東北大学における標準ガスの製造および濃度スケールの維持について

Preparation and calibration of greenhouse gases at Tohoku University

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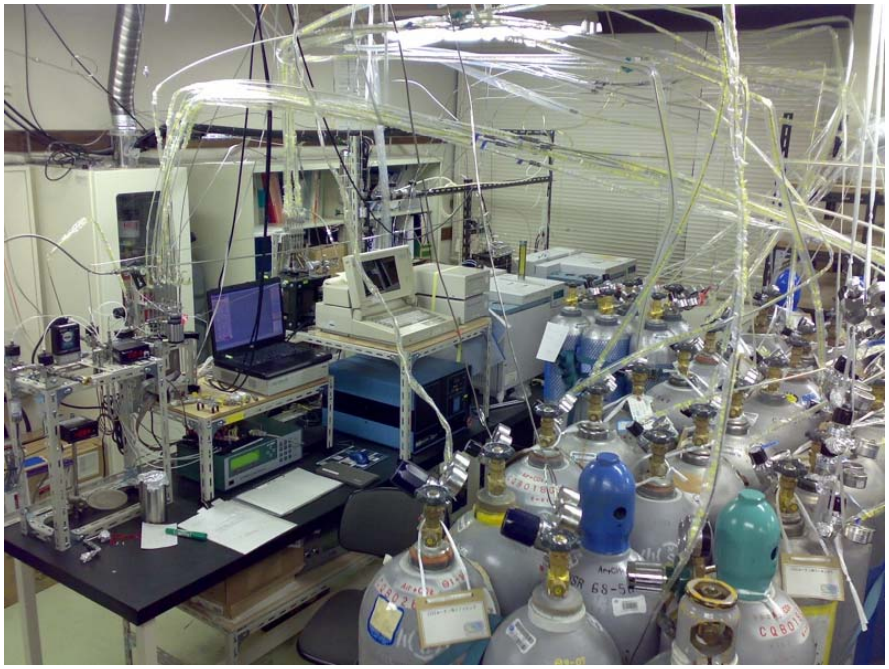
Analytical components at CAOS/ Tohoku Univ.

- Concentration

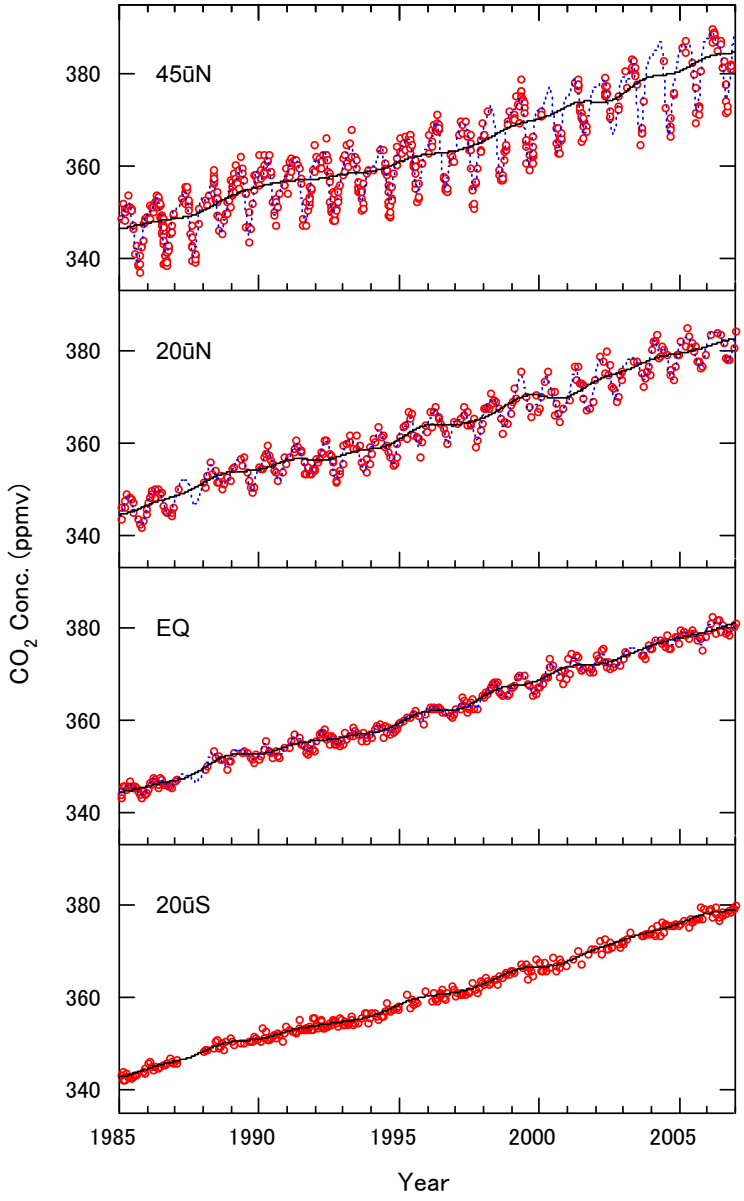
  CO_2, CH_4, N_2O, CO,
  SF_6, H_2, O_2/N_2

- Isotopic ratio

  CO_2: ^{13}C & ^{18}O
  CH_4 : ^{13}C & D
  N_2O : ^{15}N & ^{18}O



Variations of Atmospheric CO_2 Concentration over the Western Pacific Ocean



Amplitude of seasonal CO_2 variations:

20-1 ppmv

Secular CO_2 trend: 1-2 ppmv yr^{-1}

Irregular variations of CO_2 increase:

~ 0.1 ppmv

Requirements for CO_2 standard gases

- Precision $<$ 0.1ppmv
- Long-term stability

CO_2 standard gas

Primary standard gas

1983 scale: 320-370 ppmv

1987 scale: 200-475 ppmv

Nippon Sanso：1979, 1981, 1983, 1985, 1987, 1991, 1996
Taiyo-Toyo：2001, 2004
Japan Fine Products ：2006, 2008, 2010

Secondary standard gas

Semi-primary standard gas

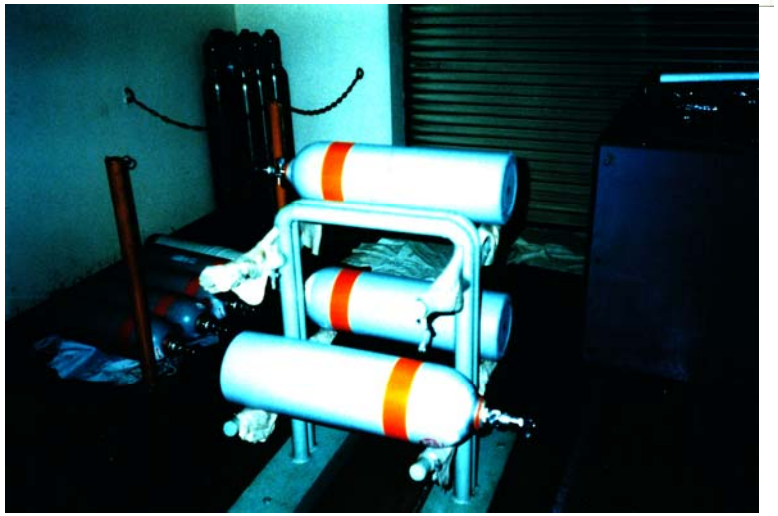
1983, 1985, 1987, 1991, 1994, 1998, 2006, 2008

1988: for pCO_2 measurements in the ocean

Working standard gas

The primary CO_2 standards

Prepared by gravimetric method and stored in 9L aluminum cylinders



Extremely precise balance

Range: 1 mg - 100 kg

Accuracy : $3\sigma = \pm$ 4.6 mg

Overall accuracy : $\pm$ 25 mg

2-stage dilution: 1979, 1981

The first stage : 1% CO_2 in air

The second stage: 310-360 ppmv CO_2 in air

Accuracy: $\pm$ 0.3-0.4 ppmv

3-stage dilution: after 1983

The first stage : 5% CO_2 in air

The second stage: ~4000 ppmv CO_2 in air

The last stage: 300-450 ppmv CO_2 in air

Accuracy: $\pm$ 0.13 ppmv

Secondary and working standard gases for CO_2 measurements

1) Secondary and working standards were stored in 48L aluminum cylinders.

2) We always stopped to use secondary and working standards at the respective pressure of about 30 kg cm^{-2} to avoid the concentration increase with deceasing pressure.

3) We purchased new cylinders for filling secondary and working standards, and those cylinders were repeatedly used for the CO_2 standard only.

Semi-primary standard gases for CO_2 measurements

1) We upgraded several sets of secondary standards to semi-primary standards considering their excellent and long-term stability of CO_2 concentration.

- Ingredients of CO_2 standards

  CO_2 : purity 99.995%, Mole weight = 44.011 g

  CO_2 free dry air : dew point temp. < -70˚C,

  CO_2 < 0.05 ppm, Mole weight = 28.960 g

- Treatment of gas cylinders

  evacuation with heating（加熱真空引き）

  forced CO_2 adsorption on inner wall of a gas cylinder（ガス処理）

  evacuation without heating（真空引き）

  filling gases（ガス充填）

  forced homogenization of gas mixture （安定化）

Results of intercomparison

1999 - 2000 WMO INTERCALIBRATION RESULTS
CARBON DIOXIDE CONCENTRATIONS

LABORATORY	ANALYSIS DATE	TANK #		
GROUP ONE		1357	1155	1224
US - NOAA	Jul.98	349.89	364.50	381.30
AU - CSIRO	Nov.98	349.90	364.47	381.24
NZ - NIWA	Dec.98	349.97	364.58	381.42
ZA - CAPE PT.	Feb.99	349.90	364.54	381.63
CA - AES	Apr.99	349.89	364.53	381.32
US - HARVARD U.	Sep.99	349.86	364.47	381.31
US - NIST	Apr.00	349.85	364.64	381.49
US - SIO	Aug.00	349.96	364.64	381.48
US - NOAA	Jun.00	349.95	364.61	381.35
GROUP TWO		1157	1164	1230
US - NOAA	Jul.98	354.10	366.51	377.46
JP - TOHOKU U.	Jan.99	354.09	366.50	377.44
JP - NIRE	Feb.99	354.05	366.47	377.44
JP - NIES	Apr.99	354.08	366.59	377.60
JP - MRI	Jul.99	354.09	366.60	377.62
JP - JMA	Aug.99	354.13	366.53	377.49
CN - CMA	Sep.99	354.07	366.36	377.39
US - NOAA	Mar.00	354.20	366.61	377.57
GROUP THREE		1988	1159	1223
US - NOAA	Jul.98	349.29	368.23	380.78
FR - CFR	Oct.98	349.25	368.33	380.88
DE - U. HEIDELBERG	Jan.99	349.06	368.05	380.63
DE - UMWELTBUND.	Feb.99	349.46	368.39	380.88
DE - IFU	Feb.99	349.13	368.05	380.79
SE - STOCKHOLM U.	Apr.99			
IT - ENEA	May.99	349.32	368.28	380.47
IT - ENEL	Jun.99	349.11	368.08	380.57
ES - IZANA	Jul.99	349.47	368.51	381.19
NL - U. GRONINGEN	May.00	349.40	368.33	380.81
HU - HMS	Jul.00	349.69	368.22	380.76
US - NOAA	Jul.00	349.34	368.36	380.93

10 Feb. 1997

Tank #	CSIRO CO2 (ppm)	Tohoku CO2 (ppm)	Difference (CSIRO- Tohoku)
CQB06581	320.30 (139)	320.34	-0.04
CQB06405	330.29 (66)	330.28	+0.01
CQB06584	339.99 (23)	340.06	-0.07
CQB06533	348.40 (54)	348.50	-0.10
CQB06534	358.60 (101)	358.57	+0.03
CQB06535	368.66 (54)	368.71	-0.05

Summary

1) We have established CO_2 standard gas system with an accuracy of ±0.13ppmv.
2) The system consists of primary, secondary and working standards.
3) The primary standards were prepared by gravimetric method with the ultra-high precision balance installed at Nippon Sanso Co Ltd.
4) The secondary and the working standards were prepared by manometric method and calibrated against higher rank standards.
5) Intercomparisons have been made many times with the other institutins which have independent concentration scales. The results indicated that the scales were agreed with each other within ± 0.1ppmv.