944, L. 21: How significant was the H_2 change in valves fitted with the Valcon-E rotor? Is this something one needs to consider when setting up the analytical system?”

AC: The difference in experimental results between Valcon M fitted rotor valves and Valcon E ones pointing to a loss in the latter polymer was 0.5 %. While it would certainly be reasonable to use Valcon M rotors in the analytical system the measurements done with Valcon E equipped systems is still unlikely to result significant biases or reduced precision. First of all, the storage time between flushing of the sample loop and before injection onto the GC-column is relatively short (20 s) compared to the holding time of H2 in the sample loop in teh procedure described in section 2.3 (ca. 6 min). Secondly, the valve switch programming is assuring always identical contact times of the sample gas with the valve rotor. In contrast to the preparation of absolute reference mixtures the GC analysis is a relative measurement. As the effect applies equally to sample and standard measurement it does not induce any bias.

RC: “P.4945, L. 4-6, Table 2: The number of experiments (n) used to determine the uncertainty for each source of error should be included.”

AC: The various sources of error and how the uncertainty of the individual parameters was derived are discussed in Table 3. In Table 2 the combined uncertainties of the pressure, temperature and mass measurements are derived from the uncertainties specified in Table 3. Whereas the uncertainties of the temperature and pressure measurements of the loop that is filled are assumed uniform for all mixtures (T range: 296-298 K; p-range: 966-1010 mbar) the weighing uncertainty differs depending on the number of weightings and the respective masses of the mixtures and their intermediate samples. Therefore, the relative weighing uncertainty is calculated by taking the root of the sum of squares of the balance uncertainty relative to the actual masses of all intermediate and final mixtures. As an example for the mixture 20083260 (p.4955, 2^{nd} line of the table) the weighing uncertainty is:

$$u_m = \sqrt{\left(\frac{0.16g}{411.5g}\right)^2 + \left(\frac{0.16g}{203.4g}\right)^2 + \left(\frac{0.16g}{371.4g}\right)^2} = \sqrt{0.04\%^2 + 0.08\%^2 + 0.04\%^2} = 0.10\%$$

with 0.16 g = balance uncertainty; 411.5 g = mass of air of pre-filling; 203.4 g = mass of pre-filling sample after pressure release; 371.4 g mass of the diluted final mixture.

RC: “P. 4945, L. 24-25: rewrite these as ‘: : :working standard results in: : :?’”

AC: This sentence actually needs to be rewritten and should read as follows:

“In contrast, a combination of a quadratic and exponential function of the following type (3) results in a good match between measured and calculated data points:

[H2]=ax^2+bx+c*(1-exp(-dx))

with a, b, c, d = regression parameters; x = peak height normalized to working standard.”

RC: “P. 4946, L. 2: ‘no’ should be ‘not’.”

AC: This probably refers to P.4948, L. 2. The sentence will be changed accordingly.

RC: “Figure 3: Are the drift rates for the series of calibrations significant? The rates and

error should be given in the figure caption.”

AC: Figure 3 displays the record of measurement results of quality control standards that are used only to monitor the long-term consistency and not for calibration. The trends in a linear fit of these data results are insignificant. Any instrumental response drift that is not captured by regular calibration would show up here but there has not been any continuing drift rate been observed in the instrumental response in this period. In our experience such response changes have rather been observed stepwise (after power-cuts, lamp changes).

RC: “Figure 5: How many tanks were used in each test? If only one tank was examined for each alloy the results could be biased as drift rates may vary among cylinders of the

same type.”

AC: The data points in Figure 5 do represent only single cylinders (the figure caption will be changed to clarify this) so only for alloy 7060 there are two individual units. We have documented in Figure 4 that individual cylinders of the same type may differ in their properties and so it is admitted that this weakens the significance of the test. Yet, we have not been able to purchase more cylinders to perform this storage test with a larger number of cylinders. With the test results displayed in Figures 4 and 5 and the discussion of literature findings in section 3.1 we do not claim that this study can conclude on the mechanism on formation of traces of hydrogen on aluminium surfaces. Yet, we would like to document all results that give indication of potential influencing properties of the material involved. Thus, we would rephrase the text:

p. 4941, L.30:

"These different properties may reflect the influence of alloying additions on the characteristic trait of the material."

p. 4942, L 10ff:

"In summary, there are various influencing factors that can explain why aluminium cylinders do not generally behave like chemically inert Al_2O_3 surfaces. On the basis of the tests performed within this study it is not possible to clearly prove the specific reasons that determine the characteristics of an individual cylinder. However, the different processes discussed can explain the variability of individual cylinders of the same type as well as systematic differences between cylinder types or cylinders from different manufacturers."

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