

## AGAGE\_scale\_2022\_v1 (updated in May 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 <sub>4</sub>	TU1987	ppb	renamed "Tohoku University" scale to "TU1987" in 2/2020
nitrous oxide	N <sub>2</sub> O	SIO-16	ppb	new SIO-16 scale implemented in 6/2017
carbon monoxide	CO	CSIRO94 WMO-X2014	ppb	the Macehead CO data has been converted to WMO-X2014 scale; the Capegrim CO data is still on CSIRO94 scale (it will be changed later)
hydrogen	H <sub>2</sub>	MPI-2009	ppb	
<b>CFCs</b>				
CFC-11	CCl <sub>3</sub> F	SIO-05	ppt	
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	SIO-05	ppt	
CFC-13	CCIF <sub>3</sub>	METAS-2017	ppt	data first released in 10/2017
CFC-113	CCl <sub>2</sub> FCCIF <sub>2</sub>	SIO-05	ppt	also includes the minor isomer CCl <sub>3</sub> CF <sub>3</sub> (CFC-113a)
CFC-114	CCIF <sub>2</sub> CCIF <sub>2</sub>	SIO-05	ppt	also includes the minor isomer CCl <sub>2</sub> FCF <sub>3</sub> (CFC-114a)
CFC-115	CCIF <sub>2</sub> CF <sub>3</sub>	SIO-05	ppt	
<b>HCFCs</b>				
HCFC-22	CHClF <sub>2</sub>	SIO-05	ppt	
HCFC-124	CHClFCF <sub>3</sub>	UB-98	ppt	data first released in 6/2019
HCFC-132b	CH <sub>2</sub> ClCCIF <sub>2</sub>	METAS-2017	ppt	data first released in 11/2020
HCFC-133a	CH <sub>2</sub> ClCF <sub>3</sub>	Empa-2013	ppt	data first released in 11/2020
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	SIO-05	ppt	
HCFC-142b	CH <sub>3</sub> CCIF <sub>2</sub>	SIO-05	ppt	
<b>HFCs</b>				
HFC-23	CHF <sub>3</sub>	SIO-07	ppt	
HFC-32	CH <sub>2</sub> F <sub>2</sub>	SIO-07	ppt	
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	SIO-14	ppt	
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	SIO-05	ppt	
HFC-143a	CH <sub>3</sub> CF <sub>3</sub>	SIO-07	ppt	
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	SIO-05	ppt	
HFC-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	SIO-14	ppt	
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	SIO-14	ppt	
HFC-245fa	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	SIO-14	ppt	
HFC-365mfc	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	SIO-14	ppt	
HFC-43-10mee	CF <sub>3</sub> (CHF) <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	SIO-14	ppt	
<b>Halons</b>				
H-1211	CBrClF <sub>2</sub>	SIO-05	ppt	
H-1301	CBrF <sub>3</sub>	SIO-05	ppt	
H-2402	C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>	SIO-14	ppt	

### **Chlorocarbons**

methyl chloride	CH <sub>3</sub> Cl	SIO-05	ppt
dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	SIO-14	ppt
chloroform	CHCl <sub>3</sub>	SIO-98	ppt
methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	SIO-05	ppt
trichloroethylene	CHClCCl <sub>2</sub>	UB-98	ppt
perchloroethylene	CCl <sub>2</sub> CCl <sub>2</sub>	NOAA-2003B	ppt
carbon tetrachloride	CCl <sub>4</sub>	SIO-05	ppt

### **Bromocarbons**

methyl bromide	CH <sub>3</sub> Br	SIO-05	ppt
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### **PFCs**

PFC-14	CF <sub>4</sub>	SIO-05	ppt
PFC-116	CF <sub>3</sub> CF <sub>3</sub>	SIO-07	ppt
PFC-218	CF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	SIO-07	ppt
PFC-318	c-C <sub>4</sub> F <sub>8</sub>	SIO-14	ppt data first released in 2/2020

### **Other fluorinated compounds**

sulfur hexafluoride	SF <sub>6</sub>	SIO-05	ppt
sulfuryl fluoride	SO <sub>2</sub> F <sub>2</sub>	SIO-07	ppt
nitrogen trifluoride	NF <sub>3</sub>	SIO-12	ppt

#### Notes:

#### 1. The SIO-16 N<sub>2</sub>O Calibration Scale (June, 2017)

The SIO-16 calibration scale for N<sub>2</sub>O 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 N<sub>2</sub>O/CO<sub>2</sub> mixtures prepared manometrically in the Keeling CO<sub>2</sub> laboratory at SIO. CO<sub>2</sub> concentrations were measured in the resulting primary mixtures, referenced to Keeling laboratory CO<sub>2</sub> standards, by GC-FID with catalytic conversion to CH<sub>4</sub> (Weiss, J. Chrom. Sci., 19, 611-616, 1981) to determine N<sub>2</sub>O prepared values from the prepared N<sub>2</sub>O/CO<sub>2</sub> ratios. The optimal transfer from the Keeling CO<sub>2</sub> 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 CO<sub>2</sub> scale propagation are at the < 0.1 ppm CO<sub>2</sub> (< 0.025%) level, and are subject to future revisions based on ongoing additional manometric measurements in the Keeling laboratory.

N<sub>2</sub>O 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" N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O 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%.