International Comparison CCQM-K41.2017
(Hydrogen sulfide in nitrogen at 10 µmol/mol)
Draft B Report

Dalho Kim[1], Young-Doo Kim[1], Sangil Lee[1], Damian Smeulders[2], Hai Wu[3], Judit Fuko[4], Janneke I.T. van Wijk[5], Adriaan M.H. van der Veen[5], James Tshilongo[6], Mudalo Jozela[6], Nompumelelo Leshabane[6], Gumani Mphaphuli[6], Napo Godwill Ntsasa[6], Florbela Dias[7], Carlos Costa[7], Leonid Konopelko[8], Olga Efremova[8], Sam Bartlett[9], Paul Brewer[9] and Arul Murugan[9].

[1]Korea Research Institute of Standards and Science (KRISS), Center for Gas Analysis
267 Gajeong, Yuseong, Daejeon 305-340, Republic of Korea

[2]National Measurement Institute, Australia (NMIA) 36 Bradfield Rd Lindfield NSW 2070, Australia

[3]National Institute of Metrology, China (NIM) No 18 Beisanhuan Donglu, Chaoyang District
Beijing 100029, P.R.China

[4]Budapest Főváros Kormányhivatala (BFKH), Nemetvolgyi ut 37-39, Budapest, 1124, Hungary

[5]Van Swinden Laboratorium B.V. (VSL), Thijsseweg 11, 2621JA Delft, The Netherlands

[6]National Metrology Institute of South Africa (NMISA), Meiring Naude Road, Brummeria, 0183, South Africa

[7]Instituto Português da Qualidade (IPQ), Rua António Gião, 2, 2829-513 Caparica, Portugal

[8]D.I. Mendeleyev Institute for Metrology (VNIIM), 19 Moskovsky pr., St. Petersburg, 190005, Russia

[9]National Physical Laboratory (NPL), Hampton Road, Teddington, Middlesex TW11 0LW, United Kingdom

Field

Amount of Substance

Subject

Comparison of hydrogen sulfide in nitrogen at an amount-of-substance fraction of 10 µmol/mol.

Organizing body

CCQM Gas Analysis Working Group

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1. Introduction

Hydrogen sulfide is a naturally occurring compound encountered in petroleum, natural gas and other drilling operations, mining, and sewers. Hydrogen sulfide is a poisonous gas which can paralyze the respiratory system, quickly leading to death. It is also a flammable gas, which will ignite explosively when exposed to heat, open flames or oxidizers. For these reasons, hydrogen sulfide is classified as a hazardous material.

This comparison is a repeat of the key comparison of the "CCQM-K41 (2005)" [1] and it is intended to compare the capabilities of the preparation and value assignment of gas standard of hydrogen sulfide in nitrogen (subsequently referred to as H_2S). The range of the nominal amount-of-substance fractions of the comparison standard is 10 µmol/mol.

2. Design and organization of the key comparison

2.1 Participants

Table 1: List of participants.

Acronym	Country	Institute
BFKH	Hungary	Budapest Főváros Kormányhivatala
IPQ	Portugal	Instituto Português da Qualidade
KRISS	Repubic of Korea	Korea Research Institute of Standards and Science
NIM	China	National Institute of Metrology, China
NMIA	Australia	National Measurement Institute
NMISA	South Africa	National Metrology Institute of South Africa
NPL	United Kingdom	National Physical Laboratory
VNIIM	Russia	D.I. Mendeleyev Institute for Metrology
VSL	The Netherlands	NMi Van Swinden Laboratorium B.V.
CEM*	Spain	Centro Espanol de Metroogia

* CEM failed to report results

2.2 Measurement schedule

The schedule for this key comparison is:

Nov., 2016: Registration and protocol circulation

Mar. 2018: Preparation of Transfer standards

Mar.~Apr. 2018: First verification measurement

Jun., 2018: Shipment of cylinders to participating laboratories

Oct., 2018: Reporting results to KRISS

Dec., 2018: Second verification measurement

Apr., 2019: Preliminary report to participants

Sep., 2019: Draft A report

Sep., 2020: Draft B report

2.3 Measurement protocol

A set of hydrogen sulfide in nitrogen gas mixtures with the nominal amount fraction of 10 µmol/mol were prepared gravimetrically (20000 µmol/mol - 1000 µmol/mol - 10 µmol/mol) and verified with gas chromatography – atomic emission detector(GC-AED) system against a KRISS reference cylinder. The gravimetric values of the amount of substance fractions were adopted as key comparison reference values (KCRVs). The parent gases were analyzed to check for impurities.

Participating laboratories were requested to specify in detail which analytical method(s) were used and how the evaluation of the measurement uncertainty was performed. Each participating laboratory was responsible for the calibration of its own equipment. For a proper evaluation of the data, participating laboratories were required to report their calibration method and calibration mixtures with their measurement results.

After each calibration, the measurements of the gas mixture had to 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) [2]. The participants were required to provide a detailed description of the uncertainty budget, including the method of evaluation.

After the measurements, the participants were responsible for the return shipment of the cylinders leaving a sufficient amount of gas (pressure at least 27 bar, 2.7MPa) for re-analysis. The participants were required to report at least three independent measurements under repeatability conditions.

2.4 Measurement standards

KRISS prepared gravimetrically a set of H_2S standard gas mixtures in nitrogen. The standard gas mixtures were verified against a set of KRISS primary standard mixtures. The pure H_2S source gas (Specialty Gases, TX, USA) was subjected to a purity analysis prior to use for preparation of the gas mixtures. The purity of the H_2S source gas was checked by several measurement techniques (Table 2). The nitrogen used was free of H_2S and had also been checked for impurities.

The filling pressure in the cylinders was more than 73 bar (7.3 MPa). Aluminium cylinders having a 6 L water volume from Luxfer UK with an Aculife IV treatment were used. The amount-of-substance fractions as obtained from gravimetry and purity verification of the parent gases were used as KCRVs. Each cylinder had its own reference value. The nominal amount-of-substance fraction of H_2S was 10 µmol/mol.

Table 2. Results of Impurity Analysis for H_2S source gas

Component	Amount fraction, cmol/mol	U, cmol/mol, $k=2$	Methods
C_3H_6	0.01400	0.00026	GC/FID
THC	0.0110	0.0031	GC/FID
COS	0.004900	0.000061	GC/SCD
CH_3SH	0.000390	0.000032	GC/SCD
$(CH_3)_3CSH$	0.00029	0.00014	GC/SCD
CS_2	0.000200	0.000019	GC/SCD
unknown sulfur	0.00360	0.00014	GC/SCD
O_2, Ar	0.00000050	0.00000058	GC/PDD
N_2	0.00270	0.00010	GC/TCD
CO	0.00000150	0.00000087	GC/PDD
CH_4	0.00700	0.00017	GC/PDD

H_2	0.00000100	0.00000058	GC/PDD
CO_2	0.00000150	0.00000087	GC/PDD
H_2O	0.010000	0.000013	DPM (dew point)

To validate the stability, the standard gas mixtures were compared with the PSMs maintained in KRISS.

The stability of the standard gas mixtures was in the range of analysis uncertainty and therefore the uncertainty component from stability was considered to be negligible during this key comparison (Figure 1).
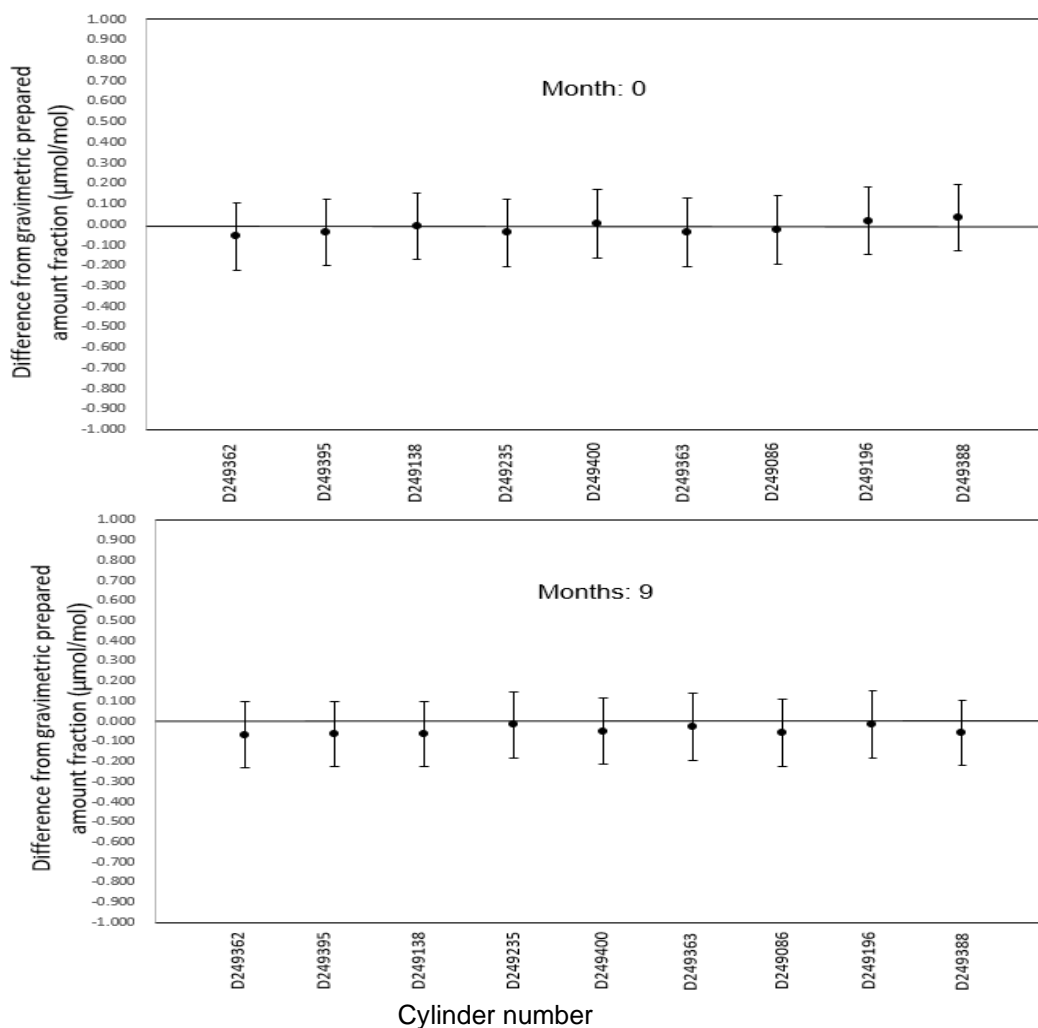

Figure 1: Preparation and verification data of the transfer standards used in this key comparison (1st verification: month 0, 2nd verification: month 9).

2.5   Measurement equation

To assign the amount-of-substance fraction to a gravimetrically prepared cylinder, the following uncertainty components have been considered:

gravimetric preparation (weighing process) ($x_{i,\text{grav}}$)

purity of the parent gases ($\Delta x_{i,\text{purity}}$)

stability of the gas mixture ($\Delta x_{i,\text{stab}}$)

"Δx_i " is the contribution to $x_{i,\text{grav}}$ resulting from purity or stability components.

Previous experience has indicated that there are no stability issues so $\Delta x_{i,\text{stab}}$ is assumed to be zero.

The amount-of-substance fraction $x_{i,\text{prep}}$ of a particular component in mixture i, can be expressed as[3, 4]:

$$x_{i,\text{prep}} = x_{i,\text{grav}} + \Delta x_{i,\text{purity}} \tag{1}$$

The equation for calculating the associated standard uncertainty expressed as

$$u^2(x_{i,\text{prep}}) = u^2(x_{i,\text{grav}}) + u^2(\Delta x_{i,\text{purity}}) \tag{2}$$

ISO 6143 [5] describes the general procedure for the comparison of two values. The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement.

$$|\,x_{i,\text{prep}} - x_{i,\text{ver}}\,| \;\le 2\sqrt{u^2(x_{i,\text{prep}}) + u^2(x_{i,\text{ver}})} \tag{3}$$

The uncertainty associated with the verification relies on the measurement capability and experimental design. Returning to the definition of the reference value, the standard uncertainty of the reference value for a key comparison can be expressed as

$$u(x_{i,\text{ KCRV}}) = \sqrt{u^2(x_{i,\text{ref}})} \;=\; \sqrt{u^2(x_{i,\text{prep}}) + u^2(x_{i,\text{ver}})} \tag{4}$$

The preparation and verification data for the gas mixtures used in this key comparison (Figure 1) agree well. The values for $u(x_{i,\text{prep}})$ and $u(x_{i,\text{ver}})$ are listed in Table 3.

Table 3. KCRVs and their uncertainties of the transfer standards (values in µmol mol^{-1})

Cylinder	x_{KCRV}	$u(x_{i,\text{prep}})$	$u(x_{i,\text{ver}})$	$u(x_{i,\text{KCRV}})$
D249362	10.274	0.0045	0.082	0.082
D249395	10.083	0.0046	0.081	0.081
D249138	9.928	0.0043	0.079	0.080
D249235	10.205	0.0043	0.082	0.082
D249400	10.407	0.0047	0.083	0.083
D249363	10.396	0.0043	0.083	0.083
D249086	10.359	0.0041	0.083	0.083
D249196	10.368	0.0043	0.083	0.083
D249388	10.055	0.0043	0.080	0.081

2.6 Degrees of equivalence

The degree of equivalence for each participating laboratory was calculated with the equation:

$$d_i = x_{i,\text{lab}} - x_{i,\text{KCRV}} \tag{5}$$

d_i: difference

$x_{i,\text{lab}}$: the value reported by each participant

$x_{i,\text{KCRV}}$: key comparison reference value (KCRV)

$$u^2(d_i) = u^2(x_{i,\text{lab}}) + u^2(x_{i,\text{KCRV}}) \tag{6}$$

$u^2(d_i)$: uncertainty of d_i

$u(x_{i,\text{lab}})$: the standard uncertainty of $x_{i,\text{lab}}$

$u(x_{i,\text{KCRV}})$: the standard uncertainty of $x_{i,\text{KCRV}}$

2.7 Measurement methods

The details of the measurement methods used by the participants are described in the individual participant's report. A summary of the calibration method, date of measurement, and the way in which metrological traceability is established is given in Table 4.

Table 4. Summary of the measurement methods of the participants.

NMI	Cylinder	Measurement Period	Calibration Standards	Instrument Calibration	Measurement Techniques
NIM	D249362	Oct. 12, 2018~Nov.1, 2018	Own standards	one point	GC-SCD
IPQ	D249395	Aug. 6, 2018~Aug. 10, 2018	Own standards	multiple point	NDUV
VNIIM	D249138	Oct. 4, 2018~Oct. 18, 2018	Own standards	one point	GC-FPD
BFKH	D249235	Nov. 19, 2018~Nov.23, 2018	Own standards	one point	UVD
NMIA	D249400	Aug. 14, 2018~Oct. 12, 2018	Own standards	multiple point	GC-FPD
NPL	D249363	Oct. 18, 2018~Oct. 29, 2018	Own standards	multiple point	GC-SCD
NMISA	D249086	Jul. 25, 2018~Oct. 14, 2018	Own standards	multiple point	NDUV, UV fluorescence, GC-PDHID
KRISS	D249196	May. 17, 2018~May 19, 2018	Own standards	one point	GC-AED
VSL	D249388	Oct. 2, 2018~Oct. 4, 2018	Own standards	multiple point	electrochemical analysis

3. Results

Results from this key comparison are summarized in Table 5

Table 5. Summary of the results (µmol/mol) for CCQM-K41.2017

NMI*	Cylinder	$x_{i,\text{KCRV}}$	$u(x_{i,\text{KCRV}})$	$x_{i,\text{lab}}$	$u(x_{i,\text{lab}})$	d_i	$U(d_i)$, $k=2$
NIM	D249362	10.274	0.082	10.097	0.039	-0.177	0.182
IPQ	D249395	10.083	0.081	10.080	0.100	-0.003	0.257
VNIIM	D249138	9.928	0.080	10.030	0.045	0.102	0.183
BFKH	D249235	10.205	0.082	10.370	0.180	0.165	0.395
NMIA	D249400	10.407	0.083	10.430	0.150	0.023	0.343
NPL	D249363	10.396	0.083	10.290	0.050	-0.106	0.194
NMISA	D249086	10.359	0.083	10.329	0.046	-0.030	0.190
KRISS	D249196	10.368	0.083	10.370	0.042	0.002	0.186
VSL	D249388	10.055	0.081	10.053	0.030	-0.002	0.172

* : random order

The values in Table 5 indicate that the reported results agree well with the KCRV within their associated uncertainties as shown in Figure 2.

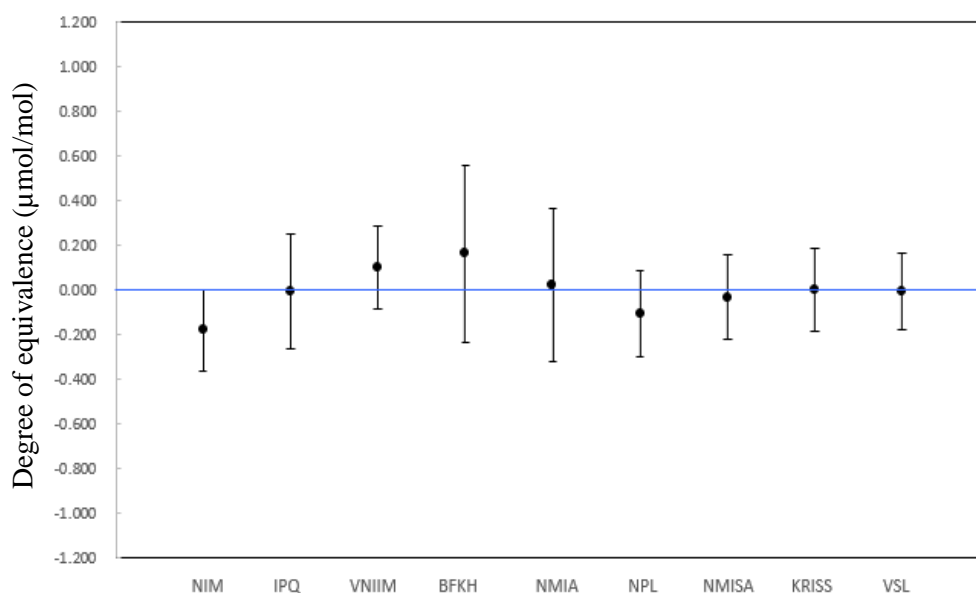Figure 2. Degree of Equivalence for the CCQM-K41.2017

4. Supported CMC claims

This key comparison can be used to assess Calibration and Measurement Capabilities (CMCs) for hydrogen sulfide in nitrogen or air, at an amount of substance fraction between 1 µmol/mol and 500 µmol/mol. Detailed CMC claims regarding how far the light shines follows "CCQM-GAWG strategy for comparisons and CMC claims".

5. Conclusion

This key comparison compares the measurement capability of H_2S at a level of 10 µmol/mol. The results of 9 participants are consistent with their KCRV. Therefore, it is possible for this key comparison to offer a good traceability and a harmonization among the global distribution data of H_2S.

References

[1] F.R. Guenther et al. 2007 International Comparison CCQM-K41: Hydrogen sulfide in nitrogen *Metrologia Technical Supplement*, 44, 08004

[2] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML, 2008 Guide to the Expression of Uncertainty in Measurement – GUM 1995 with minor corrections JCGM100: 2008

[3] Adriaan M.H. van der Veen et al, "Degrees of equivalence across key comparisons in gas analysis", *Metrologia* 40 (2003), pp. 18-23

[4] Adriaan M.H. van der Veen et al. 2017 International Comparison CCQM-K111: Propane in nitrogen *Metrologia Technical Supplement*, 54, 08009

[5] International Organization for Standardization, ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd edition

Coordinator

Korea Research Institute of Standards and Science (KRISS)
Center for Gas Analysis
267 Gajeong, Yuseong, Daejeon 305-340
Republic of Korea
Dalho Kim
dhkim@kriss.re.kr

Project Reference: CCQM-K41.2017

Completion Date: Dec. 2020

Annex A : Measurement reports

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information		
Institute	National Institute of Metrology, China	
Address	No 18 Beisanhuan Donglu, Chaoyang District Beijing 100029 P.R.China	
Contact person	Hai Wu	
Telephone	+86 10 6452 5330	**Fax** +86 10 8425 2306
Email	wuhai@nim.ac.cn	
Transfer standard information		
Date of reception	Sep. 1, 2018	
Serial number of cylinder received	D249362	
Cylinder pressure as received	8MPa	
Cylinder pressure before shipment to KRISS	6.5MPa	

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	12/10/18	10.11	0.19%	7
No. 2	12/10/18	10.12	0.36%	7
No. 3	01/11/18	10.12	0.29%	7
No. 4	01/11/18	10.09	0.71%	14
No. 5	01/11/18	10.07	0.59%	14
No. 6	01/11/18	10.10	0.38%	14
No. 7	01/11/18	10.13	0.50%	14
No. 8	01/11/18	10.08	0.79%	14
No. 9	01/11/18	10.05	0.48%	14

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(*)
Hydrogen sulfide	10.097	0.039	0.077	2

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

Details of the measurement method used:

Pleas complete the following data regarding the description of the methods and the uncertainty evaluation.

Reference Method:
Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

A GC-SCD (7890B, Agilent, USA), equipped with a capillary column of DB sulfur-Low Sulfur (60m×0.32mm×1μm), was adopted to conduct the measurement of H2S. The data was collected by using the program of Agilent workstation.

The parameters of GC-SCD used were set as follow: Oven=60℃, Injection Port=180℃, Split ratio=20:1. The analysis of both standards and sample was done at room temperature and ambient pressure. In order to cancel the drift effect of GC-SCD on the measurement result, A-B-A mode was used. The standard and sample were injected alternatively.

The response of PFPD (in sulfur mode) is quadratic linear to the sulfur concentration in gas sample. That means the square root of the PFPD response is first-order linear to the sulfur concentration. Here single point calibration method was taken to obtain the H2S concentration in the sample.

Calibration Standards:
Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

The calibration standards of H2S in nitrogen were prepared by gravimetric method according to ISO 6142-2001. In order to obtain the PRM(Primary Reference Materials) of 10ppm H2S/N2, the pure H2S was 2-step diluted by N2. The pure H2S was firstly diluted to a pre-mixtures of around 650ppm by using loop-injection technique, in which around 0.36g pure H2S as weighed by Satorius balance (capacity of 610g with resolution of 0.1mg) and then added into a 4L coated cylinder. BIP high purity N2 (6N) of around 450g was then filled into the cylinder to obtain the pre-mixtures. In the second dilution step, around 6.3g of pre-mixtures and 410g of N2 were blended into a 4L coated cylinder, in order to achieve the 10ppm H2S/N2 mixtures.

Through above dilution scheme, three PRMs were prepared as below:

Cyl. No.	H$_2$S Conc. (µmol/mol)	Exp. Uncertainty(µmol/mol)	Exp. Relative *Uncerttainty	Remarks
75601147#	9.974	0.056	0.56%	H$_2$S/N$_2$
75601083#	10.02	0.056	0.56%	H$_2$S/N$_2$
75601140#	10.08	0.056	0.56%	H$_2$S/N$_2$

According to the formula provided by ISO 6142-2001, the standard uncertainty from gravimetric method was 0.24% relative. While the relative standard uncertainty due to verification(inhomogeneity) was 0.15%. So the relative standard uncertainty in the certified value of the our PRM is 0.28%(k=1). The adsorption effect was also verified by decanting half amount of H2S gas mixtures from the mother cylinder to a treated vacuum daughter cylinder. The comparison between the mother and daughter cylinder showed no obvious loss due to inner surface adsorption, and therefore the adsorption effect could be negligible.

Instrument Calibration:
Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):

Because SCD is linear to the Sulfur content, the following mathematical model was adopted:
$$c_{spl} = c_{std} \cdot f_r$$

symbol	unit	definition
c_{spl}	µmol/mol	Concentration of H2S in comparison sample
c_{std}	µmol/mol	Concentration of H2S in standard
f_r	1	Ratio of sample response to standard response at SCD

Finally, the PRM of 75601140# was used to calibrate the GC-SCD, and based on which the D249362# was measured in two different days.

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 8MPa was read before we started the measurement. The pressure decrease to around 6.5MPa after the measurement was finished.

1 reference cylinder (our own prepared standards) and the comparison sample cylinder were

connected to a high pressure needle valve, respectively. The outlets of needle valve were connected to the inlets of a switch valve (Valco, 4-port valve), via 1/16" SS tube. The gas from outlet of the valve was introduced into GC sample loop, via 1/16" SS tube. The sample loop size was 1mL. Sample gas flow rate was controlled by the needle valve at 50mL/min.

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.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from ISO-Standards, ISO-6142 and ISO-6143.

a. Uncertainty related to the balance and mass pieces

b. Uncertainties related to the gas cylinder

c. Uncertainties related to the component gases

d. Uncertainties related to the analysis

In this measurements, two type of balances were used as below:
Satorius balance, capacity of 610g with resolution of 0.1mg;
Mettler Toledo balance, capacity of 26kg with resolution of 1mg.

Based on a rough evaluation of the sources according to ISO6142, the standard uncertainty regarding the 0.36g of pure H_2S was 0.0005g in case of using Satorius balance; while the standard uncertainty of around 0.020g for 450g BIP N_2 in case of using Mettler Toledo balance.

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Uncertainty table: Hydrogen sulfide 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 $u_I(y)$ (umol/mol)
c_{std}	10.08 µmol/mol	B	Norm.	0.0282 µmol/mol	1.0016	0.0283
f_r	1.0016	A	Norm.	0.00262	10.08 µmol/mol	0.0264
c_{spl}	10.097 µmol/mol	A	Norm	0.0387 µmol/mol		

Coverage factor or degree of freedom:
Expanded uncertainty: 0.077ppm

Optional
You may provide additional data like the raw measurement data, information on your measurement procedure etc:

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information	
Institute	Instituto Português da Qualidade
Address	Rua António Gião, 2 2829-513 Caparica Portugal
Contact person	Florbela Dias; Carlos Costa
Telephone	00351 212948175 **Fax** 003510212948188
Email	florbelad@ipq.pt

Transfer standard information	
Date of reception	2018-07-20
Serial number of cylinder received	D249395
Cylinder pressure as received	1378 psi (95 bar)
Cylinder pressure before shipment to KRISS	943 psi (65 bar)

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	06/08/18	9,99	0,5	3
No. 2	09/08/18	10,07	0,3	3
No. 3	10/08/18	10,16	0,2	3
No. 4				
No. 5				

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(*)
Hydrogen sulfide	10,08	0,10	0,20	2,0

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

Details of the measurement method used:

Reference Method:
ISO 6143:2001 (E)

Calibration Standards:
PRM274 (5,00 x10^{-6}); VSL4982 (10,01 x10^{-6}); PRM0273 (25,03 x10^{-6}); PRM0282 (48,30 x10^{-6}); VSL0536 (200,0 x10^{-6})

Instrument Calibration:
Manual calibration (zero and span are calibrated separately by pressing the analyzer system display and control unit softkeys).
Software: XGenline (NPL)
Analyzer: LIMAS11, NDUV

Sample Handling:
After arrival the cylinder was stabilized at laboratory temperature for at least 24 hours. All cylinders were rolled for at least one hour to ensure the homogeneity of the mixture.
The samples were transferred to the instrument by an Autosampler / Software Sira version 2.0.

Uncertainty:

The uncertainty of each run was obtained according to ISO-Standard ISO-6143 (XGenline (NPL)).
The potential sources that influence the uncertainty of the final measurement result:
a. Uncertainty related to the repeatability
b. Uncertainties related to the Reproducibility
c. Uncertainties related to the Calibration
These standard uncertainties were combined and then the combined uncertainty was multiplied by the Coverage factor to calculate the expanded uncertainty.

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Uncertainty table: Hydrogen sulfide in N_2

Uncertainty source X_l	Estimate x_l	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_l	Contribution to standard uncertainty $u_l(y)$ (umol/mol)
Repeatability			normal	$1,76 \times 10^{-8}$	1	$1,76 \times 10^{-8}$
Reproducibility			normal	$5,05 \times 10^{-8}$	1	$5,05 \times 10^{-8}$
Calibration			normal	$8,43 \times 10^{-8}$	1	$8,43 \times 10^{-8}$

Coverage factor or degree of freedom: 2
Expanded uncertainty: 0,20

Optional
Measurement procedure PT7020005507 - Certification/Calibration of gas mixtures

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

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Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

20D

Participant information

Institute	D.I. Mendeleyev Institute for Metrology (VNIIM)
Address	19 Moskovsky pr., St. Petersburg, Russia, 190005
Contact persons	Leonid Konopelko, Olga Efremova
Telephone	+7 812 315 11 45
Fax	+7 812 315 15 17
Email	fhi@b10.vniim.ru

Transfer standard information

Date of reception
20.08.2018

Serial number of cylinder received   D249138

Cylinder pressure as received   7.3 MPa

Cylinder pressure before shipment to KRISS   4.9 MPa

Measurement	Date (dd/mm/yy)	Result (µmol/mol)	Standard uncertainty (% relative)	Number of sub-measurements

№ 1	04/10/2018	10,072	0,53	30
№ 2	10/10/2018	10,025	0,63	30
№ 3	17/10/2018	9,980	0,47	20
№ 4	18/10/2018	10,042	0,70	30

Result

Gas mixture	Result (µmol/mol)	Standard uncertainty (µmol/mol)	Assigned expanded uncertainty (µmol/mol)	Coverage factor
H_2S/N_2	10,03	0,045	0,09	2

Details of the measurement method used:

Reference Method:

Gas chromatography with flame photometric detection.
Instrument:
Gas chromatograph "Crystal-5000.2" (Chromatec, Russia)
High resolution capillary column: DB-1, 30 m × 0,32 mm, 5 µ, Agilent J α W GC Columns
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ t=100°C
Carrier gas: He (grade A, purity 99,995 %), gas-flow rate – 10 ml/min, split ratio 1:3
Sampling valve loop: V=0,1 ml, t=100°C
Data collection: Software support "Chromatec Analytic 2.0".

Calibration Standards:

Calibration was carried out using Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142-1:2015 Preparation of calibration gas mixtures -- Part 1. Characteristics of pure substances used for preparation of the calibration gas mixtures are shown in the tables 1 and 2.

Table 1 – Purity table for hydrogen sulfide

Cylinder № 17/1		
Substance	Mole fraction	Standard uncertainty (µmol/mol)
H_2S	99,76 %	-
H_2O	1500 µmol/mol	200
COS	600 µmol/mol	30
N_2	100 µmol/mol	58
O_2	100 µmol/mol	58
CO	40 µmol/mol	0,5
CO_2	30 µmol/mol	1,5
CH_4	5 µmol/mol	2,9

Table 1 – Purity table for Nitrogen

Cylinder № 17/1

Substance	Mole fraction	Standard uncertainty (μmol/mol)
N_2	99,9998672 %	-
Ar	0,916 μmol/mol	0,017
H_2O	0,4 μmol/mol	0,23
CH_4	0,0025 μmol/mol	0,0014
CO	0,0025 μmol/mol	0,0014
CO_2	0,0025 μmol/mol	0,0014
H_2	0,0025 μmol/mol	0,0014
O_2	0,0015 μmol/mol	0,0009

Preparation from pure substances was carried out in 3 stages. On the first stage H_2S/N_2 gas mixtures were prepared on the concentration level of 1,9 %. On the second stage these mixtures were diluted to the concentration level of 430 μmol/mol. Then the last mixtures were diluted to target concentration level of 10 μmol/mol. There were prepared 3 mixtures at each stage in order to provide each stage verification.

The amount fractions and standard uncertainties of hydrogen sulfide in these mixtures are shown in the table 3.

Table 3

Cylinder number	Component	Concentration (μmol/mol)	Standard uncertainty due to weighing and purity (μmol/mol)
D216074	H_2S	9,395	0,005
D249373	H_2S	10,025	0,005
D249403	H_2S	10,496	0,005

All final gas mixtures were prepared in aluminum cylinders (Luxfer, V=5l) with Aculife IV + Aculife III treatment.

Instrument Calibration:

There were made 4 independent measurements under repeatability conditions in 4 days. The sample of the comparison mixture was fed to chromatograph through 6-port gas sampling valve in turn with calibration mixtures. One single measurement consisted of 3×10 sub-measurements. Each of 30 sub-measuments included "calibration$\rightarrow$measurement$\rightarrow$calibration"sequence in order to exclude a drift of the instrument.

Analysis function used

$$X = C \times \left(H/H_C\right)^a$$

(1),

where X – the amount fraction of analyte in the comparison mixture, C – the amount fraction of analyte in the calibration mixture, H and H_c - peak heights for comparison and calibration mixtures, a – the exponent.

Sample Handling:

The cylinders had been kept at least for 24 hrs at the room where the measurements were made.

The room was thermostatted at $t = (20 \pm 2)$ ºC.
All the gas supply lines and the sampling valve loop had sulfinert coating.

Uncertainty

Standard uncertainty in accordance with equation (1) was calculated as follows

$$u = \sqrt{(\frac{\partial X}{\partial C})^2 u_C^2 + (\frac{\partial X}{\partial a})^2 u_a^2 + (\frac{\partial X}{\partial \ H / Hc})^2 u_{H/Hc}^2} =$$

$$= \sqrt{(\frac{H}{H_C})^{2a} u_C^2 + C^2 (\frac{H}{H_C})^{2a} ln^2(\frac{H}{H_C}) u_a^2 + a^2 C^2 (\frac{H}{Hc})^{2a-2} u_{H/Hc}^2}$$

(2)

Uncertainty table: Hydrogen sulfide in N_2

Uncertainty source		Estimate	Evaluation type (A or B)	Assumed distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty, (µmol/mol)
Amount fraction of H_2S in calibration gas mixtures		10,496 µmol/mol	B	Rectangular	0,0050	0,962	0,0048
Calibra-tion	Determination of the exponent (a) of calibration curve	0,505	A	Normal	0,006	-0,776	0,0047
	Measurement of (H/Hc)	0,926	A	Normal	0,0044	5,51	0,024
Between day variation		10,030 µmol/mol	A	Normal	0,038	1	0,038
Combined standard uncertainty							0,0454
Expanded uncertainty (k=2)							0,09

Authors: L.A. Konopelko, Y.A. Kustikov, A.V. Kolobova, A.Y. Klimov, O.V. Efremova

PARTICIPANT: BFKH

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

Authors: Tamás BÜKI
                            Judit FÜKŐ
                            Zsófia NAGYNÉ SZILÁGYI

Comparison coordinator: Dalho Kim
                            dhkim@kriss.re.kr
                            Center for Gas Analysis
                            Korea Research Institute of Standards and Science
                            267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information	
Institute	BFKH
Address	Nemetvolgyi ut 37-39. Budapest 1124 Hungary
Contact person	Judit Fuko
Telephone	+3614585988
Fax	+36-1-458-5937
Email	fuko.judit@bfkh.gov.hu

Transfer standard information	
Date of reception	26.07.2018
Serial number of cylinder received	D249235
Cylinder pressure as received	1120 psi
Cylinder pressure before shipment to KRISS	609 psi

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements

No. 1	19-11-2018	10.365	0.46	3
No. 2	20-11-2018	10.357	0.48	7
No. 3	21-11-2018	10.364	0.47	12
No. 4	22-11-2018	10.401	0.47	3
No. 5	23-11-2018	10.369	0.47	7

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(*)
Hydrogen sulfide	10.37	0.18	0.36	2

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

Details of the measurement method used:

Reference Method:

Instrument: AMETEK Model 9900RM Analyzer
The Analyzer measures the absorbance of ultraviolet radiation by a gas species.

Calibration Standards:

Preparation of the mixtures:

The hierarchy of gravimetric mixtures prepared by BFKH for this comparison is show Figure 1.
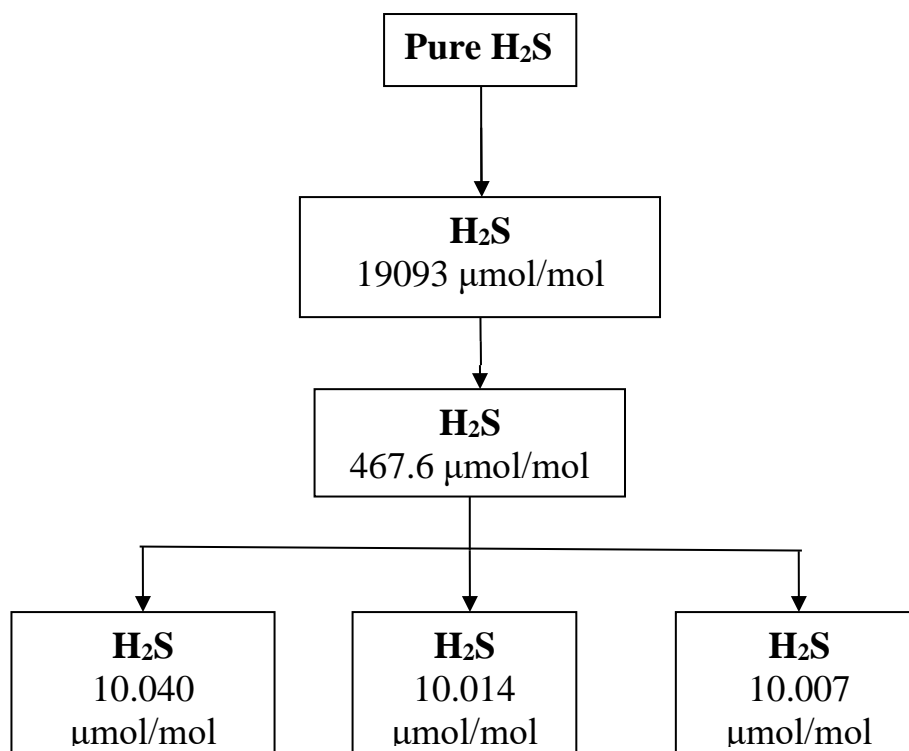
Figure 1. The hierarchy of the gravimetric mixtures of H_2S/N_2 prepare by BFKH

We used 10 L aluminum cylinders (Luxfer, Aculife 4+3) with stainless steel valves DIN1. All three mixtures were prepared with dilution series.

First the pure H_2S was filled into the properly prepared cylinder. After the pure nitrogen gas was filled directly gravimetrically, and the measurement of the gases mass was carried out by a high precision top-load balance – Mettler Toledo XP26003L.

BFKH H2S CRM	concentration (µmol/mol)	U (µmol/mol)	k
5706376	10.040	0.20	2
D521799	10.014	0.20	2
NG230	10.007	0.20	2

Instrument Calibration:

Three primary reference gases were prepared for this key comparison work, and one-point-calibration was used for the analysis since the prepared concentrations are very close to unknown sample's concentration.

Sample Handling:

The pressure of the sample gas and the standard gas cylinders was controlled by Vargha-Valve (with Minimal Dead Volume). The sample went through a Valco stainless steel crosses to the Analyser.
The sample gas was transferred with flow-rate of 50 mL/min which was measured in the output gas flow.

Uncertainty:

Uncertainty was calculated according to ISO-6142 and ISO-6143.

Detailed uncertainty budget:

Uncertainty table: Hydrogen sulfide in N_2

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$
Standard reference material	10.371 (µmol/mol)	Normal	0.100 (µmol/mol)
Hydrogen sulfide analyzer	10.371 (µmol/mol)	Normal	0.150 (µmol/mol)
Standard deviation of the 5 measurement series	10.371 (µmol/mol)	Normal	0.017 (µmol/mol)
Variancia			0.181 (µmol/mol

Coverage factor: 2
Expanded uncertainty: 0.36 (µmol/mol)

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information	
Institute	NMIA
Address	National Measurement Institute 36 Bradfield Rd Lindfield NSW 2070 Australia
Contact person	Dr Damian Smeulders
Telephone	P: +61-2-8467 3534 M: 0420959026 **Fax**
Email	damian.smeulders@measurement.gov.au
Transfer standard information	
Date of reception	August 2018
Serial number of cylinder received	D249400
Cylinder pressure as received	Not measured
Cylinder pressure before shipment to KRISS	Not measured

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	14/08/18	10.412	1.1%	12
No. 2	16/08/18	10.579	1.1%	12
No. 3	20/08/18	10.422	1.1%	12
No. 4	13/09/18	10.207	1.1%	12
No. 5	14/09/18	10.368	1.1%	12

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 6	17/09/18	10.296	1.1%	12
No. 7	19/09/18	10.405	1.1%	12
No. 8	02/10/18	10.278	1.1%	12
No. 9	04/10/18	10.622	1.1%	12
No. 10	05/10/18	10.390	1.1%	12
Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 11	08/10/18	10.410	1.1%	12
No. 12	09/10/18	10.497	1.1%	12
No. 13	11/10/18	10.429	1.1%	12
No. 14	12/10/18	10.531	1.1%	12
*Concentrations not corrected for impurities.				

Result:

Gas mixture	Result (μmol/mol)	standard uncertainty (μmol/mol)	Assigned expanded uncertainty (μmol/mol)	Coverage factor(*)
Hydrogen sulfide	10.43	0.15	0.30	2

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

Details of the measurement method used:

Please complete the following data regarding the description of the methods and the uncertainty evaluation.

Reference Method:
Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

Instrument: Varian 450 GC with PFPD (Pulsed Flame Photometric Detector)
GC Column: CP7475, CP-Sil 5CB 60m x 0.32mm, df = 8µm,
Oven Temperature 120°C, He carrier = 2 ml/min, Split x 5.
Injections carried out using 6-port Valco Valve made with Hastelloy-C body
PFPD: data sampling at 10 Hz.

Calibration Standards:
Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

NMI STD	Amount fraction (μmol/mol)	Preparation uncertainty (μmol/mol)
MK0800	8.0064	0.0082
MK0801	9.4979	0.0076
MK0802	10.485	0.0095
MK0809	10.504	0.0081
MK0812	10.692	0.0078
MK0813	10.798	0.0083
MK0814	11.108	0.0082
MK0803	12.005	0.0102

The Hydrogen Sulphide at approximately 10% was analyzed for impurities. The H2S was found to contain a trace amount of another Sulphur component, tentatively identified as COS. COS was estimated to be present at 0.07 % (700 ppm) in the nominally pure hydrogen sulphide.

Instrument Calibration:
Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):

Plot: SQRT of PFPD Signal vs H2S Concentration.
Quadratic Equation (power 2) used in plot.
The "Sulphur Saturate Test" Method makes twelve injections during each 16 minute run.
Strategy: Inject from lowest to the highest standard, and vice versa i.e. highest to lowest standard, each time bracketing the sample cylinder D249400 between MK0801 and MK0802 standards.
Random injection of the cylinders in any order was used the least.

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).:

Cylinder rolled after arrival, analyses commenced after 2 weeks of equilibrium in the analytical laboratory.
Cylinder connected to a two-stage Sulfinert treated regulator fitted with a needle valve at the outlet.
Configuration incorporates a three way connection to the vacuum to facilitate cylinder change.
The GC waste was vented through a rotameter to maintain same flow (approx. 10 ml/min) for all the cylinders.
Samples changed manually for this study.
Regulator connected to the GC by 1/16" Sulfinert tubing, Injection valve body material Hastelloy-C.

Uncertainty:
There are potential sources that influence the uncertainty of the final measurement result. Depending

on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

Preparation uncertainty was estimated in accordance with ISO 6142-1. The preparation uncertainty was a small fraction of the reported uncertainty.
The reported uncertainty covers the standard deviation observed in the analytical results.
We do not have enough data on the stability of H2S with the current cylinder treatment to provide an uncertainty estimate for stability.

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Uncertainty table: Hydrogen sulfide 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 $u_I(y)$ (umol/mol)

Coverage factor or degree of freedom:
 Expanded uncertainty:

Optional
You may provide additional data like the raw measurement data, information on your measurement procedure etc:

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information	
Institute	National Physical Laboratory
Address	Hampton Road Teddington Middlesex TW11 0LW, United Kingdom
Contact person	Sam Bartlett
Telephone	+44 (0) 20 8943 6372 **Fax**
Email	sam.bartlett@npl.co.uk

Transfer standard information	
Date of reception	16/07/2018
Serial number of cylinder received	D249363
Cylinder pressure as received	1102 psi
Cylinder pressure before shipment to KRISS	566 psi

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	18/10/2018	10.288	0.6	29
No. 2	19/10/2018	10.289	0.6	83
No. 3	29/10/2018	10.284	0.3	101

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(*)
Hydrogen sulfide	10.29	0.05	0.10	2

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

Details of the measurement method used:

Reference Method:

The amount fraction of hydrogen sulfide in the KRISS mixture was measured using an Agilent Technologies 7890A gas chromatograph (GC) system coupled with an Agilent Technologies 355 sulfur chemiluminescence detector (SCD). The GC-SCD system was fitted with a HP-1 column (L = 60 m, D = 0.530 mm, FT = 5.00 μm) and operated using the Agilent ChemStation software. The oven temperature for the method was kept isothermal at 30 °C.

Calibration Standards:

Three NPL primary reference materials (NPL PRMs) of nominally 10 μmol/mol hydrogen sulfide in nitrogen were prepared in accordance with ISO 6142-1 from three different sources of hydrogen sulfide. The purity of the three different sources of hydrogen sulfide (gas phase) were analyzed and found to be > 99.69 %. The NPL PRMs were prepared in BOC-supplied 10 litre cylinders that had undergone BOCs SPECTRA-SEAL passivation. Additionally, each cylinder was conditioned prior to use using a NPL proprietary treatment. Mixtures were prepared in one stage by dilution of nominally 100 μmol/mol hydrogen sulfide in nitrogen mixtures (by direct filling) followed by the addition of nitrogen (by direct filling). All three mixtures were used in determining the amount fraction of the KRISS mixture. The amount fractions of the three NPL PRMs (NPL A614, NPL A616 and NPL 2603) are 10.064 ± 0.007, 9.998 ± 0.007 and 10.121 ± 0.027 μmol/mol respectively (uncertainties are stated as gravimetric expanded ($k = 2$) uncertainties).

Instrument Calibration:

As the NPL PRMs described above were prepared with hydrogen sulfide amount fractions that differed by less than 3 % (relative) from the nominal concentration of the KRISS mixture, this ensured that the uncertainty contribution from any deviation from the linearity of the analyzer response was negligible.

The lines were thoroughly purged and flowrates allowed to stabilize before commencing analysis. The method was set-up to alternate between NPL and KRISS mixtures every 2 minutes. Up to 120 injections of each mixture were performed in order to obtain a comprehensive dataset.

Sample Handling:

The KRISS mixture and an NPL PRM were connected to the GC (via an automated switching valve) using an appropriate cylinder valve stem connector and a purpose-built minimized dead volume connector respectively, and Sulfinert-passivated $^1/_{16}$" internal diameter stainless steel tubing. NPL-designed flow restrictors were used to allow a stable sample flow of 20 ml min^{-1} to be maintained throughout the analysis. The NPL PRMs were rolled for at least two hours following preparation. The cylinders were left to reach equilibrium with laboratory temperature before commencing analysis.

Uncertainty:

In support of this action, a list of potential uncertainty sources is given:

a. Uncertainty related to the balance and mass pieces
b. Uncertainties related to the gas cylinder
c. Uncertainties related to the component gases
d. Uncertainties related to purity of the source gases
e. Uncertainties related to the analysis

Detailed uncertainty budget:

The ratio of the GC-SCD response from the KRISS mixture and the NPL PRM was calculated using:

$$r = \frac{2A_{u,m}}{(A_{s,m} + A_{s,m+1})}$$

Where $A_{u,m}$ is the peak area from repeat m of the KRISS mixture, and $A_{s,m}$ is the peak area from repeat m of the NPL PRM.

And the average ratio ($\bar{r}$) is calculated by:

$$\bar{r} = \frac{\sum r}{n}$$

Where n is the number of ratios. The amount fraction of the propane in the KRISS mixture, x_u, is then calculated by:

$$x_u = x_s \bar{r}$$

Where x_s is the amount fraction of hydrogen sulphide in the standard. The standard uncertainty of the measurand, $u(x_u)$, is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{x_s^2} + \frac{u(\bar{r})^2}{\bar{r}^2}}$$

The expanded uncertainty of the measurement, $u(x_u)$ ($k = 2$) is calculated by:

$$U(x_u) = 2u(x_u)$$

The table which follows details the uncertainty analysis for an example measurement.

Uncertainty table: Example from Measurement no.1

Uncertainty source	Estimate	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard u/c
X_I	x_I			$u(x_i)$	c_i	$u_i(y)$(umol/mol)
x_s	10.06	A	Normal	0.0033	1.02	0.0335
$\bar{r}$	1.02	A	Normal	0.0034	10.06	0.00345
x_u						10.272
$u(x_u)$						0.0370
$U(x_u)$						0.0739

Coverage factor or degree of freedom: $k = 2$

The table below details the overall uncertainty calculation

Uncertainty table: Calculation of uncertainty from averaged measurements

quantity	unit	value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_1	µmol/mol	10.29	0.07	0.33	0.02	A	normal
x_2	µmol/mol	10.29	0.07	0.33	0.02	A	normal
x_3	µmol/mol	10.28	0.04	0.33	0.01	A	normal
x_f	µmol/mol	10.29					
$u(x_f)$	µmol/mol	0.036					
$U(x_f)$	µmol/mol	0.072					

The total uncertainty ($U(x_f)$) was increased to 0.1 µmol mol^{-1} to account for additional uncertainty components such as adsorption of the target component to the cylinder wall and stability of the NPL reference materials after preparation.

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information		
Institute	National Metrology Institute of South Africa	
Address	CSIR Scientia Campus Meiring Naude Road Brummeria 0183 South Africa	
Contact person	Dr James Tshilongo	
Telephone	+27 12 841 2589	**Fax** +27 12 841 2131
Email	jtshilongo@nmisa.org	
Transfer standard information		
Date of reception	04 July 2018	
Serial number of cylinder received	D249086	
Cylinder pressure as received	**1015,26 psi**	
Cylinder pressure before shipment to KRISS	**609.16 psi**	

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	25/07/2018	10,304	0,022	3
No. 2	25/07/2018	10,303	0,021	3
No. 3	25/07/2018	10,302	0,022	3

Note: UV Fluorescence analyser measurements

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	24/08/2018	10,310	0,068	7
No. 2	24/08/2018	10,302	0,060	7
No. 3	24/08/2018	10,315	0,067	7
No. 4	13/09/2018	10,360	0,089	6
No. 5	13/09/2018	10,344	0,077	6
No. 6	13/09/2018	10,338	0,089	6
No. 7	13/09/2018	10,348	0,091	6

Note: Gas Chromatography coupled with PDHID measurements

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	12/10/2018	10,32	0,18	4
No. 2	12/10/2018	10,34	0,13	4
No. 3	13/10/2018	10,36	0,17	4
No. 4	13/10/2018	10,34	0,19	4
No. 5	14/10/2018	10,36	0,18	4

Note: NDUV analyser measurements

Result:

Gas mixture	Result (μmol/mol)	standard uncertainty (μmol/mol)	Assigned expanded uncertainty (μmol/mol)	Coverage factor at 95 % confidence level
Hydrogen sulfide	10,329	0,046	0,092	k=2

Details of the measurement method used:

Pleas complete the following data regarding the description of the methods and the uncertainty evaluation.

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

Three techniques were used for the analysis of the comparison sample:

For Non-dispersive ultra violet (NDUV) technique:

ABB LIMAS 11 UV analyser was purged with high pure nitrogen before and after every sample analysis using FEP tubing connected to a multi-position valve sampler box. Data acquisition was done by using in-house LabView software program.

Table 1: NDUV analytical conditions

Purging time	180s
Number of measurements taken	30s
Number of cycle repeats	4
Sample flow	300 ml/min

For Ultra Violet Fluorescence technique:

Teledyne T101 UV fluorescence analyser was used for the analysis of the comparison sample. The sample and primary standard gas mixture (PSGM) were introduced through the molbloc system for constant flow and mass flow controller to control sample flow. Data was recorded manually.

Table 2: UV Fluorescence analytical conditions

Purging time	5 minutes
Sample measurements taken	16
Number of repeats	3
Sample flow	200 ml/min

For Gas Chromatography (GC) technique:

Agilent 7890B GC-PDHID system was used for the analysis of the comparison sample. Both sample and the PSGM were connected to the sampler box using a sulfinert treated tubing. Data acquisition was done using OpenLab software program. The regulators for both sample and PSGM were purged before use. The sample flow was set at 35 ml/min using the mass flow controller. 15 injections were done with minimum of four repeats.

Table 3: GC - PDHID Analytical conditions

Column	Hayesep Q, 80/100, 2m, ID(2.1mm), 1/8"
Oven temperature	120 º C isothermal
Detector temperature	150 º C
Sample loop	1 ml
Carrier gas	Helium
Run time	2 minutes
Sample flow (mass flow controller)	35 ml/min

Calibration Standards:
Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

The H_2S in nitrogen primary standard gas mixtures (PSGMs) used for calibration were prepared in accordance with ISO 6142:2015 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method). The calibration standards were prepared in four dilution steps from a high purity H_2S (Source from Takachiho in JAPAN) and BIP nitrogen (Air Products Southern Africa). The gravimetric mole fractions of the calibration standards were verified using ISO 6143:2001 (Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures).

Instrument Calibration:
Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.):

For Non-dispersive ultra violet (NDUV) analyser
The determination of hydrogen sulphide in nitrogen (H_2S in N_2) was done using multi-point calibration curve which ranged from a mole fraction of 8 to 12 µmol/mol. The calibration standards used are listed in Table 4. Calibration standards and comparison sample were connected randomly on the ABB LIMAS UV analyser. The generated data was analysed using a generalized least square method.

Table 4: Multi-point calibration standards

Cylinder Number	Mole Fraction (µmol/mol)	Expanded uncertainty (µmol/mol), K=2
D67 9551	7,9777	0,0033
D67 9596	9,9860	0,0036
D67 9392	8,9689	0,0032
D67 9504	10,9815	0,0040
D67 9342	11,9977	0,0043

The second-order polynomial mathematical function was used for multipoint calibration:

$$x = b_0 + b_1 y + b_2 y^2$$

For UV Fluorescence analyser:
The determination of hydrogen sulphide in nitrogen (H_2S in N_2) was done using a single point calibration with a 10 µmol/mol H_2S in nitrogen PSGM. The regulator and bullnose connected to the comparison sample was left with H_2S gas overnight for conditioning. The comparison sample and PSGM were connected on the same line through the molbloc system to the analyser. The mole fraction for the sample was calculated using the following model equation:

$$C_{unknown} = \frac{c_{known}}{A_{known}} A_{unknown}$$

For GC- PDHID system:

The determination of hydrogen sulphide in nitrogen (H_2S in N_2) was done using a single point calibration with a 10 μmol/mol H_2S in nitrogen PSGM. The sample and PSGM were connected on the Multi-position sampler box to the GC. The mole fraction for the sample was calculated using the following model equation:

$$C_{unknown} = \frac{c_{known}}{A_{known}} A_{unknown}$$

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):

After arrival, the comparison sample was kept in the laboratory to stabilize to the laboratory's environmental conditions. The cylinders (standards and sample) were connected through the Tescom 316L stainless steel pressure regulator. These pressure regulators were purged before connecting to the automatic sampler box with a 16-port multi-position valve. The sample flow rate was set to about 300 ml/min.

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 result, they must be considered or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from ISO-Standards, ISO-6142 and ISO-6143.

The uncertainty contributors associated with the certified H_2S mole fraction are as follows

    a. Gravimetric uncertainty from the calibration standard
    b. Long term stability of the H_2S gas mixtures
    c. Adsorption of H_2S on the inner surface of the cylinder
    d. Verification uncertainty (Repeatability)

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Uncertainty table: Hydrogen sulfide (H_2S) in N_2

Table 5: Uncertainty measurement for H_2S in N2

Uncertainty source X_I	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$ (umol/mol)
Verification	A	Normal	0,045	1	0,045
Stability	A	Normal	0,0057	1	0,0057
Adsorption	A	Normal	0,0032	1	0,0032

Coverage factor: k = 2 at 95 % Confidence level
Expanded uncertainty: 0,092 μmol/mol

Optional

You may provide additional data like the raw measurement data, information on your measurement procedure etc.

Table 6: Purity analysis for high pure H_2S

Component	Mole Fraction (µmol/mol)	Expanded uncertainty (µmol/mol), K=2
H_2	2800	140
N_2	2,37	0,12
Ar	61,6	6,2
H_2S	997135,60	140,16

Table 7: Purity analysis for BIP N_2

Component	Mole Fraction (µmol/mol)	Expanded uncertainty (µmol/mol), K=2
Ar	63,6	6,4
CO	0,0500	0,0050
CO_2	0,0500	0,0050
CH_4	0,0100	0,0010
C_2H_6	0,0050	0,0060
O_2	0,00400	0,00040
H_2O	0,010	0,012
H_2	0,50	0,58
N_2	999935,73100	0,00064

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator:
Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information			
Institute	Korea Research Institute of Standards and Science		
Address	267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea		
Contact person	Dalho Kim		
Telephone	82-42-868-5356	**Fax**	82-42-868-5042
Email	dhkim@kriss.re.kr		
Transfer standard information			
Date of reception			
Serial number of cylinder received		D249196	
Cylinder pressure as received		1100 psi	
Cylinder pressure before shipment to KRISS		600 psi	

Measurement	Date (dd/mm/yy)	Result (μmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	17/05/18	10.377	0.14	3
No. 2	18/05/18	10.375	0.02	3
No. 3	18/05/18	10.381	0.03	3
No. 4	19/05/18	10.348	0.06	3
No. 5	19/05/18	10.375	0.12	3

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(*)
Hydrogen sulfide	10.37	0.042	0.084	2

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

Details of the measurement method used:

Pleas complete the following data regarding the description of the methods and the uncertainty evaluation.

Reference Method:

A HP6890 GC-AED was used for the analysis. A gas switching valve at 100 ℃ was used with a 2 mL sample loop. Sample gas was continuously passed through the sampling loop during the analysis. The sample flow rate was controlled using a MFC located at the front of the sampling valve. A CP-SIL 5CB GC column was used (30 m x 0.53 mm ID x 5 μm thickness with dimethylsilicon). The GC oven temperature was set to the isothermal condition of 60 ℃ (isothermal). The column flow of carrier gas was set as 6 mL/min and an EPC was used for constant column flow. High purity helium was used as a carrier gas. The sample gas was injected through at VI inlet (split 6:1) before transferring to the GC column. The AED transfer-line temperature was set as 250 ℃ and the cavity temperature was set as 250 ℃. High purity helium was used as AED discharge gas, which was supplied with EPC control. The AED cavity pressure was maintained at 1.5 psi. High purity hydrogen was used for the AED with EPC controlled pressure at 8.6 psi. High purity oxygen was also used for AED with EPC controlled pressure of 17.5 psi. The AED signal was acquired by Agilent Chemstation software and the GC-AED data was processed using Chemstation software. The sulfur emission line of 181 nm was monitored for sulfur analysis by AED.

Calibration Standards:

KRISS Primary Standard Gas Mixtures (PSMs) of nominally 10 μmol/mol hydrogen sulfide in nitrogen were prepared by three step gravimetric dilution in accordance with ISO 6142. The purity of the parent

hydrogen sulfide was analysed using several analytical technic. The mixtures were prepared in Luxfer UK 6 liter cylinders treated with Aculife IV.

Result of purity analysis for parent hydrogen sulfide.

Component	Conc, cmol/mol	U, cmol/mol, k=2	Methods
C_3H_6	0.014	0.00026	GC/FID
THC	0.011	0.0031	GC/FID
COS	0.0049	0.000061	GC/SCD
CH_3SH	0.00039	0.000032	GC/SCD
$(CH_3)_3CSH$	0.00029	0.00014	GC/SCD
CS_2	0.00020	0.000019	GC/SCD
unknown sulfur	0.0036	0.00014	GC/SCD
O_2, Ar	0.0000005	0.00000058	GC/PDD
N_2	0.0027	0.00010	GC/TCD
CO	0.0000015	0.00000087	GC/PDD
CH_4	0.0070	0.00017	GC/PDD
H_2	0.000001	0.00000058	GC/PDD
CO_2	0.0000015	0.00000087	GC/PDD
H_2O	0.010	0.000013	DPM(dew point)

Instrument Calibration:
One point calibration was used for the analysis since the prepared concentrations are very close to CCQM-K41 sample's concentration. At the same time, GC-AED analysis of H_2S gave good linearity with passing origin always.
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-...).
Lab temperature were kept 24 ℃ ±1 ℃ and atmospheric pressure were between 1000 ~ 1015 hPa. Since no appreciable change in temp and pressure were noticed, no correction for the temperature and pressure were made for the measurement.

Sample Handling:

Cylinder was stored at room temperature before analysis. The sample gas was transferred (with flow-rate of 100 mL/min) to gas sampling valve of GC through "Sulfinert" coated regulator and tubing. MFC was mounted between sample inlet-line and gas sampling valve to control constant flow of sample to the valve.

Uncertainty:

Following uncertainty components were major uncertainty sources considered for sample measurement.
- Gravimetric preparation of PSMs.
- Purity of the parent gases used for preparing the PSMs.
- Reproducibility of sample measurement

Detailed uncertainty budget:

Uncertainty table: Hydrogen sulfide in N_2

Uncertainty source	Estimate	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
Gravimetric preparation	10.36	A and B	normal	0.0041		
Purity of parent gas	99.945	A and B	normal	0.0015		
Reproducibility of measurement	10.37	A	normal	0.042		

Coverage factor or degree of freedom: k=2.0

Expanded uncertainty: 0.084 µmol/mol

Result Form CCQM K41.2017 : Hydrogen sulfide in nitrogen

This form should be completed by participants in the key comparison CCQM-K41.2017 after completion of the measurements described in the protocol of the comparison.

Please complete and return the form by email to dhkim@kriss.re.kr.

Comparison coordinator: Dalho Kim
dhkim@kriss.re.kr
Center for Gas Analysis
Korea Research Institute of Standards and Science
267 Gajeong-Ro Yusung-gu, Daejeon 305-340 Korea

Participant information	
Institute	VSL
Address	Thijsseweg 11 2629JA Delft The Netherlands
Contact person	Janneke I.T. van Wijk / Adriaan M.H. van der Veen
Telephone	+31 152691500 **Fax**
Email	jvwijk@vsl.nl; avdveen@vsl.nl
Transfer standard information	
Date of reception	2018-11-07
Serial number of cylinder received	D249388
Cylinder pressure as received	76 bar
Cylinder pressure before shipment to KRISS	56 bar

Measurement	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (% relative)	number of sub-measurements
No. 1	2018-10-02	10.053	0.3	3
No. 2	2018-10-03	10.051	0.3	3
No. 3	2018-10-04	10.056	0.3	3
No. 4				
No. 5				

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(*)
Hydrogen sulfide	10.053	0.030	0.06	2

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

Details of the measurement method used:

Pleas complete the following data regarding the description of the methods and the uncertainty evaluation.

Reference Method:
The instrument used is an Interscan RM17 gas analyzer based on electrochemical analysis with a continuous flow gas cell.

Calibration Standards:
The standards used are mixtures H_2S (hydrogen sulfide) in N_2 (nitrogen) prepared according to ISO 6142-1:2015 prepared between March 2015 and April 2018.
The nominally pure H_2S used as starting point was checked for purity and N_2, CO_2 (carbon dioxide) and COS 9carbonyl sulfide) were found and quantified. The relative expanded uncertainty on the amount fraction of the pure H_2S is 0.001 % (k = 2).
The overall preparative expanded uncertainty for the calibration gas mixtures used is 0.08 % (k=2). The expanded uncertainty due to instability is 0.2 % (k = 2).

Instrument Calibration:
7 Primary Standard Mixtures were used to create the calibration curve in the range between 3 µmol/mol and 20 µmol/mol. The calibration curve used is a second order model. 3 sets of measurements were performed and the average of the 3 was used as the result of 1 measurement cycle in the reporting form. The analyzer was flushed with nitrogen the night before measurement and one test mixture was used to stabilize the analyzer before measurement. The relative standard uncertainty due to analysis repeatability is 0.02 %.

Sample Handling:
All mixtures are kept in a temperature stabilized storage room and are placed in the laboratory the night before measurement. All mixtures are equipped with a pressure reducing valve the night before the actual analysis and the reducing valves are flushed in 2 cycles. The first cycle when the cylinders are placed in the laboratory and the second cycle before analysis. A multi position valve is used to connect

the mixtures to the analyzer and every position of the multi position valve is flushed with the connected mixture before analysis.

Uncertainty:

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Uncertainty table: Hydrogen sulfide 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 $u_I(y)$ (μmol/mol)
Purity H_2S	0.001 %	A and B	Normal, $k = 2$	0.0005 %	1	0.00005
Preparation	0.08 %	A and B	Normal, $k = 2$	0.04 %	1	0.004
Stability	0.20 %	A	Normal, $k = 2$	0.1 %	1	0.010
Analysis	0.4 %	A	Normal, $k = 2$	0.1 %	1	0.020
Reproducibility analysis	0.20 %	A	Normal, $k = 2$	0.1 %	1	0.010

Coverage factor or degree of freedom: $k = 2$
 Expanded uncertainty: 0.06 μmol mol^{-1}

Optional
You may provide additional data like the raw measurement data, information on your measurement procedure etc: