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, contaminations environmental monitoring and annually level comparison. 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^{-5}), 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 21 November, 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: 30 April 2021
Distribution of samples: June 2021
Deadline for submission of results: 21 November 2021
First presentation of the results: April 2022 at IAWG meeting

Contact Details

Please send completed report form by e-mail no later than **21 November, 2021** to:

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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 (total element) (F, Cl, Br, I)				—			
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)			K161 (PO_4^{3-}) – or high level; mass fraction range crosses low/high level boundary K161 (Cl^-, Br^-, SO_4^{2-}, NO_3^-)				
Small organo-metallics							
Proteins							
Nanoparticles							