Preparation of nitrous oxide (N_2O) in air standard being traceable to SI by gravimetric method

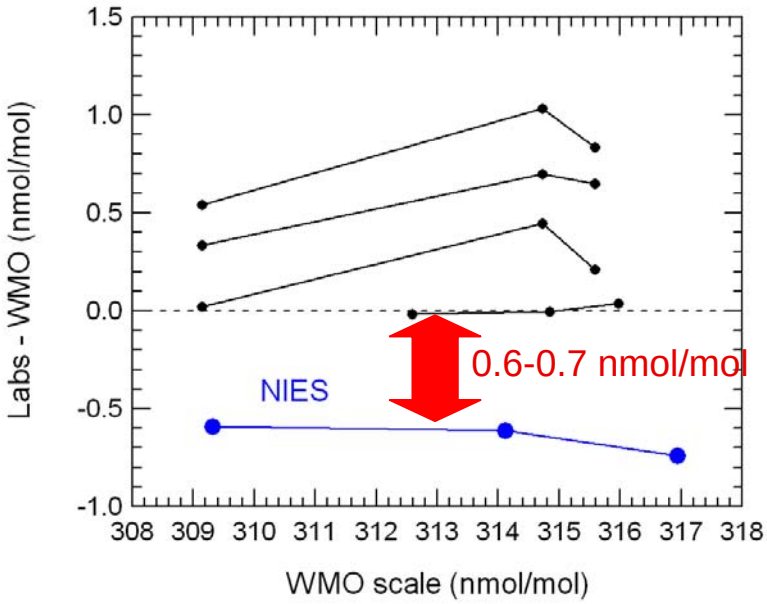
15th WMO Meeting of Experts on Carbon Dioxide,
Other Greenhouse Gases, and Related Tracer Measurement Techniques
September 7th, 2009
Jena, Germany

Nobuyuki Aoki, Takuya Shimosaka, Nobuhiro Matsumoto, Kenji Kato
(National Metrology Institute of Japan, AIST)

Keiichi Katsumata, Toshinobu Machida
(National Institute for Environmental Studies)

N_2O standard

WMO Round-Robin intercomparison (2002-2007)



courtesy of Dr. Zhou Lingxi

International comparison among National Metrology Institutes (NMI)

CIPM
International Committee of Weights and Measures

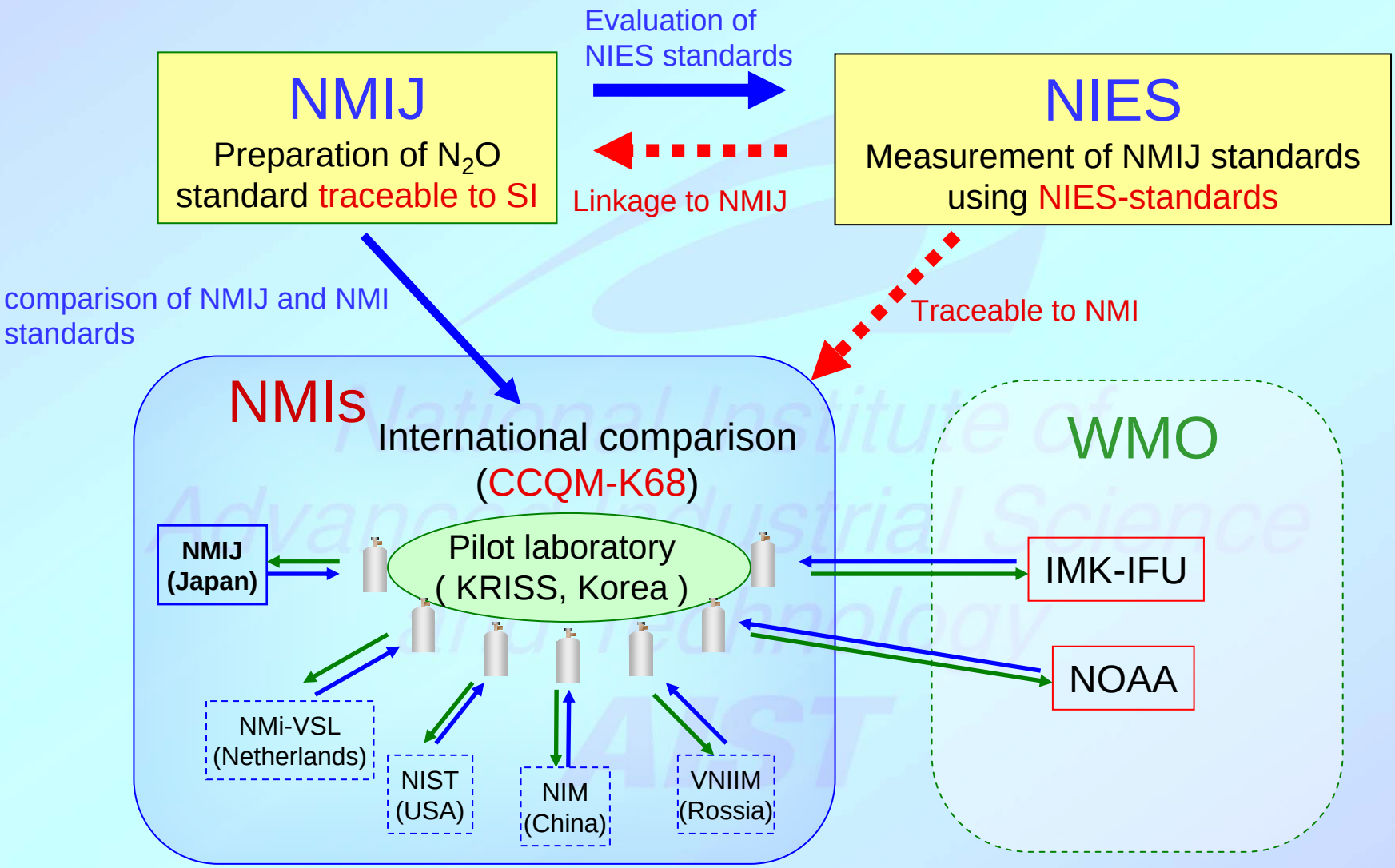
CCQM
the Consultative Committee for Amount of Substance

CCQM-K68

Analysis of N_2O standard prepared in pilot laboratory (KRISS)

- Component: N_2O in air
- Concentration: 320nmol/mol
- Time of measurement: 2008-2009
- Status: in progress

This study

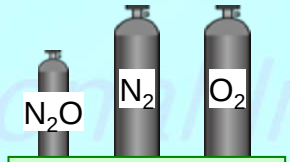

Evaluation of NIES standards
NMIJ
Preparation of N_2O standard traceable to SI
Linkage to NMIJ
NIES
Measurement of NMIJ standards using NIES-standards
comparison of NMIJ and NMI standards
Traceable to NMI
NMIs
International comparison (CCQM-K68)
NMIJ (Japan)
Pilot laboratory (KRISS, Korea)
NMi-VSL (Netherlands)
NIST (USA)
NIM (China)
VNIIM (Rossia)
WMO
IMK-IFU
NOAA

Gravimetric method traceable to SI

Gravimetric value

$$x_i = \sum_{A=1}^{P} \left(\frac{x_{i,A} \cdot m_A}{\sum_{j=1}^{n} x_{j,A} \cdot M_j} \right) \Bigg/ \sum_{A=1}^{P} \left(\frac{m_A}{\sum_{j=1}^{n} x_{j,A} \cdot M_j} \right)$$

$x_{j,A}$: mol fraction of the component in parent gas



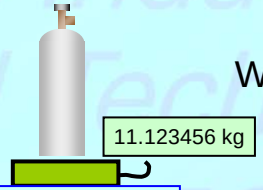
purity analysis

Measurement of Impurity with primary standards

SI

Amount of substance (mol)

m_A: mass of parent gas



Weighing

Weighing amount of gases by standard mass piece

Mass (kg)

Verification

M_j: Molar mass of component

IUPAC Atomic weight

Relative mass

Purity analysis of raw materials

Purity table of N_2O

Components	Applied concentration (μmol/mol)	Standard uncertainty (μmol/mol)	Analytical method
N_2	0.983	0.567	Micro GC
O_2	1.020	0.589	Micro GC
CO_2	0.128	0.006	GC-FID with methanizer
CH_4	0.019	0.003	GC-FID
CO	0.056	0.032	GC-FID with methanizer
H_2O	0.439	0.253	Capacitance-type moisture meter
N_2O	**999997.36**		

Purity table of N_2

Components	Applied concentration (μmol/mol)	Standard uncertainty (μmol/mol)	Analytical method
O_2	0.819	0.473	Micro GC
CO_2	0.010	0.006	FT-IR
CH_4	0.026	0.015	FT-IR
CO	0.175	0.101	FT-IR
H_2O	0.439	0.253	Capacitance-type moisture meter
N_2O	0.00002	0.00001	Clyo. conc. /GC/MS
N_2	**999998.53**		

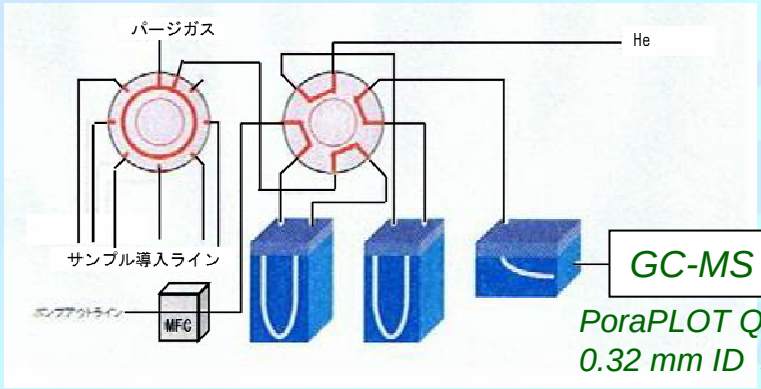
Purity table of O_2

Components	Applied concentration (μmol/mol)	Standard uncertainty (μmol/mol)	Analytical method
N_2	0.090	0.052	GC-TCD
Ar	0.087	0.050	GC-TCD
CO_2	0.056	0.004	FT-IR
CH_4	0.003	0.002	FT-IR
CO	0.005	0.003	FT-IR
H_2O	0.439	0.253	Capacitance-type moisture meter
N_2O	0.00002	0.00001	Clyo. conc. /GC/MS
O_2	**999999.32**		

Purities of all raw materials are more than 99.999 %

N_2O concentrations in O_2 and N_2

Analytical system for impurity N_2O



PoraPLOT Q
0.32 mm ID × 25 m

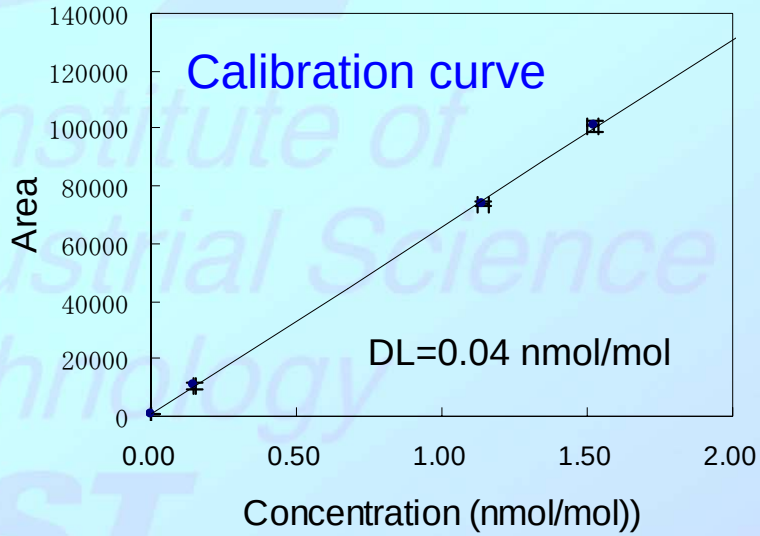
	Module 1	Module 2	Module 3
adsorbent	Tenax	Glass beads	Capillary colmn
Trap Temp.	-120	-150	-180
Desorb Temp	20	150	70

Calibration standards

N_2O in He
(gravimetric method)

0.149, 1.141, 1.521 nmol/mol

Calibration curve



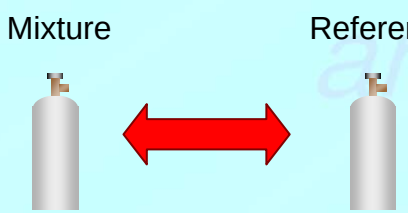
N_2O concentrations in O_2 and N_2 are less than 0.04 nmol/mol

Weighing

Main sources of uncertainty

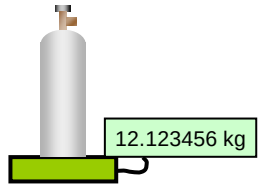
- Balance
- Buoyancy effect
- Absorption and adsorption to external cylinder surface
- …. etc.

Comparative Weighing



Weighing room

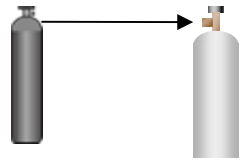
25° C, 50%



an hour after filling parent gases
five hours after filling dilution gases

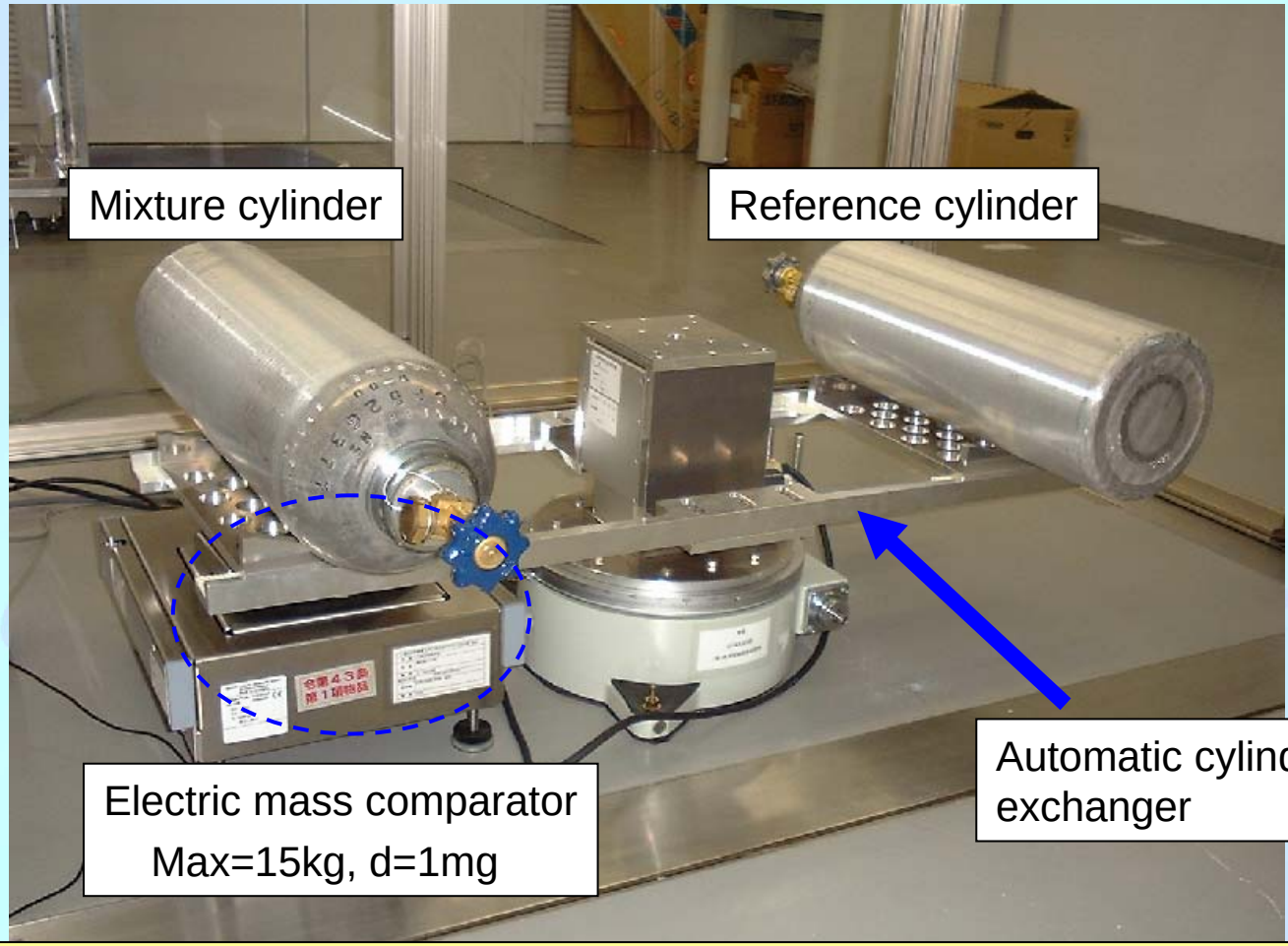
Filling room

24° C, 20~80%



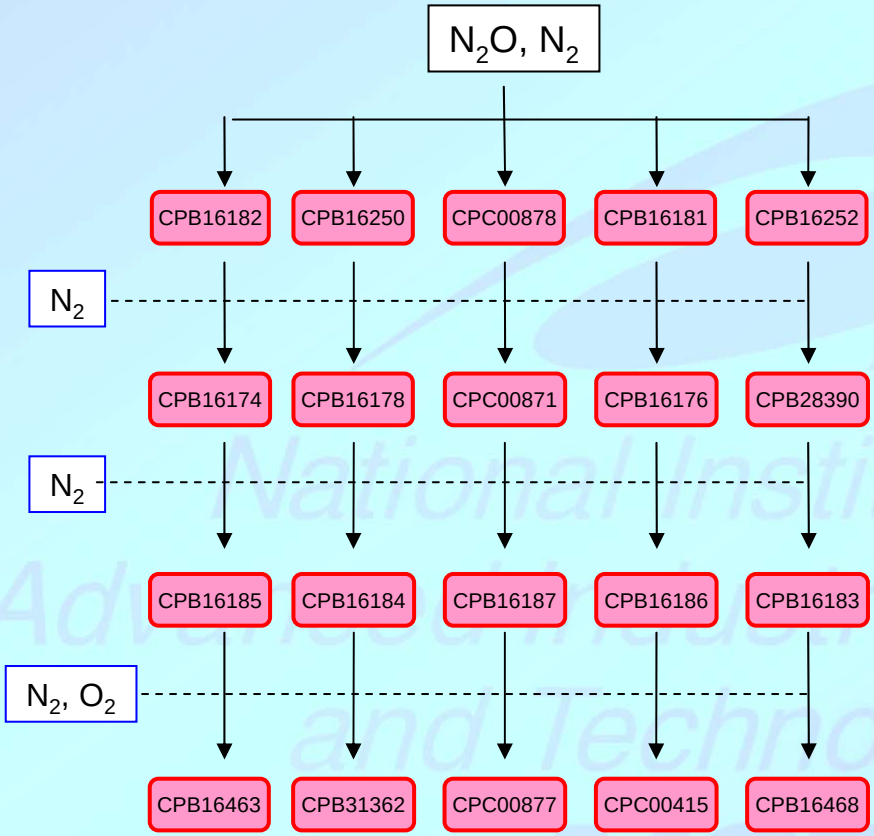
N_2O or N_2O in N_2
N_2 or O_2

Weighing system of NMIJ



Standard deviation of balance system : 2.6 mg !

Preparation sequence



1.3-1.5 %mol/mol
Expanded uncertainty: 0.04 %

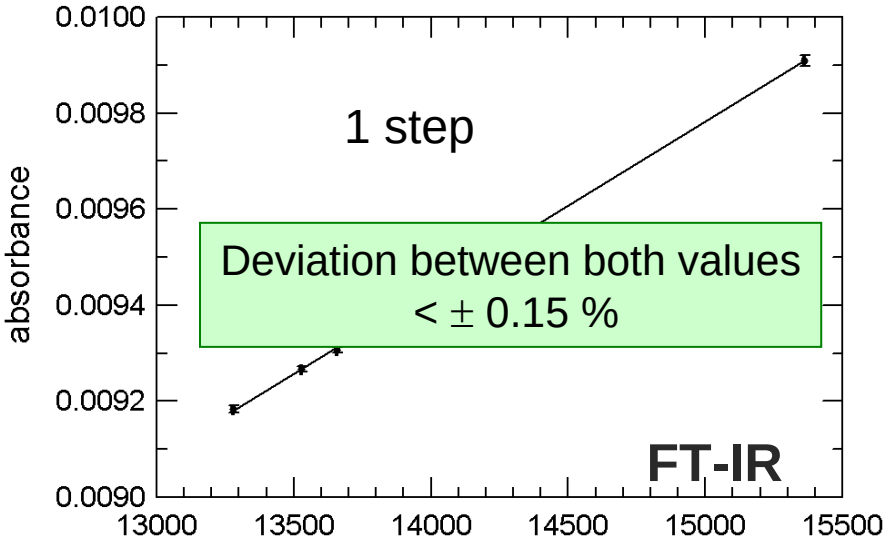
280-300μmol/mol
Expanded uncertainty: 0.05 %

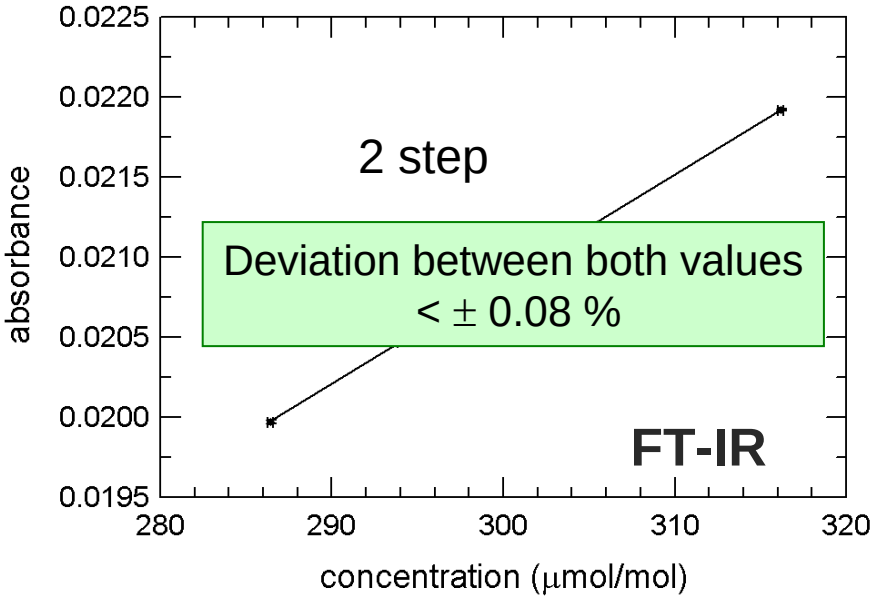
9.0-10μmol/mol
Expanded uncertainty: 0.06 %

300-345nmol/mol
Expanded uncertainty: 0.06 %

Five standards of 4th step were independently prepared !

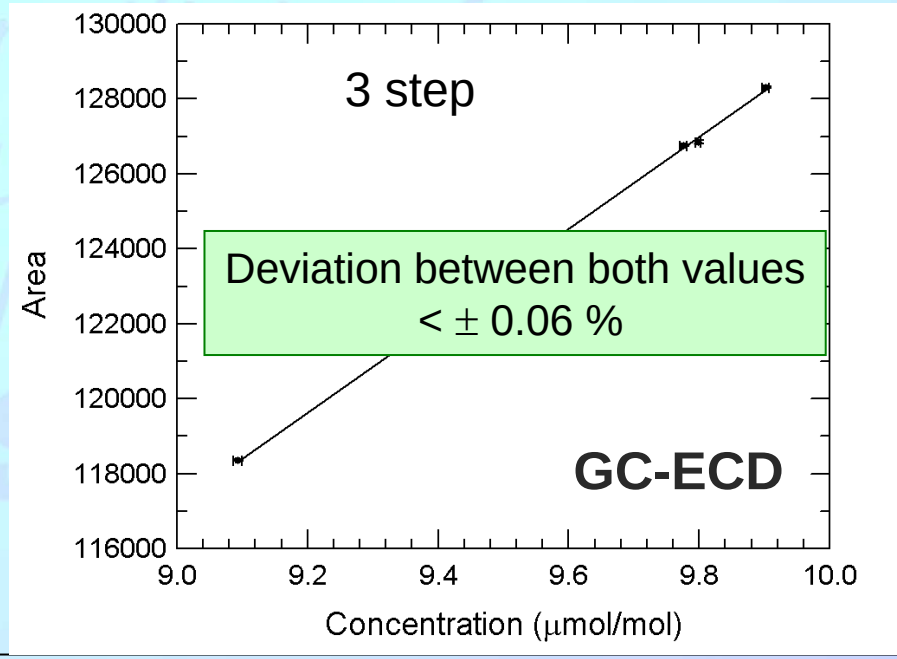
Verification of intermediated gases



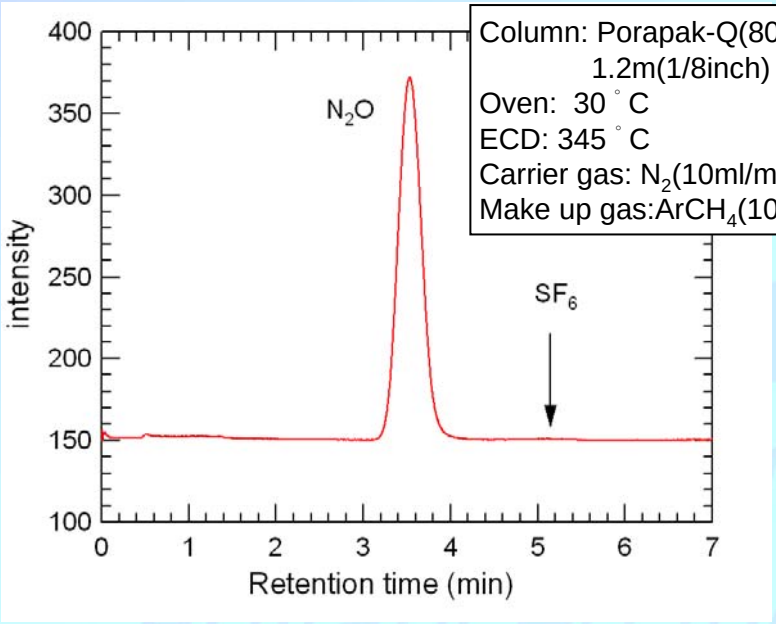


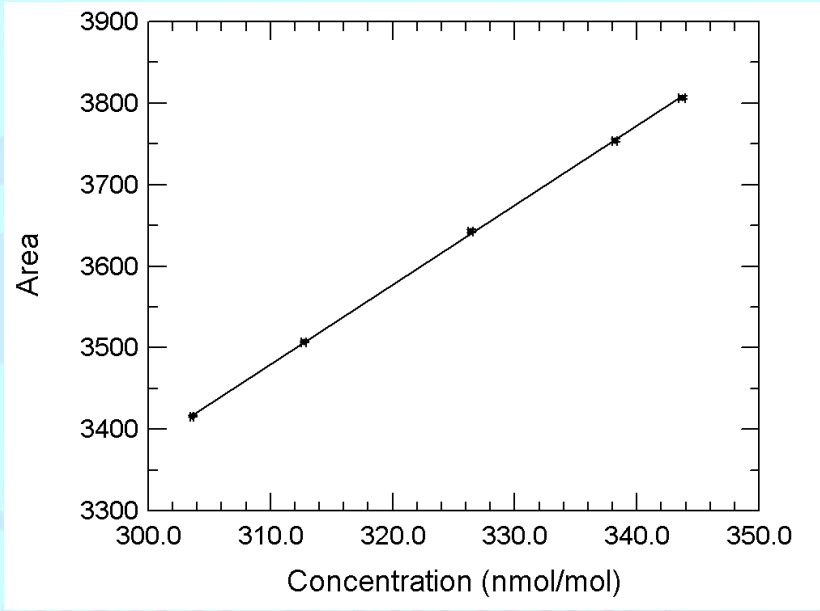
Internal consistency test

- check that gravimetric value is consistent with analytical value
- highlight significant errors in the preparation process



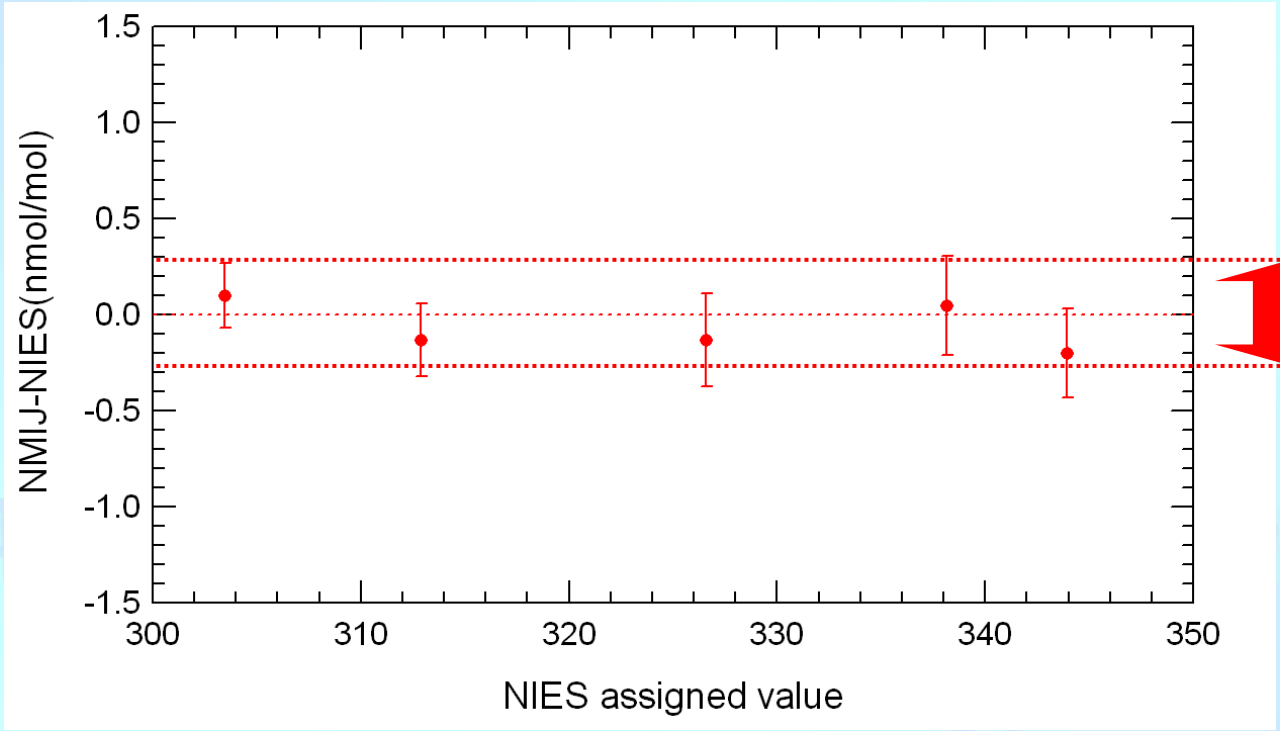
N_2O standards of NMIJ





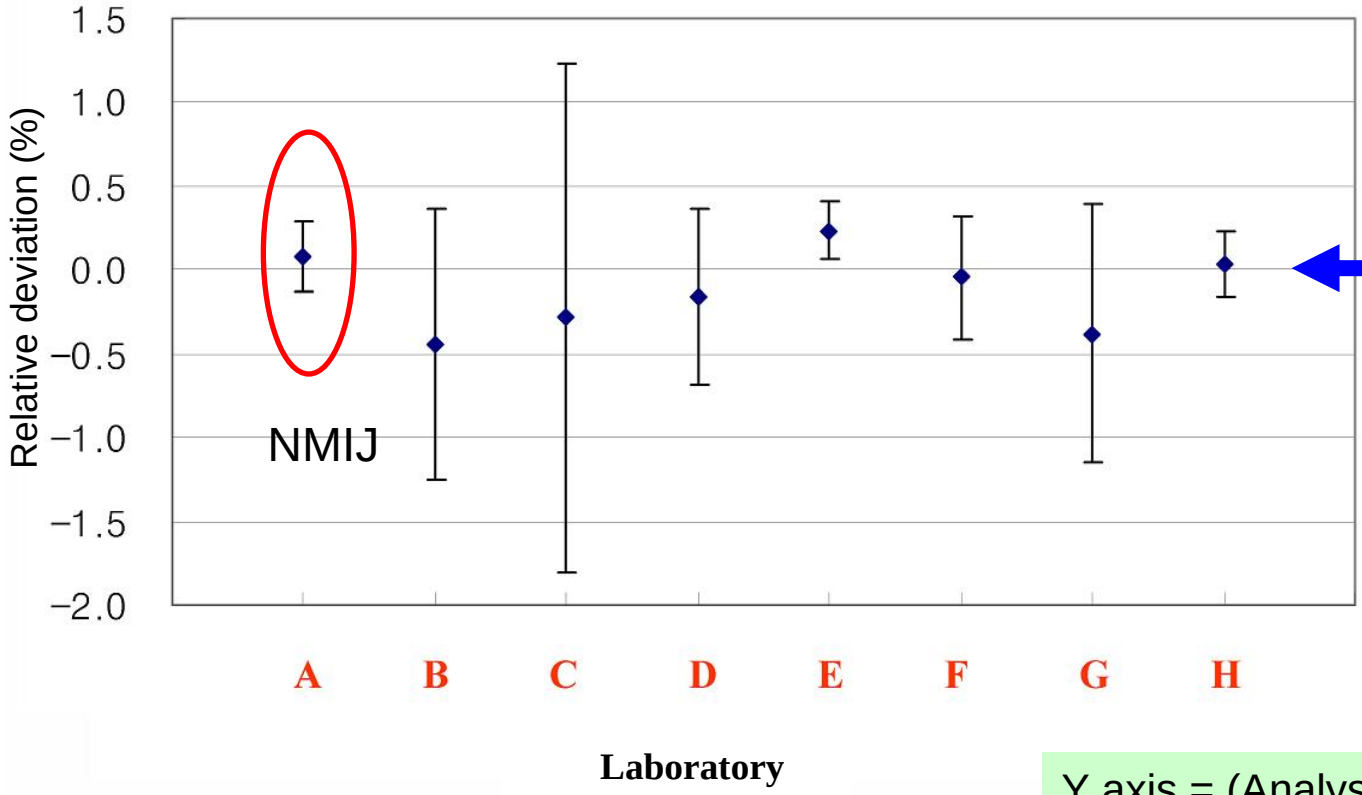
Cylinder number	Gravimetric Value (nmol/mol)	Expanded uncertainty [k=2] (nmol/mol)	Concentration with calibration carve (nmol/mol)	Deviation (nmol/mol)
CPB00877	303.57	0.13	303.54	0.03
CPB31362	312.77	0.19	312.84	-0.07
CPB16468	326.44	0.20	326.37	0.07
CPC00415	338.20	0.20	338.10	0.10
CPB16463	343.73	0.23	343.84	-0.11

Comparison between NMIJ and NIES standards



NIES scale is comparable to SI

Draft report of CCQM-K68



Key comparison reference value (KCRV)

Y axis = (Analysis value)-(KCRV)

Analysis result of NMIJ is in excellent agreement with key comparison reference value (KCRV)

Summary

- N_2O standards traceable to SI have been prepared at NMIJ
- The scale of NIES-standards is linkage to the scale of NMIJ-standards
- Analysis result of NMIJ is in excellent agreement with KCRV in CCQM-K68
- The scale of NIES-standards will be comparable to NMI

International comparison among NMi

- **Measurement capability**
  CCQM-K68 : Nitrous oxide 320 nmol/mol in artificial Air

- **Gravimetric preparation of N2O by coordinating lab.**
  Purity Assessment + Weighing Technique + Stability + Verification
  N2O 300 ~ 350 nmol/mol ± 0.06 % (95 % confidence level)

- **How far does the light shine**
  This key comparison will support the measurement capability of N_2O at ambient level

- **Participation(8)**
  KRISS, NIM, NIST, NMIJ, GMD/NOAA, VSL, IMK-IFU, VNIIM

Uncertainty

Main source of uncertainty

- Purity of raw material
- Balance
- mass piece
- adsorption/desorption
- buoyancy effect
- molar mass