AGAGE_scale_2022_v2 (updated in Oct. 2022)

Standard scales used in archived species from the measurement of AGAGE GC-MD and GC-MS instruments

species	formula	scale	units	comments
methane	CH_4	TU1987	ppb	renamed “Tohoku University” scale to “TU1987” in 2/2020
nitrous oxide	N_2O	SIO-16	ppb	new SIO-16 scale implemented in 6/2017
carbon monoxide	CO	CSIRO94 WMO-X2014A	ppb	the Macehead CO data has been converted to WMO-X2014A scale; the Capegrim CO data is still on CSIRO94 scale (it will be changed later)
hydrogen	H_2	MPI-2009	ppb	
CFCs				
CFC-11	CCl_3F	SIO-05	ppt	
CFC-12	CCl_2F_2	SIO-05	ppt	
CFC-13	$CClF_3$	METAS-2017	ppt	data first released in 10/2017
CFC-113	CCl_2FCClF_2	SIO-05	ppt	also includes the minor isomer CCl_3CF_3 (CFC-113a)
CFC-114	$CClF_2CClF_2$	SIO-05	ppt	also includes the minor isomer CCl_2FCF_3 (CFC-114a)
CFC-115	$CClF_2CF_3$	SIO-05	ppt	
HCFCs				
HCFC-22	$CHClF_2$	SIO-05	ppt	
HCFC-124	$CHClFCF_3$	UB-98	ppt	data first released in 6/2019
HCFC-132b	$CH_2ClCClF_2$	METAS-2017	ppt	data first released in 11/2020
HCFC-133a	CH_2ClCF_3	Empa-2013	ppt	data first released in 11/2020
HCFC-141b	CH_3CCl_2F	SIO-05	ppt	
HCFC-142b	CH_3CClF_2	SIO-05	ppt	
HFCs				
HFC-23	CHF_3	SIO-07	ppt	
HFC-32	CH_2F_2	SIO-07	ppt	
HFC-125	CHF_2CF_3	SIO-14	ppt	
HFC-134a	CH_2FCF_3	SIO-05	ppt	
HFC-143a	CH_3CF_3	SIO-07	ppt	
HFC-152a	CH_3CHF_2	SIO-05	ppt	
HFC-227ea	CF_3CHFCF_3	SIO-14	ppt	
HFC-236fa	$CF_3CH_2CF_3$	SIO-14	ppt	
HFC-245fa	$CHF_2CH_2CF_3$	SIO-14	ppt	
HFC-365mfc	$CH_3CF_2CH_2CF_3$	SIO-14	ppt	
HFC-43-10mee	$CF_3(CHF)_2CF_2CF_3$	SIO-14	ppt	
Halons				
H-1211	$CBrClF_2$	SIO-05	ppt	
H-1301	$CBrF_3$	SIO-05	ppt	
H-2402	$C_2Br_2F_4$	SIO-14	ppt	

Chlorocarbons

methyl chloride	CH_3Cl	SIO-05	ppt	
dichloromethane	CH_2Cl_2	SIO-14	ppt	
chloroform	$CHCl_3$	SIO-98	ppt	
methyl chloroform	CH_3CCl_3	SIO-05	ppt	
trichloroethylene	$CHClCCl_2$	UB-98	ppt	
perchloroethylene	CCl_2CCl_2	NOAA-2003B	ppt	
carbon tetrachloride	CCl_4	SIO-05	ppt	

Bromocarbons

methyl bromide	CH_3Br	SIO-05	ppt	

PFCs

PFC-14	CF_4	SIO-05	ppt	
PFC-116	CF_3CF_3	SIO-07	ppt	
PFC-218	$CF_3CF_2CF_3$	SIO-07	ppt	
PFC-318	*c*-C_4F_8	SIO-14	ppt	data first released in 2/2020

Other fluorinated compounds

sulfur hexafluoride	SF_6	SIO-05	ppt	
sulfuryl fluoride	SO_2F_2	SIO-07	ppt	
nitrogen trifluoride	NF_3	SIO-12	ppt	

Notes:

1. The SIO-16 N2O Calibration Scale (June, 2017)

The SIO-16 calibration scale for N2O is based on a suite of 17 primary standard mixtures: 6 covering the 297-322 ppb concentration range that were also the basis of the SIO-98 calibration scale, and 11 covering the 310-354 ppb concentration range that were prepared for this new scale. Each primary standard was prepared by diluting high-precision pure N2O/CO2 mixtures prepared manometrically in the Keeling CO2 laboratory at SIO. CO2 concentrations were measured in the resulting primary mixtures, referenced to Keeling laboratory CO2 standards, by GC-FID with catalytic conversion to CH4 (Weiss, J. Chrom. Sci., 19, 611-616, 1981) to determine N2O prepared values from the prepared N2O/CO2 ratios. The optimal transfer from the Keeling CO2 calibration scale was established from 9 reference cylinders based on Keeling manometric and optical measurements and improved CG-FID measurements with improved nonlinearity fitting. Uncertainties in this CO2 scale propagation are at the < 0.1 ppm CO2 (< 0.025%) level, and are subject to future revisions based on ongoing additional manometric measurements in the Keeling laboratory

N2O concentrations in these 17 primary standards were measured against each other by GC-ECD (Prinn et al., J. Geophys. Res., 105, 17,751-17,792, 2000) and were fitted to a smooth curve of sensitivity vs. concentration to assign a “best estimate” N2O concentration (dry air mole fraction) to each standard mixture. The relative standard deviation of the corrections applied to the 17 individual prepared values is 0.017%.

The resulting SIO-16 N2O primary calibration scale was then propagated through the AGAGE “R1 scale” consisting of tanks of compressed whole air (Miller et al., Anal. Chem., 80, 1536-1545, 2008), to the entire AGAGE N2O atmospheric record from the beginning of the use of the R1 scale in AGAGE. Changes were also made in how the results were calculated: 1) The nonlinearity correction was changed to take concentration into account, instead of sample/standard ratio, and; 2) The new N2O scale was propagated to the R1 scale using a revised GC-ECD nonlinearity which has been constant since 2004, rather than the nonlinearity determined in 1998 that was used in the earlier propagation.

The resulting new AGAGE global atmospheric N2O values reported on the SIO-16 calibration scale have risen gradually compared to those reported previously, by from 0.0 ppb to approximately +0.8ppb over 20 years (+0.04 ppb/year). Approximately 20% of this increase is due to the use of the concentration based nonlinearity propagation, and about 80% of this increase is due to the use of the post-2004 GC-ECD non-linearity measurements. Importantly, there was no evidence of drift in the 6 original SIO-98 primary standards, and had the new calculation methods described above been used to propagate the SIO-98 scale, the corrections to present-day

values, even though they are ~8 ppb above the range of these older standards, would have been much smaller than the changes reported here.

2. Comments for CFC-113 and CFC-114
   Measurements of CFC-113 are a combination of CFC-113 (1,1,2-Trichlorotrifluoroethane, CAS 76-13-1) and CFC-113a (1,1,1-Trichlorotrifluoroethane, CAS 354-58-5). Measurements of CFC-114 are a combination of CFC-114 (1,2-Dichlorotetrafluoroethane, CAS 76-14-2) and CFC-114a (1,1-Dichlorotetrafluoroethane, CAS 374-07-2), see Vollmer et al., ACP, 2018

3. Comments for Methane TU1987 scale
   The methane scale was renamed from “Tohoku University” to “TU1987” in Feb. 2020. This is to differentiate from the new Tohoku University 2008 (TU2008) scale, see Fujita et al., JGR, 2018.

4. Comments for METAS-2017 scale
   The METAS-2017 primary calibration scales for CFC-13 and HCFC-132b are described in Guillevic et al., 2018 (https://doi.org/10.5194/amt-11-3351-2018). Eleven mixtures at near ambient molar fractions were prepared in synthetic air (oxygen and nitrogen). All prepared mixtures were measured vs each other to check for internal consistency. The expanded uncertainty (95% confidence interval, similar to 2 sigma) after internal consistency check is 2%.