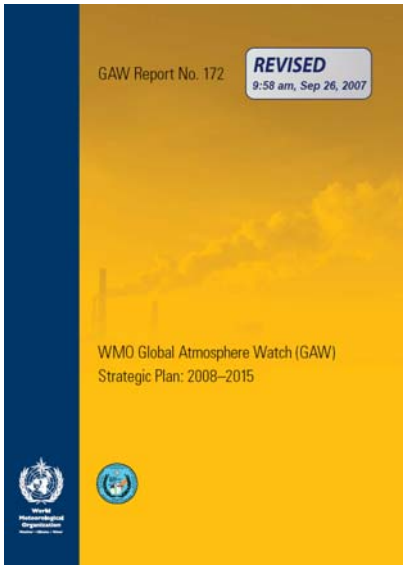
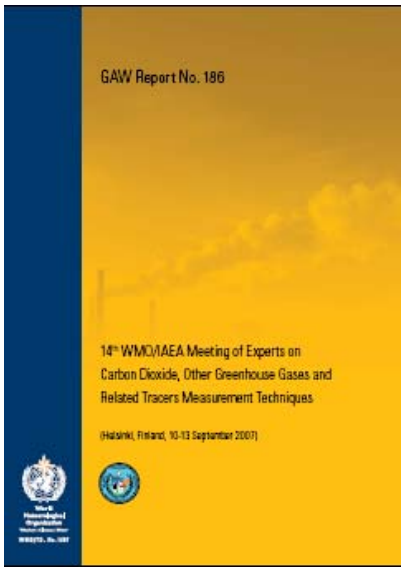
Is it time for a WMO Hydrogen calibration scale?

Armin Jordan and Bert Steinberg

Max-Planck-Institute for Biogeochemistry
07745 Jena, Germany

15th WMO/IAEA Meeting of Experts on Carbon Dioxide,
Other Greenhouse Gases and Related Tracer Measurement Techniques
Jena, September 7th, 2009





14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniq

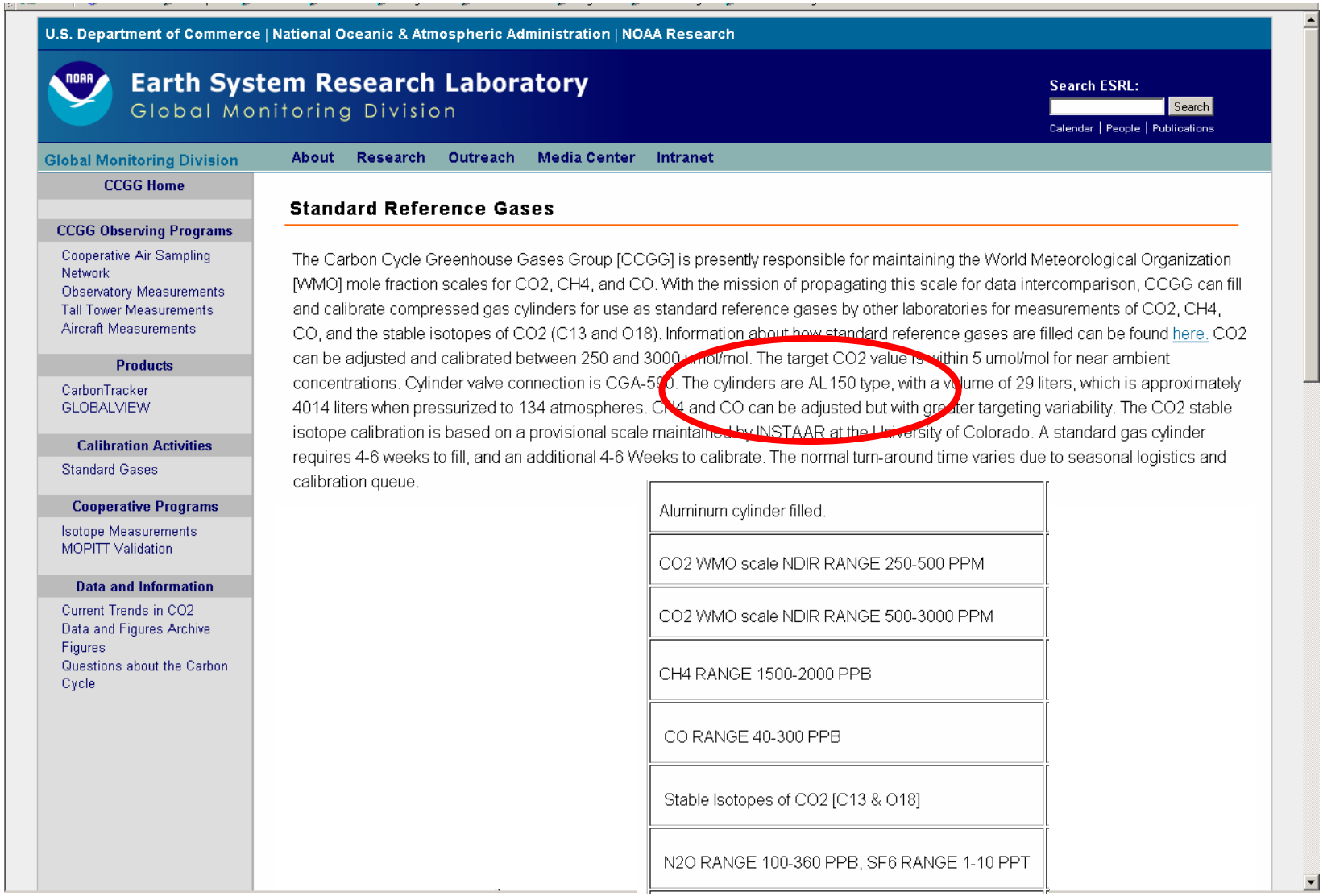
(Helsinki, Finland, 10-13 September 2007)

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 ..

http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html

No global supplier of H_2 standard gases



U.S. Department of Commerce | National Oceanic & Atmospheric Administration | NOAA Research

Earth System Research Laboratory
Global Monitoring Division

Search ESRL: Search
Calendar | People | Publications

Global Monitoring Division | About | Research | Outreach | Media Center | Intranet

CCGG Home

CCGG Observing Programs
- Cooperative Air Sampling Network
- Observatory Measurements
- Tall Tower Measurements
- Aircraft Measurements

Products
- CarbonTracker
- GLOBALVIEW

Calibration Activities
- Standard Gases

Cooperative Programs
- Isotope Measurements
- MOPITT Validation

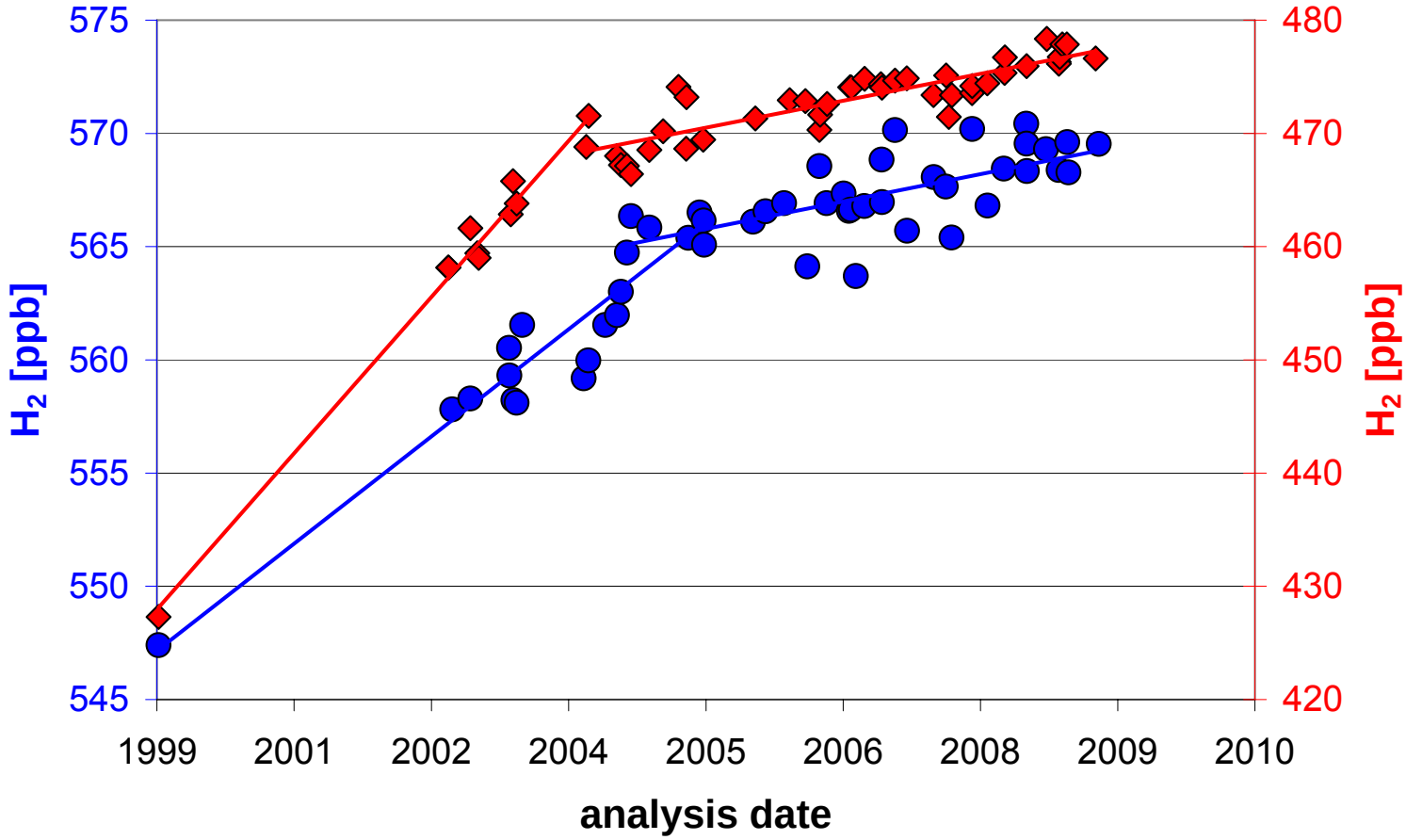
Data and Information
- Current Trends in CO2
- Data and Figures Archive Figures
- Questions about the Carbon Cycle

Standard Reference Gases

The Carbon Cycle Greenhouse Gases Group [CCGG] is presently responsible for maintaining the World Meteorological Organization [WMO] mole fraction scales for CO2, CH4, and CO. With the mission of propagating this scale for data intercomparison, CCGG can fill and calibrate compressed gas cylinders for use as standard reference gases by other laboratories for measurements of CO2, CH4, CO, and the stable isotopes of CO2 (C13 and O18). Information about how standard reference gases are filled can be found here. CO2 can be adjusted and calibrated between 250 and 3000 umol/mol. The target CO2 value is within 5 umol/mol for near ambient concentrations. Cylinder valve connection is CGA-590. The cylinders are AL150 type, with a volume of 29 liters, which is approximately 4014 liters when pressurized to 134 atmospheres. CH4 and CO can be adjusted but with greater targeting variability. The CO2 stable isotope calibration is based on a provisional scale maintained by INSTAAR at the University of Colorado. A standard gas cylinder requires 4-6 weeks to fill, and an additional 4-6 Weeks to calibrate. The normal turn-around time varies due to seasonal logistics and calibration queue.

Aluminum cylinder filled.
CO2 WMO scale NDIR RANGE 250-500 PPM
CO2 WMO scale NDIR RANGE 500-3000 PPM
CH4 RANGE 1500-2000 PPB
CO RANGE 40-300 PPB
Stable Isotopes of CO2 [C13 & O18]
N2O RANGE 100-360 PPB, SF6 RANGE 1-10 PPT

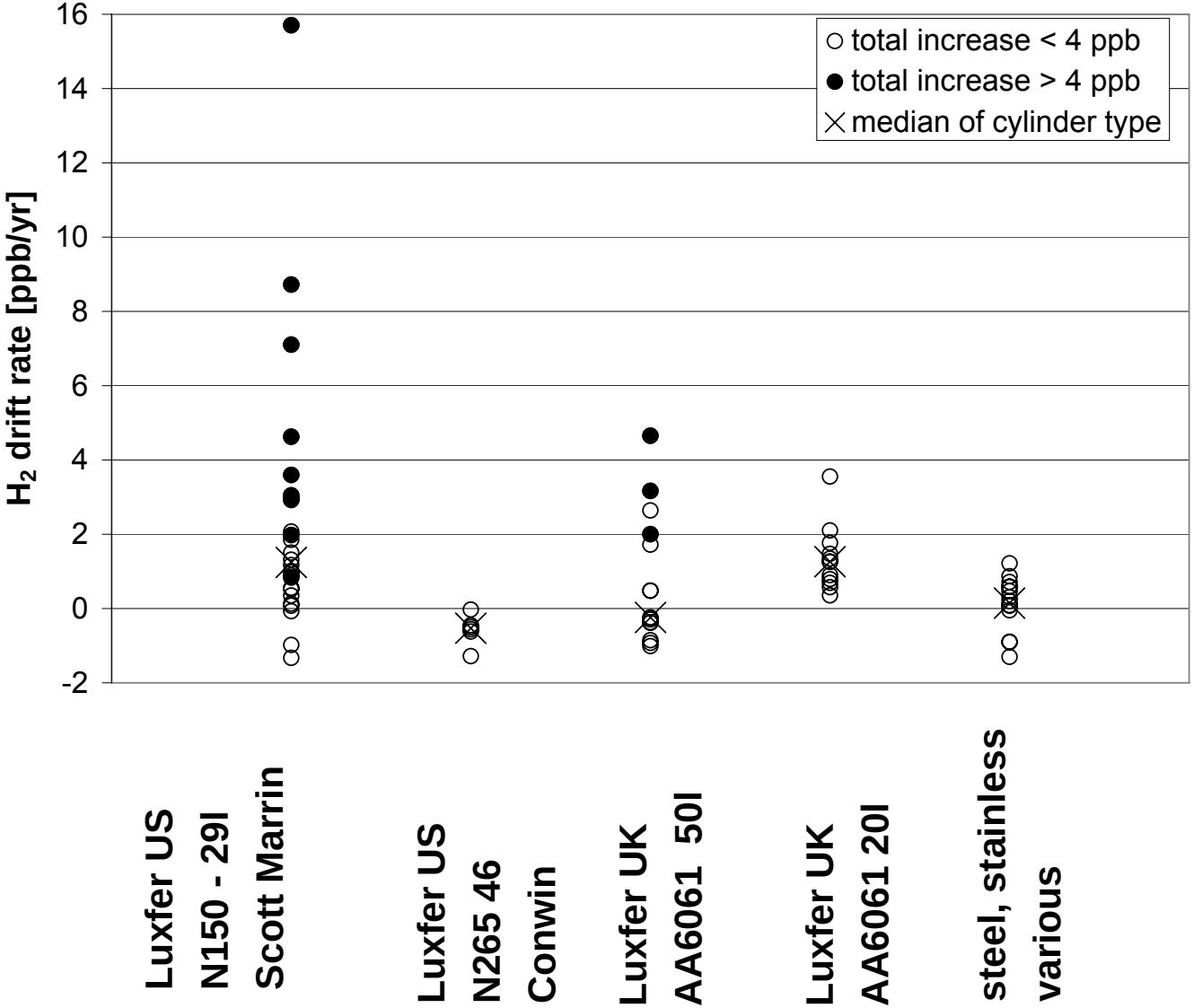
H_2 mixing ratios unstable in AL150 type cylinders



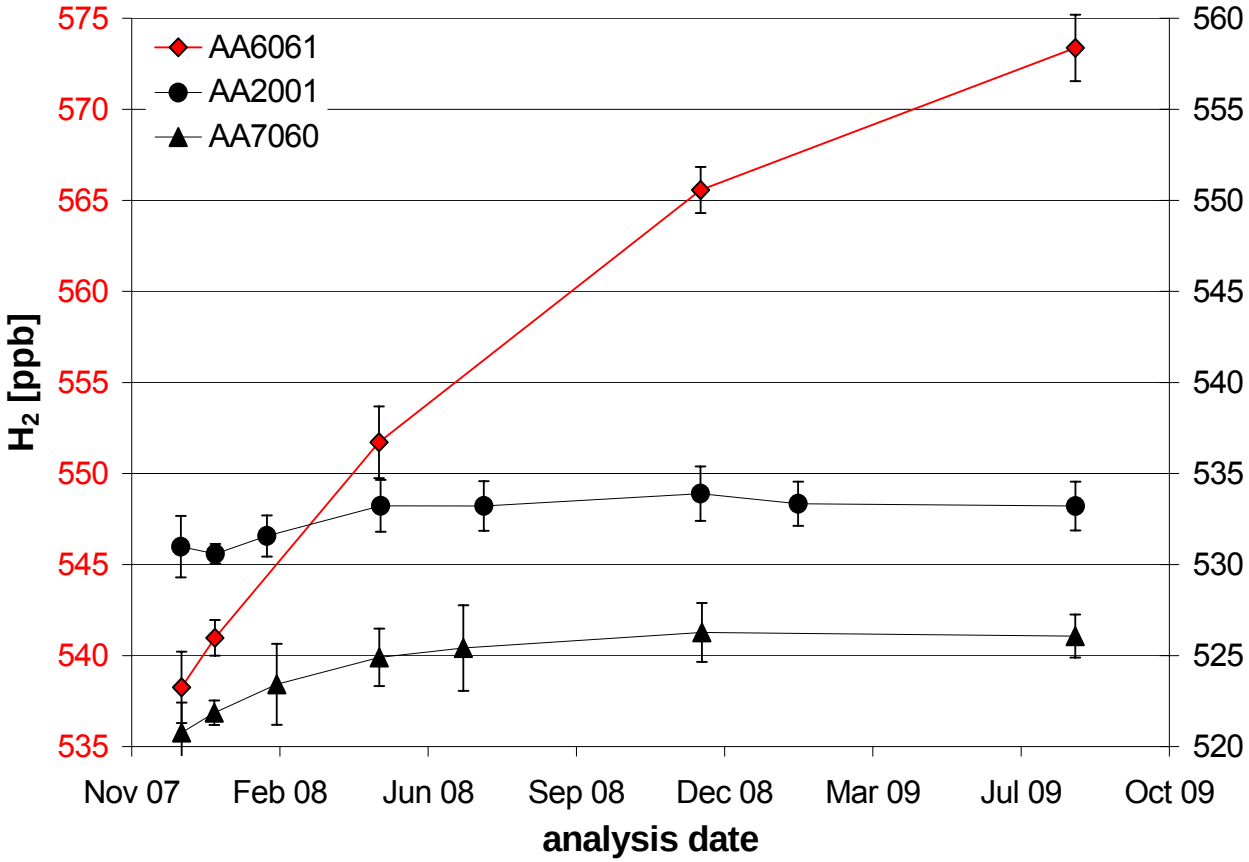
H_2 drift rates CA01601: 3.5 ppb/yr → 0.9 ppb/yr

CA01650: 10 ppb/yr → 1.8 ppb/yr

Observed H_2 stability depending on cylinder type

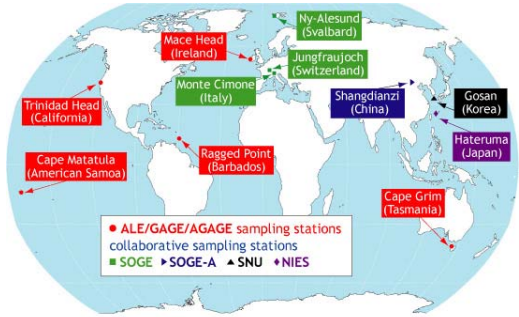


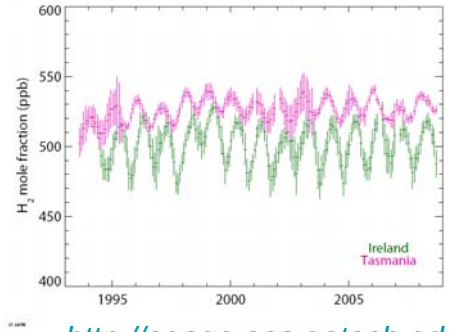
Dependence of standard stability on alloy



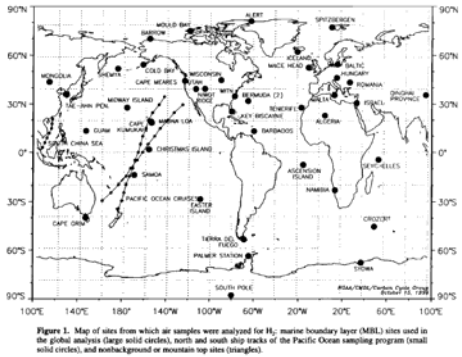
Registered International Designation											
No. [17]	Date	By	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti
6061	1954	USA	0.40-0.8	0.7	0.15-0.40	0.15	0.8-1.2	0.04-0.35	...	0.25	0.15
2001	1979	FRANCE	0.20	0.20	5.2-6.0	0.15-0.50	0.20-0.45	0.10	0.05	0.10	0.20
7060	1986	FRANCE	0.15	0.20	1.8-2.6	0.20	1.3-2.1	0.15-0.25	...	6.1-7.5	0.05

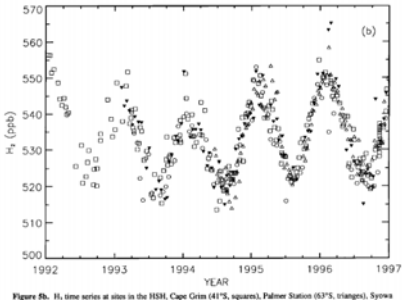
H_2 Monitoring Networks



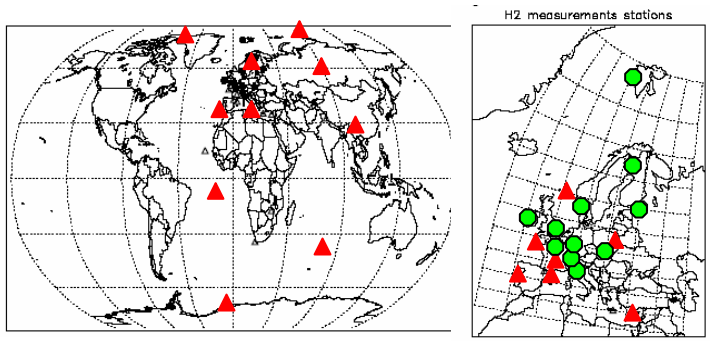


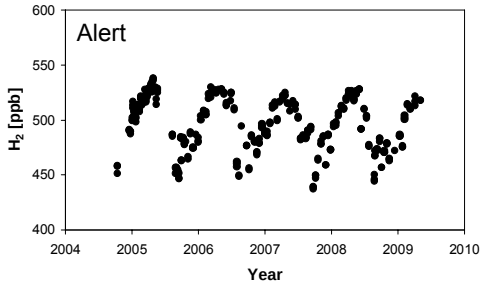
http://agage.eas.gatech.edu/



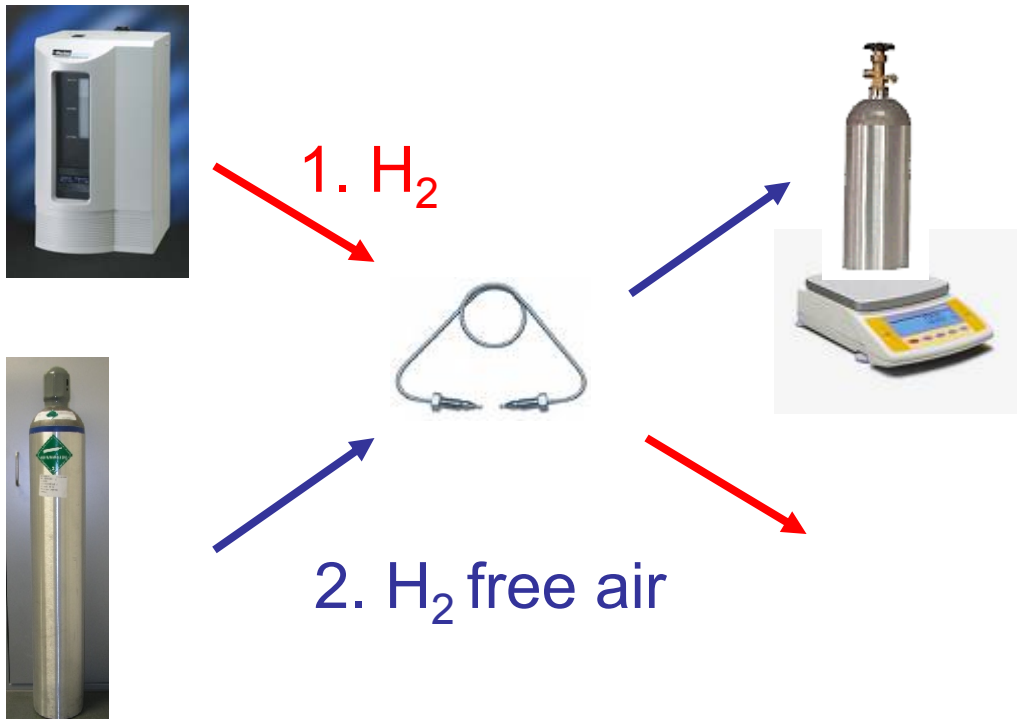


Novelli et al. (1999), JGR104, 30,427





EuroHydros calibration activities: Standard preparation by precise mixing of H_2 in air

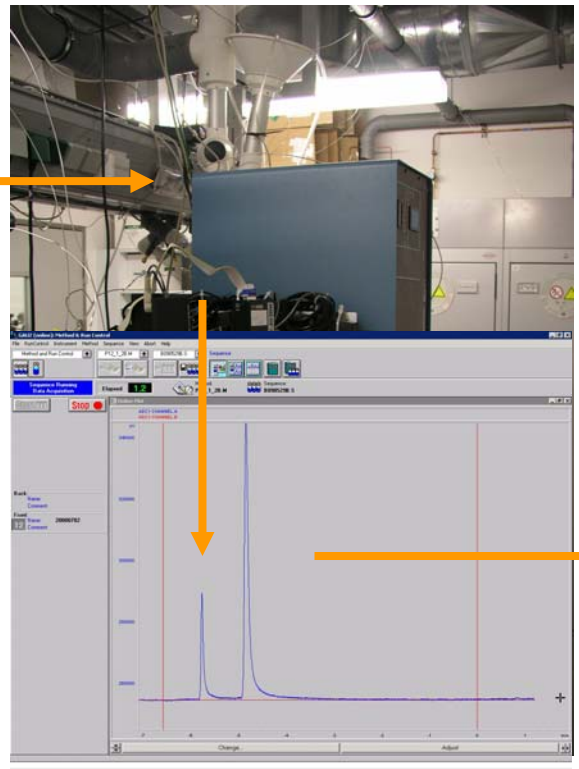


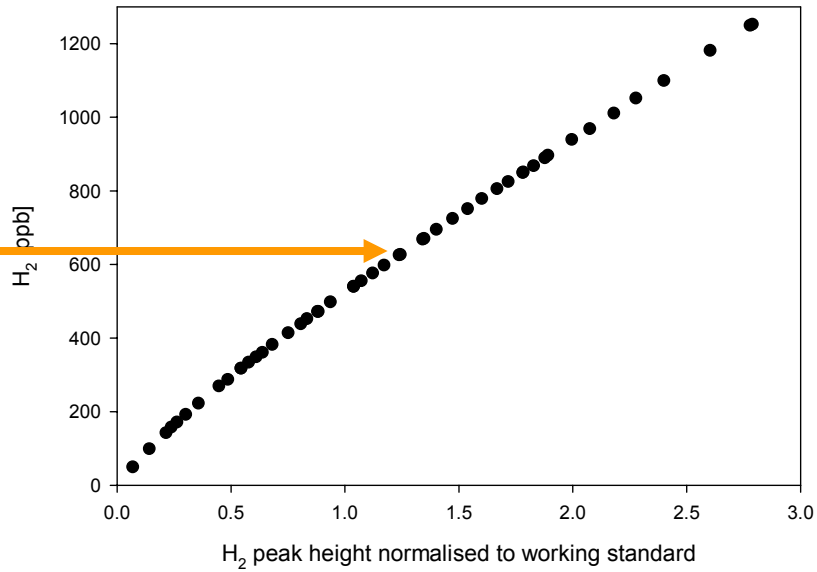
moles H_2= (344.6 µl * 99226 Pa) / (297.87 K * 8314.5 (Pa* L/K*mol))

moles air = 639.7 g / (28.965 g/mol)

$\Rightarrow$ [H_2] = 625.6 ppb

Preparation of standard gases by precise mixing of H_2 in air

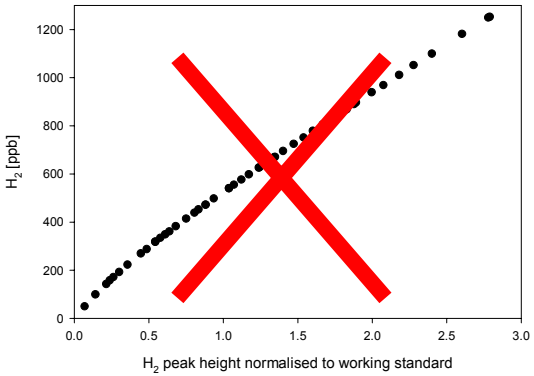




$[H_2]$ = 625.6 ppb

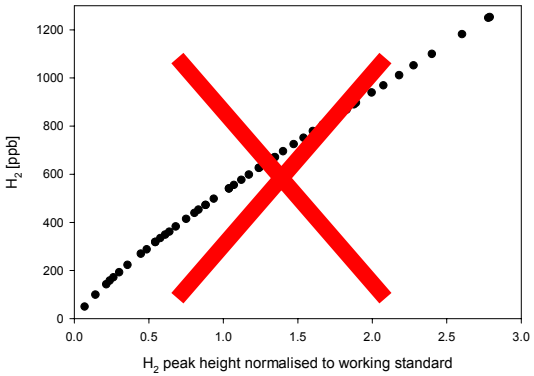
→ 28.973 mV

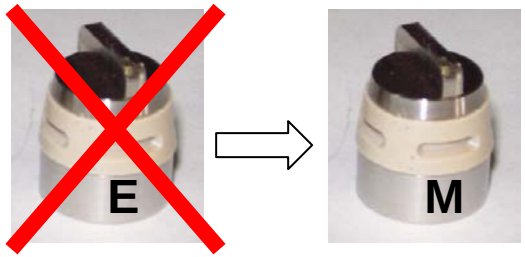
Interfering factors for accuracy of standards



RGA response dependent on oxygen content of gas:

peak height decreases wit increasing O_2

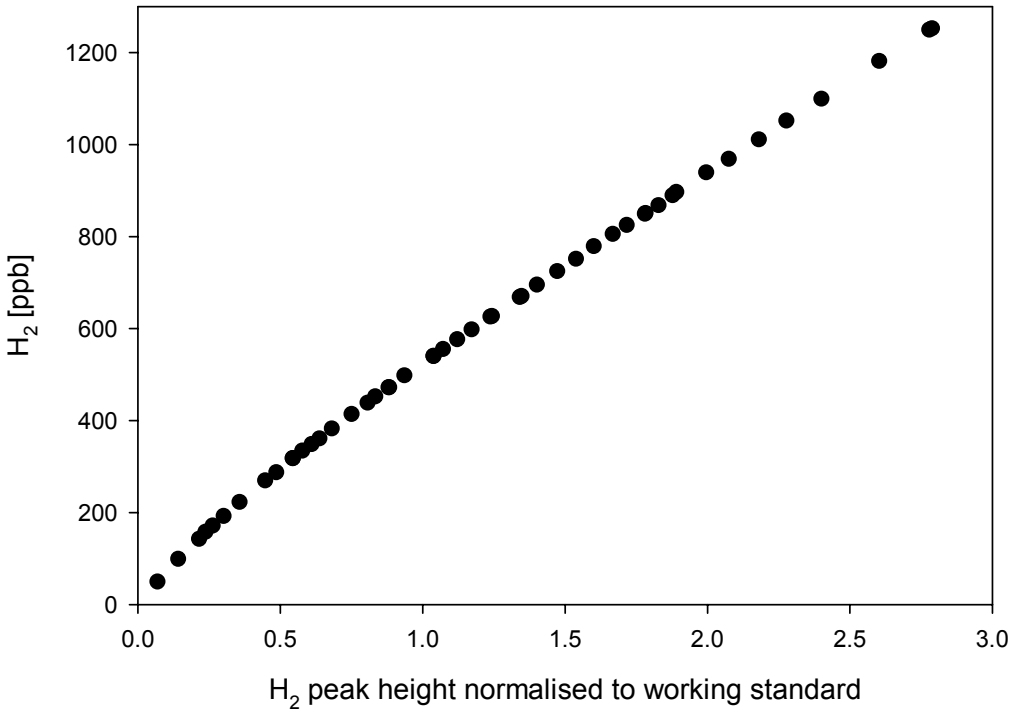


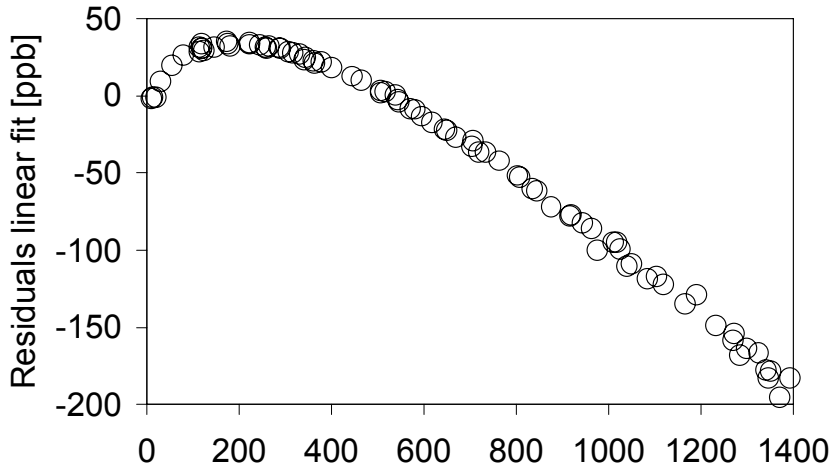


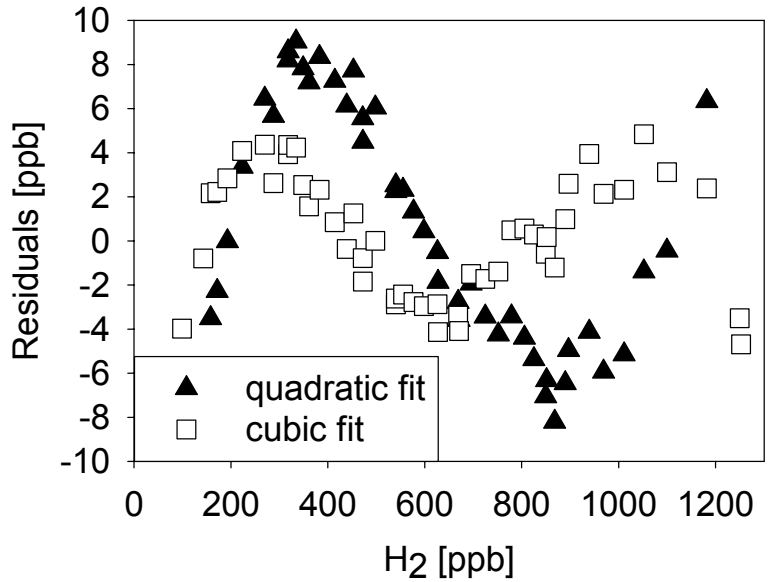
Hydrogen depletion by diffusion into Valcon E polymer

→ no H_2 depletion with Valcon M rotor

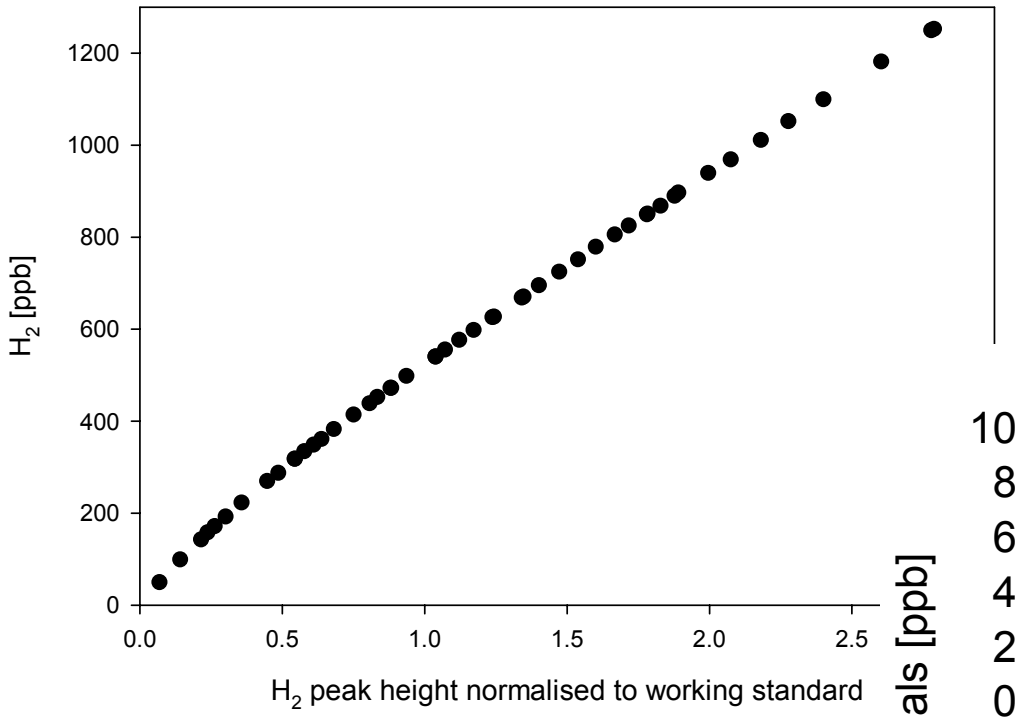
Non-linearity of RGA response function



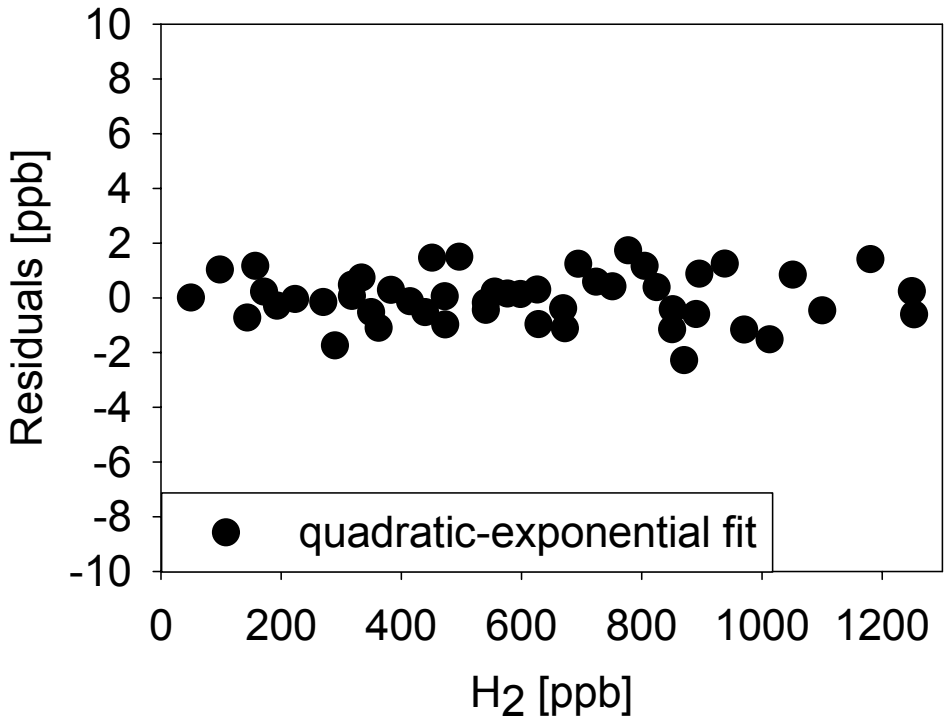




RGA response function fit



$$f = a*x+b*x^2+c*(1-e^{-d*x})$$



Accuracy limits from sensors and balances

	abs. uncertainty	result	rel. uncertainty
Pressure	0.15 mbar	1000 mbar	0.015%
Temperature	0.1-0.2 K	295 K	0.05%
Volume	0.2 µl	344 µl	0.06%
Mass	0.1-0.2 g	200-600g	0.02-0.1%

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

pressure

GE Druck DPI 142

temperature

Greising GTF175

volume

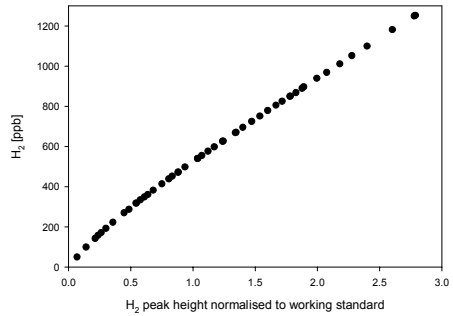
Mettler AT261

air mass

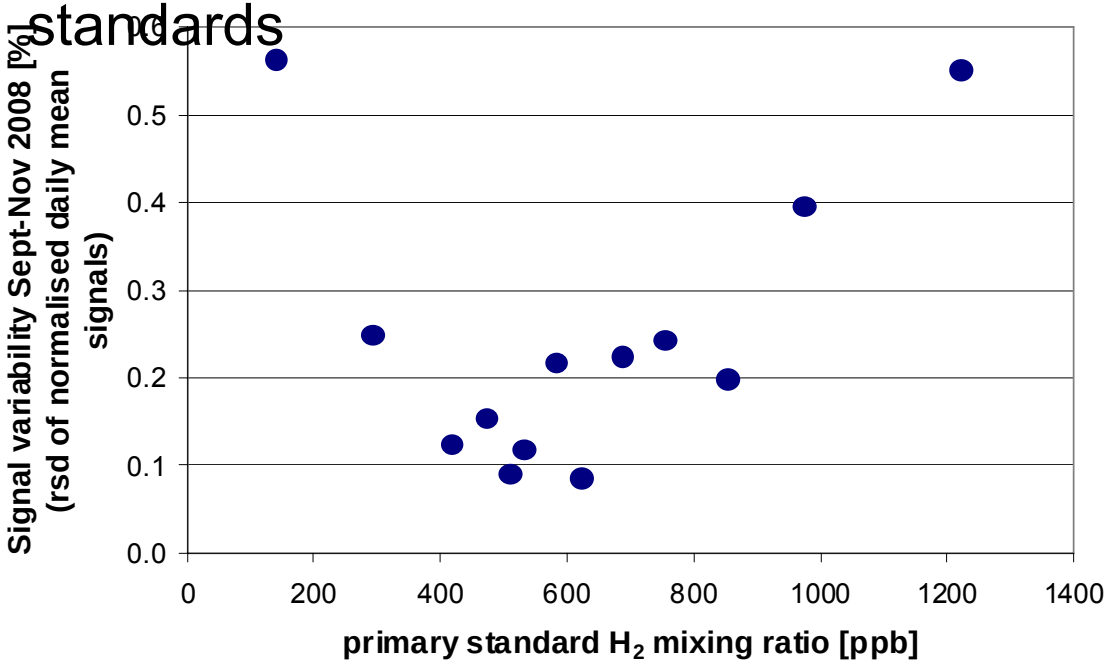
Sartorius 8201-0CE

Accuracy of transfer of mixing ratios

period of preparation of 50 reference mixtures: Sept-Nov 2008



variability of repeated analyis of 13 EuroHydros calibration standards



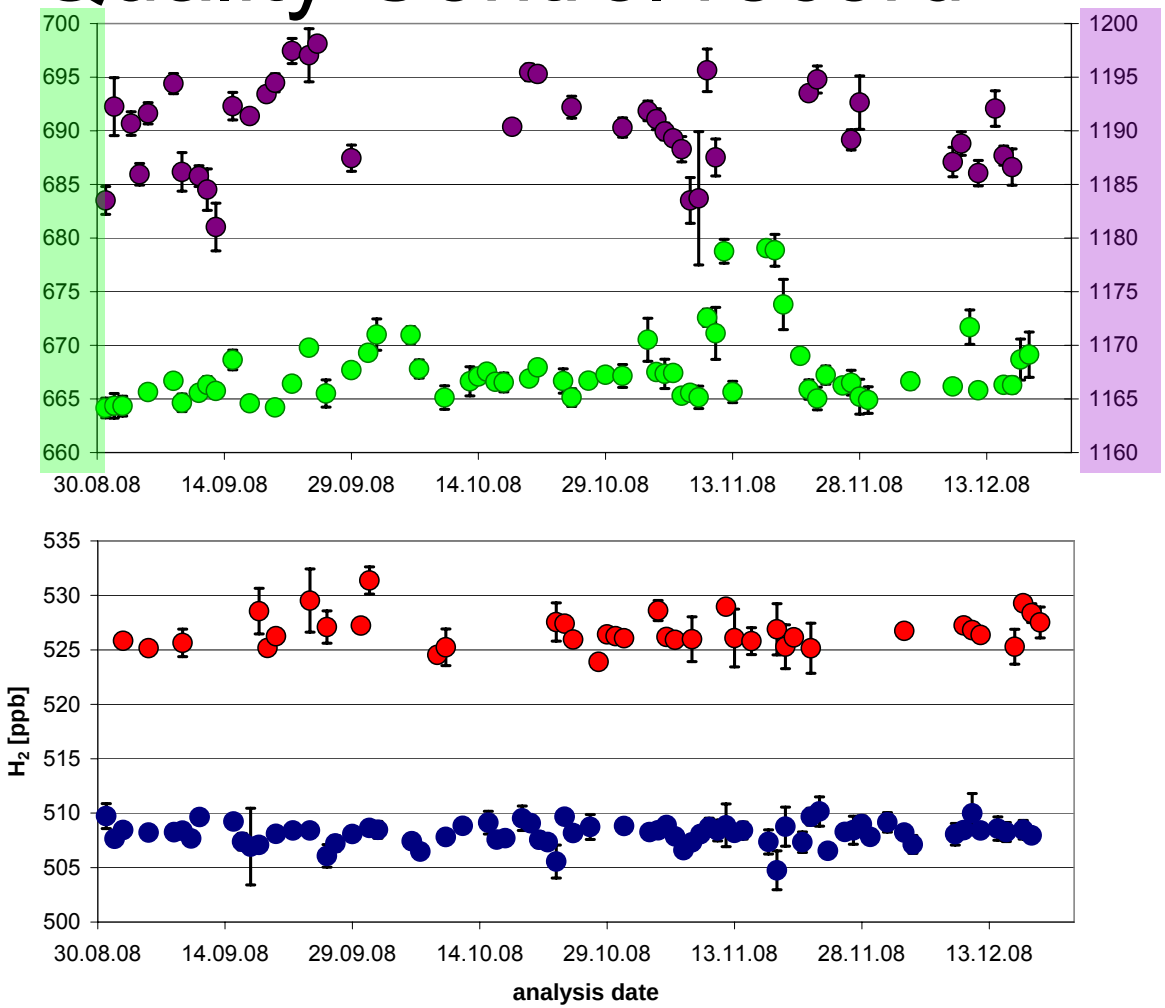
reproducibility:

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 %

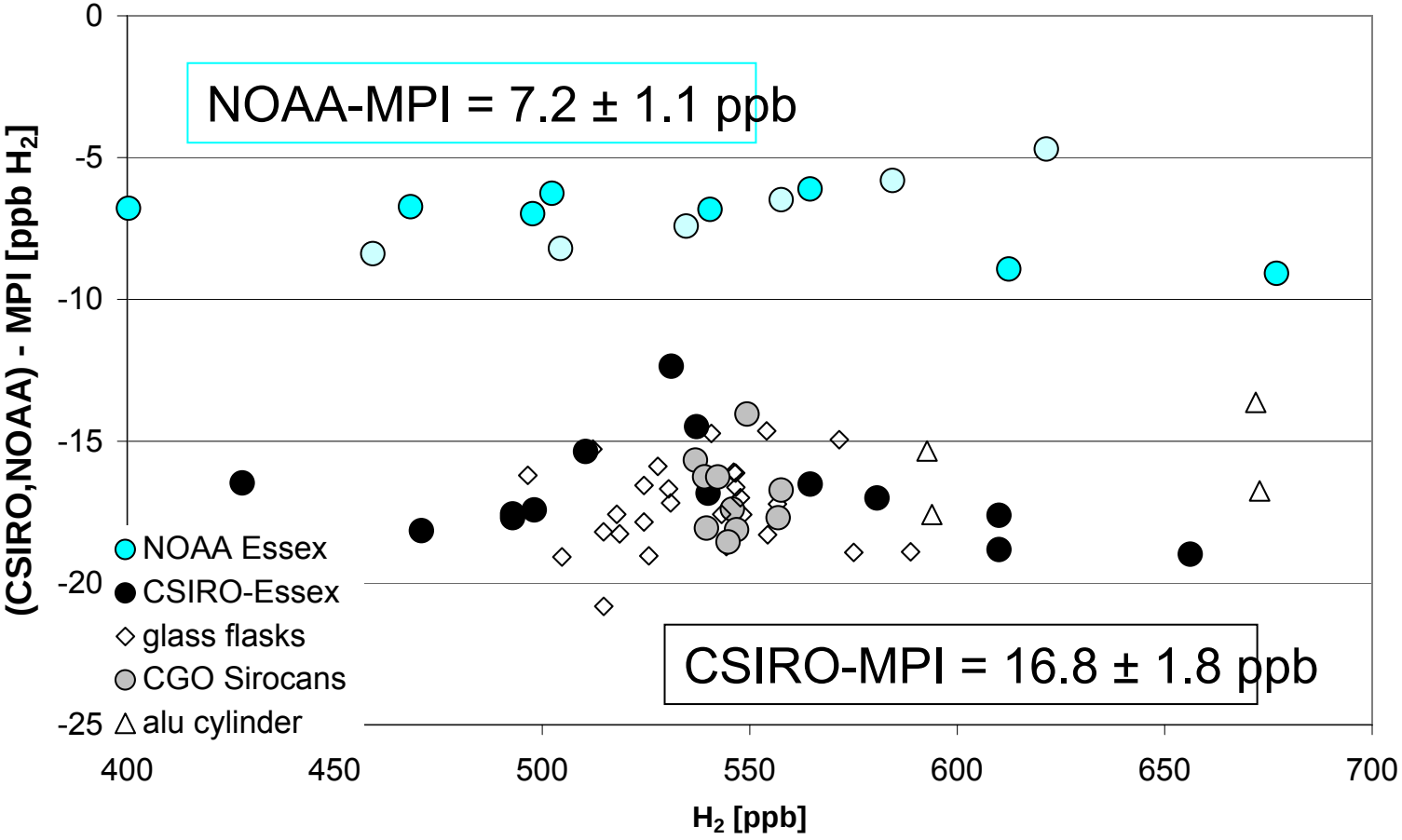
1190 ppb: 0.35 %

CSIRO94 scale → MPI2009 scale

Manufacturer	Vol [l]	Press [bar]	Material	standard filling date	H_2 [ppb]	H_2 MPI2009
Essex	35	60	SS	26.04.2007	135	**139**
Graeven	50	25	SS	13.02.2007	273	**290**
Graeven	27	25	SS	07.02.2007	399	**416**
Essex	35	60	SS	22.08.2004	456	**471**
Essex	35	60	SS	04.08.2004	492	**508**
Linde	50	200	SS	10.06.2003	512	**529**
Linde	50	200	Alu	22.11.2004	562	**581**
Linde	50	200	SS	22.02.2007	604	**622**
Essex	35	60	SS	10.12.2005	664	**685**
Graeven	50	25	SS	15.02.2007	730	**753**
Graeven	27	25	SS	07.02.2007	824	**853**
Graeven	50	25	SS	09.02.2007	935	**971**
Graeven	27	25	SS	05.04.2006	1183	**1219**

difference @ 500 ppb = 16 ppb

Scale comparison with CSIRO94 and NOAA2008



Summary

- most common cylinders for trace gas standards H_2 usually not suitable for H_2 standards
- steel cylinders do generally not cause H_2 drifts, cylinders of o 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 variou longterm intercomparison exercises with CSIRO

⇒ **preconditions for coming to a common calibration scale now fulfilled**

Thank you and many thanks to

Ray Langenfelds and Paul Steele (CSIRO)
Paul Novelli (NOAA)
for valuable discussion and good cooperation

Bert Steinberg, Frank Hilbert, Michael Targan
for lab support preparing the reference mixtures

Michael Hielscher
for database support

EU funding : FP6-2005-Global-4, Eurohydros Contract Nr. 036916