Better Standards, Better Life

Development of International VOC Standards for GAW Measurement of Background Monitoring on Earth

Counting number of molecules in gas phase in cylinder

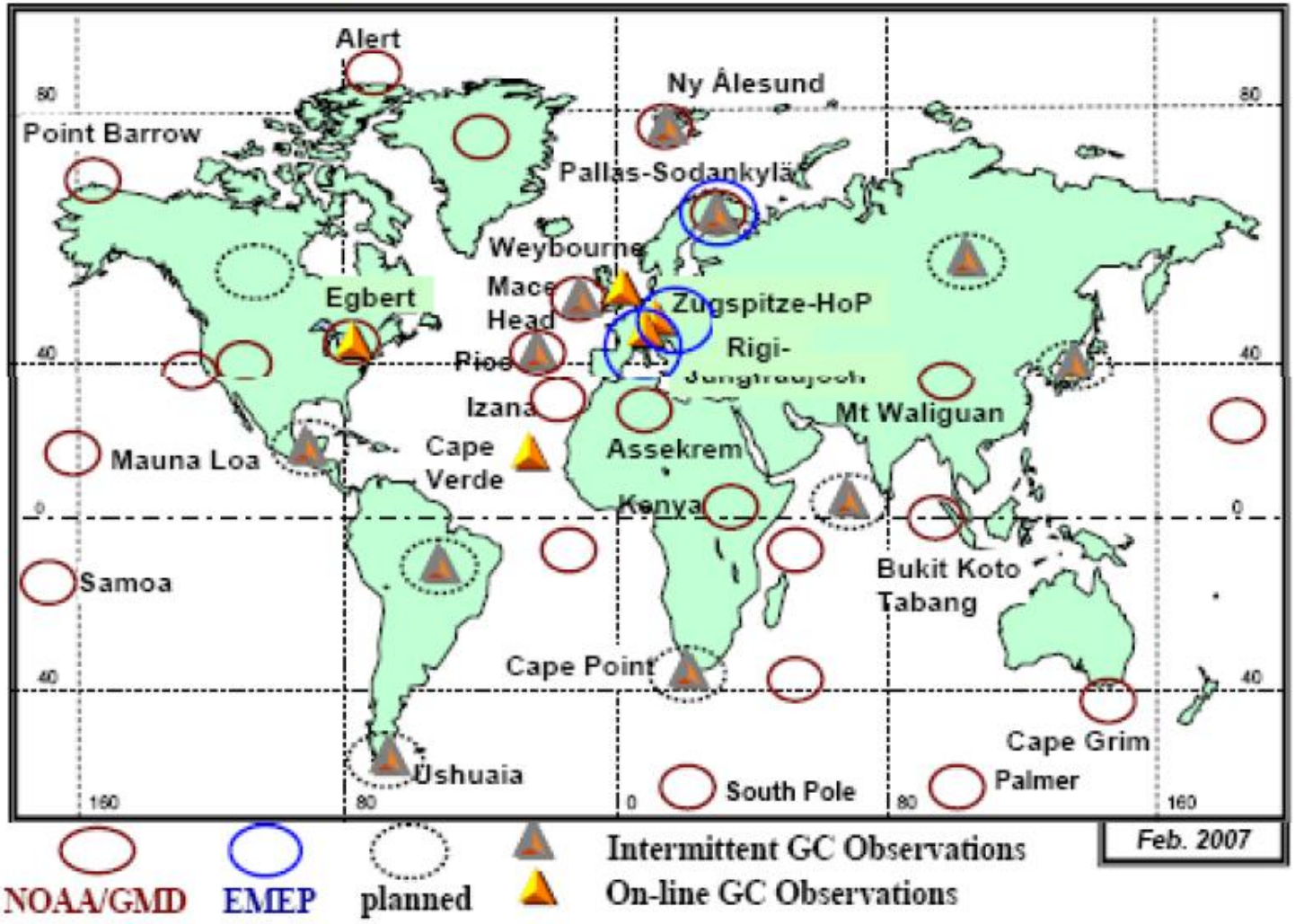
Gwi Suk Heo, Yong Doo Kim, Mi-Eon Kim

Background WMO_GAW - BIPM GAWG

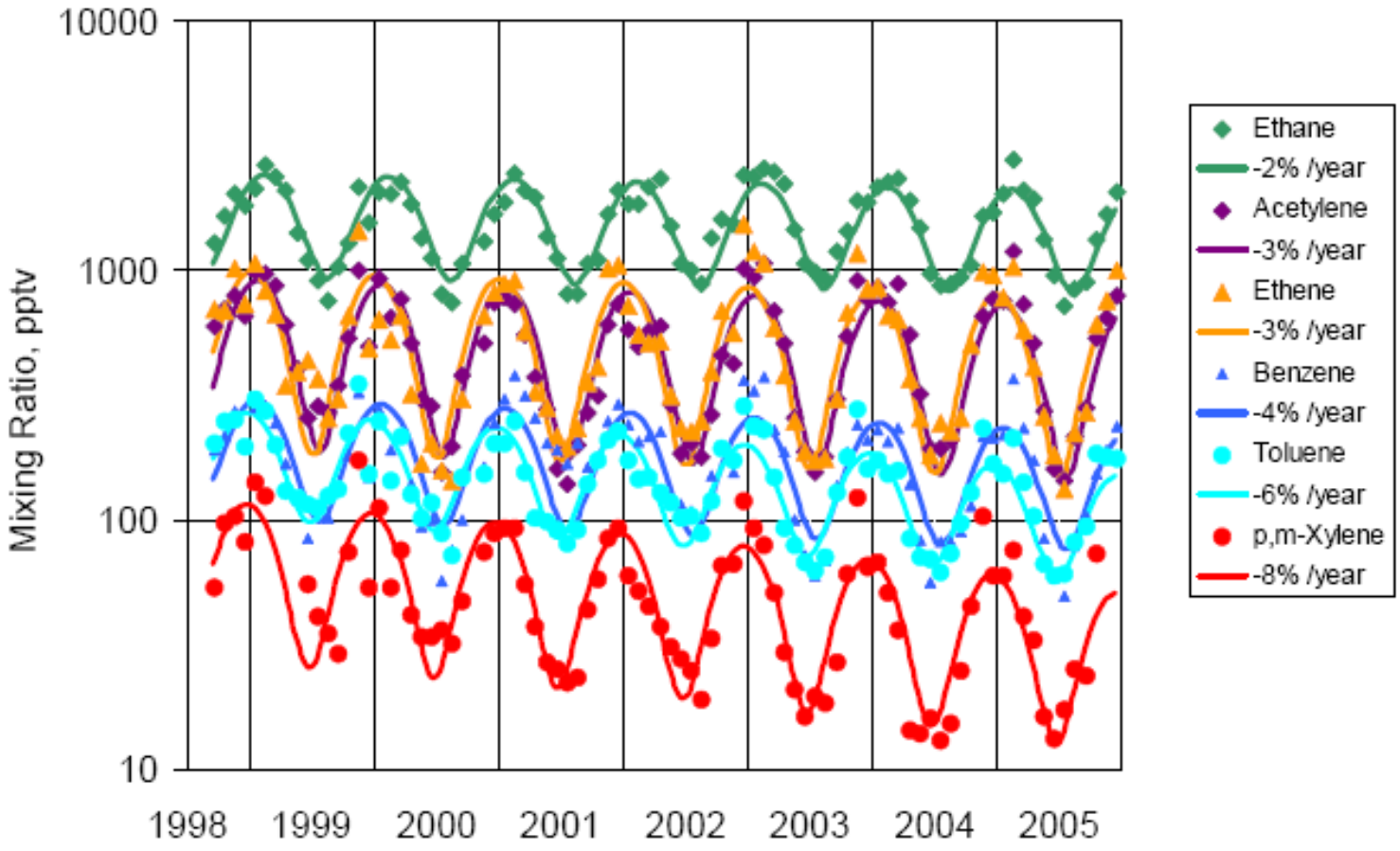
GAW - VOC compounds and objectives, GAW report 171

Molecule	Lifetime (1E6 OH)	Importance / Changing Atmosphere
Ethane Propane Acetylene I,n-Butane I,n-Pentane Benzene Toluene	1.5 months 11 days 15 days 5 days 3 days 10 days 2 days	• Atmospheric composition, Trends • Source attribution (HC pattern): biomass burning, traffic, oceans, ... • Ozone production • Oxidizing capacity • Chemistry (HC ratios): Role of OH / O3 / NO3 / halogen chemistry • Precursor to particulates • Sources of methane (HC pattern)
Isoprene Terpenes	3 hours 1-5 hours	• Biosphere products • Sensitive to temperature/land use/climate change • Precursors to O3, HCHO, organic aerosol • Oxidizing capacity
Formaldehyde	1 day	• Indicator of VOC/isoprene oxidation • Biomass burning • Comparison with satellites
Acetone	2 months	• Abundant oxidation product • Free radical source in the upper troposphere
Methanol Ethanol	12 days 4 days	• Sources in the biosphere • Abundant oxidation product • Tracer of alternative fuel usage
Acetonitrile	1.5 year	• Biomass burning
DMS	2 day	• Major natural sulphur source • Sulphate aerosol / climate • Tracer of marine bioproductivity

Prospective GAW VOC Network



VOC - Trends at Hohenpeissenberg



VOC QA / QC

GAW
- Report 111, 171
- Intercomp.+audits by WCC
- training (GAWTEC)

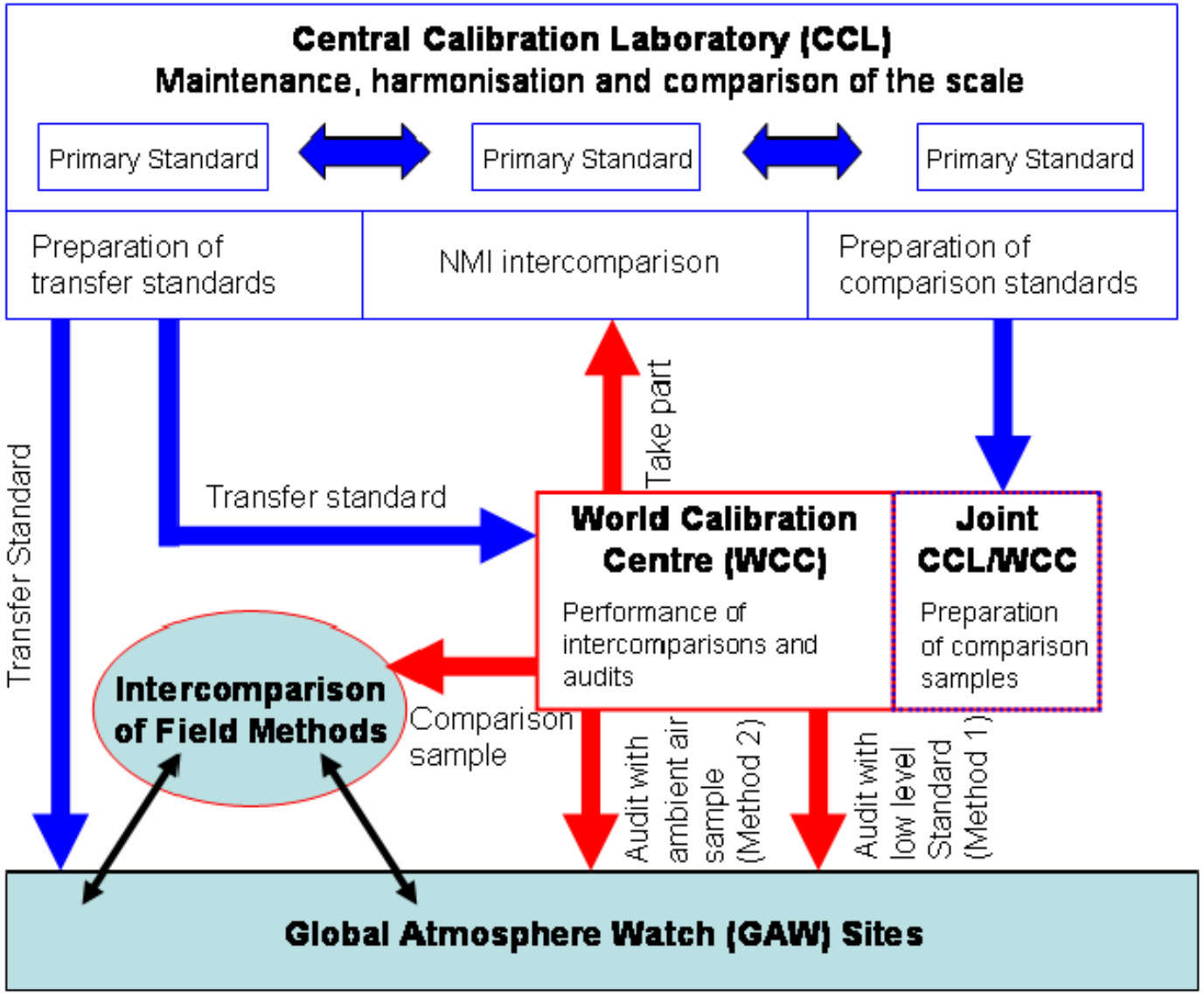
EMEP
- Manual (EMEP/CCC-1/95)
- intercomp.+audits by NILU
- data screening by NILU and local laboratories

VOC Data Quality Objectives

uncertainty VOC: 10 - 20 %

uncertainty VOC 15-25%

no common calibration gas standards
no accepted QA / QC protocol
no SOP‘s


Central Calibration Laboratory (CCL)
Maintenance, harmonisation and comparison of the scale
Primary Standard
Primary Standard
Primary Standard
Preparation of transfer standards
NMI intercomparison
Preparation of comparison standards
Transfer Standard
Transfer standard
Take part
World Calibration Centre (WCC)
Performance of intercomparisons and audits
Joint CCL/WCC
Preparation of comparison samples
Intercomparison of Field Methods
Comparison sample
Audit with ambient air sample (Method 2)
Audit with low level Standard (Method 1)
Global Atmosphere Watch (GAW) Sites

The GAW-VOC Target Compounds

Standards for **C2-C9 hydrocarbons** are readily available

Proposed tasks for preparing a world standard for **other VOC**

- prepare 4-component mixtures of methanol, ethanol, acetone, and acetonitrile at 0.25-2.5 ppm in N2 in gas cylinders
- prepare adsorption tubes loaded with defined amounts of monoterpene mixtures in the ng range
- prepare monoterpene mixture in N2 at about 0.25 ppm in gas cylinder
- develop calibration system for CH2O and DMS
- develop a dynamic dilution device to dilute standards from high pressure gas cylinders by a factor of 500 in air or N2, according to standard operating procedures

Action Plan

1. Components to be included in the C2-C9 NMHC standard [April 2007 - done]
2. Agree on (tests for) calibration procedures for other VOC [April 2007 –> 07/2008]
3. Agree to a schedule for comparisons of C2-C9 NMHC standards with participation of GAW-WCC, starting with EUROMET 886 [April 2007 - started]
4. Develop and agree to a statistical approach that can relate the Degrees of Equivalence arising from comparisons organized according to the CIPM guidelines with the requirement for a "scale" for the GAW CCL. [June 2007 –> 07/2008].
5. Agree to a strategy for dissemination of values for the "scale" and prepare an outline of a publication – (might lead to certificates with a GAW scale value as well as values from a NMI's own methodology!). [Oct 2007 –> 07/2008]
6. Memorandum of co-operation - NMI, NIST, KRISS, NPL +? [Oct 2007 –> draft]

MEMORANDUM OF COOPERATION

between

The National Institute of Standards and Technology - NIST
Gaithersburg, MD., United States of America,

The Netherlands Measurements Institute - NMi
Delft, The Netherlands,

National Physical Laboratory – NPL
Teddington, Middlesex, United Kingdom,

Korean Research Institute of Standards and Science – KRISS
Taejon, Korea,

And

World Metrology Organization, Global Air Watch Program

Cooperative Program for maintenance of volatile organic compound gas standards for the World Metrology Organization, Global Air Watch Program

Next Steps

- NIST, NMI-VFL and KRISS will have the other-VOC program on board (2009 ?)
- NIST, NMI-VFL have started with Terpenes, Alcohols, Acetone
- Tasks and Responsibilities:
  - NMHCs and "scale": Martin Milton, NPL
  - Alcohols, Acetone: Rob Wessel, NMI-VFL
  - Monoterpenes: Jerry Roderick, NIST
  - DMS, Formaldehyde, Acetonitril: Jin Seog Kim, KRISS
- GAW will organize a Workshop GAW/GAWG in summer 2008 (2nd week of July?) at EMPA (Zürich, CH)
- GAW VOC intends to have a Workshop in summer 2008
- Have all CCLs in place 2010

Development of DMS and acetonitrile standards in KRISS

Counting number of molecules in gas phase in cylinder

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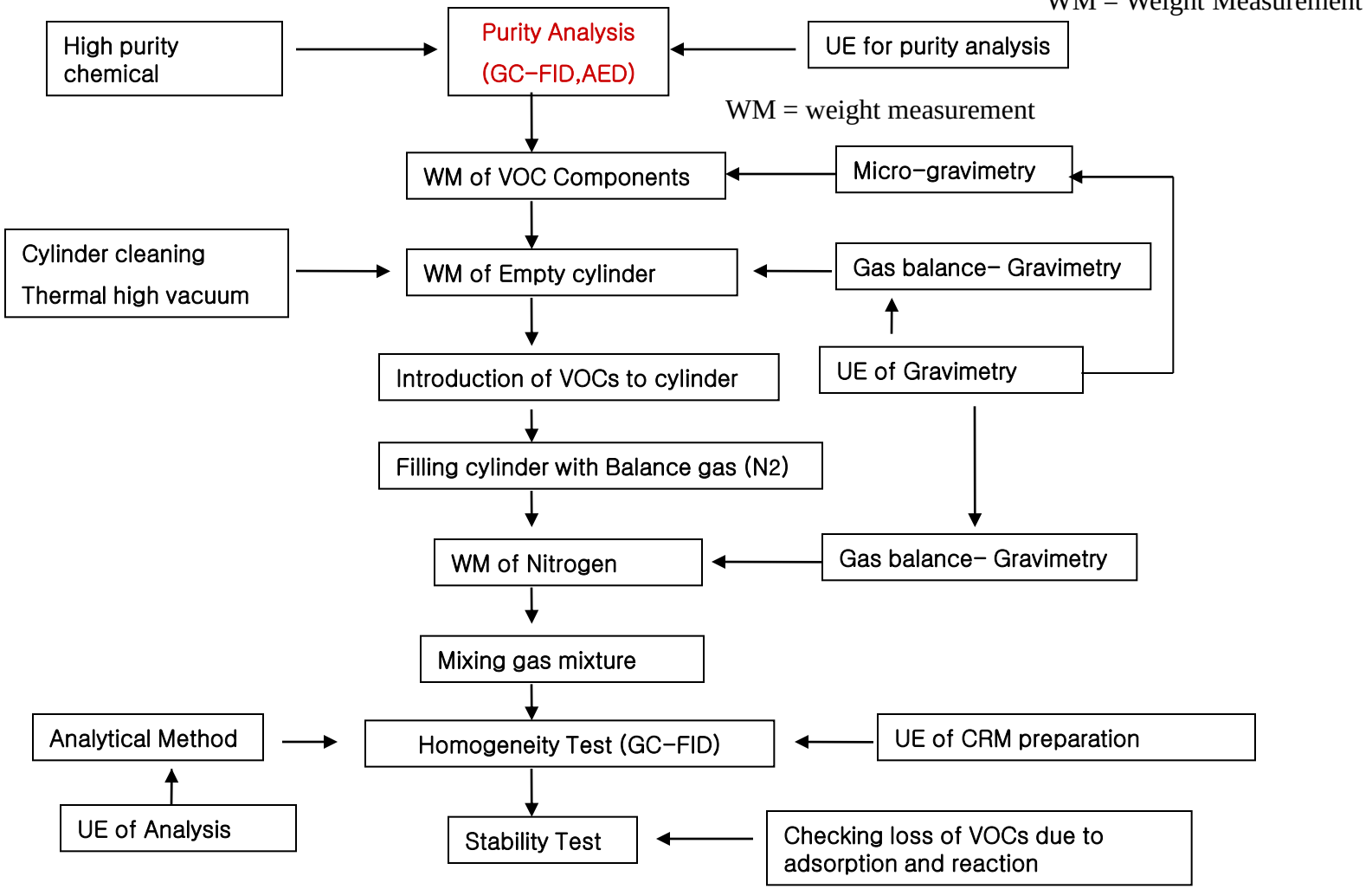
Preparation Scheme of DMS CRM

UE = Uncertainty Evaluation
WM = Weight Measurement



Uncertainty evaluation for preparation of low μmol/mol DMS CRM : Modeling Equation

Modeling Equation

$$C_{DMS} = \frac{n_{DMS}}{(n_{DMS}+n_{N2})} \times 10^6 \times f_{purity} \times f_{Ads} \times f_{\mathrm{Re}} \times f_S$$

Where,

C_{DMS} : Concentration of DMS (μmole/mole)

n_{DMS} : Mole of DMS in CRM (mole),

$n_{DMS}=m_{DMS}/M_{DMS}$

m_{DMS} : Amount of liquid DMS reagent in CRM (g)

M_{DMS} : Molecular weight of DMS (g/mole)

n_{N2} : Mole of N2 in CRM(mole),

$n_{N2}=m_{N2}/M_{N2}$

m_{N2} : Amount of N2 gas in CRM (g)

M_{N2} : Molecular weight of N2 (g/mole)

f_{purity} : Factor for purity of liquid DMS reagent

f_{Ads} :: Factor for adsorption loss of DMS in cylinder

f_{Re} : Factor for Preparation reproducibility of DMS CRM

f_S : Factor for stability of DMS in cylinder

Purity determination of DMS

Reagents

- Dimethyl sulfide : anhydrous, ≥99.0% (Aldrich, USA)

Instruments

- GC-FID and GC-SCD (Agilent, 6890N)
- FT-IR (Bruker, IFS 120HR)

Purity Measurement

- Pure dimethyl sulfide

  : Total hydrocarbons (GC-FID), Total sulfur (GC-SCD, FTIR),

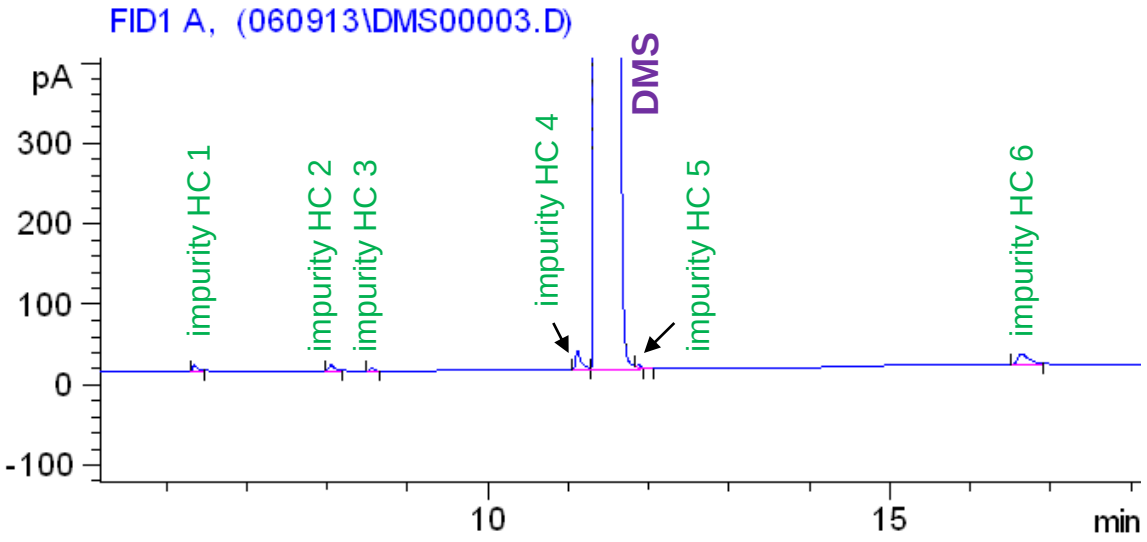
  Moisture (Karl Fisher coulometer)

Impurity Analysis of DMS by GC-FID

Measurements gas Total hydrocarbons

Analysis conditions

- Column : J&W GS-Q, 30 m x 0.53 mm , Carrier gas : 10 mL/nin
- Sample loop 1.0 mL , Sample injection 0.4 μL, Split ratio 2:1
- Sample valve Temp. : 150 ℃ :
- Detector : FID, Temp. : 250 ℃
- GC oven Temp. : 100 ℃ (3 min) →10℃/min → 220 ℃(4 min)



Purity determination of DMS

- Measurement techniques: **GC-FID, GC-SCD, FTIR, Karl-Fischer coulometer**

- **GC-FID** was used for analysis of total impurity hydrocarbons (4,063 μmol/mol)
- **GC-SCD** was used for analysis of total sulfur (<1 μmol/mol)
- **Karl-Fischer coulometer** was used for analysis of moisture (1,471 μmol/mol)

- Therefore,

  total of 0.1% of uncertainty was assigned to **DMS purity result of 99.5%.**

Preparation Scheme of DMS CRM

UE = Uncertainty Evaluation
WM = Weight Measurement

Purity Analysis (GC-FID,AED)

UE for purity analysis

WM = weight measurement

WM of VOC Components

Micro-gravimetry

Cylinder cleaning
Thermal high vacuum

WM of Empty cylinder

Gas balance- Gravimetry

Introduction of VOCs to cylinder

UE of Gravimetry

Filling cylinder with Balance gas (N2)

WM of Nitrogen

Gas balance- Gravimetry

Mixing gas mixture

Analytical Method

ID)

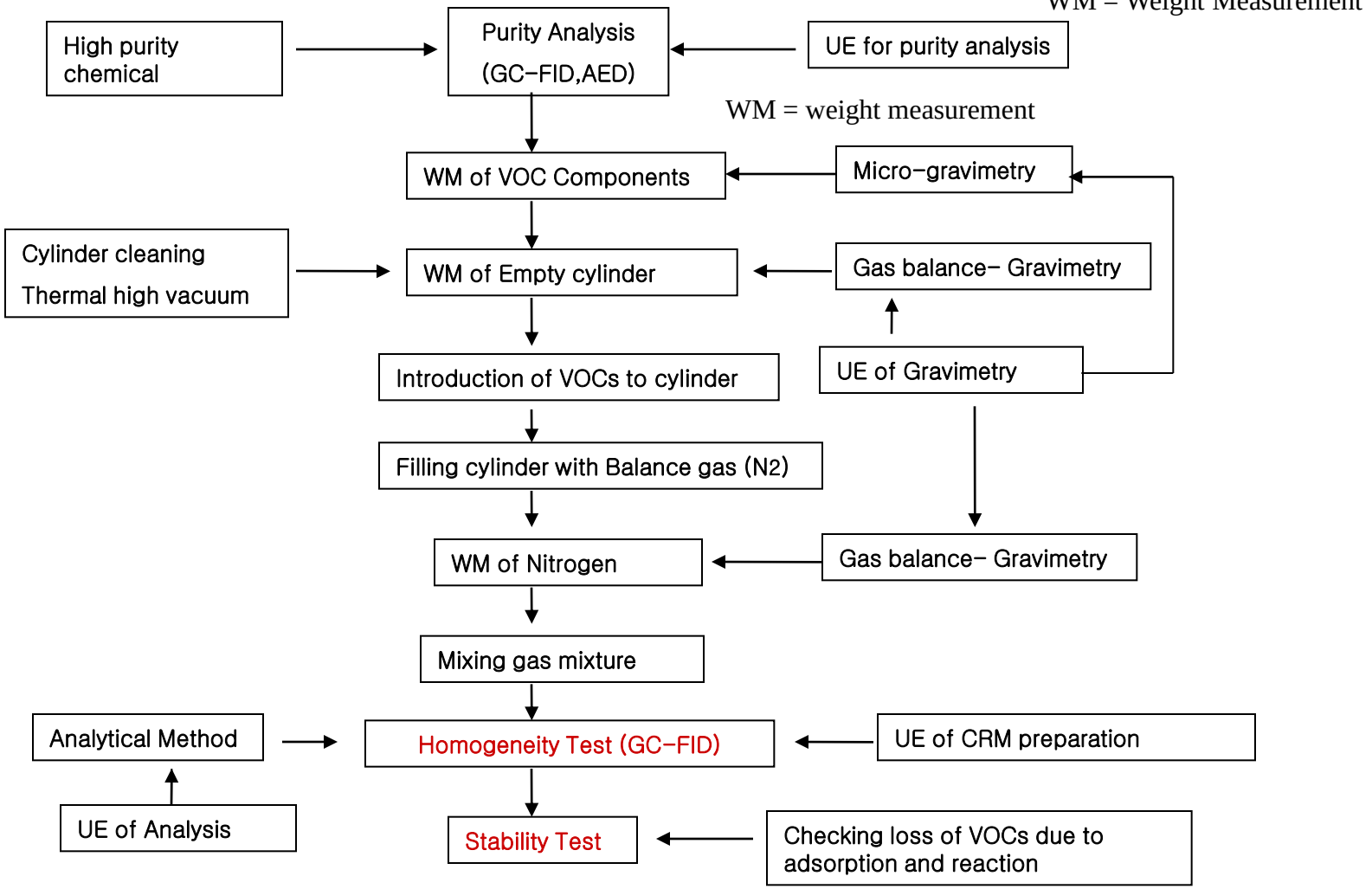
UE of CRM preparation

UE of Analysis

Checking loss of VOCs due to adsorption and reaction

Preparation Scheme of DMS CRM

UE = Uncertainty Evaluation
WM = Weight Measurement

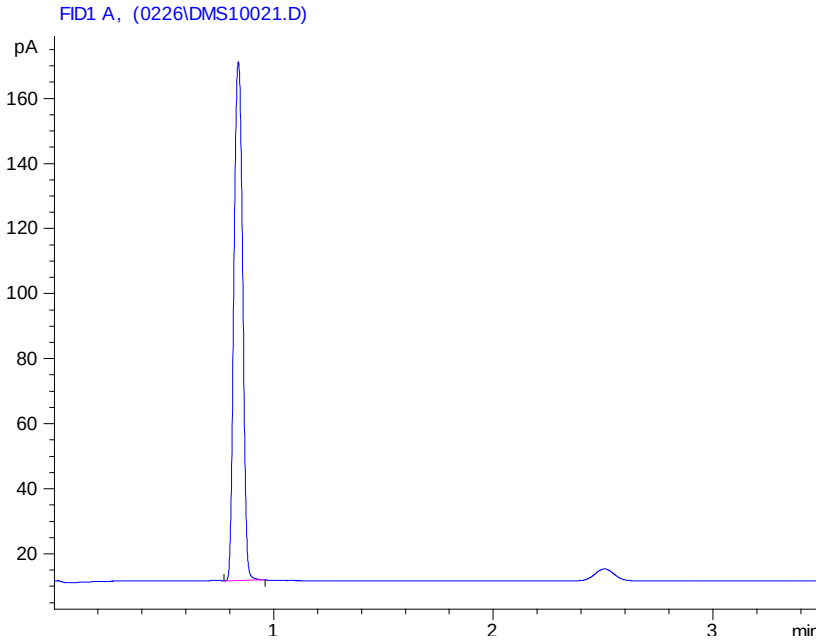


Preparation reproducibility test of DMS CRMs

Preparation reproducibility of low μmol/mol level DMS gas standards was **checked by GC-FID**

Analytical Conditions

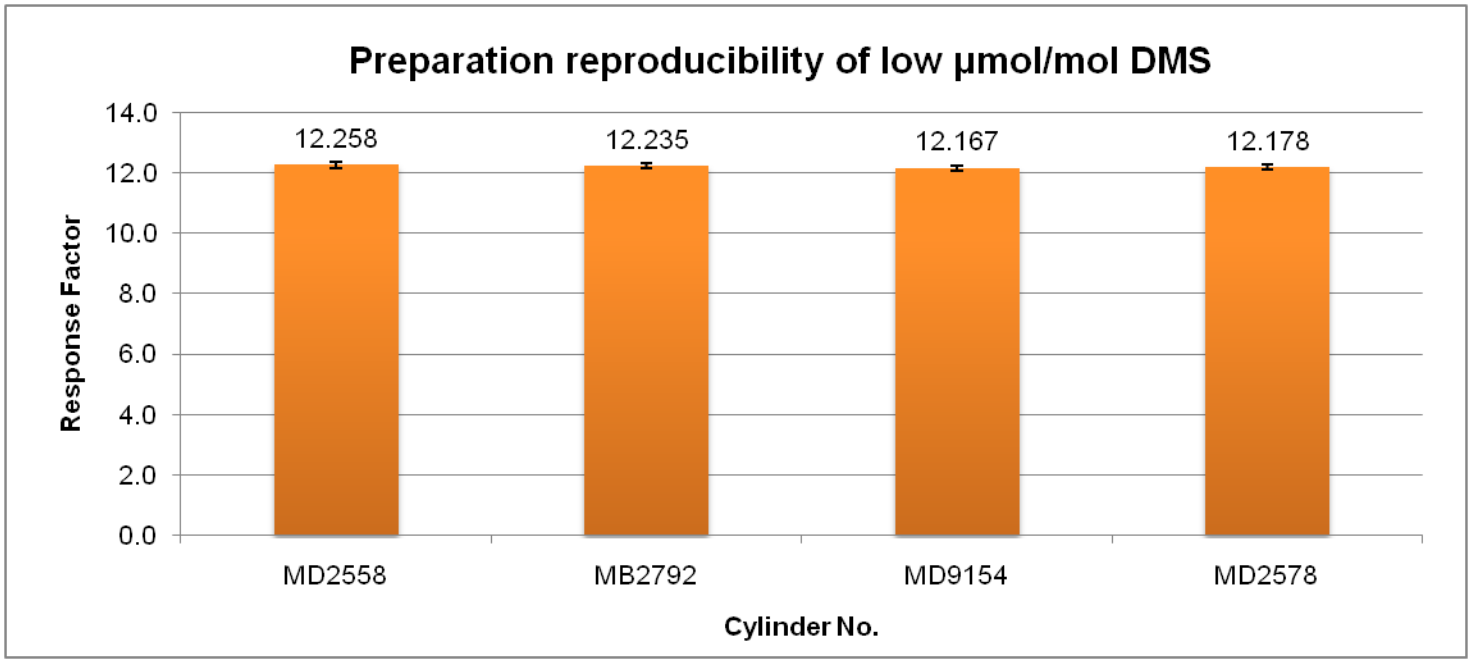
- Column : CP-Sil 5B, 25 m x 0.53 mm
  Carrier gas : N2,
- Injection : Sample valve temp. : 100 ℃,
  Sample loop 1.0 mL Sample flow 100 mL/min, Split ratio 20 :1
- GC oven Temp. 70 ℃ (3.5 min)
- Detector : FID, Temp. : 250 ℃



Analysis Chromatogram of DMS

Preparation reproducibility of low μmol/mol DMS

Preparation reproducibility : 0.36 %



Cylinder No.	Conc. of preparation (μmol/mol)	Means (± S.D)	RSD (%)	Response factor	Difference (%)	Date of preparation
MD2578	3.710	45.18	0.11	12.18	0.26	000628
MD9154	5.440	66.19	0.12	12.17	0.35	000628
MB2792	6.018	73.63	0.28	12.24	-0.21	000628
MD2558	6.443	78.98	0.10	12.26	-0.40	991205
					RSD(%)	**0.36**

DMS loss test due to reaction with cylinder : immediate reaction, short term stability

Reaction with the inner surface of cylinder and cylinder valve

Very important to counting number of molecules getting out from cylinder: how many molecules are getting out without loss from cylinder?

Adsorption loss test of DMS during the preparation of CRMs

Low μmol/mol CRM :

- Loss of DMS due to adsorption to inner surface of cylinder was evaluated by distributing equal amount of low micromole/mole DMS to other empty cylinder, then second cylinder again was distributed to another empty cylinder.
- The three cylinders were analyzed and compared their FID response factors to check the adsorption loss of DMS.
- **Result : very small loss**, 0.11 % loss at first distribution, 0.35 % loss at second distribution.

DMS loss test due to reaction with cylinder : immediate reaction, short term stability

Absorption result of 10 umol/mol Dimethyl sulfide

200103

Cylinder No	Conc. of preparation	Means (± S.D)	RSD(%)	Response factor	Differance(%)	Cylinder pressure (psi)	
DM9154	5.440	25604	0.12	4707		700	Mother
MD6097	5.440	25542	0.14	4695	0.24	700	First
MD6092	5.440	25153	0.10	4624	1.76	300	Second
				actual loss(%)	**0.11**	**1500**	First
					0.35	**1500**	Second

Stability test of DMS CRMs

- **Stability of low μmol/mol DMS** standard gas was evaluated by comparing with newly prepared μmol/mol CRM.
- The old CRMs and new CRM gave the same FID response factors with **difference of 0.2 %.**

Analytical Conditions

- Column : HP-1, 30 m x 0.53 mm,

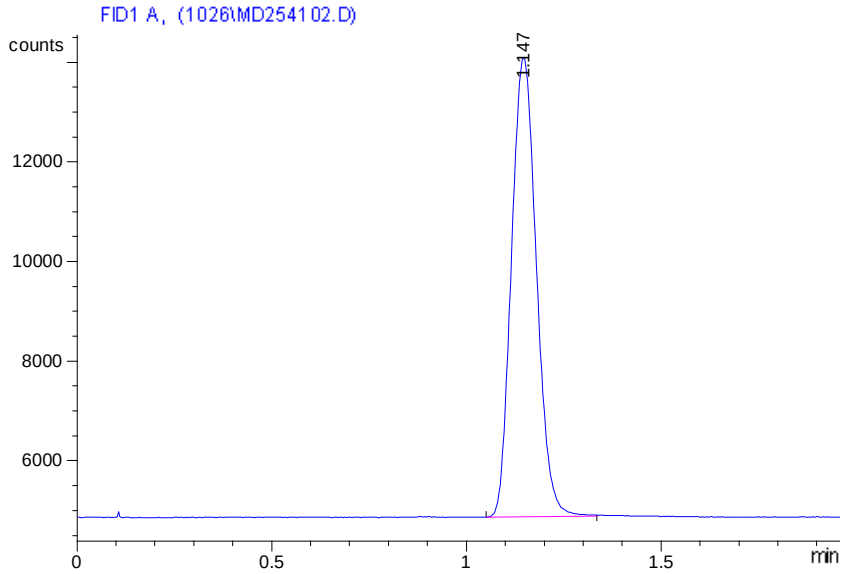
  Carrier gas : 5 mL/min

- Injection : Sample Inlet Temp. 100 ℃,

  Sample loop 1.0 mL, Sample flow 200 mL/min, Sample valve Temp. : 100 ℃

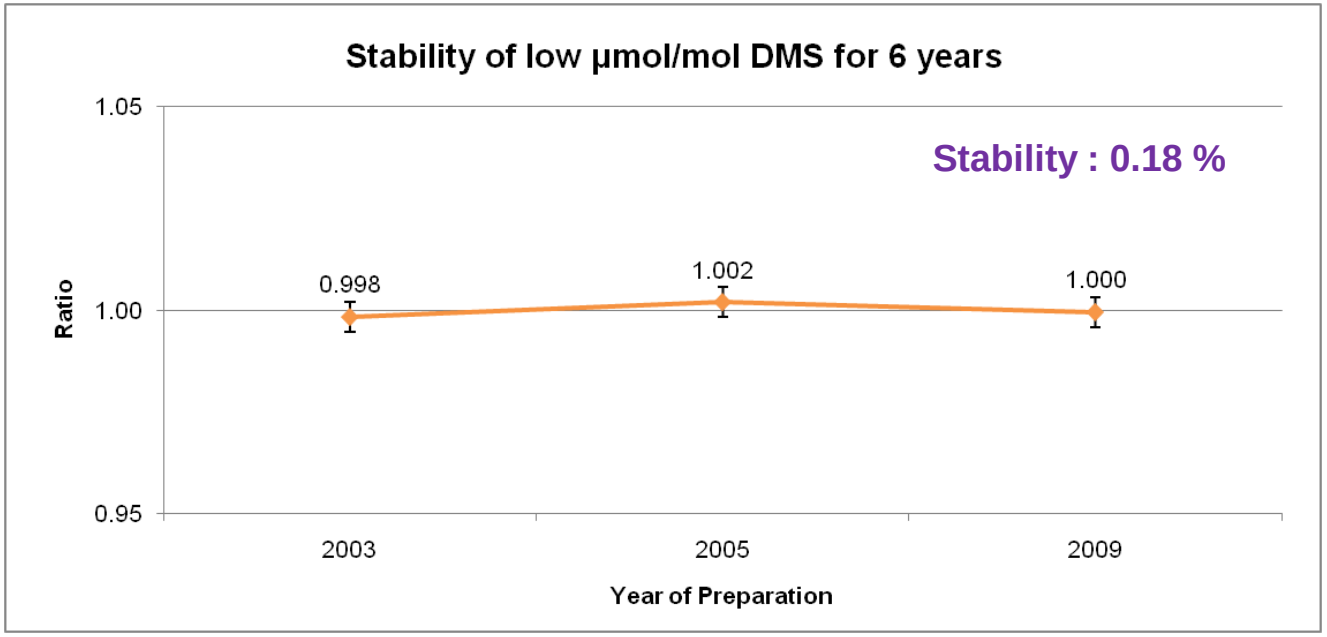
- GC oven Temp. 120℃ (10 min)

- Detector : FID, Temp. 250 ℃



Analysis Chromatogram of DMS

Stability of low µmol/mol DMS for 6 years



Cylinder No.	Conc. of preparation (µmol/mol)	Means (± S.D)	RSD (%)	Response factor	Difference (%)	Date of preparation
MD2541	12.612	42110	0.17	3338.884	0.04	091021
MD2558	11.542	38631	0.25	3346.978	-0.20	050805
MD6097	20.453	68211	0.07	3335.029	0.16	030220
					RSD (%)	0.18

Development and preparation of DMS CRM

- Preparation of dimethyl sulfide CRM by gravimetry (ISO 6142)
- **Preparation reproducibility** was checked by preparation four DMS CRMs : **< 0.36 %**
- **Six years stability** of the CRMs had been checked by comparing newly prepared CRM with old CRMs : **< 0.18 %**

Uncertainty evaluation for preparation of low μmol/mol DMS CRM : Modeling Equation

Modeling Equation

$$C_{DMS} = \frac{n_{DMS}}{(n_{DMS}+n_{N2})} \times 10^6 \times f_{purity} \times f_{Ads} \times f_{\mathrm{Re}} \times f_S$$

Where,

C_{DMS} : Concentration of DMS (μmole/mole)

n_{DMS} : Mole of DMS in CRM (mole),

$n_{DMS}=m_{DMS}/M_{DMS}$

m_{DMS} : Amount of liquid DMS reagent in CRM (g)

M_{DMS} : Molecular weight of DMS (g/mole)

n_{N2} : Mole of N2 in CRM(mole),

$n_{N2}=m_{N2}/M_{N2}$

m_{N2} : Amount of N2 gas in CRM (g)

M_{N2} : Molecular weight of N2 (g/mole)

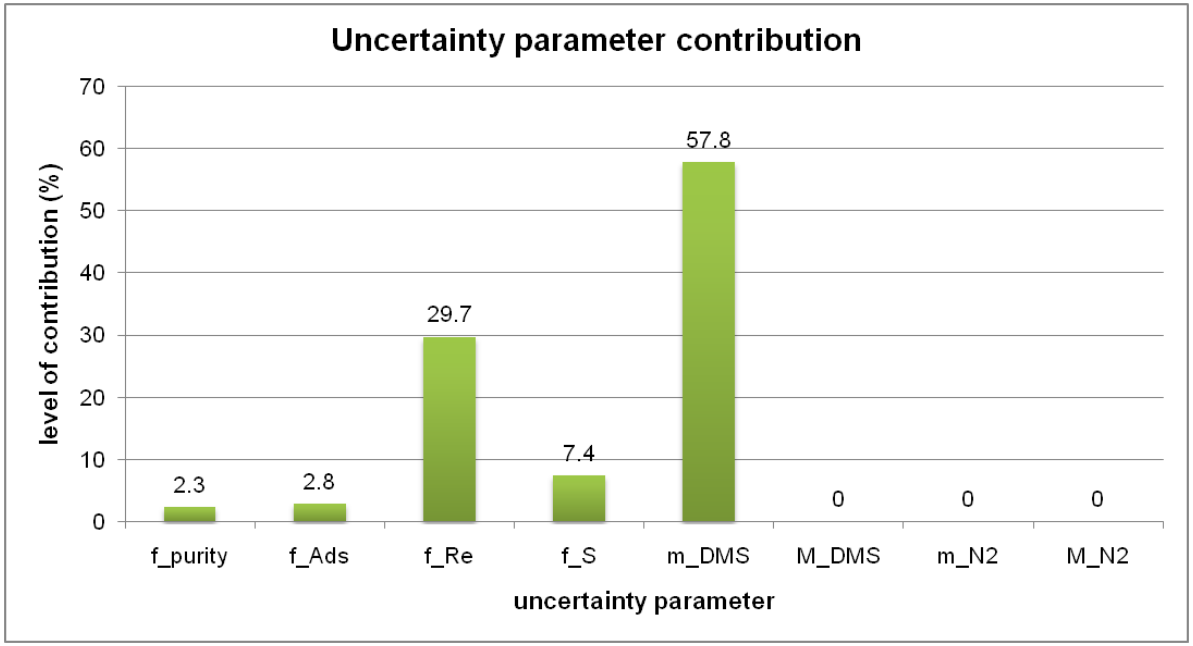
f_{purity} : Factor for purity of liquid DMS reagent

f_{Ads} :: Factor for adsorption loss of DMS in cylinder

f_{Re} : Factor for Preparation reproducibility of DMS CRM

f_S : Factor for stability of DMS in cylinder

Uncertainty evaluation for preparation of low μmol/mol DMS CRM : Uncertainty parameter contribution



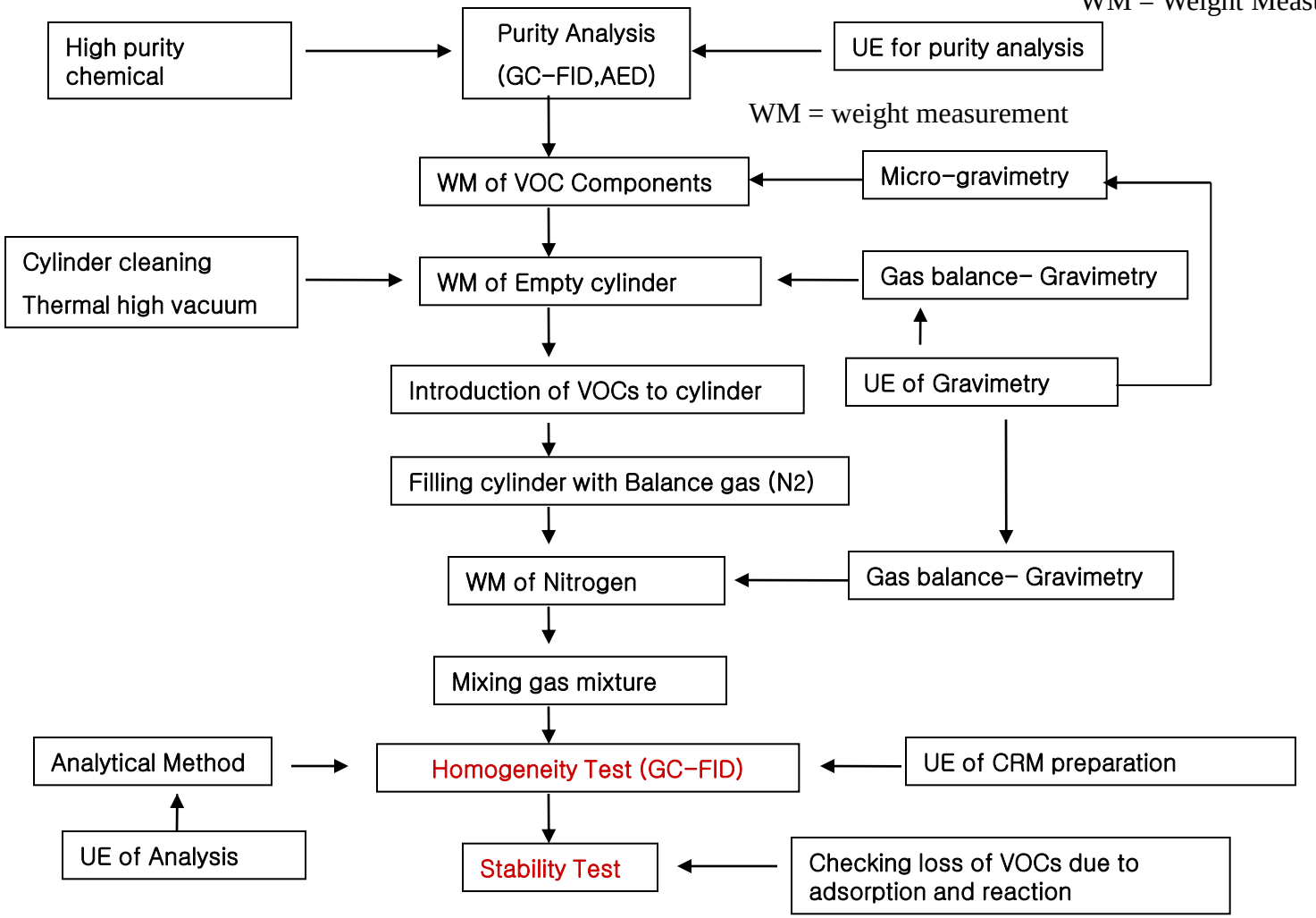
Concentration of DMS : 12.612 μmol/mol
Relative Expanded uncertainty : 1.3 %

	uncertainty parameter	level of contribution (%)
f_purity	Factor for purity of liquid DMS reagent	2.3
f_Ads	Factor for adsorption loss of DMS in cylinder	2.8
f_Re	Factor for reproducability for manufacture of DMS CRM	**29.7**
f_S	Factor for stability of DMS in cylinder	7.4
m_DMS	Amount of liquid DMS reagent in CRM	**57.8**

Establishing KRISS standards for acetonitrile

Preparation Scheme of MeCN CRM

UE = Uncertainty Evaluation
WM = Weight Measurement



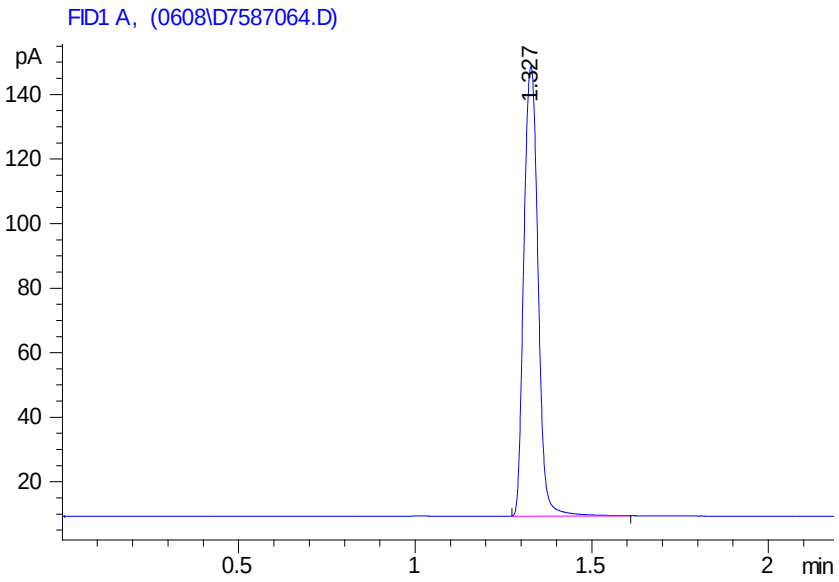
Preparation reproducibility test of CH_3CN CRMs

Preparation reproducibility of CH_3CN gas standards was **checked by GC-FID**

Analytical Conditions

- Column : Carrier gas : 6 mL/min,

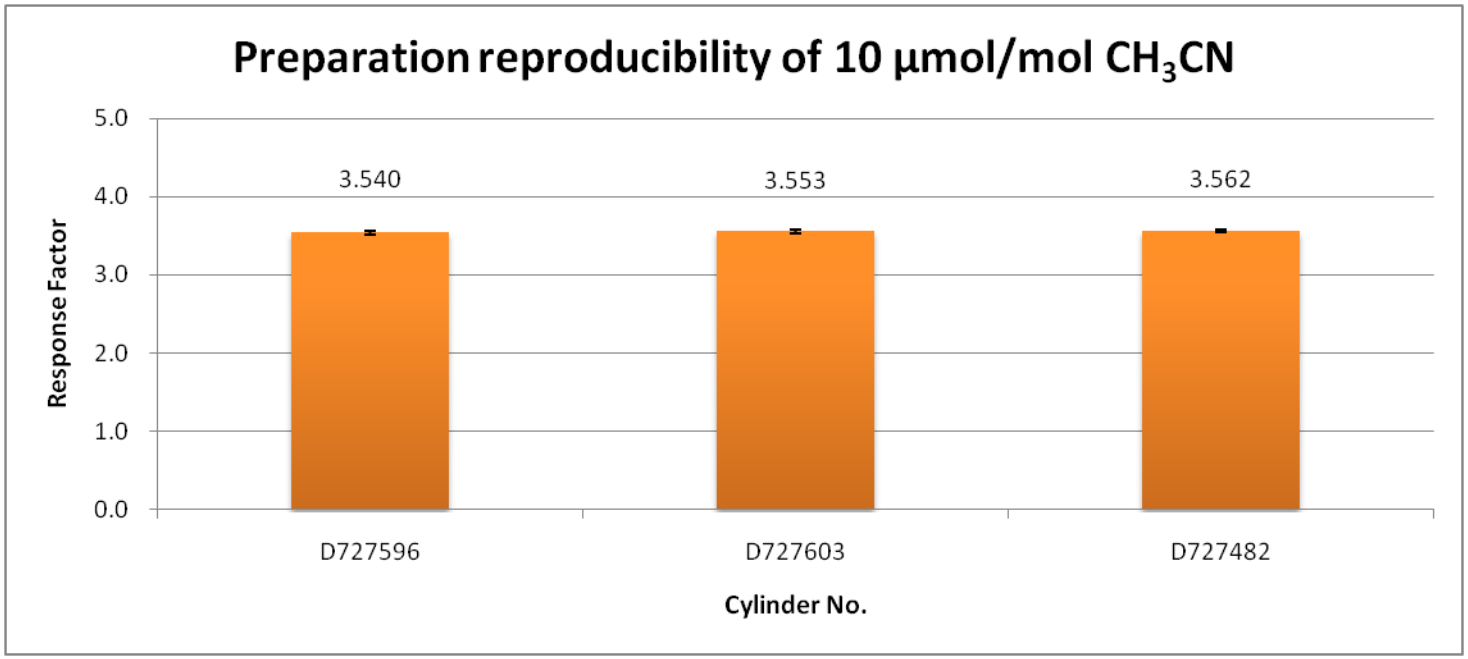
  CP-SIL 5CB, 30 m x 0.53 mm x 5 μm,
- Injection : Split ratio 2 : 1, Sample loop 1.0 mL, Sample flow : 100 mL/min
- GC oven Temp. : 100 ℃ (2.2min)
- Detector : FID, Temp. 250 ℃
- Sample valve temp. : 100 ℃



Analysis Chromatogram of CH_3CN

Preparation reproducibility of low 10 µmol/mol CH_3CN

Preparation reproducibility : 0.31 %



Cylinder No.	Conc. of preparation (µmol/mol)	Means (± S.D)	RSD (%)	Response factor	Difference (%)	Date of preparation
D727596	10.052	35.6	0.49	3.540	0.33	100614
D727603	10.051	35.7	0.06	3.553	-0.04	
D727482	10.049	35.8	0.10	3.562	-0.29	
					RSD(%)	**0.31**

CH_3CN loss test due to reaction with cylinder : immediate reaction, short term stability

Reaction with the inner surface of cylinder and cylinder valve

Very important to counting number of molecules getting out from cylinder: how many molecules are getting out without loss from cylinder?

Adsorption loss test of CH_3CN during the preparation of CRMs

10 µmol/mol CRM :

- Loss of CH_3CN due to adsorption to inner surface of cylinder was evaluated by distributing equal amount of 10 µmole/mole CH_3CN to other empty cylinder..
- The two cylinders were analyzed and compared their FID response factors to check the adsorption loss of CH_3CN.
- **Result : very small loss**, 0.18 % loss at first distribution.

Development and preparation of CH_3CN CRM

- Preparation of acetonitrile CRM by gravimetry (ISO 6142)

- **Preparation reproducibility**

  100 µmol/mol was checked by preparation four CH_3CN CRMs : **< 0.21%**

  10 µmol/mol was checked by preparation three CH_3CN CRMs : **< 0.31%**

  >> 10 µmol/mol CH_3CN CRM manufactured by gravimetric dilution with 100 µmol/mol CH_3CN CRM and N_2 gas.

- **Stability test is in progress.**

Uncertainty evaluation for preparation of 10 μmol/mol CH_3CN CRM : Modeling Equation

Modeling Equation

$$C_{CH3CN} = \frac{\frac{n_{CH3CN} \times m_{CH3CN}}{n_{CH3CN} \times M_{CH3CN} + n_{N2'} \times M_{N2}}}{\frac{m_{CH3CN}}{n_{CH3CN} \times M_{CH3CN} + n_{N2'} \times M_{N2}} + \frac{m_{N2}}{n_{N2} \times M_{N2}}} \times 10^6 \times f_{Ads} \times f_{\mathrm{Re}}$$

Where,

C_{CH3CN} : Concentration of CH_3CN (μmole/mole)

n_{CH3CN} : Mole of CH_3CN in CRM (mole)

m_{CH3CN} : Amount of liquid CH_3CN reagent in CRM (g)

M_{CH3CN} : Molecular weight of CH_3CN (g/mole)

$n_{N2'}$: Mole of N_2 in 100 μmol/mol CRM (mole)

M_{N2} : Molecular weight of N_2 (g/mole)

m_{N2} : Amount of N_2 gas in CRM (g)

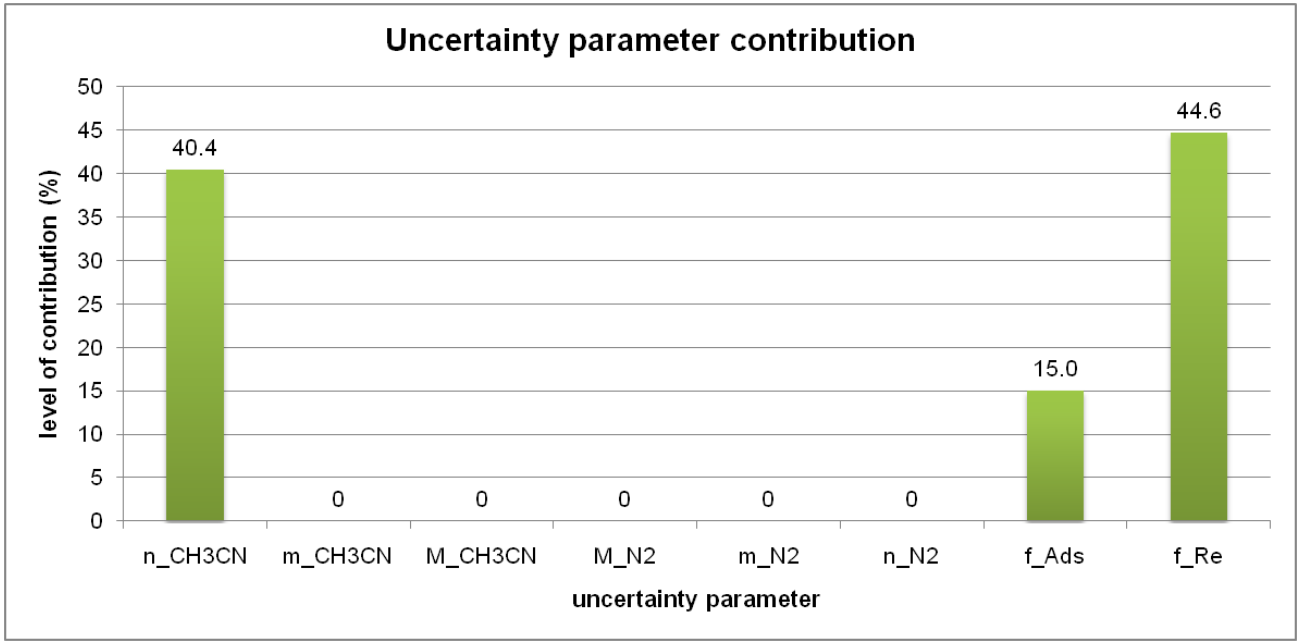
n_{N2} : Mole of N_2 in CRM (mole)

n_{N2} Mole of N_2 in CRM (g)

f_{Ads} :: Factor for adsorption loss of CH_3CN in cylinder

f_{Re} : Factor for Preparation reproducibility of CH_3CN CRM

Uncertainty evaluation for preparation of 10 μmol/mol CH_3CN CRM : Uncertainty parameter contribution



Concentration of CH_3CN : 10.051 μmol/mol
Relative Expanded uncertainty : 0.93 %

uncertainty parameter		level of contribution (%)
n_CH3CN	Mole of CH_3CN in CRM	**40.4**
f_Ads	Factor for adsorption loss of CH_3CN in cylinder	15.0
f_Re	Factor for reproducability for manufacture of CH_3CN CRM	**44.6**

Next Plan:

- Establishing 10 nmol/mol DMS and MeCN standard by dynamic dilution
  - 10,000 times dilution system setup by MFC and Molblock, or Sonic nozzle
- Developing transfer standard of cylinder or other container
  - Certify with the dynamic dilution standard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