CCQM-K161
Anions in Seawater

Key Comparison

Final Report

May 2024

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SUMMARY

Anions or nutrients in seawater are very important targets for oceanographic research and environmental monitoring of contaminations. Quantification of minor and trace anions in seawater has always been a challenge for the extremely high salinity, disparate levels of analyte and matrix ions, and even need to be measured at levels close to the detection limits of the method performance. Evidence of successful participation in formal, relevant international comparisons is needed to support calibration and measurement capability claims (CMCs) made by the national metrology institutes (NMIs) and designated institutes (DIs).

The CCQM-K161 Anions in Seawater was organized by the Inorganic Analysis Working Group (IAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) to assess the abilities of the NMIs and DIs for the accurate determination of minor and trace anions in seawater. The measurands covered chloride (16 mg/g-25 mg/g), sulfate (1 mg/g-4 mg/g), bromide (30 mg/kg-100 mg/kg), nitrate (1 mg/kg-5 mg/kg) and phosphate (60 µg/kg-300 µg/kg). Twelve national metrology institutes and designated institutes participated in this key comparison. Participants were requested to evaluate the mass fractions, expressed in mg/g for chloride and sulfate, mg/kg for bromide and nitrate, and µg/kg for phosphate (as phosphorus) in a mixed natural seawater that was spiked with the phosphate. A variety of techniques including isotope dilution inductively coupled plasma mass spectrometry (IDMS), isotope dilution gas chromatography-mass spectrometry (ID-GC-MS), ion chromatography (IC), UV visible spectrophotometry (UV-Vis), flow injection analysis (FIA) was used by the participants for the determination.

The NIST Decision Tree was used to assign the KCRV estimate and to calculate the degrees of equivalence of each participants following the IAWG Guidance on Using NIST Decision Tree for Comparison Reporting from 30 June 2023.

Successful participation in CCQM-K161 demonstrates measurement capabilities for determination of anions in seawater. Considering the IAWG Core Capability Matrix, this material falls into the matrix challenge called ‘High salts content’, which corresponds to the CCQM amount-of-substance category sea water, and so will support CMCs for the anions in a mass fraction range from 60 µg/kg to 25 mg/g.

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ACRONYMS/SYMBOLS

APMP	Asia Pacific Metrology Programme
ANOVA	analysis of variance
u_{bb}	between-bottle (in) homogeneity
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CE	capillary electrophoresis
CIPM	International Committee of Weights and Measures
CMC	calibration and measurement capability
tau	dark uncertainty
°C	degree Celsius
DoE	degrees of equivalence
DI	designated institute
D_i	difference from KCRV
FIA	flow injection analysis
GC-ICP-MS	gas chromatography – inductively coupled plasma – mass spectrometry
GC-MS	gas chromatography – mass spectrometry
HDPE	high density polyethylene
HPLC-ICP-MS	high performance liquid chromatography – inductively coupled plasma – mass spectrometry
IAWG	Inorganic Analysis Working Group
IC	ion chromatography
ICP-MS	inductively coupled plasma – mass spectrometry
IDMS	isotope dilution mass spectrometry
IS	internal standard
KC	Key Comparison
KCRV	Key Comparison Reference Value
mg/g	milligram per gram
mg/kg	milligram per kilogram
µg/kg	microgram per kilogram
µm	micrometre
NMI	national metrology institute
NDT	NIST Decision Tree
%	percentage
PET	polyethylene terephthalate
pH	decimal logarithm of the reciprocal of the hydrogen ion activity
PS	pilot study
PTFE	polytetrafluoroethylene
u(KCRV)	standard uncertainty of the Key Comparison Reference Value
TCQM	Technical Committee for Amount of Substance
QQQ-ICP-MS	triple quadrupole inductively coupled plasma – mass spectrometry
UV-Vis	ultraviolet and visible spectrophotometry

INTRODUCTION

Anions or nutrients such as nitrate and phosphate in seawater are very important targets for oceanographic research and environmental monitoring of contaminations. Quantification of minor and trace anions in seawater has always been a challenge for the extremely high salinity, disparate levels of analyte and matrix ions, and even need to be measured at levels close to the detection limits of the method performance.

At the Asia Pacific Metrology Programme (APMP) meeting in November 2018, the National Institute of Metrology, China (NIM) initially proposed to organize an APMP supplementary comparison of determination of anions in seawater, thereby responding to the urgent need for monitoring eutrophication and pollution in the Asia-Pacific region after discussion on APMP Clean Water Focus Group meeting. The proposal was then presented at the CCQM IAWG meetings in April 2019. After discussion, the working group supported running a CCQM key comparison (CCQM-K161) and pilot study (CCQM-P207) for anions determination in seawater. In December 2019, the APMP Technical Committee for Amount of Substance: Metrology in Chemistry and Biology (TCQM) approved the parallel-run Pilot Study (PS) numbered APMP.QM-P37.

The comparison is aimed to test the NMI/DI's measurement capabilities for anions (as part of speciation analysis) and supports CMCs within category 5 which corresponds to matrix challenge of 'high salts content' in the IAWG core capability table. The selected anions including chloride, sulfate, bromide, nitrate and phosphate in candidate seawater and the mass fraction range from very high (10^{-2}) to very low level (10^{-8}), and this broadens the scope and a degree of complexity of earlier measurements in this field. The comparison facilitates to investigate the core capabilities of participants to measure trace, minor and major anions and/or halogens in high salts matrix water, indicate the method performance such as ion chromatography, UV-Vis or herein flow injection analysis based on UV-Vis, HPLC-ICP-MS, ICP-MS, IDMS etc. Successful participation in CCQM-K161 will support NMIs claim their Calibration and Measurement Capabilities of anions determination in a wide mass fraction range of high salts matrix water.

The following sections of this report document the time schedule of CCQM-K161, the sample, instruction to participants, participants, results, and the measurement capability claims that participation in CCQM-K161 can support. The Appendices reproduce the official communication materials.

TIMELINE

Table 1 lists the timeline for CCQM-K161.

Table 1. Timeline for CCQM-K161

Date	**Action**
November 2018	Proposed to CCQM
April 2019	IAWG authorized CCQM-K161
March 2021	Call for participation to IAWG members
April 2021	Deadline for registration
June 2021	Distribution of samples
January 2022	Original deadline for submission of results
February 2022	Extended deadline for submission of results
April 2022	Initial results summary
November 2022	Presentation/discussion of results at IAWG meeting
April 2023	Presentation/discussion of results at IAWG meeting
February 2024	Draft A report
March 2024	Draft B report
May 2024	Final report approved by IAWG

MEASURANDS

The measurands and their expected mass fractions are listed in Table 2.

Table 2. Measurands and expected mass fraction range

Anions	**Expected mass fraction**
Chloride	(16-25) mg/g
Sulfate	(1-4) mg/g
Bromide	(30-100) mg/kg
Nitrate	(1-5) mg/kg
Phosphate (as phosphorus) Phosphate	(20-100) µg/kg (60-300) µg/kg

STUDY MATERIALS

Sample preparation

The candidate sample was a mixture of surface seawater sampling from East China Sea and North Pacific with the PO_4^{3-} spiking. About 25 L of mixed candidate seawater in pre-cleaned HDPE plastic drum was filtered to another via 0.2 μm filter membrane for removing bacterial retention. The level of phosphate in seawater was gravimetrically adjusted by adding aliquots of known masses of phosphate standard solution which was prepared from monopotassium phosphate solid. After thorough mixing with a mechanical stirrer for 4 h, the whole drum was placed into a large autoclave and sterilized at 121 °C in 105 kPa (relative pressure) for 3 h. The procedure of autoclaving was performed twice about two days apart. The seawater was filled into the 60 mL polypropylene bottles manually in Class 100 clean room after cooling and sealed in aluminized PET sachets. The polypropylene bottles were cleaned with ultrapure water, oven dried, sealed in double bags and sterilized with ultraviolet lamps in the clean room before filling. Then all the samples were stored at 4 °C.

Homogeneity Assessment of Study Material

The homogeneity study was conducted by analyzing 15 randomly selected bottles using ion chromatography (for chloride, sulfate and bromide) and flow injection analysis (for nitrate and phosphate) based on UV-Vis spectrophotometry. The results were subjected to an ANOVA test and the *F* values were less than 1.23. The relative standard uncertainty due to between-bottle inhomogeneity were less than 0.62 %. The comparison sample was found to be sufficiently homogeneous and fit the objective of the comparison. The results are summarized in Table 3.

Table 3. Results of the homogeneity assessment for measurands

Anions	ANOVA test		Relative standard uncertainty due to between-bottle inhomogeneity, u_{bb} (%)
	F-statistics	Critical value	
Chloride	1.06	2.42	0.05
Sulfate	1.14		0.09
Bromide	0.82		0.62
Nitrate	1.23		0.13
Phosphate	0.98		0.62

Stability Assessment of Study Material

The short-term stability was conducted over a period of 3 weeks at -20 °C and 65 °C using isochronous approach. Two randomly selected sample bottles were transferred from the storage condition (4 °C) to -20 °C and 65 °C on three occasions (1 week, 2 weeks and 3 weeks) over the

study period. Two subsamples were then taken from each bottle. Using Student's *t*-test on the slope of the linear regression at 95 % level of confidence, no significant instability of the measurands was observed upon exposure to -20 °C and 65 °C up to 3 weeks. The results are summarized in Table 4 and graphically represented in Figure 1 and Figure 2.

Table 4. Results of the short-term stability assessment

Measurand	Student's *t*-test			*p*-value	
	Calculated test statistics		Critical value	-20 °C	65 °C
	-20 °C	65 °C			
Chloride	0.450	0.711	4.303	0.697	0.554
Sulfate	0.247	0.597	4.303	0.828	0.611
Bromide	0.233	0.857	4.303	0.837	0.481
Nitrate	0.577	0.471	4.303	0.622	0.684
Phosphate	0.325	0.734	4.303	0.776	0.539

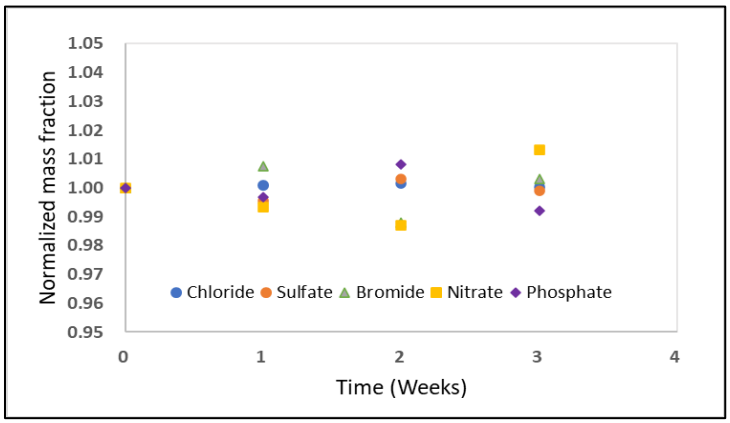


Figure 1. Short-term stabilities of the measurands at -20 °C

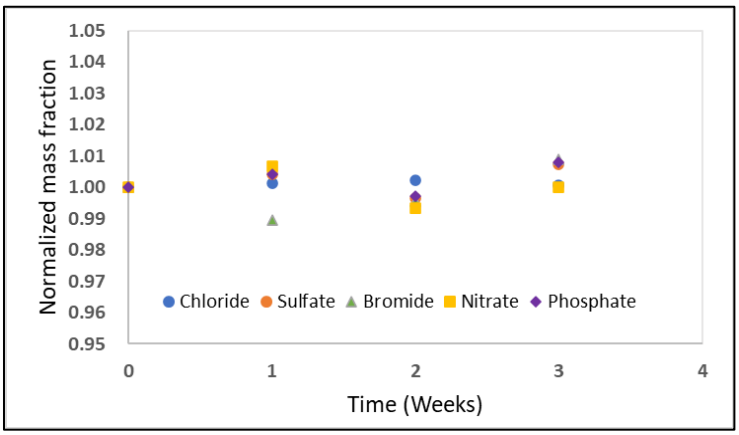


Figure 2. Short-term stabilities of the measurands at 65 °C

The long-term stability of five anions in the comparison sample at 4 °C was assessed using the classical approach, for a period of 38 months that encompassed the sample dispatch and the completion of the comparison. For each occasion of the stability testing, at least two bottles were randomly selected, and two subsamples were taken from each bottle. Student's *t*-test on the slope of the linear regression at 95 % level of confidence was used for the evaluation of instability of the measurands. No instability was observed during the duration of the comparison at the recommended storage temperature. The results are summarized in Table 5 and graphically represented in Figure 3.

Table 5. Results of the long-term stability assessment

Measurand	**Student's *t*-test**		***p*-value**
	Calculated test statistics	**Critical value**	
Chloride	0.597	4.303	0.572
Sulfate	0.225	4.303	0.829
Bromide	0.475	4.303	0.652
Nitrate	0.577	4.303	0.584
Phosphate	0.873	4.303	0.416

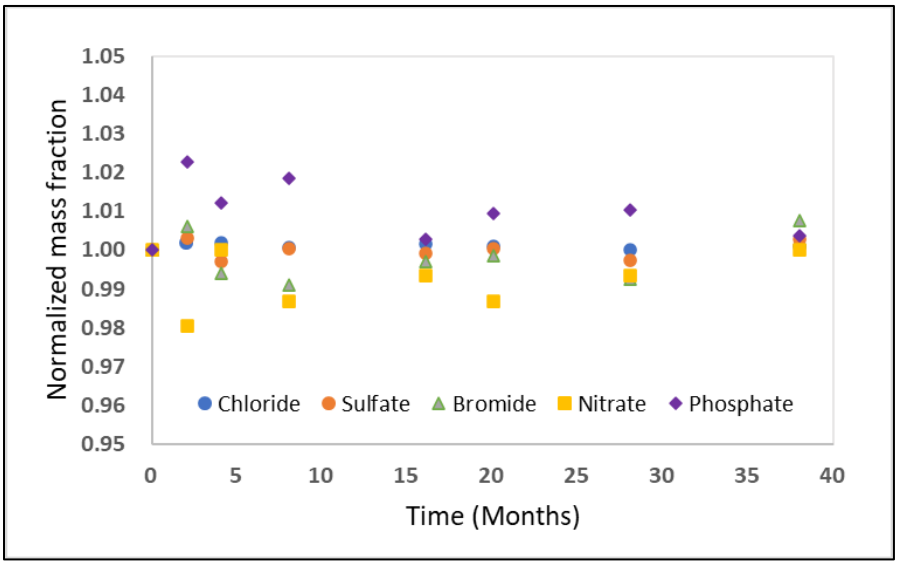


Figure 3. Long-term stabilities of the measurands at 4 °C

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The first call for participation was distributed in August 2020 with the intent of distributing samples in December 2020. Due to the COVID-19 pandemic, the second call was distributed in

March 2021, and the sample distribution was extended to 19 June 2021. Table 6 lists the institutions that registered for CCQM-K161. As listed in Table 6, twelve national metrology institutes and designated institutes registered in the CCQM-K161 key comparison. Table 6 also present information regarding the analytes registered, sample number, distribution of samples date, reporting date and analytes reported for each registered participant.

Participating laboratories provided with two bottles (or more samples if participants required) of comparison sample containing about 50 mL of seawater each. The samples were transported with a temperature strip pasted on aluminized PET sachet to monitor the temperature during the transportation. All participants received the samples at the end of June 2021 except for NIS received samples in December 2021. The hard copy of Sample Receipt Form, Technical Protocol and Report Form were provided to the participating NMIs/DIs with the sample delivery and the electronic version (in Microsoft Word format) was sent to the participants. Appendix A presents the Technical Protocol, Appendix B presents the Registration Form, Appendix C presents the Sample Receipt Form, and Appendix D presents the Report Form.

Participants were allowed to use any appropriate methods of their choice. Calibrations were required to be carried out using standards with metrological traceability to the SI. It should be noted that calibration standards from commercial entities do not comply with the requirements of CIPM MRA-P-11 (https://www.bipm.org/documents/20126/43742162/CIPM-MRA-P-11.pdf/71fe65ae-d97b-82c2-83cf-bdca2909e8af).

Table 6. Registered institutes, contacts, analytes registered, shipping instructions

Participant	Country	Contact	Sample number	Analytes registered	Sample deliver date/ receipt date	Reporting date	Analytes reported
NRC	Canada	Patricia Grinberg	9, 66, 84, 63	Nitrate, Phosphate	June 19, 2021 June 21, 2021	January 20, 2022	Nitrate, Phosphate
NIM China	China	Chao Jingbo	138, 212, 245	Chloride, Sulfate, Bromide, Nitrate, Phosphate	/	January 28, 2022	Chloride, Sulfate, Bromide, Nitrate, Phosphate
INMC	Colombia	Henry Torres Quezada	227, 232	Chloride as Pilot study	June 19, 2021 June 25, 2021	November 30, 2021	Chloride
NIS	Egypt	Ibrahim Tahoun	271, 274	Chloride, Sulfate, Bromide, Nitrate, Phosphate	June 19, 2021 December 19, 2021	January 30, 2022	Chloride, Sulfate, Bromide, Nitrate
PTB	Germany	Olaf Rienitz	55, 59	Sulfate, Bromide	June 19, 2021 June 25, 2021	January 26, 2022	Sulfate, Bromide
GLHK	Hong Kong, China	Wai-hong Fung, Po-kwan LAU	176, 182, 190	Chloride, Sulfate, Nitrate	June 19, 2021 June 23, 2021	January 28, 2022	Chloride, Sulfate, Nitrate
NMIJ	Japan	Chikako Cheong	139,127, 117, 146, 151,121	Chloride, Sulfate, Bromide, Nitrate, Phosphate	June 19, 2021 June 23, 2021	January 31, 2022	Chloride, Sulfate, Bromide, Nitrate, Phosphate
VNIIFTRI	Russia	Sergey Prokunin, Vladimir Dobrovolskiy	41, 29	Chloride, Sulfate, Bromide, Nitrate, Phosphate	June 19, 2021 June 25, 2021	February 22, 2022	Chloride, Sulfate, Bromide, Nitrate, Phosphate
VNIIM-UNIIM	Russia	Alena Sobina	200, 215	Chloride, Sulfate, Bromide, Nitrate, Phosphate	June 19, 2021 June 25, 2021	February 28, 2022	Chloride, Sulfate, Bromide
HSA	Singapore	Richard Shin	100, 106, 96	Chloride, Sulfate, Phosphate	June 19, 2021 June 24, 2021	February 24, 2022	Chloride, Sulfate

Participant	Country	Contact	Sample number	Analytes registered	Sample deliver date/ receipt date	Reporting date	Analytes reported
NIMT	Thailand	Nongluck Tangpaisarnkul	19, 7	Chloride, Sulfate, Bromide, Nitrate	June 19, 2021 June 23, 2021	January 30, 2022	Chloride, Sulfate, Bromide, Nitrate
TUBITAKUME	Turkey	Süleyman Can	234, 248	Chloride, Sulfate, Bromide, Nitrate, Phosphate	June 19, 2021 June 28, 2021	February 28, 2022	Chloride, Sulfate, Bromide, Nitrate, Phosphate

RESULTS

Participants were requested to report results for the measurands at least 5 subsamples using their method of choice. In order to allow a sufficient evaluation of the comparison, a complete information including individual results, detailed uncertainty budget, details about the method used such as instruments, calibration standards, sample preparation, interference correction method, reference material used for quality assurance were also requested to be provided. Considering multiple methods used during the comparison, the result with the smallest uncertainty will be chosen for the calculation of the reference value.

INMC participated in CCQM-P207 when registration, but the participant contact coordinator want report CCQM-K161 key comparison results when submitted report. VNIIM-UNIIM did not submit results for nitrate and phosphate, NIS did not submit result for phosphate.

Methods Used by Participants

Participants were free to use any appropriate method of their choice. Table 7 summarized the sample preparation, measurement method (including calibration strategy) by the participating NMIs/DIs for CCQM-K161.

In this comparison, NRC used ID-GC-MS for nitrate determination, HSA used ID-HPLC-ICP-MS for the determination of chloride and sulfate. Ion chromatography with different detector, UV-Vis, FIA and ion pair-reversed phase-liquid chromatography methods were used by other participants, the calibration strategy including external calibration with/without matrix matching, standard addition with/without internal standard, etc.

Calibration Materials Used by Participants

Participants were allowed to establish the metrological traceability of their results to the SI using a direct realization via a primary method, certified reference materials (CRMs) from an NMI/DI having the required CMC claims, or by preparing their own calibration standards using commercially available high purity materials for which they determined the purity themselves.

Most of the participating NMIs/DIs used NIST CRMs: SRM 3182 chloride, SRM 3181 sulfate, SRM 3184 bromide, SRM 3185 nitrate and SRM 3186 phosphate as calibration solution. NIM China used high purity salt CRM such as GBW(E) 060024 sodium chloride, GBW 06205 potassium bromide, GBW 08665 sodium sulfate to prepare primary standard, used solution CRMs GBW(E) 080265 nitrate and GBW(E) 080431 phosphate as calibration standards. NMIJ used NMIJ CRM 3802, 3803, 3808, 3806 and 3807 as calibration standards. VNIIFTRI used pX GET 171-2011 and VNIIM-UNIIM used GSO 4391-88, GSO 7619-99 and GSO 7253-96 as the primary calibrants, respectively.

Table 7. Summary of sample preparation, measurement method and calibration strategy

Participant	Analytes	Sample preparation	Measurement method	Calibration strategy	Reference materials used
NRC	Nitrate, Phosphate	Nitrate: Isotope dilution with $^{15}NO_3^-$; elimination of NO_2^- by sulfamic acid; ethylation of NO_3^- by Et_3O^+ $[BF_4]^-$ to yield volatile $EtONO_2$ Phosphate: Derivatization of PO_4^{3-} with molybdenum blue chemistry	Nitrate: Headspace GC-MS in NCI mode Phosphate: UV-vis spectroscopy	Nitrate: exact-matching quadrupole isotope dilution Phosphate: external calibration with matrix matching	Nitrate: Primary standard: NIST SRM 3185 Phosphate: Primary standard: NIST SRM 3186
NIM China	Chloride, Sulfate, Bromide, Nitrate, Phosphate	Sample dilution by gravimetric method with matrix matching except chloride	Chloride, Sulfate, Bromide: Ion Chromatography Nitrate: Flow injection analysis (FIA) Phosphate: FIA, UV-Vis after derivatization to phosphomolybdate	Chloride, Sulfate, Bromide: one point calibration with matrix matching (except chloride) Nitrate, Phosphate: five points external calibration	GBW(E) 060024 GBW06205 GBW08665 GBW(E) 080265 GBW(E) 080431
INMC	Chloride	Dilution	IC (Ion Chromatography): Conductivity detector, capillary column CE (Capillary Electrophoresis): UV detection to 230 nm	Bracketing external calibration	Standard Reference Material 919b NIST Certified Reference Material LGC6020
NIS	Chloride, Sulfate, Bromide, Nitrate	Gravimetric dilution	Chloride, Sulfate, Bromide: Ion Chromatography Nitrate: Ion Chromatography (IC) &Ion Pair-Reversed Phase-Liquid Chromatography	Chloride, Sulfate: external calibration Bromide: external calibration & matrix matched calibration Nitrate: standard addition calibration	NIST SRM 3182 NIST SRM 3181 NIST SRM 3184 NIST SRM 3185

Participant	Analytes	Sample preparation	Measurement method	Calibration strategy	Reference materials used
PTB	Sulfate, Bromide	1 g sample + 0 to 2 g standard solution, topped up to 100 g using water	IC, conductivity	Standard addition (3 solutions) using Cl^- as the IS	NIST SRM 3181 NIST SRM 3184
GLHK	Chloride, Sulfate, Nitrate	Chloride, Sulfate: dilution with deionized water with internal standard (formate for chloride, oxalate for sulfate) Nitrate: 3 g of sample was spiked with 0/1/2 g of calibration standard solution and diluted to 7.5 g with 3.1% NaCl solution	Chloride, Sulfate: Ion Chromatography with conductivity detector Nitrate: Flow injection analysis (FIA)	Gravimetric standard Addition	NIST SRM 3182 NIST SRM 3181 NIST SRM 3185
NMIJ	Chloride, Sulfate, Bromide, Nitrate, Phosphate	Gravimetric preparation	Ion Chromatography	Standard addition	NMIJ CRM 3802-a04 NMIJ CRM 3803-a03 NMIJ CRM 3808-a04 NMIJ CRM 3806-a03 NMIJ CRM 3807-a03
VNIIFTRI	Chloride, Sulfate, Bromide, Nitrate, Phosphate	Filtering/Dilution	IC with suppressor	5 points calibration	Primary standard pX GET 171-2011
VNIIM-UNIIM	Chloride, Sulfate, Bromide	Dilution with water 1:4000 and 1:2000	Ion Chromatography	Linear calibration	GSO 4391-88 GSO 7619-99 GSO 7253-96
HSA	Chloride, Sulfate	Chloride: an exact-matching IDMS method was used. Enriched isotope ^{37}Cl from Oak Ridge National Laboratory (USA) was used as the internal standard. Chloride was precipitated from the blends using silver nitrate solution. The silver chloride was	Chloride: Agilent 8900 Triple quadrupole ICP-MS using hydrogen reaction gas. Sulfate: Agilent 1260 Infinity II Bioinert HPLC coupled to an Agilent 8900 Triple quadrupole ICP-MS using oxygen reaction gas.	IDMS	Chloride: Sodium Chloride (NaCl) Standard (NIST SRM 919b). ^{37}Cl (95.20%) isotopic spike from Oak Ridge National Laboratory (USA)

Participant	Analytes	Sample preparation	Measurement method	Calibration strategy	Reference materials used
		redissolved in concentrated ammonia, diluted with water, followed by TQ-ICP-MS measurements. Sulfate: An exact-matching IDMS method was used. Enriched isotope ^{34}S from Isoflex (USA) was used as the internal standard. The blends were analysed by HPLC (AS14 column) coupled to TQ-ICP-MS.			Sulfate: Sulfate Anion (SO_4^{2-}) Standard Solution (NIST SRM 3181). ^{34}S (99.26%) isotopic spike from ISOFLEX USA.
NIMT	Chloride, Sulfate, Bromide, Nitrate	Chloride, Sulfate: Sample dilution by gravimetric method Bromide, Nitrate: No sample preparation	Chloride, Sulfate: IC-EC Bromide, Nitrate: IC-UV	External calibration (5-points)	NIST SRM 3182 NIST SRM 3181 NIST SRM 3184 NIST SRM 3185
TUBITAK UME	Chloride, Sulfate, Bromide, Nitrate, Phosphate	Samples were diluted with DI water, no digestion applied	Ion Chromatography	Standard addition	NIST SRM 3182 NIST SRM 3181 NIST SRM 3184 NIST SRM 3185 NIST SRM 3186

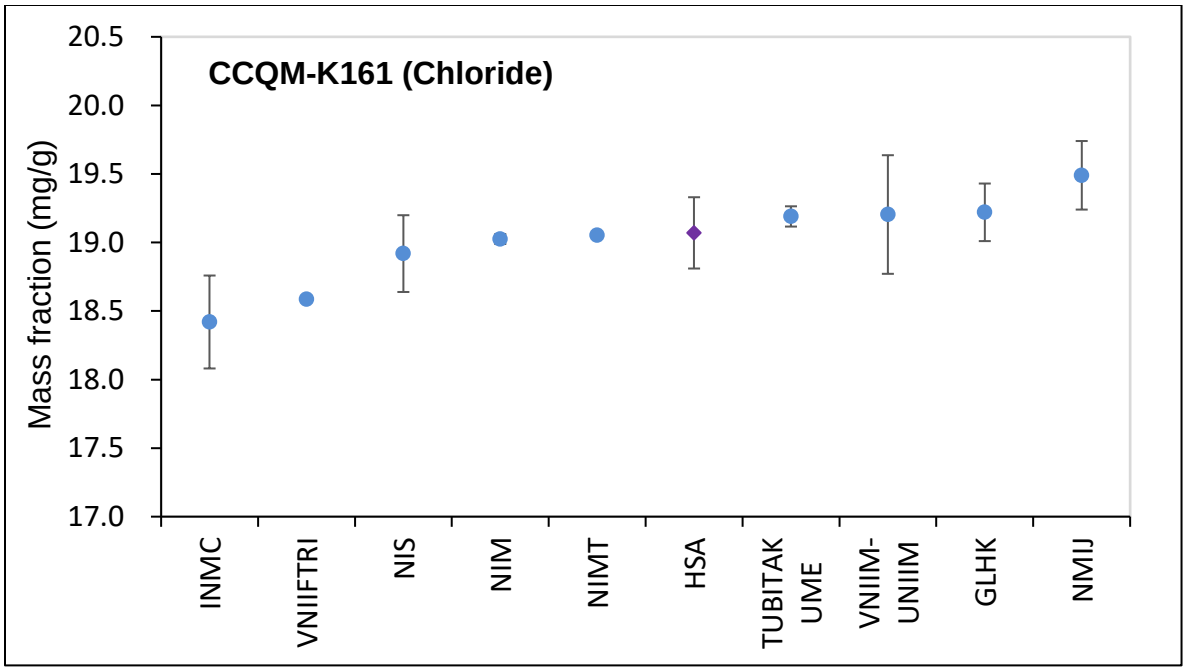
Participant Results for Chloride, Sulfate, Bromide, Nitrate and Phosphate

The results of CCQM-K161 for the determination of chloride, sulfate, bromide, nitrate and phosphate (as phosphorus) are present in Table 8 to Table 12 and graphically presented in Figure 4 to Figure 8, respectively.

In Table 10 and Table 11, the value in brackets for bromide and nitrate were recalculated by NIMT because they found calculation error after all the results opened to participants in IAWG meeting, so the bromide and nitrate from NIMT were excluded from KCRV calculation. The degrees of freedom were estimated from the reported coverage factor.

Table 8. Reported results of chloride

Participant	Reported value (mg/g)	Standard deviation (mg/g)	Combined standard uncertainty u_c (mg/g)	Expanded uncertainty U (mg/g)	n	Coverage factor (k)	Degrees of freedom
INMC	18.42	0.275	0.339	0.67	5	1.97	238
VNIIFTRI	18.5857	0.001922	0.007094	0.014187	5	2	60
NIS	18.919	0.107	0.280	0.560	5	2	60
NIM	19.025	0.0188	0.036	0.072	6	2	60
NIMT	19.052	0.0121	0.01252	0.02555	5	2	60
HSA	19.07	0.19	0.26	0.53	6	2	60
TUBITAKUME	19.19	0.15	0.074	0.15	5	2	60
VNIIM-UNIIM	19.204	0.258	0.4326	0.865	6	2	60
GLHK	19.22	0.104	0.21	0.42	5	2	60
NMIJ	19.49	0.51	0.25	0.49	6	2	60



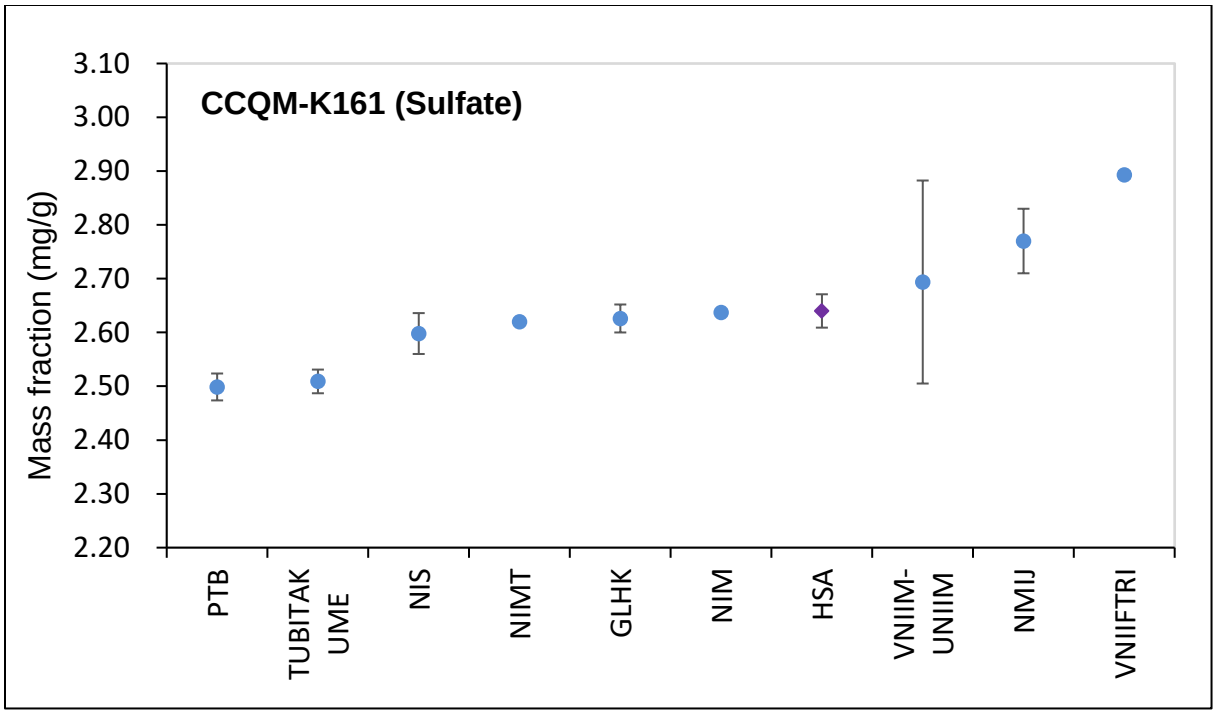
Purple: IDMS; Blue: Ion chromatography

Figure 4. Reported results of chloride in mg/g

Error bars represent the combined standard uncertainties (u_c, k=1)

Table 9. Reported results of sulfate

Participant	Reported value (mg/g)	Standard deviation (mg/g)	Combined standard uncertainty u_c (mg/g)	Expanded uncertainty U (mg/g)	n	Coverage factor (k)	Degrees of freedom
PTB	2.4987	0.0248	0.025	0.050	10	2	60
TUBITAK UME	2.509	0.051	0.022	0.045	6	2	60
NIS	2.598	0.017	0.038	0.076	5	2	60
NIMT	2.620	0.0016	0.00234	0.004689	5	2	60
GLHK	2.626	0.0107	0.026	0.052	5	2	60
NIM	2.637	0.0066	0.006	0.013	6	2	60
HSA	2.640	0.025	0.031	0.086	6	2.78	4
VNIIM-UNIIM	2.6938	0.1768	0.1887	0.3774	6	2	60
NMIJ	2.77	0.16	0.06	0.12	8	2	60
VNIIFTRI	2.8931	0.002077	0.007108	0.014216	5	2	60



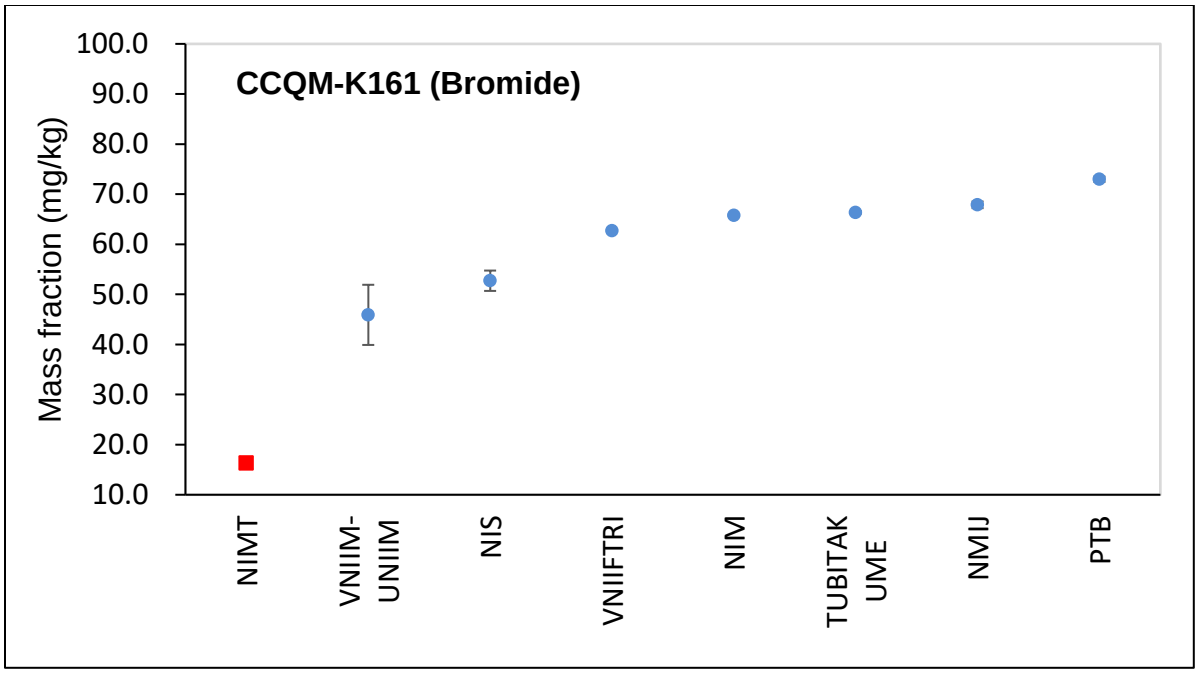
Purple: IDMS; Blue: Ion chromatography

Figure 5. Reported results of sulfate in mg/g

Error bars represent the combined standard uncertainties (u_c, k=1)

Table 10. Reported results of bromide

Participant	Reported value (mg/kg)	Standard deviation (mg/kg)	Combined standard uncertainty u_c (mg/kg)	Expanded uncertainty U (mg/kg)	n	Coverage factor (k)	Degrees of freedom
NIMT	16.345 (47.21)	0.1045	0.10455	0.20910	5	2	60
VNIIM-UNIIM	45.91	4.53	6.005	12.01	6	2	60
NIS	52.72	1.46	2.03	4.06	5	2	60
VNIIFTRI	62.6697	0.01438	0.01086	0.02173	5	2	60
NIM	65.77	0.2719	0.207	0.413	6	2	60
TUBITAK UME	66.36	0.33	0.25	0.49	6	2	60
NMIJ	67.87	1.59	0.66	1.32	7	2	60
PTB	72.98	0.50	0.53	1.1	7	2	60



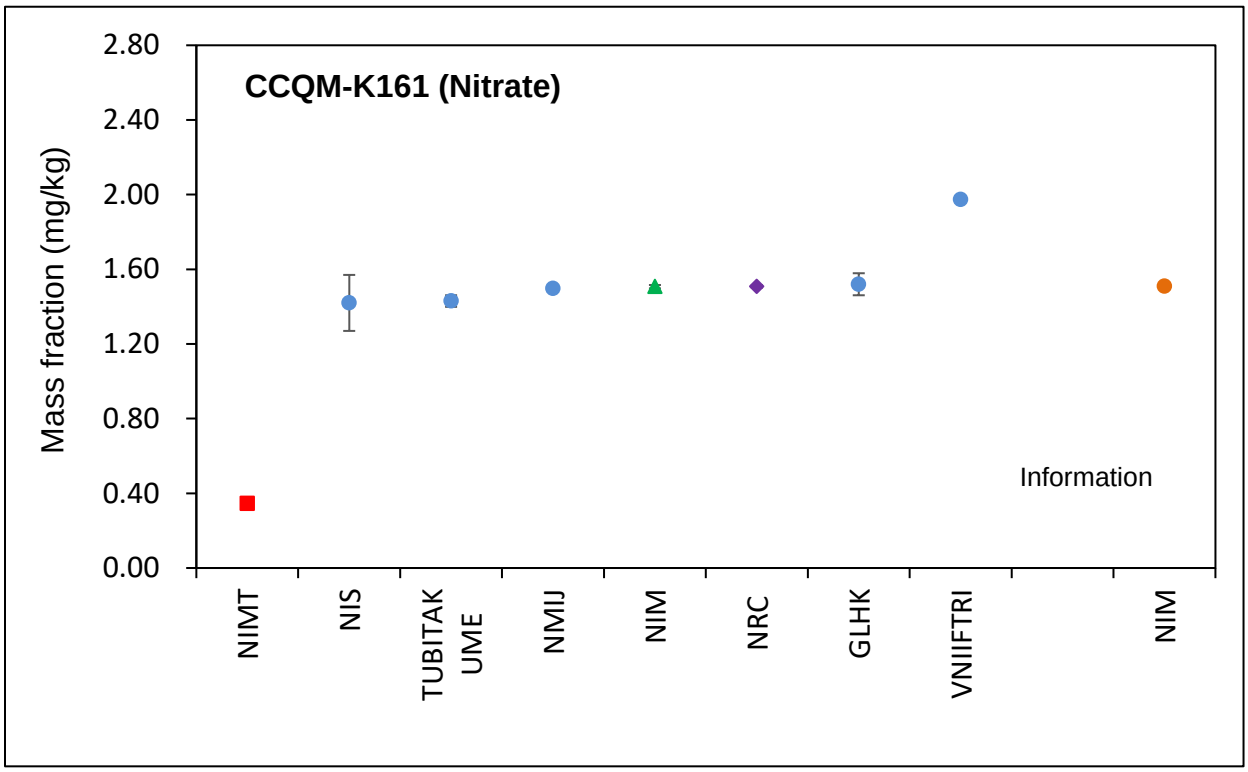
Red: Incorrect data; Blue: Ion chromatography

Figure 6. Reported results of bromide in mg/kg

Error bars represent the combined standard uncertainties (u_c, k=1)

Table 11. Reported results of nitrate

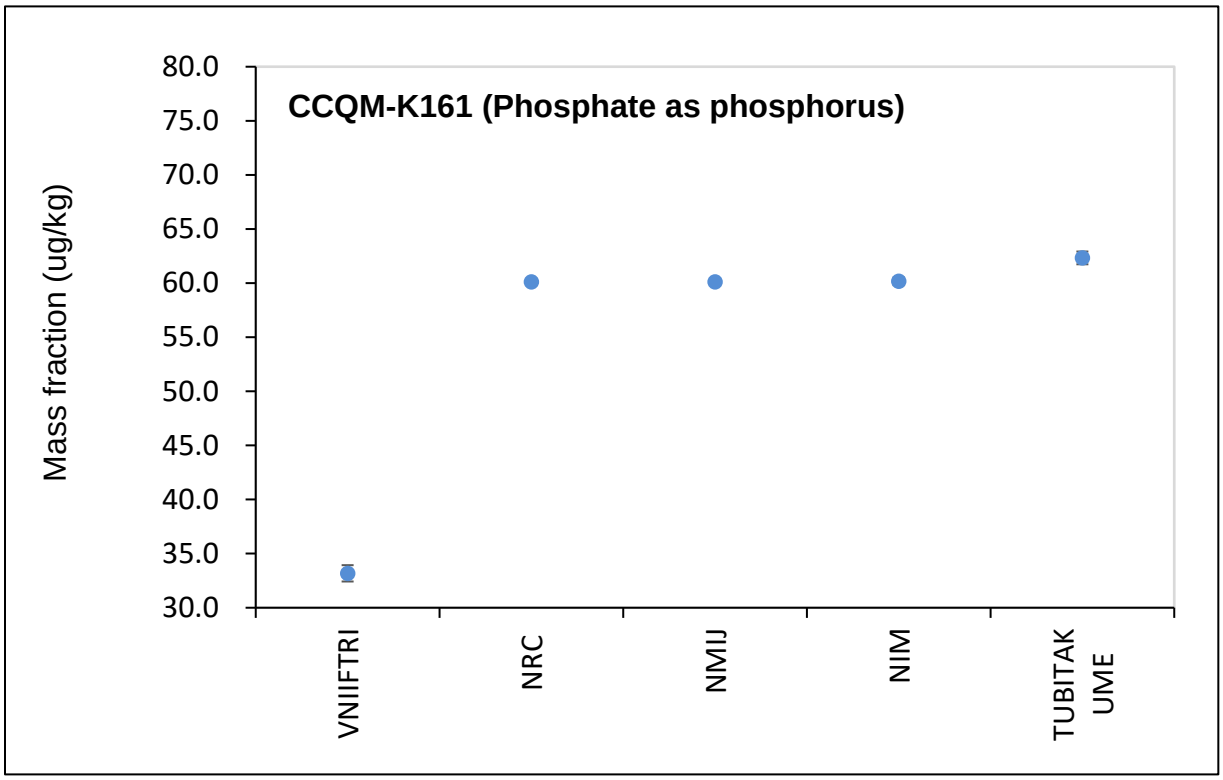
Participant	Reported value (mg/kg)	Standard deviation (mg/kg)	Combined standard uncertainty u_c (mg/kg)	Expanded uncertainty U (mg/kg)	n	Coverage factor (k)	Degrees of freedom
NIMT	0.346 (1.432)	0.0074	0.007661 (0.03085)	0.015322	5	2	60
NIS	1.42	0.12	0.15	0.30	5	2	60
TUBITAK UME	1.430	0.068	0.031	0.062	5	2	60
NMIJ	1.498	0.031	0.014	0.027	8	2	60
NIM	1.507	0.0079	0.009	0.018	6	2	60
NRC	1.5087	0.0052	0.0073	0.015	11	2	60
GLHK	1.520	0.0335	0.059	0.118	6	2	60
VNIIFTRI	1.9740	0.01381	0.01062	0.021232	5	2	60
NIM (Information value)	1.509	0.0249	0.013	0.027	6	2	60



Red: Incorrect data; Orange: Information value
Purple: IDMS; Green: Flow injection analysis; Blue: Ion chromatography
Figure 7. Reported results of nitrate in mg/kg
Error bars represent the combined standard uncertainties (u_c, k=1)

Table 12. Reported results of phosphate

Participant	Reported value (µg/kg)	Standard deviation (µg/kg)	Combined standard uncertainty u_c (µg/kg)	Expanded uncertainty U (µg/kg)	n	Coverage factor (k)	Degrees of freedom
VNIIFTRI	33.1810	1.3062	0.7542	1.5083	5	2	60
NRC	60.12	0.10	0.20	0.40	12	2	60
NMIJ	60.13	0.10	0.31	0.62	14	2	60
NIM	60.17	0.4016	0.358	0.716	6	2	60
TUBITAK UME	62.33	1.05	0.59	1.17	6	2	60



Blue: Ion chromatography

Figure 8. Reported results of phosphate (as phosphorus) in µg/kg
Error bars represent the combined standard uncertainties (u_c, k=1)

Discussion of Results

The compiled data of the five anions in seawater for the CCQM-K161 Key Comparison was circulated among the participants in early April, 2022 for the purpose of checking any transcription and typographical errors. The data was first presented during the IAWG meeting on 12th April, 2022. Participating institutes were instructed to review and verify their own results and to notify the coordinator of any technical problems that might have resulted in errors in the reported data.

NIMT reported a calculation mistake for bromide and nitrate, and as a result, the data for bromide and nitrate from NIMT were removed from the KCRV calculations. Other participating laboratories did not provide any feedback regarding technical issues or calculation errors.

KEY COMPARISON REFERENCE VALUE (KCRV)

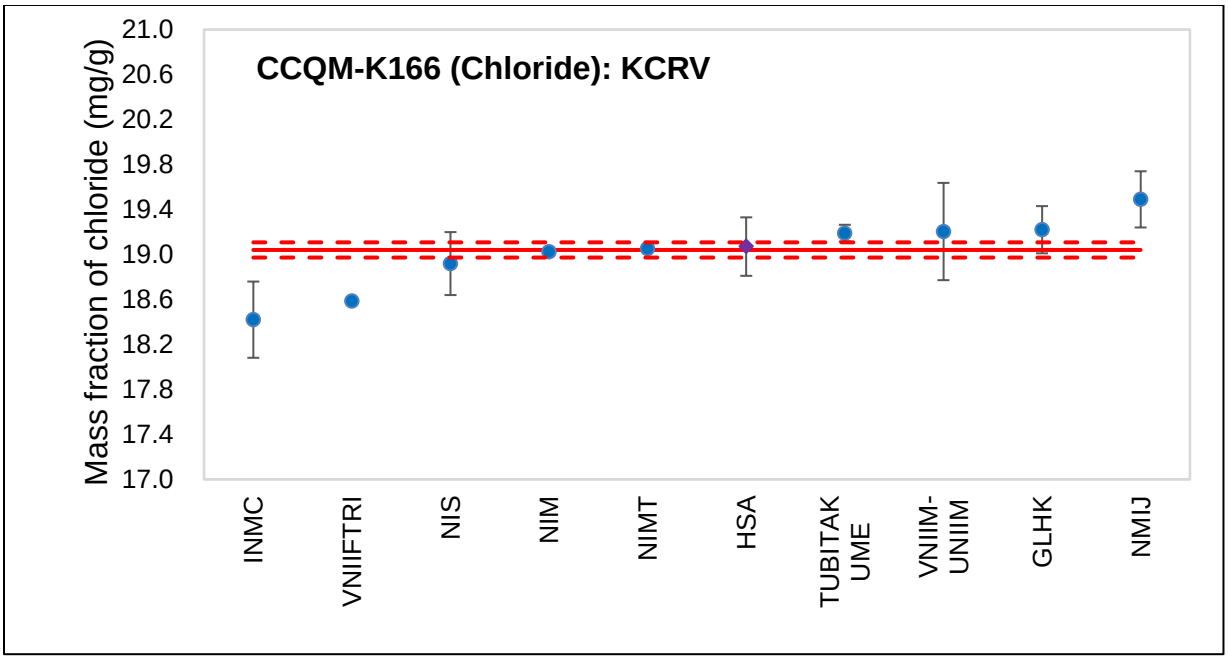
The decision to use the NIST Decision Tree (Version 1.0.4) for calculating the KCRV and Degrees of Equivalence of each participant was made during the IAWG meeting in early November 2022. The NIST Decision Tree requires the identification of the participant, reported results, uncertainty,

and degrees of freedom as input. After conducting a series of hypothesis tests for homogeneity, symmetry, and normality (Gaussian shape), the NIST Decision Tree recommends the best statistical model for calculating the KCRV and Degrees of Equivalence.

The KCRVs for all five anions were proposed using the NIST Decision Tree and obtained using the Hierarchical Laplace-Gauss statistical model. The results of the hypothesis tests are listed in tables 13 to 17, and the graphical representation of participants' reported results relative to the KCRV can be found in Figures 9 to 13. In these figures, the candidate KCRV is depicted by a solid horizontal red line, while the dashed red lines represent the standard uncertainty of the candidate KCRV, denoted as u(KCRV). Each measured value displayed in Figure 9 to Figure 13 is represented by a blue dot (x_i), and a thin vertical black line segment ($x_i \pm u_i$) represents the combined standard uncertainty (u_i) reported by participants.

Table 13. Decision tree hypothesis test results for chloride in CCQM-K161

Decision tree hypothesis	Results	Answers
Cochran's test for homogeneity	p<0.001 Q=1192(Reference Distribution: Chi-Square with 9 Degrees of Freedom) tau est.=0.3235 tau/median(x)=0.01697 tau/median(u)=1.407	Assume Homogeneity? No (p-value<0.05)
Miao-Gel-Gastwirth test of Symmetry	p=0.4062	Assume Symmetry? Yes (p-value>0.01)
Shapiro-Wilk test for Normality	p=3.995e-7	Assume Normality? No (p-value<0.05)
Recommended Approach	Hierarchical Laplace-Gauss	
KCRV, mg/g	19.04	
Standard uncertainty (u), mg/g	0.06761	
Dark uncertainty (σ), mg/g	0.2228	

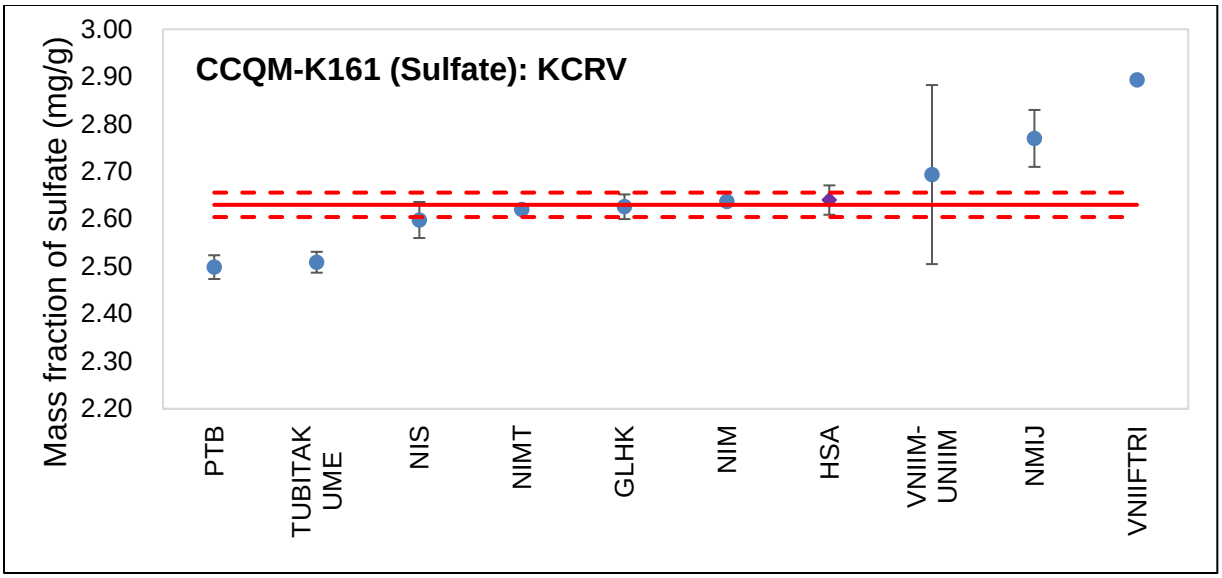


Purple: IDMS; Blue: Ion chromatography

Figure 9. Plots of participants' reported results relative to the KCRV for chloride
Error bars represent the combined standard uncertainties (u_i, k=1)
(Using Hierarchical Laplace-Gauss for KCRV estimation)

Table 14. Decision tree hypothesis test results for sulfate in CCQM-K161

Decision tree hypothesis	Results	Answers
Cochran's test for homogeneity	p<0.001 Q=1414(Reference Distribution: Chi-Square with 9 Degrees of Freedom) tau est. = 0.1236 tau/median(x) = 0.04695 tau/median(u) =4.845	Assume Homogeneity? No (p-value<0.05)
Miao-Gel-Gastwirth test of Symmetry	p=0.531	Assume Symmetry? Yes (p-value>0.01)
Shapiro-Wilk test for Normality	p=2.718e-5	Assume Normality? No (p-value<0.05)
Recommended Approach	Hierarchical Laplace-Gauss	
KCRV, mg/g	2.63	
Standard uncertainty (u), mg/g	0.02578	
Dark uncertainty (σ), mg/g	0.1103	



Purple: IDMS; Blue: Ion chromatography

Figure 10. Plots of participants' results relative to the KCRV for sulfate
Error bars represent the combined standard uncertainties (u_i, k=1)
(Using Hierarchical Laplace-Gauss for KCRV estimation)

Table 15. Decision tree hypothesis test results for bromide in CCQM-K161

Decision tree hypothesis	**Results**	**Answers**
Cochran's test for homogeneity	p<0.001 Q=910.9(Reference Distribution: Chi-Square with 6 Degrees of Freedom) tau est. = 3.16 tau/median(x) = 0.04805 tau/median(u) =5.963	Assume Homogeneity? No (p-value<0.05)
Miao-Gel-Gastwirth test of Symmetry	p=0.065	Assume Symmetry? Yes (p-value>0.01)
Shapiro-Wilk test for Normality	p=2.194e-5	Assume Normality? No (p-value<0.05)
Recommended Approach	Hierarchical Laplace-Gauss	
KCRV, mg/kg	64.25	
Standard uncertainty (u), mg/kg	2.497	
Dark uncertainty (σ), mg/kg	8.196	

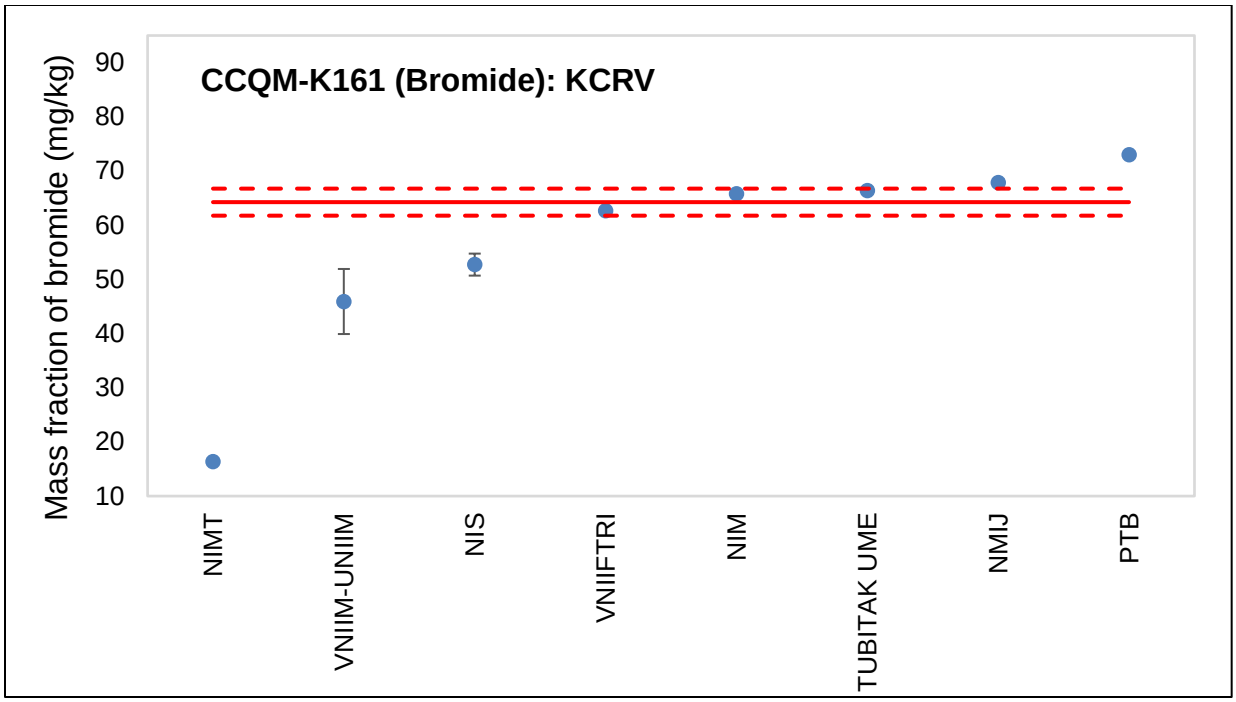
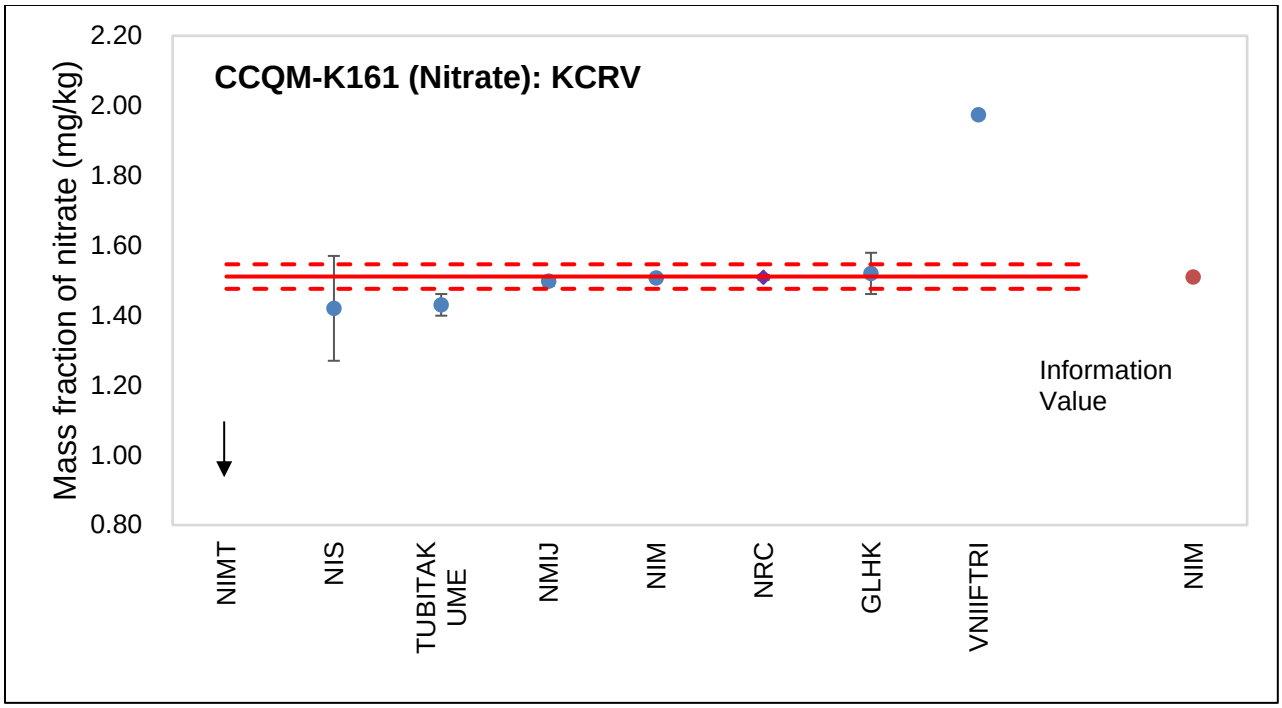


Figure 11. Plots of participants' results relative to the KCRV for bromide
Error bars represent the combined standard uncertainties (u_i, k=1)
(Using Hierarchical Laplace-Gauss for KCRV estimation)

Table 16. Decision tree hypothesis test results for nitrate in CCQM-K161

Decision tree hypothesis	Results	Answers
Cochran's test for homogeneity	p<0.001 Q=1588(Reference Distribution: Chi-Square with 6 Degrees of Freedom) tau est. = 0.2179 tau/median(x) = 0.1446 tau/median(u) =15.57	Assume Homogeneity? No (p-value<0.05)
Miao-Gel-Gastwirth test of Symmetry	p=0.4402	Assume Symmetry? Yes (p-value>0.01)
Shapiro-Wilk test for Normality	p=1.896e-5	Assume Normality? No (p-value<0.05)
Recommended Approach	Hierarchical Laplace-Gauss	
KCRV, mg/kg	1.511	
Standard uncertainty (u), mg/kg	0.03507	
Dark uncertainty (σ), mg/kg	0.1329	



Purple: IDMS; Orange: Information value

Figure 12. Plots of participants' results relative to the KCRV for nitrate
Error bars represent the combined standard uncertainties (u_i, k=1)
(Using Hierarchical Laplace-Gauss for KCRV estimation)

Table 17. Decision tree hypothesis test results for phosphate in CCQM-K161

Decision tree hypothesis	Results	Answers
Cochran's test for homogeneity	p<0.001 Q=1256(Reference Distribution: Chi-Square with 4 Degrees of Freedom) tau est. = 6.354 tau/median(x) = 0.1057 tau/median(u) =17.75	Assume Homogeneity? No (p-value<0.05)
Miao-Gel-Gastwirth test of Symmetry	p=0.3836	Assume Symmetry? Yes (p-value>0.01)
Shapiro-Wilk test for Normality	p=0.001753	Assume Normality? No (p-value<0.05)
Recommended Approach	Hierarchical Laplace-Gauss	
KCRV, µg/kg	59.18	
Standard uncertainty (u), µg/kg	2.723	
Dark uncertainty (σ), µg/kg	8.585	

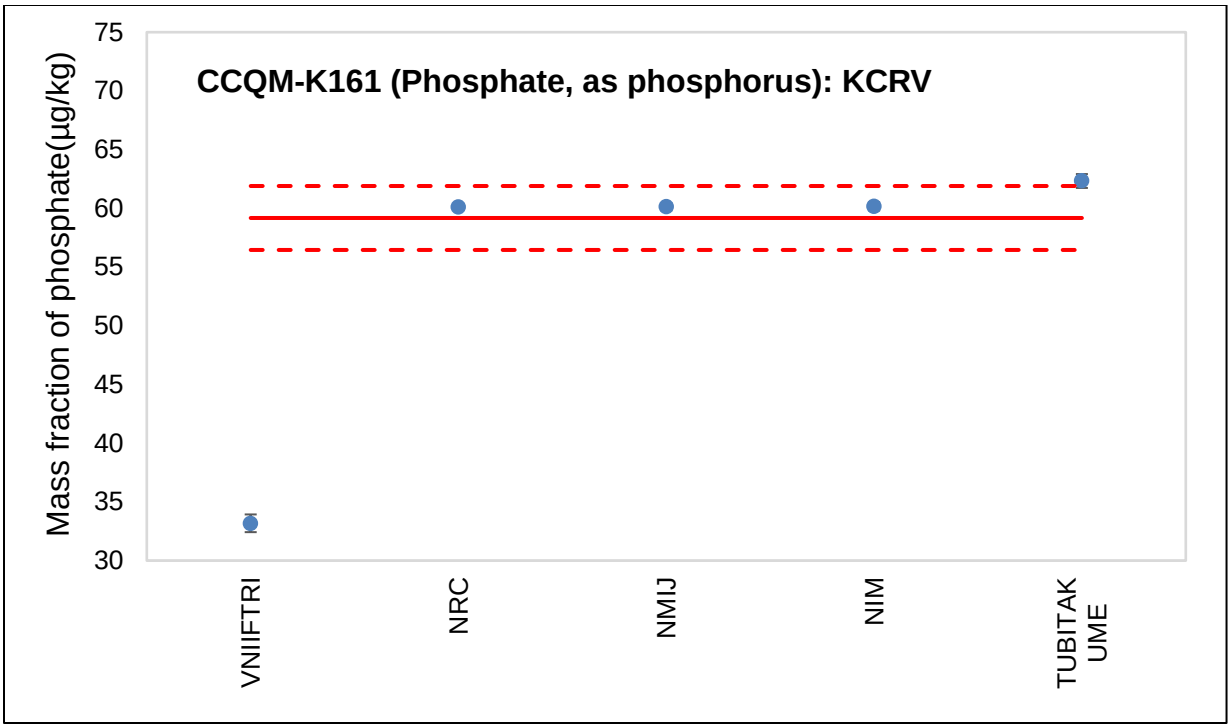


Figure 13. Plots of participants' results relative to the KCRV for phosphate
Error bars represent the combined standard uncertainties (u_i, k=1)
(Using Hierarchical Laplace-Gauss for KCRV estimation)

DEGREES OF EQUIVALENCE (DoE)

The DoEs for all the five anions proposed using NIST Decision Tree were obtained in Hierarchical Laplace-Gauss statistical model and listed in tables 18 to 22, plots of participants' DoEs were graphically presented in Figures 14 to 18. In these tables, all results are sorted by increasing *x*. In the u_i' column, the uncertainties with symbol * were the sum total of the respective reported standard uncertainty $u(x_i)$ along with the contribution of dark uncertainty *(tau)*, i.e. $(\sqrt{\tau^2 + u^2(x_i)})$. For participants without an asterisk (*), u_i' corresponds to their reported standard uncertainty $u(x_i)$. The absolute degrees of equivalence for the participants in CCQM-K161 are estimated as the signed difference between the combined value and the KCRV: $D_i = x_i$ – KCRV. For the Bayesian procedure (Hierarchical Laplace-Gauss) used to estimate each of the KCRVs, the expanded uncertainty of D_i, $U(D_i)$, is half the shortest interval centered on D_i that is believed to encompass the true value with 95 % probability, where the endpoints of the interval are derived directly from a large sample drawn from the corresponding posterior probability distribution. Therefore, the error bars in the plots represent the expanded uncertainties of D_i at 95 % confidence level, $U(D_i)$. In these figures, the horizontal line denotes perfect agreement with the KCRV, the blue dot represents the D_i value, and a thick vertical black line segment represents $U(D_i)$.

Table 18. Degrees of equivalence for chloride in CCQM-K161

Participant	x_i (mg/g)	u_i' (mg/g)	D_i (mg/g)	$U(D_i)$ (mg/g)	$D_i/U(D_i)$
INMC	18.42	0.339	-0.623	0.678	-0.92
VNIIFTRI	18.5857	0.222*	-0.457	0.556	-0.82
NIS	18.919	0.280	-0.124	0.572	-0.22
NIM	19.025	0.036	-0.018	0.154	-0.12
NIMT	19.052	0.01252	0.009	0.141	0.06
HSA	19.07	0.26	0.027	0.531	0.05
TUBITAK UME	19.19	0.074	0.147	0.201	0.73
VNIIM-UNIIM	19.204	0.4326	0.161	0.863	0.19
GLHK	19.22	0.21	0.177	0.442	0.40
NMIJ	19.49	0.25	0.447	0.520	0.86

In the u_i' column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature

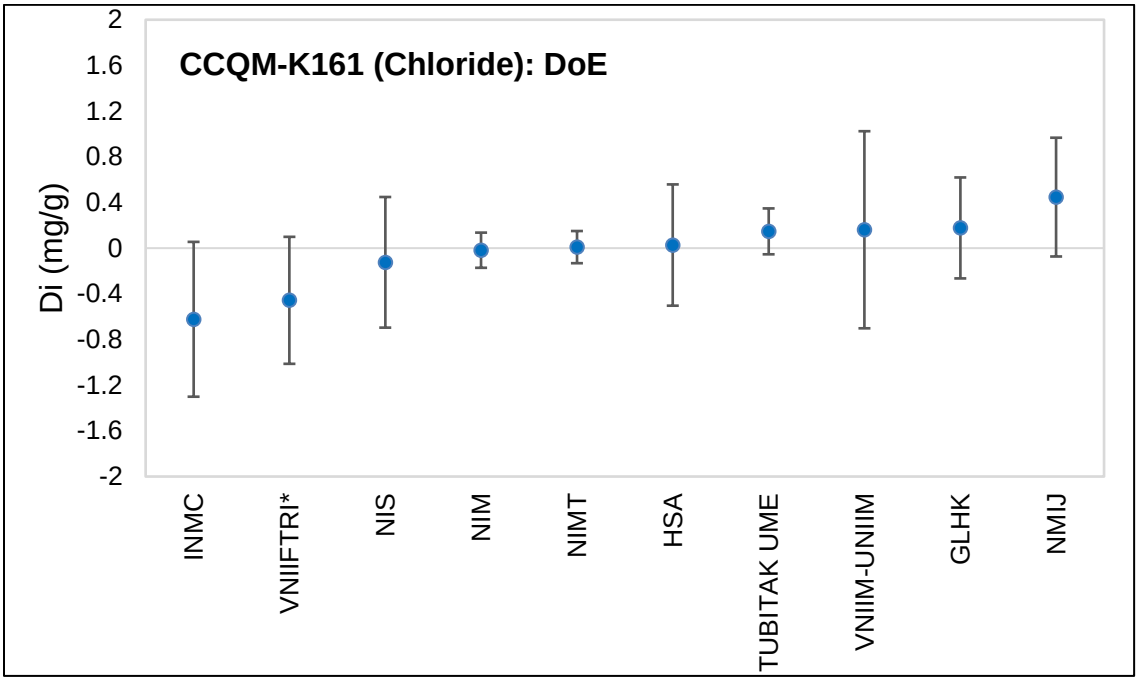


Figure 14. Degrees of Equivalence (DoE) for chloride
*Indicates error bar incorporates dark uncertainty

Table 19. Degrees of equivalence for sulfate in CCQM-K161

Participant	x_i (mg/g)	u_i' (mg/g)	D_i (mg/g)	$U(D_i)$ (mg/g)	$D_i/U(D_i)$
PTB	2.4987	0.1131*	-0.131	0.264	-0.50
TUBITAK UME	2.509	0.1125*	-0.121	0.265	-0.46
NIS	2.598	0.038	-0.032	0.090	-0.36
NIMT	2.620	0.00234	-0.010	0.053	-0.19
GLHK	2.626	0.026	-0.004	0.073	-0.05
NIM	2.637	0.006	0.007	0.054	0.13
HSA	2.640	0.031	0.010	0.090	0.11
VNIIM-UNIIM	2.6938	0.1887	0.064	0.376	0.17
NMIJ	2.77	0.1256*	0.140	0.284	0.49
VNIIFTRI	2.8931	0.1105*	0.263	0.263	1.00

In the u_i' column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature

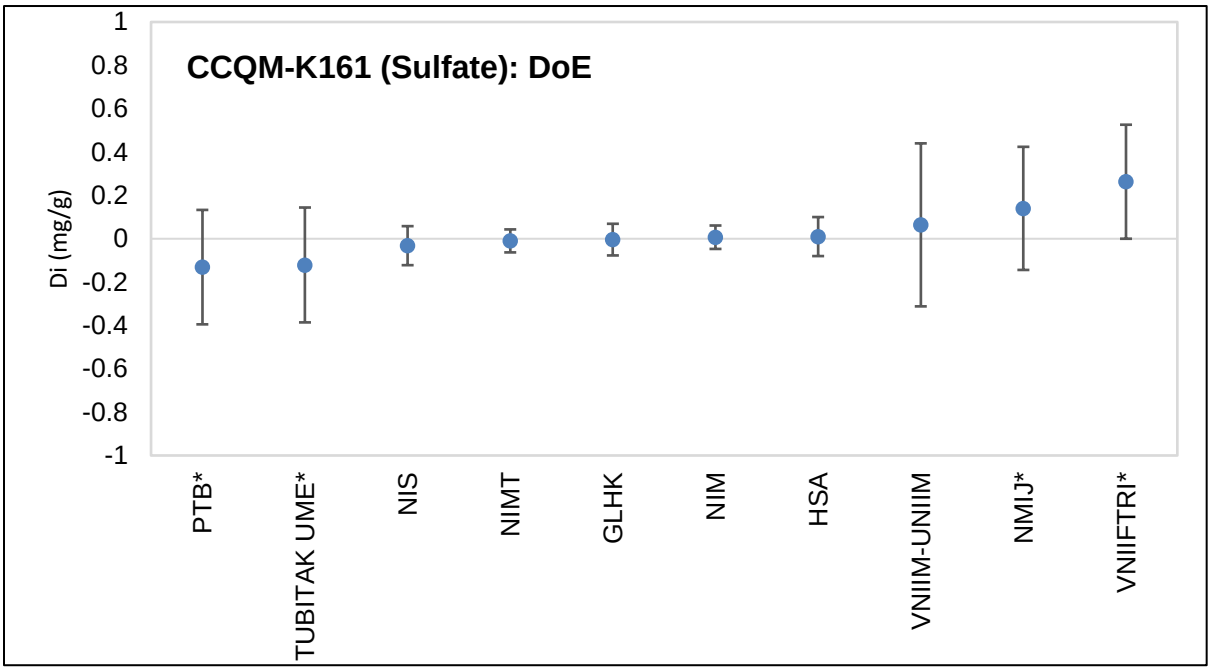


Figure 15. Degrees of Equivalence (DoE) for sulfate
*Indicates error bar incorporates dark uncertainty

Table 20. Degrees of equivalence for bromide in CCQM-K161

Participant	x_i (mg/kg)	u_i' (mg/kg)	D_i (mg/kg)	$U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NIMT#	16.345 (47.21[#])	8.197*	-47.91	20.77	-2.31
VNIIM-UNIIM	45.91	10.16*	-18.34	23.69	-0.77
NIS	52.72	8.444*	-11.53	21.0	-0.55
VNIIFTRI	62.6697	0.01086	-1.584	4.945	-0.32
NIM	65.77	0.207	1.516	4.953	0.31
TUBITAK UME	66.36	0.25	2.106	4.983	0.42
NMIJ	67.87	0.66	3.616	5.13	0.70
PTB	72.98	8.213*	8.726	20.6	0.42

In the x_i column, the data in parenthesis accompanied by a hash ([#]) was corrected data from participant. In the u_i' column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature

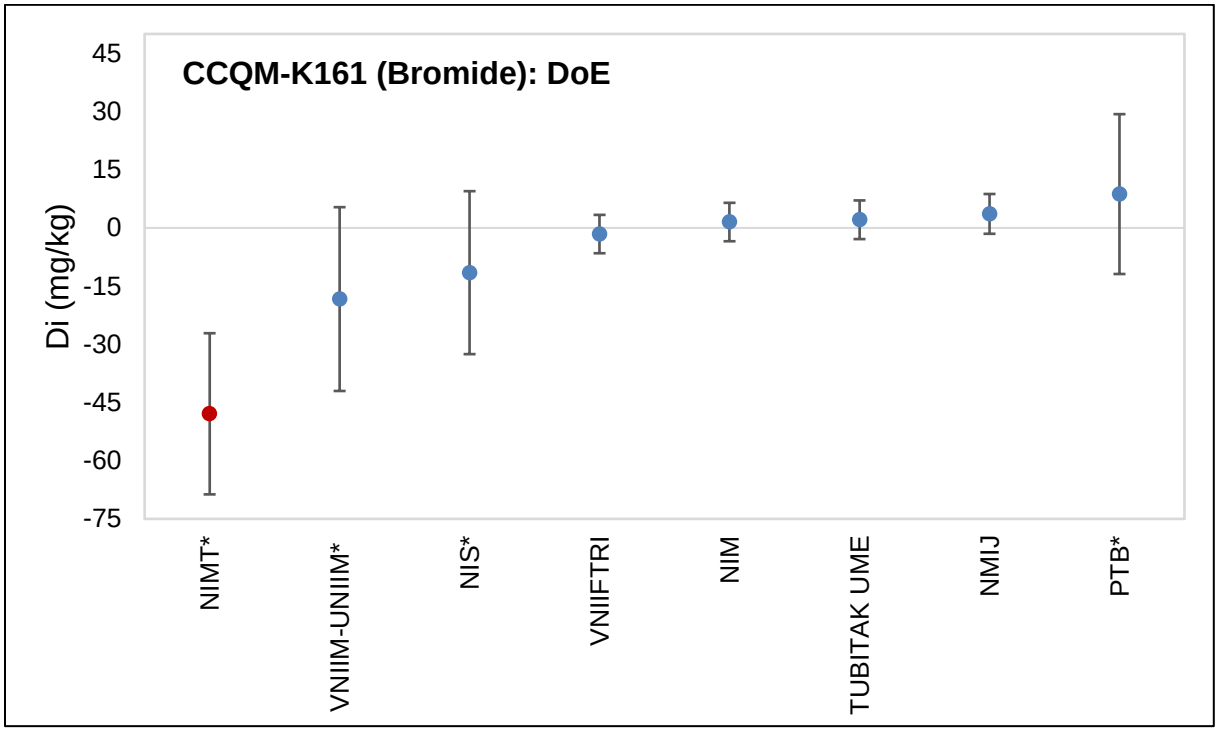


Figure 16. Degrees of Equivalence (DoE) for bromide
The result presented in red shall not be used for CMC claim. It is for information only
*Indicates error bar incorporates dark uncertainty

Table 21. Degrees of equivalence for nitrate in CCQM-K161

Participant	x_i (mg/kg)	u_i' (mg/kg)	D_i (mg/kg)	$U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NIMT	0.346 (1.432[#])	0.1331*	-1.165	0.336	-3.47
NIS	1.42	0.15	-0.091	0.304	-0.30
TUBITAK UME	1.430	0.031	-0.081	0.094	-0.86
NMIJ	1.498	0.014	-0.013	0.077	-0.17
NIM	1.507	0.009	-0.004	0.074	-0.05
NRC	1.5087	0.0073	-0.002	0.074	-0.03
GLHK	1.520	0.059	0.009	0.136	0.07
VNIIFTRI	1.9740	0.1333*	0.463	0.332	1.39

In the x_i column, the data in parenthesis accompanied by a hash ([#]) was corrected data from participant. In the u_i' column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature

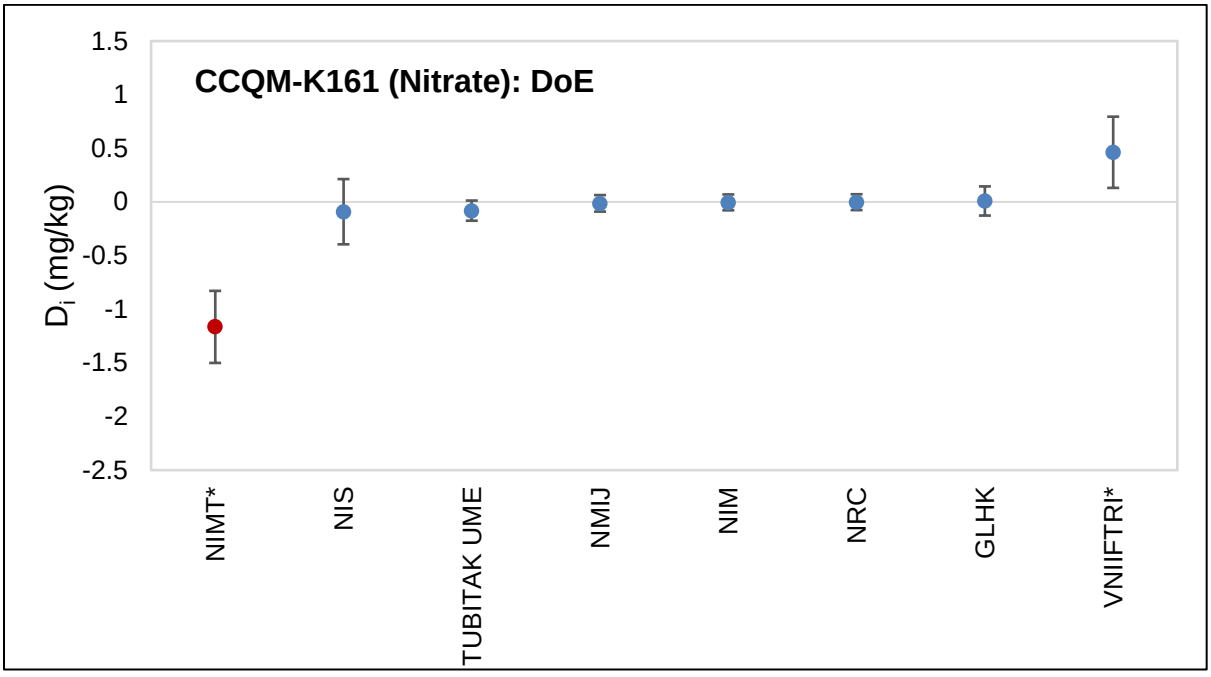


Figure 17. Degrees of Equivalence (DoE) for nitrate
The result presented in red shall not be used for CMC claim. It is for information only
*Indicates error bar incorporates dark uncertainty

Table 22. Degrees of equivalence for phosphate in CCQM-K161

Participant	x_i (µg/kg)	u_i' (µg/kg)	D_i (µg/kg)	$U(D_i)$ (µg/kg)	$D_i/U(D_i)$
VNIIFTRI	33.1810	8.618*	-26	23.18	-1.12
NRC	60.12	0.20	0.938	5.638	0.17
NMIJ	60.13	0.31	0.948	5.661	0.17
NIM	60.17	0.358	0.988	5.684	0.17
TUBITAK UME	62.33	0.59	3.148	5.72	0.55

In the u_i' column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature

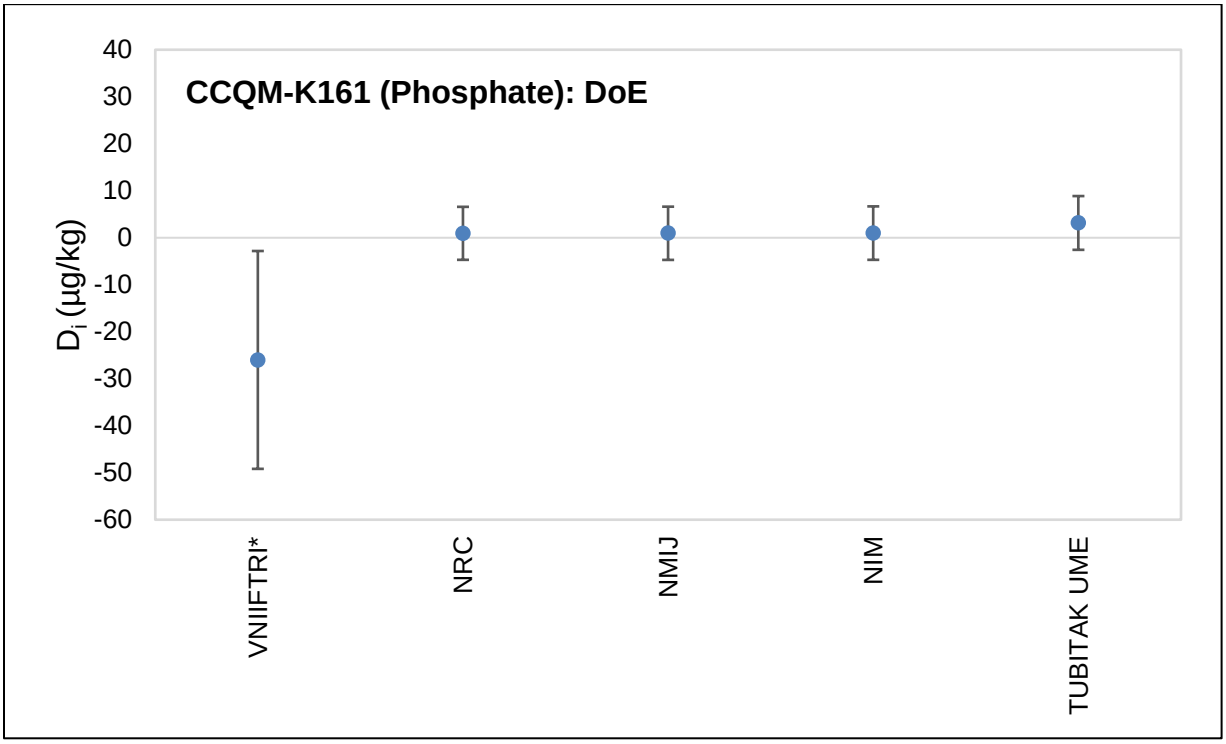


Figure 18. Degrees of Equivalence (DoE) for phosphate
*Indicates error bar incorporates dark uncertainty

USE OF CCQM-K161 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines, Core Capability Statements and CMC support

Successful participation in this key comparison will help to demonstrate measurement capabilities for determination of anions in seawater. Considering the IAWG Core Capability Matrix, this

material falls into the matrix challenge called ‘High salts content’, which corresponds to the CCQM amount-of-substance category sea water, and so will support CMCs for the anions in a mass fraction range from 60 µg/kg to 25 mg/g.

Analyte groups	Matrix challenges						Calibration materials and solutions
	Water/aqueous	High Silica content (e.g. Soils, sediments, plants, …)	High salts content (e.g. Seawater, urine, …)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, …)	Difficult to dissolve metals (Autocatalysts, …)	High volatile matrices (e.g. solvents, fuels, …)	
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)							
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)							
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)							
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)							
Non-metals (P, S, C, N, O)							
Halogens (F, Cl, Br, I)							
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)							
			K161(Cl^-, Br^-, SO_4^{2-}, NO_3^-, PO_4^{3-})				
Small organo-metallics							
Proteins							
Nanoparticles							

Table 23. Core Capability Table

CONCLUSIONS

Twelve national metrology institutes (NMIs) and designated institutes (DIs) participated in the CCQM-K161 comparison for the determination of chloride, sulfate, bromide, nitrate and phosphate in seawater. The mass fraction range of the analyzed anions was from 60 µg/kg to 25 mg/g. Ten laboratories participated in the determination of chloride and sulfate, eight laboratories determined bromide and nitrate, and only five laboratories determined phosphate. This suggests that the determination of trace phosphate in seawater or high salt solution remains a challenge for most laboratories.

Various techniques were employed by the participants for the determination, including isotope dilution inductively coupled plasma mass spectrometry (IDMS), isotope dilution gas chromatography-mass spectrometry (ID-GC-MS), ion chromatography (IC), UV visible

spectrophotometry (UV-Vis) and flow injection analysis (FIA) were used by the participants. The proposed KCRV (with corresponding expanded uncertainty) and degrees of equivalence were calculated using the NIST Decision Tree.

In general, the majority of results from NMIs/DIs agreed with the KCRV within their expanded uncertainties, indicating the success of the CCQM-K161 key comparison.

ACKNOWLEDGEMENTS

The coordinator would like to thank all of the participating laboratories for their support and providing the requested information that was used in this comparison. We also thank Dr. Michael Winchester and Dr. Antonio Possolo for helpful comments and suggestions.

REFERENCES

ISO Guide 35:2017 “Reference materials — Guidance for characterization and assessment of homogeneity and stability”, 2017, Geneva, Switzerland.

CIPM MRA-G-13 “Calibration and measurement capabilities in the context of the CIPM MRA, Guidelines for their review, acceptance and maintenance”, Version 1.1, 30/03/2021.

Possolo, A., Koepke, A., Newton, D. and Winchester, M. (2021), Decision Tree for Key Comparisons, Journal of Research (NIST JRES), National Institute of Standards and Technology, Gaithersburg, MD, [online], https://doi.org/10.6028/jres.126.007.

APPENDIX A: Technical Protocol

CCQM-K161 & P207 Anions in Seawater

Technical Protocol

Rationale

Anions or nutrients such as nitrate and phosphate in seawater are very important targets for oceanographic research and contaminations environmental monitoring. Quantification of minor and trace anions in seawater has always been a challenge for the extremely high salinity, disparate levels of analyte and matrix ions, and even need to be measured at levels close to the detection limits of the method performance.

The comparison is aimed to test the NMI/DI's measurement capabilities for anions (as part of speciation analysis) and supports CMCs within category 5 which corresponds to matrix challenge of "high salts content" in the IAWG core capability table. The selected anions including chloride, sulfate, bromide, nitrate and phosphate in candidate seawater and the concentrations range from very high (10^{-2}) to very low levels (10^{-8}), this broadens the scope and a degree of complexity of earlier measurements in this field. The comparison facilitates to investigate the core capabilities of participants to measure trace, minor and major anions and/or halogens in high salts matrix water, indicate the method performance such as ion chromatography, UV-Vis or herein flow injection analysis based on UV-Vis, HPLC-ICP-MS, ICP-MS, etc. Then support NMIs claim their Calibration and Measurement Capabilities of anions determination in a wide concentration ranges of high salts matrix water.

Sample

The candidate sample was a mixture of seawater sampling from East China Sea and North Pacific with the PO_4^{3-} spiking. About 25 L of mixed candidate seawater in pre-cleaned HDPE plastic drum was filtered to another via 0.2 μm filter membrane for removing bacterial retention. Then the whole drum was placed into a large autoclave and sterilized at 121℃ for 3h after PO_4^{3-} spiking and homogenized for 4 hours. The procedure of autoclaving was performed on two occasions about two days apart. The seawater was filled into the 60 mL polypropylene bottles manually in Class 100 clean room after cooling and sealed in aluminized PET sachets. The polypropylene bottles were cleaned with ultrapure water, oven dried, sealed in double bags and sterilized with ultraviolet lamps in the clean room before filling. Then all the samples were placed at 4 °C temperature room.

The homogeneity study was conducted by analyzing 15 randomly selected bottles use ion chromatography (chloride, sulfate, bromide) and flow injection analysis (nitrate, phosphate) based on UV-Vis spectrophotometry from the whole lot of bottles prepared. The results were subjected to an ANOVA test and the *F* values were less than 1.23, the relative standard uncertainty due to between-bottle inhomogeneity were less than 0.62%, respectively. The results are given in Table 1. Also, the short-term stability was conducted and no instability was observed for the test material at -20 °C and 65 °C during the 3-week study period. Results shows the sample is fit the objective

of the comparison. The long-term stability of the test material at 4°C will be continued until the deadline for submission of results.

Table 1. Homogeneity assessment of data

Anions	ANOVA test		Relative standard uncertainty due to between-bottle inhomogeneity, u_{bb} (%)
	F-statistics	Critical value	
Chloride	1.06	2.42	0.05
Sulfate	1.14		0.09
Bromide	0.82		0.62
Nitrate	1.23		0.13
Phosphate	0.98		0.62

Measurands

Participating laboratories will be provided with two bottles containing about 50 mL of seawater each. All the five measurands and their expected mass fractions are listed in Table 2.

Table 2. Measurands and expected concentration range

Anions	**Excepted mass fraction**
Chloride	(16-25) mg/g
Sulfate	(1-4) mg/g
Bromide	(30-100) mg/kg
Nitrate	(1-5) mg/kg
Phosphate（as P）	(20-100) μg/kg

Distribution

Each participant will receive two numbered bottles containing 50 mL sample each. Based on the analyte and measurement methods choose by participant, if more sample is needed, please tell us at the time of registration specify in the registration table. Participants will be informed the date of samples dispatching, upon receipt, the samples shall be stored at refrigerator (about 4°C) prior to analysis. It is required to confirm the receipt of the sealed samples and return receipt table to the coordinator by e-mail. If there is any damage, please contact us immediately and NIM will dispatch another one.

Methods

Participants may use any appropriate methods of their choice. Calibrations should be carried out using standards with metrological traceability, it should be noted that calibration standards from commercial entities often do not comply with the requirements of CIPM 2009-24 (https://www.bipm.org/utils/common/documents/CIPM-MRA/CIPM-MRA-Traceability.pdf). At

least five replicate samples should be analyzed in order to assess the impact of measurement replication on the overall analytical uncertainty.

Reporting

A reporting form will be sent to the participants by email after the samples are dispatched. The report should be submitted before 15 September, 2021. NIM will confirm the receipt of each report. The result should include individual results, detailed uncertainty budget, details about the method used such as instruments, calibration standards, sample preparation, interference elimination method, reference material used, etc. If more than one method were applied, please describe the details as each method.

If any participant submitted individual results by multiple methods, the result with the smallest uncertainty will be chosen for the calculation of the reference value. Results from participants of pilot study will not be used for KCRV determination.

Schedule

Call for participation: March 2021

Deadline for registration: 15 April 2021

Distribution of samples: May 2021

Deadline for submission of results: 15 September 2021

First presentation of the results: April 2022 at IAWG meeting

Contact Details

Please send completed report form by e-mail no later than **15 September, 2021** to:

Dr. Chao Jingbo

National Institute of Metrology, P. R. China

E-Mail: chaojb@nim.ac.cn; chaojingbo@sina.com

Tel: +86-10-64225471

No.18, Bei San Huan Dong Lu, Chaoyang District, Beijing 100029, China

Dr. Ma Liandi

National Institute of Metrology, P. R. China

E-Mail: mald@nim.ac.cn;

Tel: +86-10-64524704

No.18, Bei San Huan Dong Lu, Chaoyang District, Beijing 100029, China

APPENDIX B: Registration Form

CCQM-K161 & P207 Anions in Seawater

Registration Form

Institute _____

NMI/DI _____

City, Country _____

Postal address _____

_____

Postal code _____

Contact person _____ _____ _____

Title Given name Surname

E-mail _____

Telephone no. _____

Date _____

Any particular local customs / quarantine requirements / special permits for samples sent into your country are needed? _____

(* *Please delete where appropriate.*)

Please indicate the analyte(s) that you would like to determine by indicating “Yes” under the column heading of CCQM-K161&P207 as follows:

Analyte	CCQM-K161	CCQM-P207	Methods of analysis
Chloride			
Sulfate			
Bromide			
Nitrate			
Phosphate (as P)			

Other information:

a) Each participant will receive two numbered bottles containing 50 mL sample each. Based on the analyte and measurement methods choose by participant, if more sample is needed, please tell us at the time of registration.

b) A special requirement of customs entry for the sample dispatch should be described clearly, if needed.

Please send completed registration form by e-mail no later than **15 April 2021** to:

Dr. Chao Jingbo

National Institute of Metrology (NIM)

No. 18, Bei San Huan Dong Lu, Chaoyang District, Beijing, P. R. China

Email: chaojb@nim.ac.cn; chaojingbo@sina.com;

Tel: 86-10-64225471

APPENDIX C: Sample Receipt Form

CCQM-K161 & P207 Anions in Seawater

Sample Receipt Form

Institute	
City, Country	
Detail Address	
Contact person	
Tel /Fax	
Email	
Vial No.	
Receipt Date	

Confirmation of Package Content

Please choose the state of the sample: ☐ intact

☐ broken

☐ other thing:

Please fill in the temperature indicated: The thermal sensitive test paper indicated that the maximum temperature in the transportation process was ☐ below 65℃

☐ or at ___ ℃

Please fill in the form and return it to **Dr. Chao Jingbo** (chaojb@nim.ac.cn; chaojingbo@sina.com) by E-mail after receipt of the sample.

Dr. Chao Jingbo
National Institute of Metrology (NIM)
No. 18, Bei San Huan Dong Lu, Chaoyang District, Beijing, P. R. China
Email: chaojb@nim.ac.cn; chaojingbo@sina.com;
Tel: 86-10-64225471

APPENDIX D: Report Form

CCQM-K161 & P207 Anions in Seawater

Report Form

Information of participant

Institute	Full Name:
	Abbreviative Name:
Country	
Contact Person	
Analyst(s)	
Date	
Bottle No.	
Email	

*Please complete and submit this form with suitable Core Capability Table **by e-mail to Dr. Chao Jingbo (chaojb@nim.ac.cn and chaojingbo@sina.com) no later than 21 November, 2021.**

Summary of analytical method (If it is necessary, please describe it by each measurand.)

Analyte	Sample preparation/Digestion procedure	Measurement technique	Calibration method	Reference materials used

Summary of results ☐ **CCQM-K161** ☐ **CCQM-P207**

Run No.	Chloride (mg/g)	Sulfate (mg/g)	Bromide (mg/kg)	Nitrate (mg/kg)	Phosphate (as P) (µg/kg)
1					
2					
3					
4					
5					
Mean					
Standard Deviation					
Combined standard uncertainty (u_c)					
Coverage factor (k)					
Expanded uncertainty (U)					

Uncertainty Budget (Please make an uncertainty budget by each measurand)

Analyte: (for example) Chloride

Parameter	Source of uncertainty	Typical value	Standard uncertainty	Unit	Type

C_x	Mass fraction		mg/g
u_c	Combined standard uncertainty		mg/g
k	Coverage factor		
U	Expanded uncertainty		mg/g

APPENDIX E: NIST Decision Tree Reports

Chloride

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	INMC	18.4200	0.339000	238
TRUE	VNIIFTRI	18.5857	0.007094	60
TRUE	NIS	18.9190	0.280000	60
TRUE	NIM	19.0250	0.036000	60
TRUE	NIMT	19.0520	0.012520	60
TRUE	HSA	19.0700	0.260000	60
TRUE	TUBITAK UME	19.1900	0.074000	60
TRUE	VNIIM-UNIIM	19.2040	0.432600	60
TRUE	GLHK	19.2200	0.210000	60
TRUE	NMIJ	19.4900	0.250000	60

Date: 2024-01-31
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 411
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 19.04
Standard uncertainty: 0.06761
95% coverage interval: (18.9, 19.18)
Dark uncertainty (tau): 0.2228
Tau posterior 0.025 and 0.975 quantiles: (0.1027,0.5074)

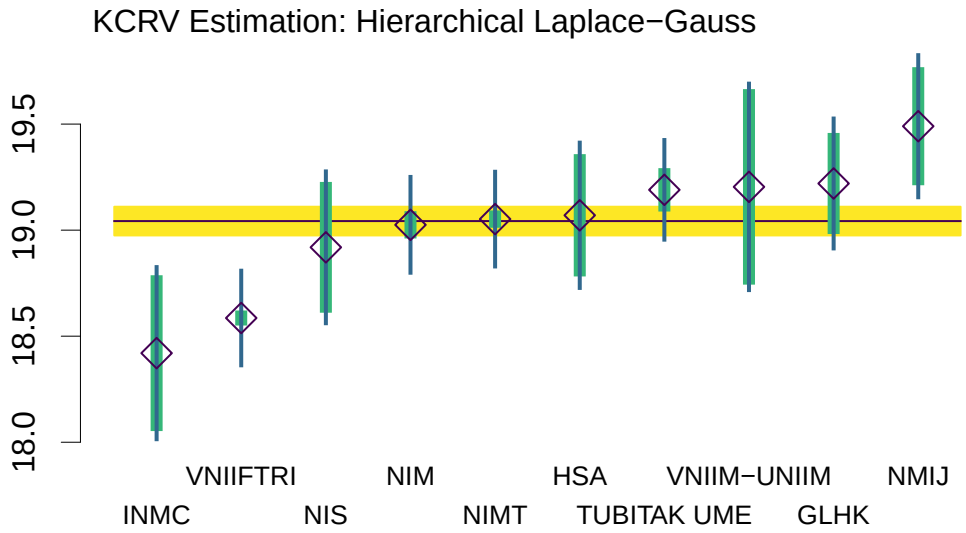
Decision Tree Hypothesis test results

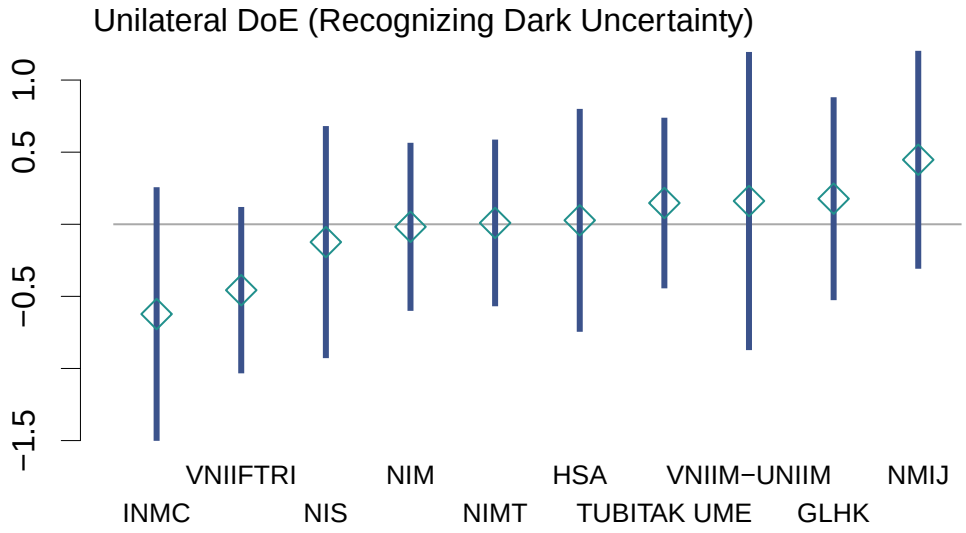
Cochran's test for Homogeneity:
p-value: $p < 0.001$
Q = 1192 (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 0.3235
tau/median(x) = 0.01697
tau/median(u) = 1.407

Shapiro-Wilk test for Normality: p = 3.955e-07

Miao-Gel-Gastwirth test of Symmetry: p = 0.4062

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
19.5
19.0
18.5
18.0
INMC
VNIIFTRI
NIS
NIM
NIMT
HSA
TUBITAK
VNIIM−UNIIM
UME
GLHK
NMIJ


Unilateral DoE (Recognizing Dark Uncertainty)
1.0
0.5
−0.5
−1.5
INMC
VNIIFTRI
NIS
NIM
NIMT
HSA
TUBITAK
VNIIM−UNIIM
UME
GLHK
NMIJ

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
INMC	INMC	-0.622700	0.8587	-1.4810	0.23600
VNIIFTRI	VNIIFTRI	-0.457000	0.5561	-1.0130	0.09904
NIS	NIS	-0.123700	0.7839	-0.9076	0.66020
NIM	NIM	-0.017720	0.5620	-0.5797	0.54420
NIMT	NIMT	0.009278	0.5571	-0.5478	0.56630
HSA	HSA	0.027280	0.7520	-0.7248	0.77930
TUBITAK UME	TUBITAK UME	0.147300	0.5708	-0.4235	0.71810
VNIIM-UNIIM	VNIIM-UNIIM	0.161300	1.0130	-0.8519	1.17400
GLHK	GLHK	0.177300	0.6827	-0.5054	0.86000
NMIJ	NMIJ	0.447300	0.7349	-0.2876	1.18200

Lab Uncertainties Table

lab	x	u	nu	ut
INMC	18.42	0.339000	238	0.4057
VNIIFTRI	18.59	0.007094	60	0.2230
NIS	18.92	0.280000	60	0.3579
NIM	19.02	0.036000	60	0.2257
NIMT	19.05	0.012520	60	0.2232
HSA	19.07	0.260000	60	0.3424
TUBITAK UME	19.19	0.074000	60	0.2348
VNIIM-UNIIM	19.20	0.432600	60	0.4866
GLHK	19.22	0.210000	60	0.3062
NMIJ	19.49	0.250000	60	0.3349

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
INMC	-0.622700	0.4399	0.8587	-1.4810	0.23600	0.34630	0.6781	-1.30100	0.05536
VNIIFTRI	-0.457000	0.2745	0.5561	-1.0130	0.09904	0.06793	0.1390	-0.59600	-0.31800
NIS	-0.123700	0.3965	0.7839	-0.9076	0.66020	0.29100	0.5725	-0.69620	0.44870
NIM	-0.017720	0.2783	0.5620	-0.5797	0.54420	0.07703	0.1538	-0.17160	0.13610
NIMT	0.009278	0.2727	0.5571	-0.5478	0.56630	0.06877	0.1408	-0.13160	0.15010
HSA	0.027280	0.3808	0.7520	-0.7248	0.77930	0.27110	0.5313	-0.50400	0.55860
TUBITAK UME	0.147300	0.2840	0.5708	-0.4235	0.71810	0.10180	0.2012	-0.05394	0.34850
VNIIM-UNIIM	0.161300	0.5166	1.0130	-0.8519	1.17400	0.44020	0.8633	-0.70200	1.02500
GLHK	0.177300	0.3466	0.6827	-0.5054	0.86000	0.22370	0.4416	-0.26430	0.61890
NMIJ	0.447300	0.3749	0.7349	-0.2876	1.18200	0.26480	0.5205	-0.07326	0.96780

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
deviance	1.001	50000
lambda[1]	1.001	50000
lambda[2]	1.001	50000
lambda[3]	1.001	32000
lambda[4]	1.001	31000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
lambda[8]	1.001	50000
lambda[9]	1.001	21000
lambda[10]	1.001	21000
mu	1.001	50000
sigma[1]	1.001	10000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
sigma[4]	1.001	27000
sigma[5]	1.001	36000
sigma[6]	1.001	47000
sigma[7]	1.001	50000
sigma[8]	1.001	45000
sigma[9]	1.001	50000
sigma[10]	1.001	50000
tau	1.001	6700

Sulfate

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	PTB	2.4987	0.025000	60
TRUE	TUBITAK UME	2.5090	0.022000	60
TRUE	NIS	2.5980	0.038000	60
TRUE	NIMT	2.6200	0.002340	60
TRUE	GLHK	2.6260	0.026000	60
TRUE	NIM	2.6370	0.006000	60
TRUE	HSA	2.6400	0.031000	4
TRUE	VNIIM-UNIIM	2.6938	0.188700	60
TRUE	NMIJ	2.7700	0.060000	60
TRUE	VNIIFTRI	2.8931	0.007108	60

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 841
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 2.63
Standard uncertainty: 0.02578
95% coverage interval: (2.577, 2.682)
Dark uncertainty (tau): 0.1103
Tau posterior 0.025 and 0.975 quantiles: (0.05962,0.2256)

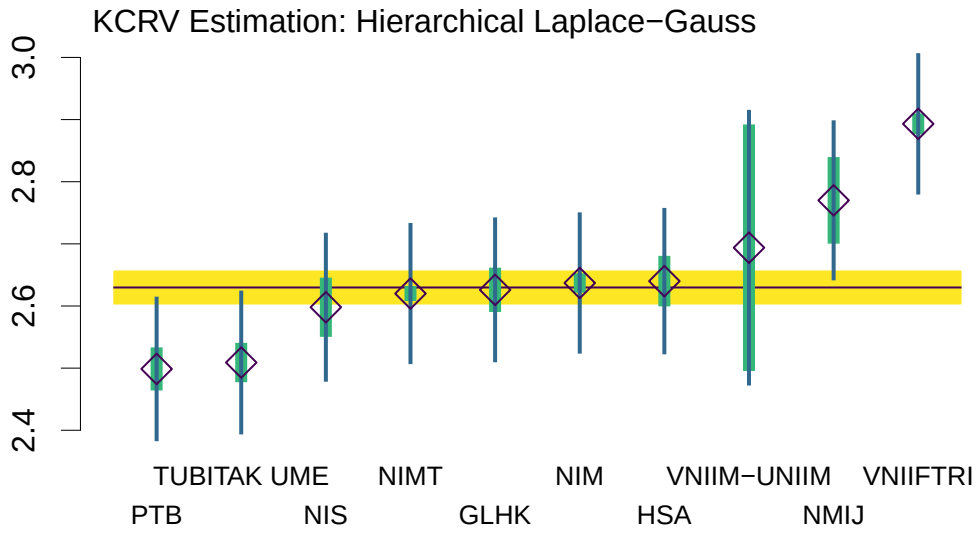
Decision Tree Hypothesis test results

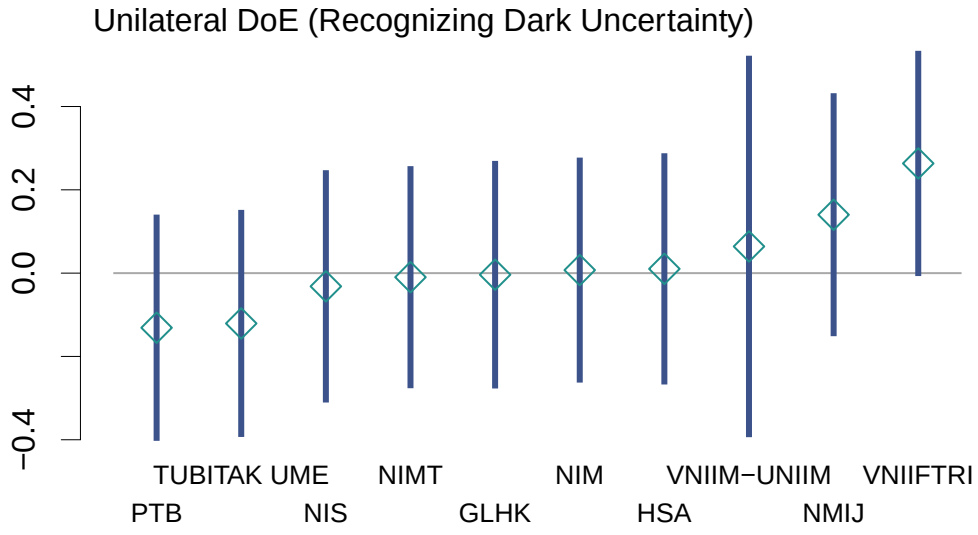
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 1412$ (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. $= 0.1236$
tau/median(x) $= 0.04695$
tau/median(u) $= 4.845$

Shapiro-Wilk test for Normality: $p = 2.718e\text{-}05$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.531$

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
3.0
2.8
2.6
2.4
TUBITAK
UME
NIMT
NIM
VNIIM−UNIIM
VNIIFTRI
PTB
NIS
GLHK
HSA
NMIJ


Unilateral DoE (Recognizing Dark Uncertainty)
0.4
0.2
0.0
−0.4
TUBITAK
UME
NIMT
NIM
VNIIM−UNIIM
VNIIFTRI
PTB
NIS
GLHK
HSA
NMIJ

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
PTB	PTB	-0.131100	0.2643	-0.3954000	0.1333
TUBITAK UME	TUBITAK UME	-0.120800	0.2654	-0.3861000	0.1446
NIS	NIS	-0.031750	0.2716	-0.3034000	0.2399
NIMT	NIMT	-0.009753	0.2593	-0.2691000	0.2496
GLHK	GLHK	-0.003753	0.2659	-0.2697000	0.2622
NIM	NIM	0.007247	0.2629	-0.2556000	0.2701
HSA	HSA	0.010250	0.2704	-0.2601000	0.2806
VNIIM-UNIIM	VNIIM-UNIIM	0.064050	0.4507	-0.3866000	0.5147
NMIJ	NMIJ	0.140200	0.2844	-0.1442000	0.4247
VNIIFTRI	VNIIFTRI	0.263300	0.2632	0.0001796	0.5265

Lab Uncertainties Table

lab	x	u	nu	ut
PTB	2.499	0.025000	60	0.1131
TUBITAK UME	2.509	0.022000	60	0.1125
NIS	2.598	0.038000	60	0.1167
NIMT	2.620	0.002340	60	0.1103
GLHK	2.626	0.026000	60	0.1133
NIM	2.637	0.006000	60	0.1105
HSA	2.640	0.031000	4	0.1146
VNIIM-UNIIM	2.694	0.188700	60	0.2186
NMIJ	2.770	0.060000	60	0.1256
VNIIFTRI	2.893	0.007108	60	0.1105

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
PTB	-0.131100	0.1312	0.2643	-0.3954000	0.1333	0.03630	0.07174	-0.20280	-0.05932
TUBITAK UME	-0.120800	0.1311	0.2654	-0.3861000	0.1446	0.03404	0.06776	-0.18850	-0.05299
NIS	-0.031750	0.1345	0.2716	-0.3034000	0.2399	0.04601	0.09042	-0.12220	0.05867
NIMT	-0.009753	0.1289	0.2593	-0.2691000	0.2496	0.02588	0.05260	-0.06236	0.04285
GLHK	-0.003753	0.1320	0.2659	-0.2697000	0.2622	0.03680	0.07323	-0.07699	0.06948
NIM	0.007247	0.1294	0.2629	-0.2556000	0.2701	0.02653	0.05390	-0.04666	0.06115
HSA	0.010250	0.1351	0.2704	-0.2601000	0.2806	0.04546	0.09003	-0.07978	0.10030
VNIIM-UNIIM	0.064050	0.2287	0.4507	-0.3866000	0.5147	0.19090	0.37570	-0.31160	0.43970
NMIJ	0.140200	0.1432	0.2844	-0.1442000	0.4247	0.06585	0.12930	0.01094	0.26950
VNIIFTRI	0.263300	0.1294	0.2632	0.0001796	0.5265	0.02676	0.05423	0.20910	0.31760

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
deviance	1.001	50000
lambda[1]	1.001	50000
lambda[2]	1.001	50000
lambda[3]	1.001	50000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	36000
lambda[7]	1.001	50000
lambda[8]	1.001	50000
lambda[9]	1.001	50000
lambda[10]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	25000
sigma[2]	1.001	36000
sigma[3]	1.001	42000
sigma[4]	1.001	19000
sigma[5]	1.001	50000
sigma[6]	1.001	50000
sigma[7]	1.001	23000
sigma[8]	1.001	46000
sigma[9]	1.001	50000
sigma[10]	1.001	50000
tau	1.001	50000

Bromide

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIMT	16.3450	0.10455	60
TRUE	VNIIM-UNIIM	45.9100	6.00500	60
TRUE	NIS	52.7200	2.03000	60
TRUE	VNIIFTRI	62.6697	0.01086	60
TRUE	NIM	65.7700	0.20700	60
TRUE	TUBITAK UME	66.3600	0.25000	60
TRUE	NMIJ	67.8700	0.66000	60
TRUE	PTB	72.9800	0.53000	60

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 728
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 64.25
Standard uncertainty: 2.497
95% coverage interval: (59.31, 69.2)
Dark uncertainty (tau): 8.196
Tau posterior 0.025 and 0.975 quantiles: (3.939,19.37)

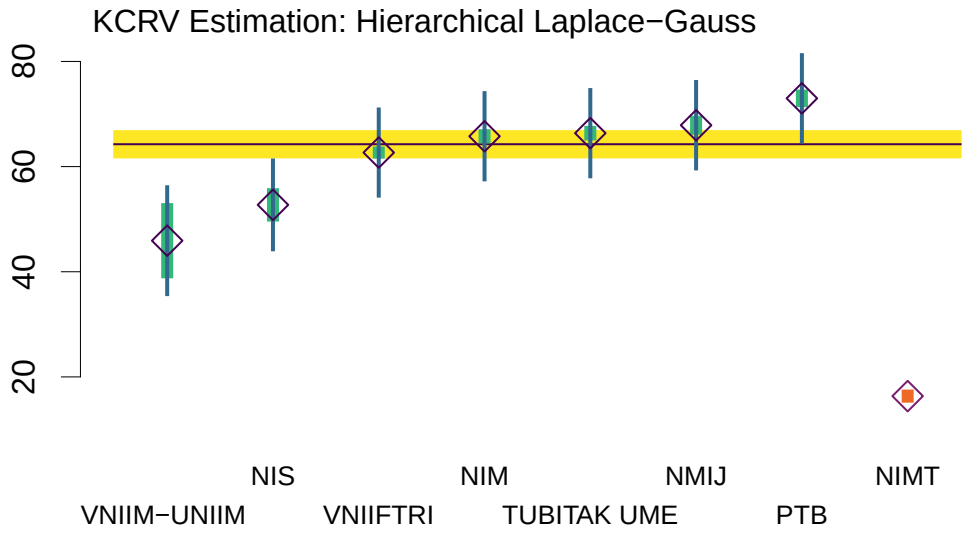
Decision Tree Hypothesis test results

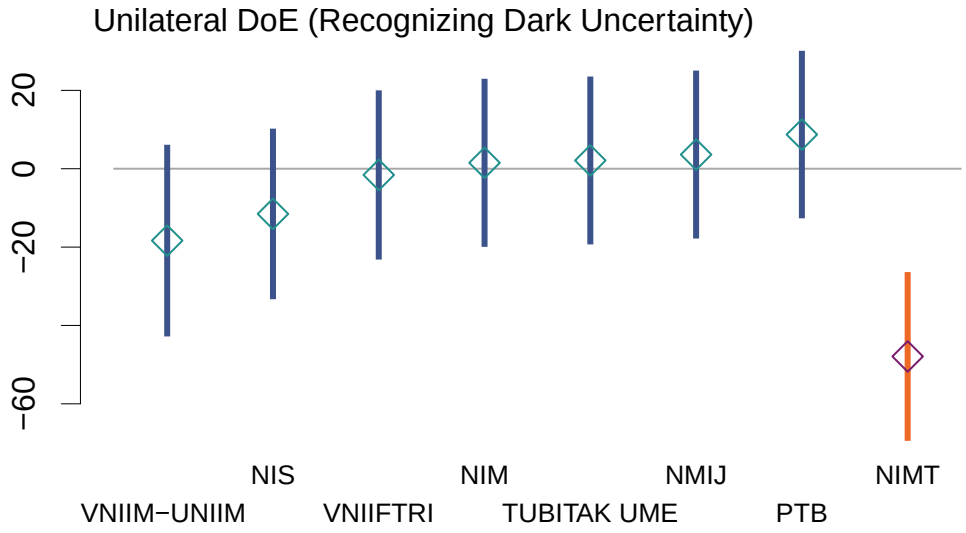
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 910.9$ (Reference Distribution: Chi-Square with 6 Degrees of Freedom)
tau est. = 3.16
tau/median(x) = 0.04805
tau/median(u) = 5.963

Shapiro-Wilk test for Normality: $p = 2.194e\text{-}05$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.065$

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
80
60
40
20
NIS
NIM
NMIJ
NIMT
VNIIM−UNIIM
VNIIFTRI
TUBITAK UME
PTB


Unilateral DoE (Recognizing Dark Uncertainty)
20
0
−20
−60
NIS
NIM
NMIJ
NIMT
VNIIM−UNIIM
VNIIFTRI
TUBITAK UME
PTB

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NIMT	NIMT	-47.910	20.77	-68.68	-27.140
VNIIM-UNIIM	VNIIM-UNIIM	-18.340	23.69	-42.04	5.350
NIS	NIS	-11.530	21.00	-32.53	9.462
VNIIFTRI	VNIIFTRI	-1.584	20.82	-22.41	19.240
NIM	NIM	1.516	20.68	-19.17	22.200
TUBITAK UME	TUBITAK UME	2.106	20.65	-18.55	22.760
NMIJ	NMIJ	3.616	20.67	-17.05	24.290
PTB	PTB	8.726	20.60	-11.88	29.330

Lab Uncertainties Table

lab	x	u	nu	ut
NIMT	16.34	0.10460	60	8.197
VNIIM-UNIIM	45.91	6.00500	60	10.160
NIS	52.72	2.03000	60	8.444
VNIIFTRI	62.67	0.01086	60	8.196
NIM	65.77	0.20700	60	8.199
TUBITAK UME	66.36	0.25000	60	8.200
NMIJ	67.87	0.66000	60	8.223
PTB	72.98	0.53000	60	8.213

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIMT	-47.910	10.32	20.77	-68.68	-27.140	2.499	4.951	-52.860	-42.960
VNIIM-UNIIM	-18.340	11.92	23.69	-42.04	5.350	6.651	13.070	-31.410	-5.277
NIS	-11.530	10.39	21.00	-32.53	9.462	3.230	6.348	-17.880	-5.186
VNIIFTRI	-1.584	10.28	20.82	-22.41	19.240	2.497	4.945	-6.529	3.361
NIM	1.516	10.21	20.68	-19.17	22.200	2.505	4.953	-3.437	6.469
TUBITAK UME	2.106	10.19	20.65	-18.55	22.760	2.509	4.983	-2.877	7.089
NMIJ	3.616	10.18	20.67	-17.05	24.290	2.581	5.130	-1.514	8.746
PTB	8.726	10.17	20.60	-11.88	29.330	2.553	5.048	3.678	13.770

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
deviance	1.001	26000
lambda[1]	1.001	50000
lambda[2]	1.001	50000

	Rhat	n.eff
lambda[3]	1.001	50000
lambda[4]	1.001	22000
lambda[5]	1.001	33000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
mu	1.001	34000
sigma[1]	1.001	50000
sigma[2]	1.001	23000
sigma[3]	1.001	12000
sigma[4]	1.001	50000
sigma[5]	1.001	50000
sigma[6]	1.001	50000
sigma[7]	1.001	50000
tau	1.001	50000

Nitrate

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIMT	0.3460	0.007661	60
TRUE	NIS	1.4200	0.150000	60
TRUE	TUBITAK UME	1.4300	0.031000	60
TRUE	NMIJ	1.4980	0.014000	60
TRUE	NIM	1.5070	0.009000	60
TRUE	NRC	1.5087	0.007300	60
TRUE	GLHK	1.5200	0.059000	60
TRUE	VNIIFTRI	1.9740	0.010620	60
FALSE	NIM			

(Information value) | 1.5090| 0.013000| 60|

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 133
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 1.511
Standard uncertainty: 0.03507
95% coverage interval: (1.438, 1.583)
Dark uncertainty (tau): 0.1329
Tau posterior 0.025 and 0.975 quantiles: (0.06638,0.3141)

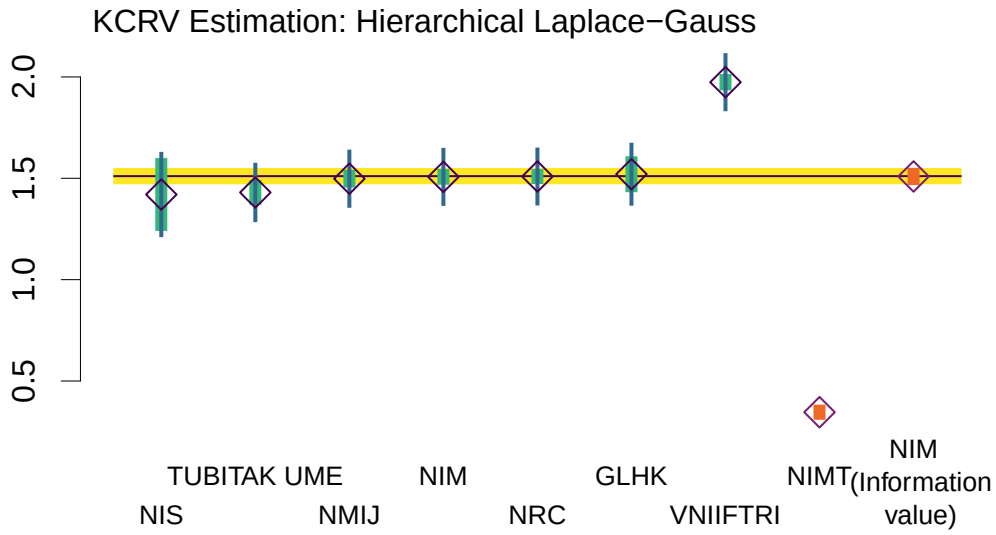
Decision Tree Hypothesis test results

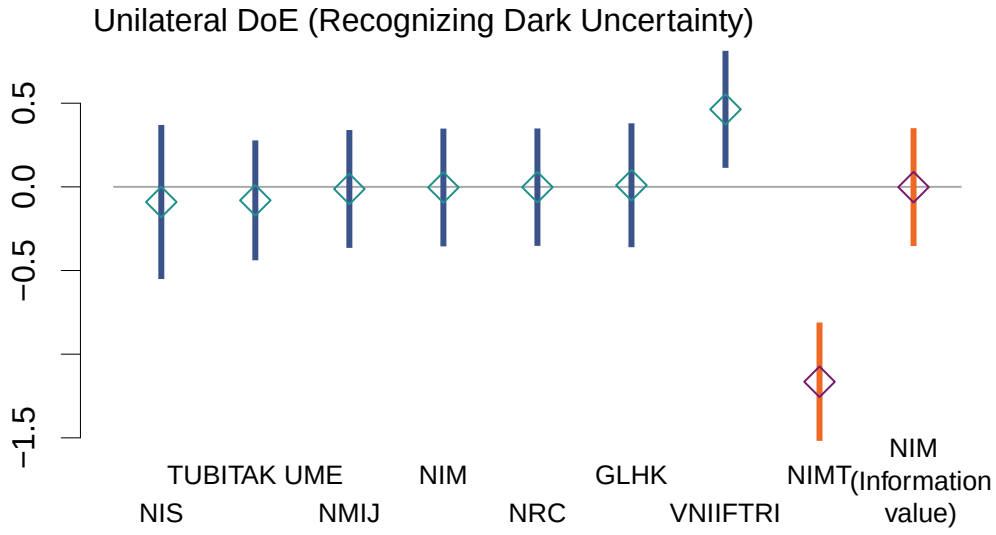
Cochran's test for Homogeneity:
p-value: $p < 0.001$
Q = 1588 (Reference Distribution: Chi-Square with 6 Degrees of Freedom)
tau est. = 0.2179
tau/median(x) = 0.1446
tau/median(u) = 15.57

Shapiro-Wilk test for Normality: p = 1.896e-05

Miao-Gel-Gastwirth test of Symmetry: p = 0.4402

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
2.0
1.5
1.0
0.5
NIS
TUBITAK
NMIJ
UME
NIM
NRC
GLHK
VNIIFTRI
NIMT
NIM (Information value)


Unilateral DoE (Recognizing Dark Uncertainty)
0.5
0.0
−0.5
−1.5
NIS
TUBITAK
NMIJ
UME
NIM
NRC
GLHK
VNIIFTRI
NIMT
NIM (Information value)

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NIMT	NIMT	-1.165000	0.3359	-1.5000	-0.8287
NIS	NIS	-0.090560	0.4425	-0.5330	0.3519
TUBITAK UME	TUBITAK UME	-0.080560	0.3404	-0.4209	0.2598
NMIJ	NMIJ	-0.012560	0.3343	-0.3468	0.3217
NIM	NIM	-0.003563	0.3341	-0.3377	0.3305
NRC	NRC	-0.001863	0.3330	-0.3348	0.3311
GLHK	GLHK	0.009437	0.3524	-0.3429	0.3618
VNIIFTRI	VNIIFTRI	0.463400	0.3317	0.1317	0.7952
NIM					

(Information value) |NIM (Information value) | -0.001563| 0.3343| -0.3359| 0.3328|

Lab Uncertainties Table

lab	x	u	nu	ut
NIMT	0.346	0.007661	60	0.1331
NIS	1.420	0.150000	60	0.2004
TUBITAK UME	1.430	0.031000	60	0.1365
NMIJ	1.498	0.014000	60	0.1336
NIM	1.507	0.009000	60	0.1332
NRC	1.509	0.007300	60	0.1331
GLHK	1.520	0.059000	60	0.1454
VNIIFTRI	1.974	0.010620	60	0.1333
NIM				

(Information value) | 1.509| 0.013000| 60| 0.1335|

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIMT	-1.165000	0.1664	0.3359	-1.5000	-0.8287	0.03590	0.07395	-1.23900	-1.09100
NIS	-0.090560	0.2238	0.4425	-0.5330	0.3519	0.15500	0.30420	-0.39480	0.21370
TUBITAK UME	-0.080560	0.1689	0.3404	-0.4209	0.2598	0.04700	0.09362	-0.17420	0.01305
NMIJ	-0.012560	0.1664	0.3343	-0.3468	0.3217	0.03787	0.07714	-0.08971	0.06458
NIM	-0.003563	0.1665	0.3341	-0.3377	0.3305	0.03622	0.07433	-0.07790	0.07077
NRC	-0.001863	0.1649	0.3330	-0.3348	0.3311	0.03580	0.07377	-0.07563	0.07191
GLHK	0.009437	0.1760	0.3524	-0.3429	0.3618	0.06912	0.13640	-0.12700	0.14590
VNIIFTRI	0.463400	0.1649	0.3317	0.1317	0.7952	0.03672	0.07501	0.38840	0.53850
NIM									

(Information value) | -0.001563| 0.1665| 0.3343| -0.3359| 0.3328| 0.03747| 0.07624| -0.07780| 0.07468|

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
deviance	1.001	50000
lambda[1]	1.001	41000
lambda[2]	1.001	50000
lambda[3]	1.001	25000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	34000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
sigma[4]	1.001	25000
sigma[5]	1.001	50000
sigma[6]	1.001	50000
sigma[7]	1.001	29000
tau	1.001	50000

Phosphate

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	VNIIFTRI	33.181	0.7542	60
TRUE	NRC	60.120	0.2000	60
TRUE	NMIJ	60.130	0.3100	60
TRUE	NIM	60.170	0.3580	60
TRUE	TUBITAK UME	62.330	0.5900	60

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 502
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 59.18
Standard uncertainty: 2.723
95% coverage interval: (53.54, 64.82)
Dark uncertainty (tau): 8.585
Tau posterior 0.025 and 0.975 quantiles: (4.005,23.85)

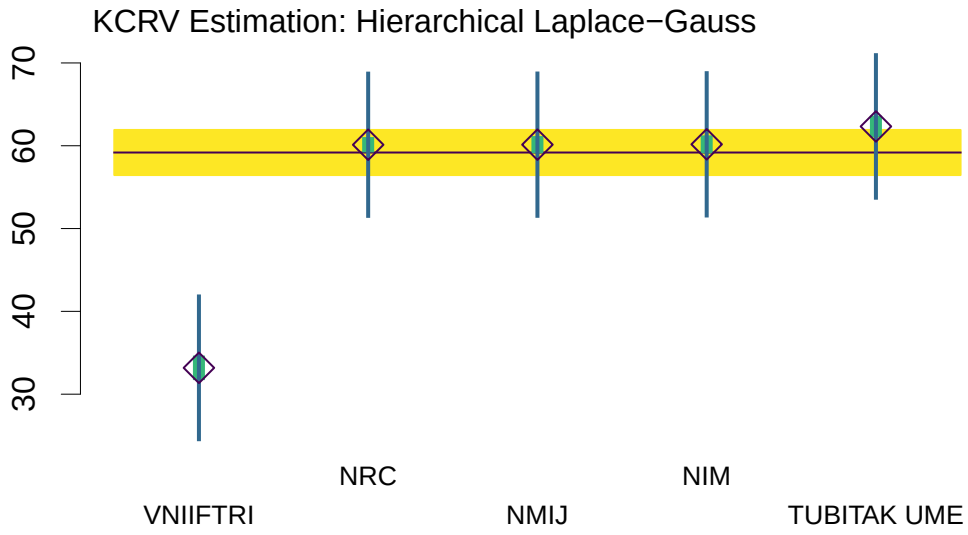
Decision Tree Hypothesis test results

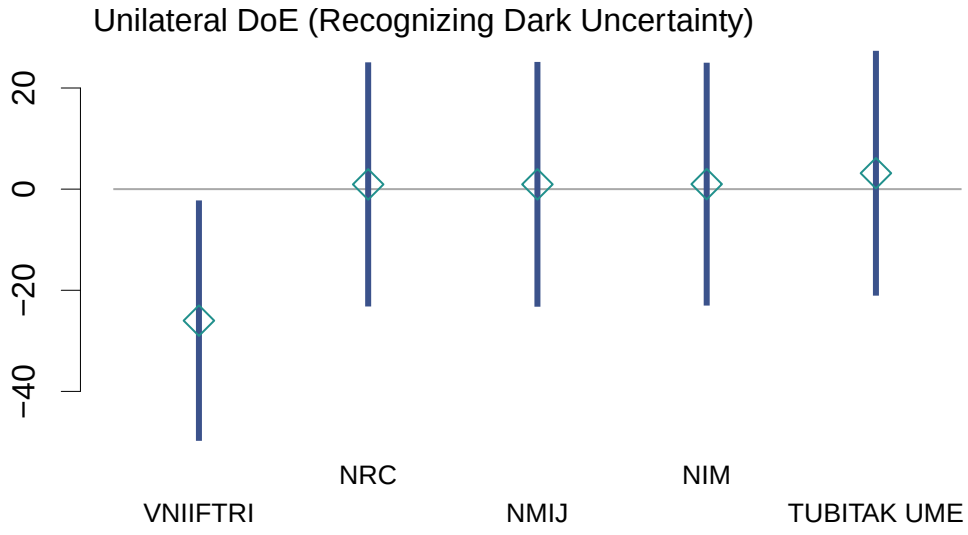
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 1256$ (Reference Distribution: Chi-Square with 4 Degrees of Freedom)
tau est. $= 6.354$
tau/median(x) $= 0.1057$
tau/median(u) $= 17.75$

Shapiro-Wilk test for Normality: $p = 0.001753$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.3836$

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
70
60
50
40
30
NRC
NIM
VNIIFTRI
NMIJ
TUBITAK UME


Unilateral DoE (Recognizing Dark Uncertainty)
20
0
−20
−40
NRC
NIM
VNIIFTRI
NMIJ
TUBITAK UME

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
VNIIFTRI	VNIIFTRI	-26.0000	23.18	-49.18	-2.826
NRC	NRC	0.9381	23.54	-22.61	24.480
NMIJ	NMIJ	0.9481	23.61	-22.66	24.560
NIM	NIM	0.9881	23.42	-22.43	24.410
TUBITAK UME	TUBITAK UME	3.1480	23.61	-20.47	26.760

Lab Uncertainties Table

lab	x	u	nu	ut
VNIIFTRI	33.18	0.7542	60	8.618
NRC	60.12	0.2000	60	8.588
NMIJ	60.13	0.3100	60	8.591
NIM	60.17	0.3580	60	8.593
TUBITAK UME	62.33	0.5900	60	8.606

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
VNIIFTRI	-26.0000	11.65	23.18	-49.18	-2.826	2.827	5.771	-31.770	-20.230
NRC	0.9381	11.67	23.54	-22.61	24.480	2.731	5.638	-4.700	6.576
NMIJ	0.9481	11.61	23.61	-22.66	24.560	2.741	5.661	-4.713	6.609
NIM	0.9881	11.73	23.42	-22.43	24.410	2.749	5.684	-4.696	6.672
TUBITAK UME	3.1480	11.69	23.61	-20.47	26.760	2.785	5.720	-2.572	8.868

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
deviance	1.001	24000
lambda[1]	1.001	45000
lambda[2]	1.001	37000
lambda[3]	1.001	50000
lambda[4]	1.001	50000
lambda[5]	1.001	38000
mu	1.001	50000
sigma[1]	1.001	43000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
sigma[4]	1.001	50000
sigma[5]	1.001	49000
tau	1.001	25000
	Rhat	n.eff