Is it time for a WMO Hydrogen calibration scale?

Armin Jordan and Bert Steinberg

Max-Planck-Institute for Biogeochemistry
07745 Jena, Germany

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Jena, September 7th, 2009
R10.2 Recommendations

a) A concerted effort to consolidate the NOAA, CSIRO/AGAGE, EuroHydros and other calibration activities is urgently needed to enable a collaborative global network for hydrogen measurements. These measurement groups are strongly encouraged to establish a common calibration scale. This scale should cover the range from 350-1000 ppb. As part of this effort the existing scales need to be harmonized ..
No global supplier of H$_2$ standard gases
H$_2$ mixing ratios unstable in AL150 type cylinders

H$_2$ drift rates

CA01601: 3.5 ppb/yr → 0.9 ppb/yr
CA01650: 10 ppb/yr → 1.8 ppb/yr
Observed H$_2$ stability depending on cylinder type

- Total increase < 4 ppb
- Total increase > 4 ppb
- Median of cylinder type

**H$_2$ drift rate [ppb/yr]**

- Luxfer US N150 - 29l
- Scott Marrin
- Luxfer US N265 46l
- Conwin
- Luxfer UK AA6061 50l
- Luxfer UK AA6061 20l
- Steel, Stainless
- Various
Dependence of standard stability on alloy

![Graph showing the dependence of standard stability on alloy]

### Registered International Designation

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H₂ Monitoring Networks

http://agage.eas.gatech.edu/

Novelli et al. (1999), JGR104, 30,427
EuroHydros calibration activities:
Standard preparation by precise mixing of \( \text{H}_2 \) in air

\[
\text{moles } \text{H}_2 = \frac{344.6 \ \mu\text{l} \times 99226 \ \text{Pa}}{(297.87 \ \text{K} \times 8314.5 \ (\text{Pa} \times \text{L}/\text{K} \times \text{mol}))} \\
\text{moles air} = \frac{639.7 \ \text{g}}{28.965 \ \text{g/mol}} \\
\Rightarrow [\text{H}_2] = 625.6 \ \text{ppb}
\]
Preparation of standard gases by precise mixing of H₂ in air

\[ [H_2] = 625.6 \text{ ppb} \]

\[ \rightarrow 28.973 \text{ mV} \]
Interfering factors for accuracy of standards

RGA response dependent on oxygen content of gas:
peak height decreases with increasing $O_2$

Hydrogen depletion by diffusion into Valcon E polymer
→ no $H_2$ depletion with Valcon M rotor
Non-linearity of RGA response function
RGA response function fit

\[ f = a \cdot x + b \cdot x^2 + c \cdot (1 - e^{-d \cdot x}) \]
## Accuracy limits from sensors and balances

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Single mixtures uncertainty: 0.1 - 0.3 % (~no of dilutions)

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### Instruments

- **Pressure**
  - GE Druck DPI 142

- **Temperature**
  - Greising GTF175

- **Volume**
  - Mettler AT261

- **Air Mass**
  - Sartorius 8201-0CE
Accuracy of transfer of mixing ratios


variability of repeated analysis of 13 EuroHydros calibration standards

reproducibility:
300 - 800 ppb < 0.25%
140 - 1200 ppb < 0.6%
Stability of RGA response Sept-Nov 2008

Quality Control record

std. dev. of daily means
510 ppb: 0.2 %
1190 ppb: 0.35 %
## CSIRO94 scale $\rightarrow$ MPI2009 scale

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**difference @ 500 ppb = 16 ppb**
Scale comparison with CSIRO94 and NOAA2008

NOAA-MPI = 7.2 ± 1.1 ppb

CSIRO-MPI = 16.8 ± 1.8 ppb
Summary

• most common cylinders for trace gas standards H₂ usually not suitable for H₂ standards
• steel cylinders do generally not cause H₂ drifts, cylinders of aluminium alloys appear promising
• procedure to prepare reference gas mixtures with adequate accuracy
• scale difference to NOAA2008 = 7 ppb
• scale difference to CSIRO = 17 ppb
• offsets have been stable to NOAA in 2008-2009 and in various longterm intercomparision exercises with CSIRO

⇒ preconditions for coming to a common calibration scale now fulfilled
Thank you and many thanks to

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