

The AGAGE atmospheric H₂ measurements made at Mace Head and Cape Grim are firmly linked to a suite of H₂-in-air calibration standards maintained at CSIRO Marine and Atmospheric Research, Aspendale, Victoria, Australia.

CSIRO's atmospheric hydrogen (H₂) measurements are made using a gas chromatographic technique, specifically a Reduction Gas Analyzer (RGA3) fitted with a mercuric oxide reduction gas detector (Trace Analytical, Inc., California).

Data are referenced against the MPI 2009 H₂ calibration scale established at the Max Planck Institute for Biogeochemistry (MPI-BGC) in Jena, Germany (Jordan and Steinberg, 2011).

- For Mace Head, a preliminary link to this MPI scale was established using the results of an intercomparison involving exchange of an air sample in a high pressure cylinder. Further intercomparisons were carried out via the exchange of several Mace Head primary standards with EMPA, Material Science and Testing Centre, Zurich, Switzerland. Reported EMPA H₂ values for these standards under the MPI2009 scale were compared with the value from MPI-BGC Jena and found to be within 0.15% of each other. A scaling factor from the intercomparison at MPI-BGC of 1.0243 was calculated. Mace Head data were adjusted from the previously used CSIRO94 H₂ scale by applying a single, constant scale factor of 1.0243 with data on the MPI scale being higher. A more direct link to the MPI scale is planned for the future through analysis at MPI-BGC of Mace Head's primary standards.
- For Cape Grim, a preliminary link to this MPI scale was established using the results of numerous intercomparison programs involving exchange of air samples in both high pressure cylinders and low pressure flasks over several years. CSIRO data were adjusted from the previously used CSIRO94 H₂ scale by applying a single, constant scale factor of 1.0314 with data on the MPI scale being higher. A more direct link to the MPI scale is planned for the future through analysis at MPI-BGC of CSIRO's primary standards.

The range of H₂ mixing ratio spanned by CSIRO's primary standard suite is currently 341 – 739 ppb. The integrity of long term trends defined by CSIRO's H₂ data is supported by monitoring of a suite of H₂-in-air mixtures in high pressure cylinders that exhibit a high level of relative stability. These mixtures have been regularly analysed over long periods (up to 20+ years), span a range of mixing ratios and cylinder pressure histories and are stored in a variety of cylinder types. Our experience has shown that H₂ mixing ratios are generally stable in clean stainless steel containers but are less reliable in

the aluminium cylinders used for CSIRO's other trace gas measurement programs.

References

Jordan, A. and B. Steinberg, Calibration of atmospheric hydrogen measurements, *Atmos. Meas. Tech.*, 4, 509–521, 2011, www.atmos-meas-tech.net/4/509/2011/doi:10.5194/amt-4-509-2011