Final Report

International Key Comparison CCQM-K94

(10 μmol/mol Dimethyl sulfide in nitrogen)

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ANNEX A

1. Field

Amount of substance.

2. Subject

Comparison of primary gas standards containing 10 μmol/mol dimethyl sulfide in nitrogen.

3. Participants

A total of five laboratories participated in this key comparison. The participants are listed in Table 1.

Table 1. List of participating laboratories

Acronym	Country	Institute
VSL	NL	Dutch Metrology Institute, Netherlands
NPL	UK	National Physical Laboratory, United Kingdom
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, Russia
NIM	CR	National Institute of Metrology, P.R.China
KRISS	KR	Korea Research Institute of Standards and Science, Republic of Korea

4. Organizing body

CCQM Gas Analysis Working Group

5. Introduction

Dimethyl sulfide (DMS) is a typical chemical trace of marine bio-productivity as it is one of the most abundant compounds emitted from biological activities in the ocean. DMS is oxidized in the atmosphere and results in the formation of aerosols. Aerosols play an important role in climate change by altering Earth's radiation budget directly and indirectly. Therefore, DMS is an important compound in monitoring climate change and is monitored by the World Meteorological Organization Global Atmospheric Watch Volatile Organic Compounds (WMO-GAW VOC) program at several monitoring sites [1]. Bacterial activity in sewage waste generates a lot of DMS which is an odorous compound, and causes environmental problems. Therefore, it is currently monitored with other sulphur compounds for controlling and managing odorous air pollution. The atmospheric lifetime of DMS is approximately a day and affected by oxidation with OH and nitrate [2]. Ambient DMS is on average about 340 pmol/mol at marine boundary [3], while DMS in urban areas is about 2 orders of magnitude higher. The WMO requires the analysis of DMS at ambient levels with 20% accuracy and 15% precision in its data quality objectives. Therefore, it is essential that measurement results are accurate and consistent among the assigned values for primary gas mixtures to meet the WMO requirement. The purpose of this comparison is to compare the measurement capability of DMS at approximately 10 μmol/mol and expectation to contribute the establishment of traceability to single measurement scale for DMS between NMIs.

6. Measurement schedule

The schedule for this key comparison was as follows

November 2011	Registration and protocol circulation
April, 2011	Preparation/verification/stability of mixtures by KRISS
May, 2012	Receiving applications for the participation from NMIs
July, 2012	Shipment of cylinders to participating laboratories
December 2012	Measurement of cylinders by participants and Received reports from VNIIM, NPL, VSL
January, 2013	Cylinder received from VNIIM, NPL, VSL
February, 2013	Second verification/stability for returned cylinders from VNIIM, NPL, VSL
March, 2013	Received report from NIM
April, 2013	GAWG Spring Meeting, Interim report
May, 2013	Received NIM cylinder
June, 2013	Finalize 2nd verification with NIM cylinder
November, 2013	GAWG Fall Meeting, Interim report
April, 2014	Draft A report
April, 2015	Draft B report

7. Measurement standards

A total of 8 primary standard gas mixtures (PSMs), DMS in nitrogen with a nominal amount-of-substance fraction of about 10 μmol/mol, was prepared gravimetrically through a two-step dilution process and verified with GC/FID (gas chromatography/flame ionization detector). Before the gravimetric preparation, a DMS solution used was analyzed to check its impurity. The amount-of-substance fractions determined by the gravimetric preparation were adopted as key comparison reference values (KCRVs). The PSMs were compared against a reference gas mixture (about 10 μmol/mol DMS in nitrogen) for their verification. After the sample cylinders were returned, KRISS reanalyzed them to assure that DMS in the cylinders remained stable throughout the comparison.

Table 2. Composition and its nominal amount of substance fraction of standard gas mixtures

Component	Nominal value/ μmol/mol
Dimethyl sulfide	10
Nitrogen	balance

8. Measurement protocol

KRISS prepared primary standard gas mixtures (PSMs) of DMS in nitrogen in 6L cylinders using the gravimetric method of ISO 6142 [4]. Participating laboratories were requested to specify in detail which analytical methods were used and how the evaluation of the measurement uncertainty was performed. Each participating laboratory was responsible for the calibration of its own analytical instrument. For a proper evaluation of the data, it was necessary that the

participants submit a detailed report to KRISS of their preparation techniques used to prepare mixtures used for the calibration of the analytical instrumentation used in this comparison.
After each calibration, the measurements of the gas mixture must be recorded. Each laboratory was required to express the uncertainty on all results submitted, as expanded uncertainty. The evaluation of the measurement uncertainty was required to be performed in accordance with the "Guide to the expression of uncertainty in measurement" (GUM) [5]. The participants were required to provide a detailed description of the uncertainty budget, including method of evaluation (type A or type B).

After the measurements, the participants were responsible for returning their sample cylinder leaving a sufficient amount of gas pressure of at least 30 bar for re-analysis by KRISS. The measurement should be repeated at least three independent times per cylinder as in the following conditions with (at least) three independent calibrations, e.g. calibration (A) → measurement (B) → calibration (A) → measurement (B) → calibration (A) → measurement (B) → calibration (A) (etc.). This was a strict requirement to come to proper statistical analysis of the reported data. One single measurement result was usually obtained from multiple readings (sub measurements), without recalibrations. The standard deviations of the measurements provided information about the performance of the measurement system.

9. Preparation of measurement standards

Seven gas mixture cylinders were prepared gravimetrically and verified with a GC/FID system against a reference cylinder prepared in 2012. Four of the cylinders were prepared in 2012 and the other three cylinders were prepared in 2010. The amount of substance fractions based on gravimetric method and purity analysis were determined and then used as reference values. Thus, each cylinder had its own reference value. The purity of dimethyl sulfide (Sigma-Aldrich Corp., MO, USA) was checked by several measurement techniques. GC-FID was used for the impurity analysis of hydrocarbons which yielded 4063 μmol/mol with an uncertainty of 345 μmol/mol ($k = 2$). GC-Sulfur Chemiluminescence Detector (SCD) was used to analyze sulfur impurities which yielded 1 μmol/mol with an uncertainty of 0.58 μmol/mol ($k = 2$). Karl-Fisher method was used to analyze moisture which yielded 1417 μmol/mol with an uncertainty of 7.3 μmol/mol ($k = 2$). Therefore, the purity of dimethyl sulfide was assigned as 99.45 cmol/mol with its relative expanded uncertainty of 0.069% ($k = 2$). The gravimetric preparation expanded uncertainties of the gas mixture cylinders were estimated at about 0.1% ($k = 2$).

10. Measurement equation

To assign the amount of substance fraction to a gravimetrically prepared cylinder, the following three groups of uncertainty components have been considered [6]:

1. gravimetric preparation (weighing process) ($x_{i,grav}$)
2. purity of the parent gases ($x_{i,purity}$)
3. stability of the gas mixture ($x_{i,stab}$)

The fractional amount of substance, $x_{i,prep}$, of a target component in mixture i, can be expressed as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} \qquad (2)$$

where $x_{i,grav}$ is the fractional amount of substance of a target component in mixture (i) gravimetrically prepared, $\Delta x_{i,purity}$ is the correction based on purity analysis, and $\Delta x_{i,stab}$ is the correction due to stability. The uncertainty of the fractional amount of substance can be estimated as

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 + u_{i,stab}^2 \qquad (3)$$

where $u_{i,prep}$ is the uncertainty from gravimetric preparation, $u_{i,grav}$ is the uncertainty from weighing process, $u_{i,purity}$ is the uncertainty from purity analysis, and $u_{i,stab}$ is the uncertainty due to stability. The long-term stability study data have shown that there are decreasing trends in the analytically determined values, even though those values agree with their gravimetric preparation values within the analytical uncertainties. Therefore, the prepared values were not corrected due to stability (i.e., $\Delta x_{i,stab} = 0$), but the maximum deviation (about 0.4%) from the gravimetric preparation value based on the stability data was estimated as the stability uncertainty (0.23%, k = 1, assumed as a rectangular distribution). Finally, the standard uncertainty of the preparation was estimated at about 0.24% (k = 1).

The gravimetrically prepared mixtures have been verified by comparing the gravimetric value with its analytical measurement value as shown in the following conditions.

$$\left|x_{i,prep} - x_{i,ver}\right| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} \qquad (4)$$

where $x_{i,ver}$ and $u_{i,ver}$ are the measurement result from verification and its standard uncertainty, respectively. Assuming that both preparation and verification are unbiased, the uncertainty associated with the verification relies on the measurement capability and experimental design. Returning to the definition on the reference value, the reference value of mixture i in a key comparison can be expressed as

$$x_{i,ref} = \langle x_{i,ref} \rangle + \delta x_{i,ref} \qquad (5)$$

where $x_{i,ref} = x_{i,prep} + \Delta x_{i,ver}$ (6)

where $\Delta x_{i,ver}$ is the correction result from the verification.

Thus, equation (6) can be expressed as

$$x_{i,ref} = \langle x_{i,prep} \rangle + \langle \Delta x_{i,ver} \rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver} \qquad (7)$$

where $\delta x_{i,prep}$ and $\delta\Delta x_{i,ver}$ are the error for the gravimetric preparation and verification, respectively. The verification experiments demonstrated that the verification values agreed with the preparation values within the preparation uncertainties. Thus, the expectation of the correction, $\langle \Delta x_{i,ver} \rangle$, was set as zero, which means that there is no correction due to the verification. Therefore, the reference value of mixture *i* is expressed as

$$x_{i,ref} = \langle x_{i,prep} \rangle + \delta x_{i,prep} + \delta\Delta x_{i,ver} \tag{8}$$

The reference value in equation (8) becomes the preparation value. The standard uncertainty of a reference value is expressed as

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2 \tag{9}$$

As far as the verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards, the reference value in equation (8) becomes the preparation value. As a result, the standard uncertainty of the reference value is expressed as

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2 \tag{10}$$

To validate the sample gas mixtures prepared by KRISS, each cylinder was analyzed against the reference cylinder before and after the comparison work. The reference cylinder, itself, was not compared against another new cylinder that was freshly prepared during the 2nd verification. However, KRISS has produced DMS (10 μmol/mol in nitrogen) since 2005. All cylinders, which were prepared from 2005 to 2012, were checked against a PRM that was newly prepared in 2012. Results showed that all cylinders were consistent within their associated preparation uncertainties (gravimetric and stability uncertainty). As shown in Figure 1, the normalized sensitivities of the cylinders were compared to the reference cylinder prepared in 2012. The maximum difference between the two periods was estimated as 0.36% which was less than their stability uncertainty (0.46%, k = 2). Therefore, the normalized sensitivities of all cylinders agreed within their preparation uncertainties (0.47%, *k* = 2), indicating that the sample cylinders are consistent with their preparation values within the preparation uncertainties. In this comparison, the standard uncertainty of verification (*k* = 1) was set as 0.077 μmol/mol (0.73% as relative standard uncertainty) based on the uncertainty of analytical measurements (0.17%, *k* = 1) and the possible maximum deviation (0.71%, k = 1) from the preparation values (i.e, the deviation was estimated as the maximum of $\left| x_{i,prep} - (x_{i,anal} \pm 2 \times u_{i,anal}) \right|$). As a result, the standard uncertainty of reference values was estimated as 0.080 μmol/mol (0.78% as relative standard uncertainty).

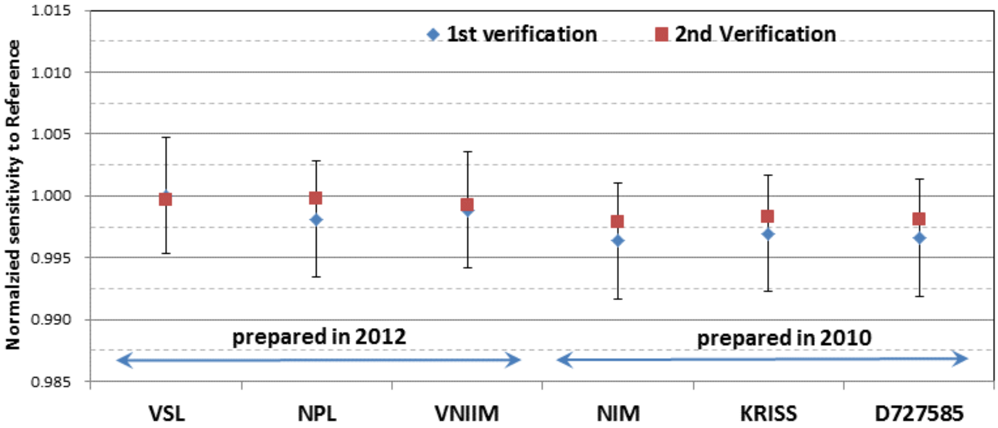

Figure 1. Results of verification measurements before and after the comparison (the error bars for the expanded uncertainties of preparation)

11. Measurement method

The details on the measurement methods used by the participants are described in the individual participant reports. A summary of the calibration method, date of measurement, and the way in which metrological traceability is established is given in Table 3.

Table 3. Summary of the measurement methods of the participants

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
VSL	D929219	Oct. 2012~ Nov. 2012	Own standards	multiple point calibration	GC-SCD
NPL	D929214	Sep. 2012	Own standards	one point calibration	GC-FID GC-MSD
VNIIM	D929234	Sep. 2012	Own standards	one point calibration	GC-FID
NIM	D727499	Mar. 2013	Own standards	one point calibration	GC-FID
KRISS	D731952	Oct. 2012	Own standards	one point calibration	GC-FID

12. Degree of equivalence (DoE)

A degree of equivalence for each participating laboratory was calculated as

$$D_i = x_{i,lab} - x_{i,KCRV} \qquad (11)$$

where $x_{i,lab}$ and $x_{i,KCRV}$ are the value reported by each participant and the key comparison reference value (KCRV), respectively. In this comparison, the preparation value is set to the KCRV value as expressed in the following.

$$x_{i,KCRV} = x_{i,ref} \qquad (12)$$

Thus, the uncertainty of the KCRV values can be expressed as

$$u_{i,KCRV} = u_{i,ref} \tag{13}$$

Therefore, the standard uncertainty of D_i can be expressed as

$$u^2(D_i) = u_{i,lab}^2 + u_{i,KCRV}^2 \tag{14}$$

where $u_{i,lab}$ and $u_{i,KCRV}$ are the standard uncertainty of $x_{i,lab}$ and $x_{i,KCRV}$, respectively

13. Results and discussion

A complete set of results from each participant is described in annex A of this report. The results of the key comparison are summarized in Table 4.

Table 4. Summary of the results (μmol/mol) for CCQM-K94

Laboratory	Cylinder	$x_{i,ref}$	$u_{i,prep}$	$u_{i,ver}$	$u_{i,ref}$	$x_{i,lab}$	$u_{i,lab}$	D_i	$U(D_i)$ $k = 2$
VSL	D929219	10.289	0.025	0.077	0.080	10.44	0.04	0.15	0.18
NPL	D929214	10.311	0.025	0.077	0.080	10.359	0.052	0.048	0.192
VNIIM	D929234	10.334	0.025	0.077	0.080	10.54	0.03	0.21	0.17
NIM	D727499	10.457	0.025	0.077	0.080	10.253	0.068	-0.204	0.211
KRISS	D731952	10.282	0.025	0.077	0.080	10.252	0.030	-0.030	0.172

The degrees of equivalence are shown in Figure 2 (as in relative deviation) and Figure 3 (as in absolute deviation). The results from the participants, except for a participant, are consistent with the KCRV values as the deviations from the KCRV values are within the associated uncertainties.

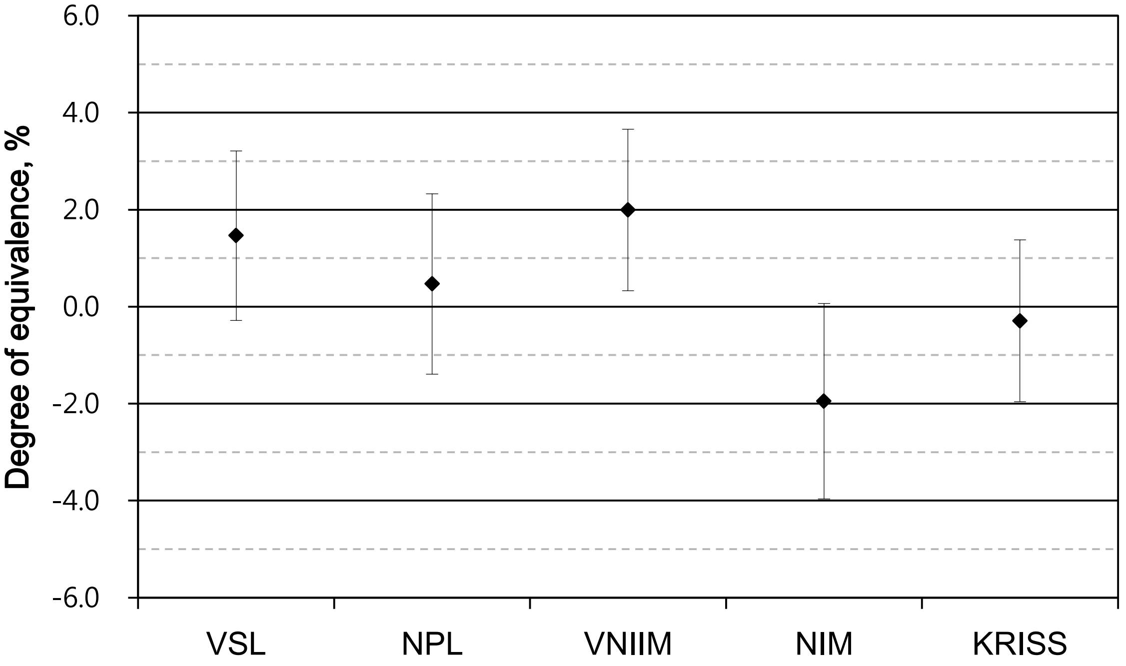

Figure 2. Relative deviations from the reference values for CCQM-K94 ($k = 2$)

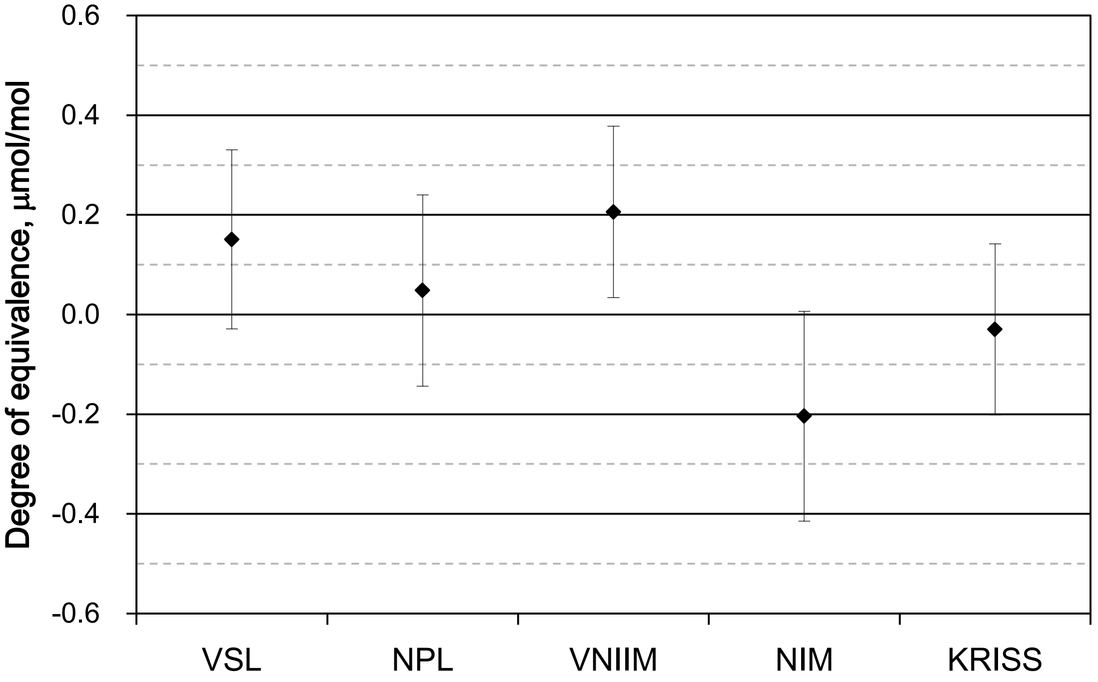

Figure 3. Degrees of equivalence for CCQM-K94 ($k = 2$)

14. Conclusion

In this key comparison, the results of four participants (VSL, NPL, NIM, and KRISS) among the five are consistent with their KCRV within the associated uncertainties. This key comparison compares the measurement capability of DMS at a level of 10 µmol/mol. Therefore, it is possible for this key comparison to offer a good traceability and a harmonization of DMS measurements.

15. How far the light shines

This key comparison supports CMC claims for the following sulphur-containing compounds in a balance gas of nitrogen or methane in the range 0.5 - 100 μmol/mol:

Carbonyl sulfide
Carbon disulfide
Dimethyl sulfide
Ethyl methyl sulfide
Diethyl sulfide
Methanethiol
Ethanethiol
2-propanethiol
1-propanethiol
2-methyl-2-propanethiol
Tetrahydrothiophene

16. References

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ANNEX A

International Key Comparison Report
On CCQM-K94 of DMS in N_2

Lab Information

Lab Code: 58
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Tel.: +86-10-84252300 Fax.: +86-10-84252306
Date of Receiving the Comparison Cylinder: Nov 2012
Cylinder No.: D727499
Initial inner pressure of the comparison cylinder when received: 8MPa
NOMINAL composition : $5\times10^{-6} - 20\times10^{-6}$mol/mol

Measurement	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	13/03/13	10.233	0.16%	15
No. 2	15/03/13	10.287	0.23%	9
No. 3	17/03/13	10.281	0.10%	12
No. 4	18/03/13	10.268	0.10%	11
No. 5	21/03/13	10.235	0.17%	7
No. 6	23/03/13	10.241	0.10%	12
No. 7	23/03/13	10.228	0.11%	12

Note: Please copy this table as many times as needed for reporting additional measurements

Result:

Gas mixture	Result (µmol/mol)	standard uncertainty (µmol/mol)	Assigned expanded uncertainty (µmol/mol)	Coverage factor(*)
DMS	10.253	0.068	0.136	2

Note: The coverage factor shall be based on approximately 95% confidence.

Details of the measurement method used:

Reference Method:

A GC-FID (Agilent 7890, USA), equipped with a capillary column of HP-5 (30m×0.32mm×0.25μm), was adopted to measure DMS in N_2. The parameters of GC-FID used were set as follow: Oven=190℃, Detector=250℃, Injection Port=160℃, Split ratio=20:1, sample loop=1mL. Carrier gas (N_2) flow rate=3.5mL/min, H_2 flow rate=30mL/min, air flow rate=400mL/min. The data was collected by using the Agilent workstation. RSD of repeatability was estimated as 0.10%~0.20% based on 7 continuous injection of 10μmol/mol gas mixtures.

The analysis of both standards and sample was done at room temperature and atmospheric pressure. In order to cancel the drift effect of GC-FID on the measurement result, A-B-A mode was used. The standard and sample were injected alternatively.

Here single point calibration method was taken to obtain the DMS concentration in the sample.

Calibration Standards:

Our own calibration standards of DMS/N_2 were prepared by gravimetric method according to ISO 6142-2001. In order to obtain the PRM (Primary Reference Materials) of 10μmol/mol DMS/N_2, the pure DMS was 2-step diluted by N_2(BIP®, Air Product).

Table 3. The purity data of DMS

Component	content (μmol/mol)	Standard Uncertainty (μmol/mol)	Method
CS_2	514	58	GC-PFPD
CH_3SH	464	60	GC-FID
CH_3CH_2SH	296	60	GC-FID
C_6H_6	188	38	GC-FID
$C_6H_5CH_3$	177	35	GC-FID
DMDS	206	104	GC-FID
H_2O	1390	400	FTIR
Other HCs(as C_6H_6)	280	56	GC-FID
DMS(P)	0.996484	0.000433	

In first dilution step, the pure DMS agent was transferred to a vacuum cylinder by syringe injection. Generally, the mass of injected DMS was around 0.8g by using top-pan balance (Mettler Toledo, capacity 260g, resolution 10μg), and the mass of N_2 was around 450g by using comparator (Mettler Toledo, capacity 10.1kg, resolution 1mg). The step 1 gas mixtures of DMS/N_2 was around 800μmol/mol. In second dilution step, around 5.5g of step 1 mixtures was diluted by 480g N_2 to obtain DMS/N_2 of around 10μmol/mol. The standard relative uncertainty of 10μmol/mol DMS/N_2 was 0.28%, which is estimated based on only gravimetric data. 4 bottles of 10μmol/mol DMS/N_2 were verified against each other by GC-FID, and results showed that they agreed within 0.30%. Another uncertainty source was due to stability of the gas mixtures over 3 month, which contribute standard uncertainty of 0.58% relative.

DMS/N_2 of 4000μmol/mol was checked by using GC-MS, GC-PFPD, GC-FID, and FTIR, in order to obtain the purity data of pure DMS agent. Purity data was showed in Table 3.

Finally, the mol fraction of our own standard gas mixtures (c_{std}) as well as its standard relative uncertainty was listed in Table 4.

Table 4. PRM list of 10μmol/mol DMS/N_2

Cyl. No.	DMS Conc. (μmol/mol)	Exp. Uncertainty(μmol/ mol)	Exp. Relative Uncerttainty	Remarks
L120702100	9.597	0.125	1.30%	DMS/N_2
L120702023	9.935	0.129	1.30%	DMS/N_2
L120702037	10.248	0.133	1.30%	DMS/N_2

Instrument Calibration:

GC-FID response is linear to the DMS content in the mixtures. The single point calibration was used to measure the sample, and the following mathematical model (1) was adopted:

$$c_{spl} = c_{std} \cdot R \tag{1}$$

symbol	*unit*	*definition*
c_{spl}	μmol/mol	Concentration of DMS in comparison sample
c_{std}	μmol/mol	Concentration of DMS in our own standard
R	1	Ratio of sample response to standard response on FID

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument (automatic, high pressure, mass-flow controller, dilution etc).:

When package box including comparison cylinder arrived at our lab, it was in good state and then stabilized at room temperature for 2 weeks. An inner pressure of about 8 MPa was read before we started the measurement. The pressure decrease to around 1.0 MPa after the measurement was finished.

The gas mixtures from cylinder (both standard and sample) were reduced by regulator and then connected to the inlets of a multi-position valve, via 1/8” Teflon tube. The gas from outlet of the multi-position valve was introduced into the 6-port valve of GC-FID via1/8” Teflon tube. The 6-port valve was driven by compressed air, and the sample loop size was 1.0mL. Sample gas flow rate was controlled at 80mL/min by an upstream mass flow controller.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipments, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

1. Estimation of the uncertainty from gravimetric method
In first dilution step, around 0.8g pure DMS agent was injected and then 450g high purity N_2(BIP) was added into a vacuum cylinder, in order to obtain around 800μmol/mol DMS/N_2. The mass of injected DMS was measured by weighing the syringe before and after injection. In order to cancel the buoyancy effect, a “tare” syringe was used. However, the buoyancy effect due the syringe plunger should be corrected when it was pulled out to take in DMS agent. In our preparation, the volume of this pulled “plunger” was 0.52mL, which could contribute buoyancy of 0.62mg with an estimated standard uncertainty of 0.12mg. Considering the uncertainty due to repeatability of balance (0.17mg), the combined standard uncertainty of injected DMS was estimated as 0.21mg, which was 0.26% relative.

While the balance gas of N_2 was weighed by using comparator (Mettler Toledo) and substitution method. The standard uncertainty of added N_2 was estimated as 0.020g in case of 450g, which could be negligible.

In second dilution step, around 5.5g of DMS/N_2 and 480g N_2 was blended into a vacuum cylinder, of which the standard uncertainty were 6mg and 20mg, respectively.

2. Estimation of the uncertainty due to the purity of parent gases
The purity of pure DMS agent as well as its uncertainty was estimated as 0.996484 ± 0.000433 (k=1) in Table 3. While the purity of BIP N_2 was checked as 5.5N, and its uncertainty contribution could be negligible in this measurement.

3. Standard uncertainty over 3 month was 0.58% relative.

Detailed uncertainty budget:

Uncertainty table: DMS in N_2

Uncertainty source X_I	Estimate x_I	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$ (*u*mol/mol)
c_{std}	10.248μmol/mol	B	Norm.	0.067μmol/mol	1.00051	0.06703
R	1.00051	A	Norm.	0.000909	10.248μmol/mol	0.00932
c_{spl}	10.253μmol/mol	A	Norm	0.068μmol/mol		

Result:
DMS content was 10.253μmol/mol with expanded uncertainty of 0.136μmol/mol (k=2).

VNIIM Report CCQM-K94: Dimethylsulfide in nitrogen

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Cylinder number: D929234

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
DMS	20/09/12	10.553	0.10	4

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
DMS	21/09/12	10.484	0.18	4

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
DMS	22/09/12	10.569	0.07	3

Result

Component	**Result (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**	**Coverage factor**
DMS	**10.54**	**0.06**	**2**

Details of the measurement method used:

Reference Method:

Gas chromatography with flame ionisation detection.
Instrument: Gas Chromatograph «Crystal 5000.2» (Chromatec);
Capillary column: Agilent J&W capillary GC column (DB-1; 30 m x 0.320 mm, 5.00 µm);
Carrier gas: helium 100 cm/sec;
Oven conditions: 70 ºC for 2 min;
Sample loop: 1 ml;
Split:1:2:
Data collection: by "Chromatec Analytic 2.6" software.

Calibration Standards:

Calibration was performed using Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method".
Characteristics of pure substances used for preparation of the calibration gas mixtures are shown in the table 1.

Table 1 – Description of pure substances

Substance	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
Dimethylsulfide	997568	32
Nitrogen	999998,63	0,04

Preparation from pure substances was carried out in 2 stages. On the first stage 3 DMS/N_2 gas mixtures were prepared on the concentration level of 200 µmol/mol. Then these mixtures were diluted to target concentration level of 10 µmol/mol.
The concentrations and standard uncertainties of dimethylsulfide in these mixtures are shown below.

Cylinder number	Component	Concentration (µmol/mol)	Standard uncertainty due to weighing and purity (µmol/mol)
D249364	DMS	10.5225	0.0021
D249389	DMS	10.5680	0.0023
D249413	DMS	10.5309	0.0021

All standard gas mixtures were prepared in aluminum cylinders (Luxfer) with Aculife IV + Aculife III treatment.

Instrument Calibration:

Single point calibration method was used to determine dimethylsulfide concentration in the gas mixture to be investigated. Measurement sequence was in the order: standard-sample-standard-sample-standard (etc.). Temperature and pressure were not corrected during the calibration procedure.

Sample Handling:

Prior to measurements cylinders were stabilized to room temperature. Each cylinder was equipped with a stainless steel pressure regulator that had been adequately purged before the sample was transferred to the sample loop. The GC lines and sampling valves were covered with Sulfinert coating (Restek). Automatic dosing to the sample loop was applied.

Uncertainty:

a) Uncertainty related to calibration standards, which takes into consideration uncertainty of the balance, weights and purity analysis of the parent gases, was calculated with the program developed in VNIIM on the base of ISO 6142:2001 “Gas analysis - Preparation of calibration gas mixtures - Gravimetric method”;
b) Uncertainty related to the analysis - Scatter of the results in 3 days
Estimate of scatter of the results in 3 days (S_x) was calculated according to the formula

$$S_x = \sqrt{S_R^2 + S_r^2 \frac{n-1}{n}}$$

$$S_R = \frac{\max \Delta x_i}{2\sqrt{3}}$$

$$S_r = \max \sqrt{\frac{\sum (x_{ij} - x_i)^2}{n(n-1)}}$$

where n – number of the results during one day;
x_{ij} – one of the single results in one of the days;
x_i – the average result in one day.

c) Uncertainty due to possible adsorption loss in preparation of calibration gas mixtures was estimated by filling an evacuated cylinder with calibration gas mixture. Adsorption loss less than 0,01 µmol/mol (0,1 %) could not be checked reliably by analysis. Therefore 0,01 µmol/mol was taken as an uncertainty due to possible adsorption.

Detailed uncertainty budget:

Uncertainty source X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$
Calibration standards (weighing + purity)	10.5680	A, B	Normal	0.0023	1.0024	0.0023
Scatter of the results in 3 days	10.543	A	Normal	0.0258	1	0.0258
Factor related to possible adsorption loss in preparation of standard	1	B	Normal	0.01	1	0.01

Combined standard uncertainty	0,028
Expanded uncertainty k=2	0.06 µmol/mol

CCQM K-94 (Dimethyl Sulfide in Nitrogen)
NPL Report

Lucy Culleton, Andrew Brown, Chris Brookes

The quantification of the amount fraction of dimethyl sulfide (DMS) in cylinder D929214 was performed at NPL during September 2012. The mixture was provided by the coordinating laboratory, KRISS.

Overview

- **Step 1**: A set of NPL Primary Standard Mixtures (PSMs) of varying DMS amount fractions were gravimetrically prepared and validated using GC-FID analysis.
- **Step 2:** The amount fraction of DMS in the unknown mixture was estimated using an NPL PSM and GC-FID analysis.
- **Step 3**: An NPL PSM of nominally identical concentration to the unknown was prepared and used to more accurately quantify the DMS amount fraction, using a more comprehensive CG-FID and GC-MS analytical methodology.
- **Step 4**: The results from the repeated analyses were averaged and the uncertainty estimated via combining the gravimetric uncertainty in the PSM, the analytical repeatability and the uncertainty in the stability of the PSM.

Analytical Methodology

GC System

GC analysis was carried out using an Agilent Technologies 7890A GC system with An Agilent 5975C MSD and an FID. Table 1 gives a description of the GC system and method parameters.

Table 3: GC System parameters

Column: Varian CP7539 50m x 530µm x 50µm	
Detectors: FID MSD	
Method Parameter:	Setting:
Run time	32.5 min
Oven temperature	60 deg C isothermal
Carrier gas	Helium
Detector temperature (FID)	250 deg C isothermal
MSD mode	Selective ion

Calibration Standards

Two hierarchies of gravimetrically prepared primary standard mixtures (PSMs) were used for the analysis, shown below in table 2.

Nominal amount fraction of DMS (µmol/mol)	Hierarchy #1	Hierarchy #2
250	NG386	NG390
10	NG388	NG393

Table 4: Hierarchy of NPL PSMs

All mixtures were made in BOC 10 litre cylinders with Spectraseal passivation. The two hierarchies were validated against each other using GC-FID analysis. Table 3 provides details of the composition of NG393, which was used to directly analyse the KRISS mixture.

NG 393 Component	Amount Fraction (µmol/mol)	Relative Gravimetric Uncertainty (%)
Dimethyl Sulfide	10.24	0.04

Table 5: Composition of NG 393, made in a balance of Nitrogen

The stated amount fractions were calculated from the gravimetric preparation process. The standard uncertainties were calculated using the NPL Software GRAVCALC2 (following ISO 6142) via the combination of uncertainties from three sources: gravimetry, relative molar masses and purity analysis.

Quantification of Impurities

Purity analysis was performed on a 250 µmol/mol DMS in nitrogen mixture (NG390). Multiple CGs were used to identify and quantify any impurities that were present in the DMS used in the preparation of the NPL PSM. The nitrogen balance gas was also purity analysed. The purity of the DMS was determined to be approximately 99.86%.

Quantification of the DMS amount fraction in the KRISS mixture

The NPL and KRISS mixtures were connected to a GC using purpose-built minimised dead volume connectors and 1/16th inch silcosteel tubing. Specialised NPL-designed flow restrictors were used to allow a stable sample flow of 20 ml/min to be maintained throughout the analysis. The lines were thoroughly purged, and flow rates were allowed to stabilise before commencing.

The method consisted of ten samplings, alternating between the two cylinders using an automated switching valve. This 32.5 minute method was repeated multiple times in order to obtain a comprehensive data set.

The detector responses were recorded as peak areas, and it was via the comparison of the NPL and KRISS DMS peak areas that the quantification of DMS amount fraction was achieved. A method involving taking a ratio of consecutive peak areas was utilised to minimise the uncertainty associated with detector drift. Equations 1 and 2 show how this was used to calculate the amount fraction of DMS in the KRISS mixture.

$$\left(\frac{A_{1,KRISS}}{A_{1,NPL}}+\frac{A_{2,KRISS}}{A_{2,NPL}}+\cdots+\frac{A_{n,KRISS}}{A_{n,NPL}}\right)n^{-1}=r$$

Equation 1: The average peak area ratio, $\boldsymbol{r}$

Where $A_{KRISS}$is the DMS peak area from the KRISS mixture, $A_{NPL}$is the DMS peak area from the NPL PRM and n is the total number of injections per mixture.

$$x_{NPL}\times r = x_{KRISS}$$

Equation 2: Calculation of unknown amount fraction from the peak area ratio, $\boldsymbol{r}$

Where $x_{NPL}$is the gravimetric amount fraction of DMS in the NPL PRM and x_{KRISS} is the calculated amount fraction of DMS in the KRISS mixture.

Evaluation of uncertainty

The uncertainty calculation takes into account uncertainties arising from three areas: gravimetric preparation of the NPL PSM (which also includes uncertainties associated with impurity analysis and molecular weight uncertainties), the stability of the PSM and the analytical uncertainty. Of these three, the measurement uncertainty has the dominating influence.

Measurement uncertainty

The measurement uncertainty is comprised of three main factors: Repeatability, Detector drift and detector linearity. Due to the analytical methodology whereby a standard of similar amount fraction is used, detector linearity effects have been considered to be negligible. The statistical methods used to process the peak area data act to negate the effects of detector drift, therefore reducing its associated uncertainty. The dominant factor in the measurement uncertainty is therefore the repeatability of the analysis. The uncertainty components are broken down in table 4.

Compound	Relative uncertainty (%)				
	Gravimetric (*k*=1)	PSM Stability (*k*=1)	Analytical (*k*=1)	Total Combined (*k*=1)	Total Combined (*k*=2)
Dimethyl Sulfide	0.04	0.20	0.45	0.49	0.99

Table 6: Breakdown of uncertainties

To calculate the combined uncertainty, the analytical and gravimetric uncertainties were combined as the square root of the sum of squares. The reported uncertainty of the result is based on standard uncertainties multiplied by a coverage factor of *k*=2, providing a level of confidence of approximately 95%.

Final Result

Table 5 provides the results of the NPL analysis of the amount fraction of DMS in the KRISS mixture (D929214).

Compound	Amount Fraction (µmol/mol)	Expanded Uncertainty (*k* = 2)	
		µmol/mol	Relative (%)
Dimethyl Sulfide	10.359	0.103	0.99

Table 7: Final result and expanded uncertainty

Report Form : Dimethylsulfide in nitrogen (CCQM K94)

Lab Code: VSL
Lab Name: Dutch Metrology Institute
Contact point and participants: Jianrong Li, Paul R. Ziel and Adriaan M.H. van der Veen
Email: jli@vsl.nl
Tel.: +31 15 2691500 Fax.: +31 15 2612971
Date of Receiving the Comparison Cylinder: 2012-08-20
Cylinder No.: D929219
Initial inner pressure of the comparison cylinder when received: 94 bar
NOMINAL composition : $5.\ 10^{-6} – 20.\ 10^{-6}$ mol/mol

Measurement	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	09/ 10/ 2012	10.41	0.21	12
No. 2	10/ 10/ 2012	10.36	0.22	9
No. 3	10/ 10/ 2012	10.45	0.22	12
No. 4	21/ 11/ 2012	10.53	0.18	12

Result:

Component	Result (µmol/mol)	standard uncertainty (µmol/mol)	Assigned expanded uncertainty (µmol/mol)	Coverage factor(*)
DMS	10.44	0.04 (0.36 %)	0.08 (0.72%)	2

Note: The coverage factor shall be based on approximately 95% confidence.

Details of the measurement method used:

Reference Method:

The measurements were taken on an Agilent GC model 6890N with model 355 SCD (Dual Plasma Sulfur Chemiluminescence Detectors) detector. A DB-1 column was used with helium as carrier gas.

Calibration standards:

Preparation: Gravimetric method

The DMS was subjected to a purity analysis. The results are given in the table below. The amount–of–substance fraction DMS was calculated by difference. The standard uncertainty associated with the amount–of–substance fraction DMS was obtained by duly propagating the uncertainties associated with the amount–of–substance fractions of the impurities.

Purity analysis:

VSL ME0515 Components	amount–of–substance fraction	Standard uncertainty (%)
Dimethylsulfide	0.998635	0.0220
Methylmercaptane	0.000225	10
Ethylmercaptane	0.001097	10
Carbon disulfide	0.000043	9

VSL standards used for assigning KRISS cylinder

DMS in N_2 mixtures	**Compositions (N_2 is the make-up gas)**		**Standard uncertainty (%)**	**Remarks**
	Component	**Concentration (µmol/mol)**		
VSL238570	Dimethylsulfide	200.02	0.020	Pre-mixture; made from ME0515; Liquid injection
VSL406388	Dimethylsulfide	29.997	0.020	Pre-mixture; made from VSL238570
VSL412671	Dimethylsulfide	19.848	0.020	End-mixture; made from VSL238570
VSL502802	Dimethylsulfide	14.911	0.022	End-mixture; made from VSL238570
VSL428537	Dimethylsulfide	9.942	0.026	End-mixture; made from VSL238570
VSL326694	Dimethylsulfide	4.999	0.021	End-mixture; made from VSL406388
VSL320117	Dimethylsulfide	0.999	0.033	End-mixture; made from VSL406388

Instrument calibration:

The gravimetrically prepared mixtures of DMS in nitrogen were used for calibrating the instrument in accordance with ISO 6143. The value assignment and uncertainty evaluation was also performed in accordance with this standard.
Measurement sequence

Sequence		
Vial nr.	Cylinder nr.	Number of injections
Vial 1	VSL320117	16
Vial 3	VSL326694	12
Vial 5	VSL428537	12
Vial 7	KRISS	12
Vial 9	VSL502802	12
Vial 11	VSL412671	12

Pressure is corrected by in-time online recording of the atmosphere pressure in the laboratory.

Sampling handling:

Sample gases were transferred to the instrument using as much as possible high pressure. One pressure reducer was used for all cylinders.

Before each sequence starts, sampling lines were flushed with the sample gases to be transferred to the instrument.

Sampling lines, injection part, and all other relevant parts of the GC are passivated.

Uncertainty:

a. Uncertainty related to the balance and the weights:

u= 0.02 % (weighing + purity analysis)

b. Uncertainty related to the gas cylinder

u = 0.5 % (stability of DMS in the relevant amount–of–substance fraction range)

c. Uncertainty related to the analysis

u = 0.36 % (includes the above and the repeatability of measurement)

Detailed uncertainty budget:

The uncertainty of the measurement is directly calculated from the calibration curve (straight line) using ISO 6143 with the mixture as the unknown and the standards to form the calibration curve. The uncertainty of the determined Dimethylsulfide amount–of–substance fraction is the average of the 4 individual results.

Measurement report: CCQM-K94 DMS in nitrogen

Laboratory: KRISS
Cylinder number: D731952

Nominal concentration: 10 µmol/mol

Measurement	Date	Result (µmol/mol)	stand. uncertainty (µmol/mol)	number of sub-measurements
No. 1	April-09-13	10.258	0.07	3
No. 2	April-10-13	10.260	0.10	3
No. 3	April-12-14	10.231	0.05	3

Result:

Gas mixture	Result (µmol/mol)	standard uncertainty (µmol/mol)	expanded uncertainty (µmol/mol)	Coverage factor (*k*)
Dimethyl sulfide	10.252	0.030	0.060	2

Note: The coverage factor shall be based on approximately 95% confidence.

Analytical Methods:

HP6890 GC-FID (Agilent, USA) was used for analysis. Gas switching valve at 100 ^{o}C temp was used with 1 mL sample loop. Sample gas was continuously passed through sampling loop during the analysis. Sample flow-rate was controlled using MFC located at front of sampling valve. A CP-SIL 5CB (Varian) GC column was used (30 m x 0.53 mm ID x 5 um thickness with dimethylsilicon). The GC was operated at isothermal condition of 100 $^{\circ}$C (3 min). The column flow was 8 mL/min and EPC used for constant column flow with helium as a carrier gas. Sample gas was split 2:1 at VI inlet before transferring to GC column. The reference cylinder A was measured between each cylinder to correct the analyzer for the drift during the comparison experiment (in sequence A-B-A-C-A-...).

Calibration Standards:

The purity of dimethyl sulfide (Sigma-Aldrich Corp., MO, USA) was checked by several measurement techniques. GC-FID was used for impurity analysis of hydrocarbons (4063 µmol/mol, U of 200 µmol/mol). GC-SCD was used for analysis of sulfur impurities (0.5 µmol/mol, U of 0.2 µmol/mol). Karl-Fisher method was used for analysis of moisture (1471 µmol/mol, U of 150 µmol/mol). Therefore, the total uncertainty of 0.05% was assigned to DMS purity result of 99.45%.

The stability of new DMS primary reference materials (PRMs) at 10 µmol/mol was evaluated by comparing with older KRISS DMS PRMs which was prepared between

2010 and 2005 (2005, 2009, 2010). Results from GC/FID analysis showed that new and old PRMs agreed within 0.4%.

The loss of DMS due to adsorption to cylinder inner surface was evaluated by distributing an equal amount of 10 μmol/mol DMS to another empty cylinder. The two cylinders were analyzed and compared their FID response factors to check the adsorption loss of DMS. Result showed that an estimated loss was less than the analytical uncertainty (0.35%).

Instrument Calibration:

A set of four gas mixtures were gravimetrically prepared within the nominal concentration of a sample cylinder (D731952) and then used to verify against each other. After that, one gas mixture (D929206) was selected and then used to verify the sample cylinder.

KRISS DMS gas mixture	Concentration (μmol/mol)	Coverage factor (*k*)	Relative gravimetric expanded uncertainty (μmol/mol)
D929206	10.284	2	0.1

Analysis of the KRISS gas mixture and the sample was repeated at 3 times with at least 3 injections for each time. A total of 3 sets of measurements were conducted. Each analytical result of the sample was obtained from the bracketed measurement of the KRISS gas mixture to correct drift in GC-FID response.

Sample Handling:
The sample cylinder was stored at room temperature before analysis.

Uncertainty Budget:

Component	**Relative uncertainty (%), *k* = 2**
Gravimetric preparation	0.1
Stability of PRMs	0.46
Analytical measurement	0.35
Combined uncertainty	0.59