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Inter-laboratory study for the certification of trace elements in seawater certified reference materials NASS-7 and CASS-6

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Abstract

Certification of trace metals in seawater Certified Reference Materials (CRMs) NASS-7 and CASS-6 is described. At the National Research Council Canada (NRC), column separation was performed to remove the seawater matrix prior to the determination of Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, U, V and Zn, whereas As was directly measured in 10-fold diluted seawater samples, and B was directly measured in 200-fold diluted seawater samples. High resolution inductively coupled plasma mass spectrometry (HR-ICPMS) was used for elemental analyses, with double isotope dilution for the accurate determination of B, Cd, Cr, Cu, Fe, Pb, Mo, Ni, U and Zn in seawater NASS-7 and CASS-6, and standard addition calibration for As, Co, Mn and V. In addition, all analytes were measured using standard addition calibration with triple quadrupole (QQQ)-ICPMS to provide a second set of data at NRC. Expert laboratories

worldwide were invited to contribute data to the certification of trace metals in NASS-7 and CASS-6. Various analytical methods were employed by participants including column separation, co-precipitation and simple dilution coupled to ICPMS detection or flow-injection analysis coupled to chemiluminescence detection, with use of double isotope dilution calibration, matrix matching external calibration and standard addition calibration.

Results presented in this study show that majority of laboratories have demonstrated their measurement capabilities for the accurate determination of trace metals in seawater. As a result of this comparison, certified/reference values and associated uncertainties were assigned for 14 elements in seawater CRMs NASS-7 and CASS-6, suitable for the validation of methods used for seawater analysis.

Key words: Dissolved trace metals, seawater, certified reference material, isotope dilution, HR-ICPMS, flow injection analysis, standard additions calibration.

Introduction

Trace metals play important roles in ocean biogeochemical processes. For example, Fe, Cu, Mn and Zn are essential elements for the growth of marine phytoplankton, and their supply is regulating primary productivity and the oceanic carbon cycle [1-3]. Other elements, such as Cd, Hg, Pb, and As are toxic to organisms when at enhanced concentrations in the marine environment [3]. Therefore, trace metal analysis in seawater can provide important information on the functioning of oceanic systems, elucidating the roles that trace elements play in biogeochemical cycles, and how human activities impact the natural environment. However, seawater has a highly complex matrix with a high salt content (ca. 35 g kg^{-1} for oceanic waters) and low elemental concentrations (often less than 1 µg kg^{-1}), making it a challenge to accurately determine trace metals.

The established methods for seawater analysis generally employ pre-concentration and matrix removal techniques prior to detection including solvent extraction [4-8], co-precipitation [9-13], ion exchange, and chelating resins [3, 14-21]. Detection is typically carried out using graphite furnace atomic absorption spectrometry (GFAAS) [4-6, 9], chemiluminescence (CL) [14], or inductively coupled plasma mass spectrometry (ICPMS) [7-8, 10-13, 15-21]. For the determination of trace elements, ICPMS is among the preferred atomic spectrometry techniques owing to its high sensitivity, low detection limits, and multi-element detection capabilities [22]. Moreover, as a mass spectrometric technique, it allows isotopic analysis. If two interference-free isotopes of a given element can be found, isotope dilution (ID) can be employed, which generally provides superior accuracy and precision over other calibration strategies [23-25]. Despite the high sensitivity and low detection limits offered by ICPMS, direct analysis of seawater is not feasible due to its high total dissolved solids (TDS) content. Typically ICPMS can tolerate approx. 0.2 % TDS in order to avoid blockage of the sample cone [22, 26]. Simple dilution of seawater samples to reduce the TDS can be used for the determination of trace metals [27], but results in poorer detection limits, increasing contamination risks and therefore is only applicable for analytes occuring at relatively high concentrations.

Seawater Certified Reference Materials (CRMs) are crucial for the validation of analytical methods used for the determination of trace metals in seawater. To address this need, the National Research Council of Canada (NRC) developed its first seawater CRMs,

NASS-1 and CASS-1, in 1985. Early methods used for the certification of NASS-1 and CASS-1 were based on off-line column separation and ICPMS or GFAAS detection, with use of large volume (500 mL) samples [21]. The new developments in on-line sample preconcentration/matrix separation systems such as seaFAST SP2 (Elemental Scientific, Omaha, NE, USA), and advances in ICPMS instruments have made possible for the contamination-free determination of trace metals in seawater with use of smaller sample sizes. For example only 6 mL/run of seawater was used in the certification of the latest seawater CRMs, NASS-7 and CASS-6 at NRC. The certified values assigned in these reference materials are traceable to the International System of Units (SI) [28] and provide measurement comparability for users [29]. The SI traceable primary standards with known purity and associated uncertainty, which were characterized by glow discharge mass spectrometry (GDMS) [30], were thus used for the determination of trace metals in the seawater CRMs NASS-7 and CASS-6 at NRC.

During this certification campaign of NASS-7 and CASS-6, several expert laboratories (as shown in Table 1) were invited and contributed results for trace metals. Instead of using a previous model of arithmetic mean of results obtained by various methods or laboratories, in this study NRC has adopted a laboratory random-effects model [31] to assign the certified or reference values in NASS-7 and CASS-6. The random effects model combines the results of participants by avoiding the homogeneity assumption, and includes both the uncertainty of individual results and the heterogeneity uncertainty between the individual results. This paper details the certification of seawater CRMs NASS-7 and CASS-6.

Table 1. Seawater inter-laboratory study: List of participating institutes

Lab Number	Institute	Country	Results reported	Reporting date
01	NRC	Canada	As, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, U, V, Zn	Oct. 30, 2015
02	NRC	Canada	As, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, U, V, Zn	Oct. 30, 2015
03	UG	Italy	As, Cr, Fe, Pb, Mn, Zn	June 30, 2015
04	GEOMAR	Germany	Cd, Co, Cu, Fe, Pb, Mn, Ni, Zn	July 09, 2015
05	KU	Japan	Cd, Co, Cu, Fe, Pb, Mn, Ni, Zn	May 18, 2015
06	RSMAS	USA	Fe, Mn	Aug. 30, 2015
07	ANU	Australia	Cd, Co, Cu, Fe, Pb, Ni, Zn	Mar. 18, 2015
08	DEP	Italy	As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, U, V	Aug. 30, 2015
09	UAF	USA	Cd, Co, Cu, Fe, Pb, Mn, V, Zn	July 13, 2015
10	LEMAR	France	Fe	June 27, 2015
11	IAC	Czech Repulic	As	Aug. 27, 2015

Experimental section

Preparation of NASS-7 and CASS-6 CRMs

The NASS-7 seawater was collected in August 2014 in the North Atlantic Ocean at a depth of 10 m, in a region off the continental shelf east of Halifax, Nova Scotia, Canada (44°16.96'N, 63°19.68'W). The sample was transferred using a peristaltic pump through acid-cleaned polyethylene lined ethyl vinyl acetate tubing and filtered in-line with sterile acrylic

copolymer filters (pore size 0.45 µm, Pall Corporation, New York, USA). The seawater was acidified to pH 1.6 with double distilled nitric acid following the transfer to 50 L acid-cleaned (10% HNO_3 soaking for a week, rinsed three times with deionized water and dried under a class-10 fume hood) polypropylene carboys (Fisher Scientific, Ottawa, ON, Canada) previously conditioned with deionized water acidified to pH 1.6. In a class-100 cleanroom at NRC, the seawater was refiltered through sterile acrylic copolymer filters (pore size 0.2 µm, Pall Corporation, New York, USA) within a week of sample collection, homogenized in an acid-cleaned polyethylene tank (Thermo Fisher Scientific, Ottawa, ON, Canada) and bottled in pre-cleaned 250 mL polyethylene bottles (Thermo Fisher Scientific, Ottawa, ON, Canada). The sample bottles were gamma irradiated to a minimum dose of 25 kGy at the Canadian Irradiation Centre (Laval, Quebec, Canada) to inhibit any bacterial activity during storage. Bottles were stored at +4°C temperature prior to analysis. The CASS-6 seawater was collected in October 2014 from Halifax harbor (Halifax, Nova Scotia, Canada). The preparation of CASS-6 was the same as for NASS-7.

Instrumentation used at NRC

A high resolution HR-ICPMS Element XR (Thermo Fisher Scientific, Bremen, Germany), equipped with a combination of cyclonic and Scott-type spray chamber and 50 µL min^{-1} MCN50 PFA nebulizer (Elemental Scientific, Omaha, NE, USA), was used for the off-line determination of trace metals in seawater. A plug-in quartz torch with a quartz injector and a platinum guard electrode were used. The Element XR is equipped with an additional Faraday cup detector in addition to the secondary electron multiplier (SEM) detector. Optimization of the HR-ICPMS Element XR was performed as recommended by the manufacturer; typical operating conditions of HR-ICPMS are summarized in Table 1S (Supplementary Information).

A triple quadrupole ICPMS (Agilent 8800, Agilent Technologies Canada Inc., Mississauga, ON, Canada) was used for the determination of trace metals using on-line column pre-concentration/matrix separation with standard additions calibration. Optimization of the ICPMS was performed according to the recommendations of the manufacturer. Typically, the extent of oxide or doubly charged ion formation was less than 1.5 %.

A seaFAST SP2 (Elemental Scientific Inc., Omaha, NE, USA) equipped with CF-N-0200 seaFAST concentrator column was used for automated off-line or on-line sample pre-concentration/matrix separation.

Additional information on instrumentations, reagents, solutions, sample preparation and analysis employed at participating laboratories are detailed in Supplementary Information. Analytical methods used for the trace metal measurements by all participants are summarized in Table 2.

Table 2. Analytical method used by participants

Analyte	NRC(1)	NRC(2)	UG	GEOMAR	KU	RSMAS
As	DD, SA, HR-ICPMS	DD, SA, QQQ-ICPMS	DD, SA, R-ICPMS	ND	ND	ND
B	DD, ID, HR-ICPMS	DD, SA, QQQ-ICPMS	ND	ND	ND	ND
Cd	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	ND	CS, ID, HR-ICPMS	CS, EC, HR-ICPMS	ND
Cr	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	CP, SA, R-ICPMS	ND	ND	ND
Co	CS, SA, HR-ICPMS	CS, SA, QQQ-ICPMS	ND	CS, SA, HR-ICPMS	CS, EC, HR-ICPMS	ND
Cu	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	ND	CS, ID, HR-ICPMS	CS, EC, HR-ICPMS	ND
Fe	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	CP, SA, R-ICPMS	CS, ID, HR-ICPMS	CS, EC, HR-ICPMS	CS, ID, HR-ICPMS
Pb	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	CP, SA, R-ICPMS	CS, ID, HR-ICPMS	CS, EC, HR-ICPMS	ND
Mn	CS, SA, HR-ICPMS	CS, SA, QQQ-ICPMS	CP, SA, R-ICPMS	CS, SA, HR-ICPMS	CS, EC, HR-ICPMS	CS, SA, HR-ICPMS
Mo	CS, ID, HR-ICPMS	DD, SA, QQQ-ICPMS	ND	ND	ND	ND
Ni	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	ND	CS, ID, HR-ICPMS	CS, EC, HR-ICPMS	ND
U	CS, ID, HR-ICPMS	DD, SA, QQQ-ICPMS	ND	ND	ND	ND
V	CS, SA, HR-ICPMS	DD, SA, QQQ-ICPMS	ND	ND	ND	ND
Zn	CS, ID, HR-ICPMS	CS, SA, QQQ-ICPMS	CP, SA, R-ICPMS	CS, ID, HR-ICPMS	CS, EC, HR-ICPMS	ND

Analyte	ANU	DEP	UAF	LEMAR	IAC
As	ND	DD, MMEC, HR-ICPMS	ND	ND	EC, HG-ICPMS
B	ND	ND	ND)	ND	ND
Cd	CS, ID, HR-ICPMS	DD, MMEC, HR-ICPMS	CS, EC, HR-ICPMS	ND	ND
Cr	ND	DD, MMEC, HR-ICPMS	ND	ND	ND
Co	CS, SAIS, HR-ICPMS	DD, MMEC, HR-ICPMS	CS, EC, HR-ICPMS	ND	ND
Cu	CS, ID, HR-ICPMS	DD, MMEC, HR-ICPMS	CS, ID, HR-ICPMS	ND	ND
Fe	CS, ID, HR-ICPMS	DD, MMEC, HR-ICPMS	CS, ID, HR-ICPMS	SA, FIA-CL	ND
Pb	CS, ID, HR-ICPMS	DD, MMEC, HR-ICPMS	CS, EC, HR-ICPMS	ND	ND
Mn	ND	DD, MMEC, HR-ICPMS	CS, EC, HR-ICPMS	ND	ND
Mo	ND	DD, MMEC, HR-ICPMS	ND	ND	ND
Ni	CS, ID, HR-ICPMS	ND	ND	ND	ND
U	ND	DD, MMEC, HR-ICPMS	ND	ND	ND
V	ND	DD, MMEC, HR-ICPMS	CS, EC, HR-ICPMS	ND	ND

Zn	CS, ID, HR-ICPMS	ND	CS, ID, HR-ICPMS	ND	ND

EC: external calibration; DD: direct measurement after dilution; CS: column separation prior to determination; CP: co-precipitation of analytes and redissolved prior to measurements; SA: standard additions calibration; SAIS: standard additions with internal standardization; MMEC: matrix match external calibration; R-ICPMS: Reaction cell ICPMS; FIA-CL: flow injection analysis with chemiluminescence.

Results and Discussion

Determination of trace metals in seawater at NRC. Isotope dilution based calibration is capable of compensating for matrix effects, instrument drift and any losses of analyte during the sample preparation procedures, providing isotopic equilibrium has been achieved prior to analysis. In addition, ID provides superior measurement accuracy and precision compared to other calibration strategies. Thus, double ID was applied for the determination of B, Cd, Cr, Cu, Fe, Pb, Mo, Ni, U and Zn in seawater using HR-ICPMS at NRC, whereas mono-isotopic elements of As, Co, Mn and as well as V were determined using standard additions calibration to avoid any possible matrix effects. The following equation was used for the calculation of analyte mass fraction in the sample using the double ID:

$$w_{\mathrm{x}} = w_{\mathrm{z}} \cdot \frac{m_{\mathrm{y}}}{m_{\mathrm{x}}} \cdot \frac{m_{\mathrm{z}}}{m'_{\mathrm{y}}} \cdot \frac{A_y - B_y \cdot K \cdot r}{B_{\mathrm{xz}} \cdot K \cdot r - A_{\mathrm{xz}}} \cdot \frac{B_{\mathrm{xz}} \cdot K \cdot r' - A_{\mathrm{xz}}}{A_{\mathrm{y}} - B_{\mathrm{y}} \cdot K \cdot r'} \cdot \frac{A_{\mathrm{r}}(\mathrm{X})}{A_{\mathrm{r}}(\mathrm{Z})} \qquad (1)$$

where:

w_x is the blank mass fraction of the analyte in the sample (μg kg^{-1});
w_z is the mass fraction of the analyte in primary standard solution (μg kg^{-1});
m_y is the mass of spike solution used to prepare the mixture of sample and spike (g);
m_x is the mass of sample used (g);
m_z is the mass of primary assay standard used (g);
m'_y is the mass of spike used to prepare the mixture of spike and primary assay standard (g);
A_y is the abundance of the reference isotope in the spike;
B_y is the abundance of the spike isotope in the spike;
A_x is the abundance of the reference isotope in the sample;
B_x is the abundance of the spike isotope in the sample;
A_z is the abundance of the reference isotope in the primary assay standard;
B_z is the abundance of the spike isotope in the primary assay standard;
K is the mass bias correction factor;
r is the measured reference/spike isotope ratio in the mixture solution of sample and spike;
r' is the measured reference/spike isotope ratio in the mixture solution of spike and primary assay standard;
A_r(X) is the atomic weight of the analyte element in the sample;
A_r(Z) is the atomic weight of the analyte element in primary assay standard.

The measurement equation can be simplified to equation 2 for all elements whose isotopic abundances are assumed invariant in nature and, therefore, $A_x = A_z = A_{xz}$, $B_x = B_z = B_{xz}$, $A_r(X) = A_r(Z)$:

$$w_{\mathrm{x}} = w_{\mathrm{z}} \cdot \frac{m_{\mathrm{y}}}{m_{\mathrm{x}}} \cdot \frac{m_{\mathrm{z}}}{m'_{\mathrm{y}}} \cdot \frac{A_y - B_y \cdot K \cdot r}{B_{\mathrm{xz}} \cdot K \cdot r - A_{\mathrm{xz}}} \cdot \frac{B_{\mathrm{xz}} \cdot K \cdot r' - A_{\mathrm{xz}}}{A_{\mathrm{y}} - B_{\mathrm{y}} \cdot K \cdot r'} \qquad (2)$$

Equation 3 was used for the calculation of the mass fraction of monoisotopic analytes and vanadium using standard additions calibration [32]:

$$\frac{m_{\text{std-i}} \cdot w_{\text{std}}}{m_{\text{s-i}}} \cdot \frac{m_{\text{xf}}}{m_{\text{x}}} = b \cdot I_{\text{i}} \cdot \frac{m_{\text{sf-i}}}{m_{\text{s-i}}} \cdot \frac{m_{\text{df-i}}}{m_{\text{d0-i}}} + \mathrm{a} \ \text{ and } \ w_{\mathrm{x}} = -\mathrm{a} \qquad (3)$$

where:

w_x is the mass fraction of the analyte in the sample (μg kg^{-1});
w_{std} is the mass fraction of the analyte in the primary standard solution (μg kg^{-1});
I_i is the measured intensity in the prepared set of samples, i=0, 1, 2;
$m_{std\text{-}i}$ is the mass of natural abundance standard added to the spiked sample (g), i=1, 2;
$m_{s\text{-}i}$ is the mass of aliquot of diluted sample used to prepared spiked sample (g), i=1, 2;

$m_{sf\text{-}i}$ is the final mass of spiked sample (g), i=1, 2;
$m_{df\text{-}i}$ is the final mass of diluted set of samples (g), i=0, 1, 2;
$m_{d0\text{-}i}$ is the mass of aliquots of spiked samples for dilution (g), i=0, 1, 2;
$m_{d0\text{-}f}$ is the final mass of aliquots of spiked samples after dilution (g), i=0, 1, 2;
m_x is the mass (g) of the original sample;
m_{xf} is the final mass of the original sample after addition of enriched spikes and 1% HNO_3 (g).

The SeaFAST SC2 automated preconcentration system with a CF-N-0200 seaFAST chelation column was able to separate Cd, Co, Cu, Fe, Pb, Mn, Mo, Ni, U, V, and Zn from seawater matrix simultaneously at pH 5.5 (shown in Figure S1 in the Supplementary Information) in an efficient manner. The set-up functioned better than our early FIAS 400 automated column separation system [15] which uses two different pH conditions in order to achieve the separation of the analytes from the seawater matrix and thus was more time consuming for sample preparation. Static measurements with off-line sample preparation provided better measurement precision compared to transient signals derived from on-line sample preparation. Thus in order to produce the most accurate and precise data set by HR-ICPMS, automated off-line column separation was performed. Chromium was separated from the seawater matrix using immobilized diphenylcarbazone column [33]. The collected elution volume (0.5 mL) was sufficient for the interference free determination of Cd, Pb, Mo and U at low resolution, and Co, Cr, Cu, Fe, Mn, Ni, V and Zn at medium resolution using HR-ICPMS. Arsenic was directly measured at high resolution in 10-fold diluted seawater.

In addition, a second set of data was produced at NRC which was based on standard additions calibration using an on-line column separation (SeaFAST SP 2) or direct 10-fold dilution and QQQ-ICPMS detection. As and V were determined directly using the on-line seaFAST 10-fold dilution in O_2 mode to ensure inference free measurements using $^{75}As^{16}O^+$ and $^{51}V^{16}O^+$. Mo and U were determined directly using the on-line seaFAST 10-fold dilution in no gas mode based on intensities of $^{98}Mo^+$ and $^{238}U^+$. All other analytes including Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were determined simultaneously using the on-line column separation with the seaFAST CF-N-0200 column at pH 5.5 based on intensities of $^{55}Mn^+$, $^{57}Fe^+$, $^{59}Co^+$, $^{60}Ni^+$, $^{63}Cu^+$, $^{66}Zn^+$, $^{111}Cd^+$ and $^{208}Pb^+$, whereas Cr was separated with immobilized diphenylcarbazone resin based on intensity of $^{52}Cr^+$.

Validation of the HR-ICPMS and QQQ-ICPMS methods was performed by analysis of CASS-5, NASS-6 and MX014 seawater CRMs at NRC, and results are summarized in Table 2S and Figure 1. Note that Figure 1 is intended to give a brief overview of all results obtained by HR-ICPMS and QQQ-ICPMS methods, thus the dash green lines represent 10 % range of the certified values, not relative expanded uncertainties of CRMs, since relative expanded uncertainties of certified values are very different in three CRMs, but majority are within 10% with the exceptions of Cr (12%) and V (11%) in CASS-5, Pb (33%) and V (11%) in NASS-6, and Mn (11%) in MX014 (see individual data in Table 2S). Spike recovery was performed for B since there are no certified B values in these CRMs. As demonstrated, results obtained for all analytes in the three CRMs by HR-ICPMS are in agreement with certified values, and quantitative spike recoveries of B were obtained for both seawater CRMs NASS-6 and CASS-5, confirming the accuracy of the method used. The measured values within reported uncertainties by QQQ-ICPMS are in agreement with the certified values, confirming the accuracy of the QQQ-ICPMS method for these analytes.

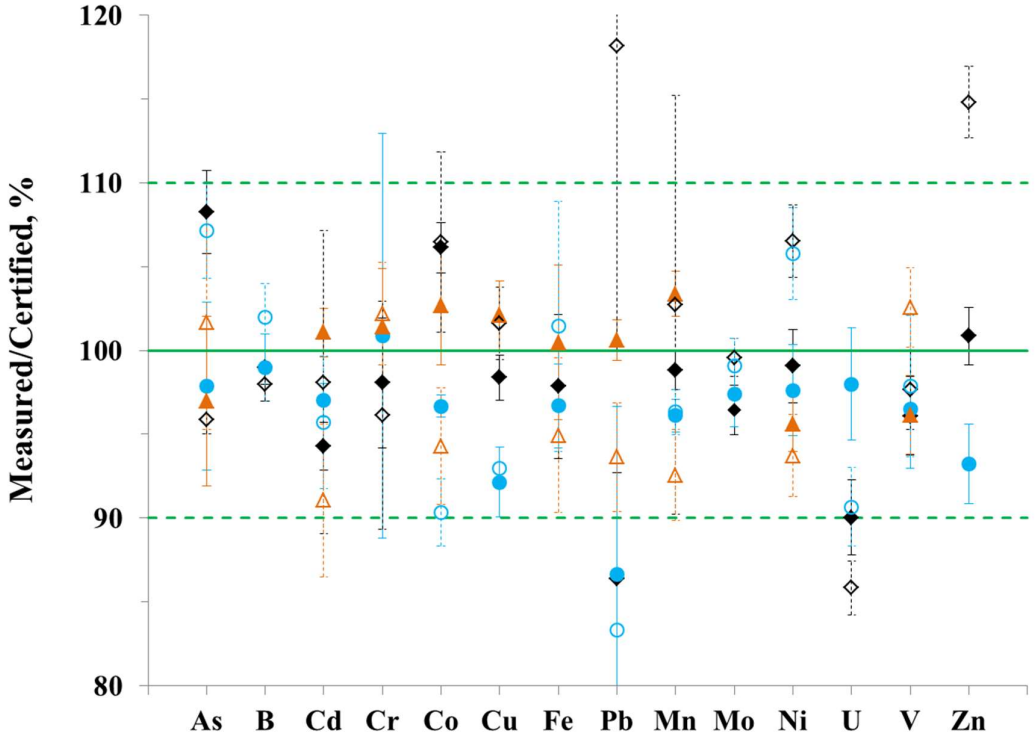

Figure 1. Comparison of measured values obtained at NRC to certified values in CASS-5 (diamonds), NASS-6 (circles) and MX014 (triangles) seawater CRMs (Ratios of measured values to certified/reference values are plotted). Error bars are 1SD. Solid symbols represent results obtained using HR-ICPMS, whereas open symbols represent results obtained using QQQ-ICPMS (see Table 2 for method details). The dash green lines represent 10 % range of the certified values, not relative expanded uncertainties of CRMs.

It is evident that the precision and accuracy of results obtained by ID HR-ICPMS were generally better than those obtained by standard addition calibration with QQQ-ICPMS, as shown in Table 2S and Figure 1. The two validated methods of HR-ICPMS and QQQ-ICPMS were applied for the determination of the new generation of seawater CRMs: NASS-7 and CASS-6 at NRC. Results obtained are summarized in Table 3S and Table 4S. Results obtained are traceable to the SI through gravimetrically prepared primary standards whose purities were established by glow discharge mass spectrometry (GDMS) at the NRC.

Results obtained by all expert laboratories. Various sample preparation methods and calibration strategies were employed by the participants, as summarized in Table 2. Results obtained from quality control (QC) samples of CASS-5 and NASS-6 seawater CRMs for method validation from external laboratories are summarized in Table 4S, Table 5S and Figure 2. It is evident that results obtained by majority laboratories are in agreement with certified values, with a few exceptions of results which are out of the certified ranges (e.g., one result for Co, three results for Fe and one result for Zn).

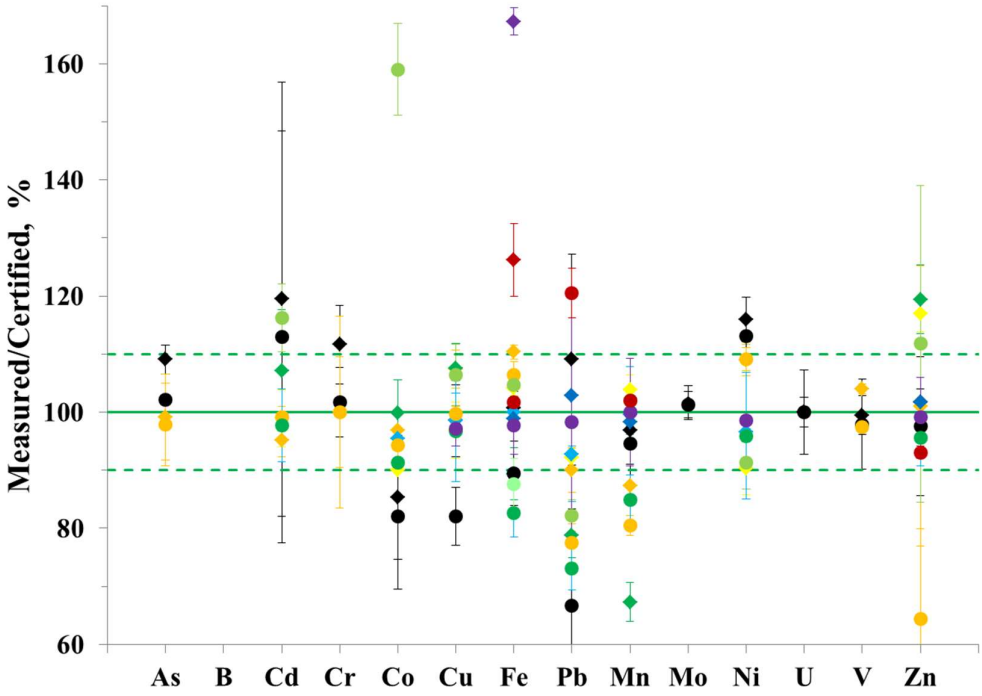

Figure 2. Comparison of measured values by external laboratories to certified/reference values in CASS-5 (diamonds), NASS-6 (circles) seawater CRMs (Ratios of measured values to certified/reference values are plotted). Error bars are 1SD and symbols represent results obtained from participating laboratories. See Table 2 for methods used and Table 2S for individual results. The dash green lines represent 10 % range of the certified values, not relative expanded uncertainties of CRMs.

Results obtained for new NASS-7 and CASS-6 CRMs from all external laboratories are also summarized in Table 3S and Table 4S. In addition, results obtained from a proficiency test (PT) [34] of AQ3 2015.1: Metals in seawater NASS-7 organized by the WEPAL-QUASIMEME, were included in the certification of NASS-7 CRM. The assigned value for the PT was established on the basis of consensus, and Cofino's model was used for the calculation of population characteristics [35]. The probability density function of the measurement results was obtained without the need for uncertainty estimates of individual results and assigned value was established as the mode of all data. Note that results of AQ3 2015.1 were given in µg L^{-1} which were converted to mass fraction using the density value ρ = 1.021 kg L^{-1} (at 21 °C), as reported in Table 3S.

To overview all results obtained by participants for this comparison study, ratios of measured values to the signed certified/reference values (See results in section of Assignment of the consensus values in CASS-6 and NASS-7 later) are plotted in Figure 3 and Figure 4 for NASS-7 and CASS-6, respectively. It is evident that results obtained from the participants showed a general good agreement, with the exception of a couple of outliers, for example, two high values of Pb, one low value of Mn and Ni in NASS-7, as well as one low value of As, Cr and Mn, and two low values of Cu in CASS-6. Despite of the-state-of-the-art instruments used, results reported by participants also show that the determination of trace levels of metals in seawater is still a challenge even for expert labs as exemplified by Pb results in NASS-7 which in general has lower mass fractions of analytes compared to CASS-6.

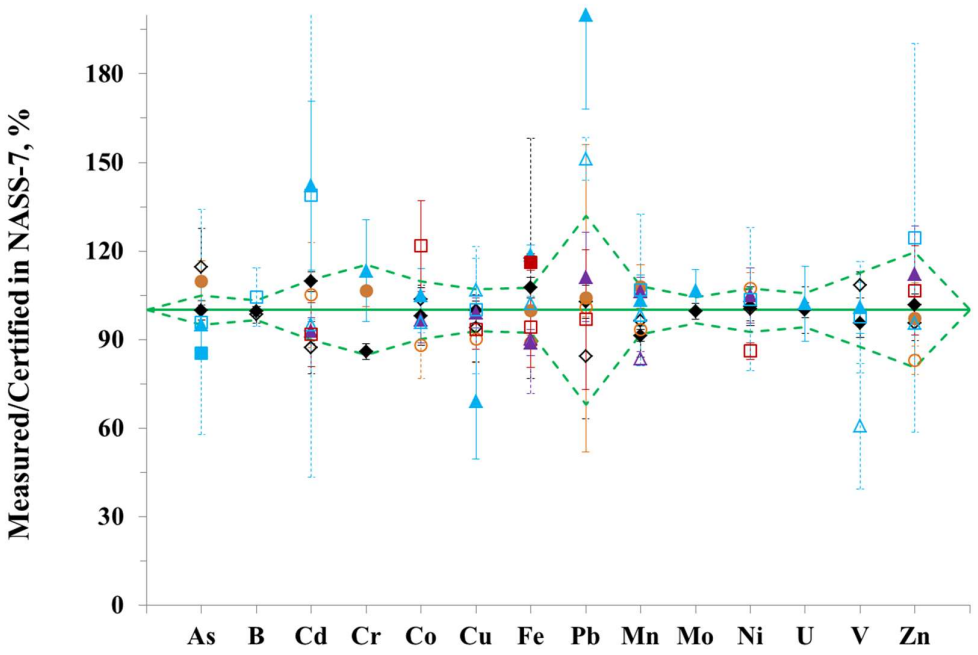

Figure 3. Comparison of measured values obtained by all participants to certified/reference values in the new NASS-7 seawater CRM (Ratios of measured values to certified/reference values are plotted). Error bars are combined standard uncertainty, K=1 and symbols represent results obtained from participating laboratories (NRC(1): filled black diamond; NRC(2): open black diamond; UG: filled orange circle; GEOMAR: open orange circle; KU: filled purple triangular; RSMAS: open purple triangular; ANU: open red square; DEP: filled blue triangular; UAF: open blue triangular; LEMAR: filled red square; IAC: filled blue square and Quasimeme: open blue square). See Table 2 for methods used, and Table 4S for individual results. The dash green lines represent relative certified ranges based on the expanded uncertainties at K=2.

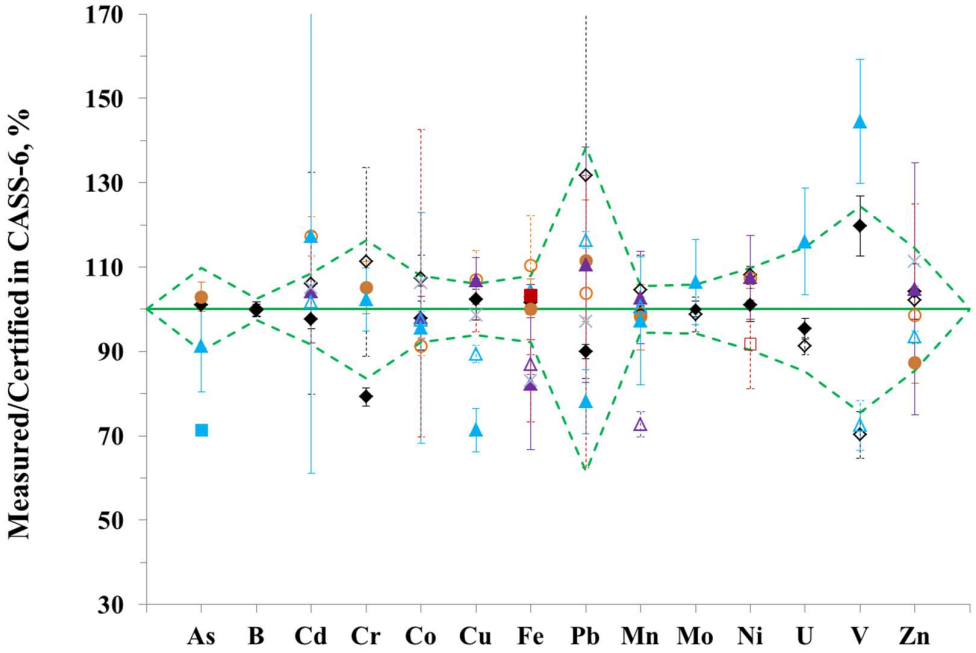

Figure 4. Comparison of measured values obtained by all participants to certified/reference values in the new CASS-6 seawater CRM (Ratios of measured values to certified/reference values are plotted). Error bars are combined standard uncertainty, K=1 and symbols represent results obtained from participating laboratories (NRC(1): filled black diamond; NRC(2): open black diamond; UG: filled orange circle; GEOMAR: open orange circle; KU: filled purple triangular; RSMAS: open purple triangular; ANU: open red square; DEP: filled blue triangular; UAF: open blue triangular; LEMAR: filled red square and IAC: filled blue square). See Table 2 for methods used, and Table 5S for individual results. The dash green lines represent relative certified ranges based on the expanded uncertainties at K=2.

For arsenic determination using ICPMS, polyatomic interferences of $^{40}Ar^{35}Cl^{+}$ and $^{36}Ar^{39}K^{+}$ need to be resolved by employing high mass resolution or a reaction cell. Five data sets reported were based on high resolution or reaction cell measurements, as shown in Tables 3S and 4S. It is evident that results obtained in CASS-6 were in agreement within their reported uncertainties. Similarly, six data sets were reported for As in NASS-7 with five data sets in agreement and one value on the low side. Low values by IAC were obtained as a sum of inorganic arsenic and methylated species, not comprising other organoarsenic species which were not forming hydrides, recently confirmed in seawater [36].

Both seawater CRMs have high boron content which makes the boron measurements less challenging than other trace metals. Evidently, results obtained by participants were in good agreement, as shown in Figure 3 and Figure 4.

All participants except DEP employed matrix separation to remove possible spectral interferences of $^{95}Mo^{16}O^{+}$, $^{114}Sn^{+}$, and $^{98}Mo^{16}O^{+}$ on cadmium isotopes. Seven and eight data sets were reported for Cd in CASS-6 and NASS-7, respectively. Despite various separation techniques and quantitation strategies used, results obtained were in agreement within the reported uncertainties, demonstrating the measurement capabilities of participating laboratories. It is evident that matrix separation prior to analysis produced more precise results for Cd whereas a larger uncertainty was reported by DEP when Cd was measured

from diluted seawater.

Spectral interferences of $^{36}Ar^{16}O^+$, $^{40}Ar^{12}C^+$, $^{40}K^{12}C^+$, $^{40}Ca^{12}C^+$, $^{37}Cl^{16}O^+$, and $^{41}K^{12}C^+$ on chromium isotopes can be separated by employing either high mass resolution mode or reaction cell with ICPMS. Matrix separation was performed by all participants except DEP who used direct dilution. Four data sets were reported for Cr in CASS-6 and NASS-7, respectively, results were in agreement except one slightly low value reported by NRC(1).

Similarly, potential polyatomic interferences of $^{40}Ar^{18}O^1H^+$, $^{43}Ca^{16}O^+$ and $^{42}K^{17}O^+$ on $^{59}Co^+$ can be resolved by using a high mass resolution approach or reaction cell with ICPMS detection. In addition, the majority of participants employed matrix separation prior to ICPMS detection. Results obtained for cobalt in CASS-6 and NASS-7 were in agreement within reported uncertainties, respectively.

For Cu determination, the majority of participants employed matrix separation technique (shown in Table 2) prior to ICPMS detection with use of high resolution or a reaction cell to remove interferences such as $^{40}Ar^{23}Na^+$, $^{40}Ar^{25}Mg^+$ and $^{136}Ba^{2+}$ on Cu isotopes, except DEP who used direct dilution. It is evident that biased results was obtained with use of external calibration in diluted seawater, whereas other results obtained were in agreement, as shown in Figure 3, Figure 4, Table 3S and Table 4S.

Iron is another difficult element for ICPMS due to spectral interferences such as $^{40}Ar^{16}O^+$, $^{40}Ca^{16}O^+$, $^{41}K^{16}O^+$, or $^{40}Ca^{16}O^1H^+$ arising from the seawater sample matrix. A high mass resolution or a reaction cell is required to resolve these interferences. It is evident that for Fe determination in NASS-7, the majority of participants demonstrated their measurement capabilities and showed agreement with the certified values within their reported uncertainties, as shown in Figure 3 and Table 3S. Results show that matrix separation with use of ID calibration (GEOMAR, ANU, RSMAS and NRC(1)) produced more accurate and precise results. CASS-6 has a higher Fe content compared to NASS-7, results obtained show agreement within reported uncertainties, as shown in Figure 4.

As shown in Figure 3 and Table 3S for Pb in NASS-7, one participant (DEP) reported a much higher value for Pb based on direct dilution method and UAF reported a slightly higher value by external calibration and column separation. It is evident, ID used at ANU, GEOMAR and NRC(1) produced more precise and accurate results, compared to those obtained by standard addition calibration used at NRC(2) and UG, and external calibration used at KU, UAF and DEP. The Pb mass fraction in CASS-6 is about 4-fold of that in NASS-7, and therefore it was less challenging to measure Pb in CASS-6. Consequently, results obtained by participants were in agreement within their stated uncertainties.

Manganese is a monoisotopic element, and matrix separation and standard addition calibration were employed by NRC(1), NRC(2), UG, GEOMAR and RSMAS, whereas KU used matrix separation with external calibration, and DEP used direct dilution with external calibration (Table 2). Spectra interferences of $^{40}Ar^{15}N^+$, $^{110}Cd^{2+}$, and $^{37}Cl^{18}O^+$ were resolved by using HR-ICPMS or reaction cell ICPMS. Results obtained were in agreement for CASS-6 with only one low value by RSMAS (Figure 4). The Mn mass fraction in NASS-7 is only the half of the value in CASS-6, and it is clear that agreement among results was poorer (Figure 3).

Seawater has a considerably higher molybdenum content compared to other trace metals, and thus presents less of a challenge for its determination using ICPMS. As a result (Figure 3 and Figure 4), results obtained by participants were in good agreement.

For the determination of Ni, spectral interferences of $^{44}Ca^{16}O^+$, $^{36}Ar^{24}Mg^+$, $^{23}Na^{37}Cl^+$, $^{36}Ar^{25}Mg^+$ and $^{36}Ar^{25}Mg^+$ can be resolved by using matrix separation, HR-ICPMS or reaction cell ICPMS. Results obtained for CASS-6 were in close agreement, whereas results obtained for NASS-7 were in agreement within reported uncertainty except one slightly low value by ANU, as shown in Figure 3 and Figure 4.

U can be determined even with use of low resolution since no significant polyatomic interferences influence U isotopes. Three sets of results were reported by NRC(1), NRC(2) and DEP which were in agreement for NASS-7 and CASS-6 within reported uncertainties, respectively.

For the determination of V, spectral interferences of $^{35}Cl^{16}O^{+}$, $^{37}Cl^{14}N^{+}$ and $^{36}Ar^{14}N^{1}H^{+}$ can be resolved by HR-ICPMS or reaction cell ICPMS. Since isobaric interferences of ^{50}Cr and ^{50}Ti on ^{50}V cannot be solved by current HR instruments, all participants employed standard addition or external calibration for the V measurements. Results obtained in NASS-7 were in close agreement with only one low value by UAF, whereas agreement of results obtained in CASS-6 was poorer, possibly due to a lower V content in this CRM, making it more challenging to measure, as shown in Figure 3 and Figure 4.

In general, it was observed that application of matrix separation with use of ID or standard addition calibrations typically produced more accurate and precise results for both new seawater CRMs NASS-7 and CASS-6, as presented in Table 3S, Table 4S, Figure 3 and Figure 4. Direct dilution with external calibration typically produced biased results for certain elements that present at very low concentration.

In addition to the range of trace metals reported in Tables 3S and 4S, one participant, DEP, reported rare earth elements in both seawater CRMs based on direct measurements after dilution and matrix match external calibration. Another participant, IAC, performed As speciation in both seawater CRMs using a previously developed method [37] based on selective hydride generation with cryotrapping coupled to ICPMS detection. Inorganic arsenic, monomethylarsenic (MeAs), dimethylarsenic (DMeAs) and trimethylarsenic (TMeAs) were found and measured. Since only one data set is available for these analytes and thus is provided as information values, results are shown in Table 7S.

Assignment of the consensus values in CASS-6 and NASS-7. Results obtained from the participating laboratories showed some inconsistencies (see Tables 3S and 4S). As a result, assigning certified/reference values for trace metals in NASS-7 and CASS-6 from such data sets is not trivial. Commonly used methods to combine results from different methods or laboratories involve the arithmetic mean, weighted mean or the median. However, these approaches have their shortcomings. For example, the arithmetic mean does not capture the uncertainty reported by individual laboratories and it assumes that any differences between the laboratories can be explained solely by the reported measurement uncertainties (fixed effects statistical model). In this study we have adopted random laboratory effects statistical model.

$$x_i = \mu + e + u_i \qquad (4)$$

This model interprets the result from each laboratory, x_i, in terms of two uncertainty components – the known measurement uncertainty reported by each laboratory, u_i, and the unknown random laboratory effect, e. In other words, the result from each laboratory is modelled as Gaussian random variable with two unknown model parameters, the unknown true value for the mass fraction of the element (also known as the consensus value), μ, and the variance due to inter-laboratory (random) effects, τ^2. This model can be summarized as $x_i \sim N(\mu, u^2_i + \tau^2)$ using standard statistical notation. In essence, the random effects model recognizes our belief that the uncertainties assigned by each laboratory to their results might not fully explain the observed differences between the laboratory results and all laboratory results might be accompanied with additional source of error captured by the variable τ^2. The statistical model shown in Eq. 4 can be solved for the unknown parameters – which include the true value for the mass fraction of the element – using a variety of statistical methods. We have adopted the simplest of approaches, the non-iterative DerSimonian-Laird method [32]. The DerSimonian-Laird estimate of μ is given as follows:

$$\mu = \frac{\sum_i w_i \cdot x_i}{\sum_i w_i} \quad (5)$$

where $w_i = (u^2_i + \tau^2)^{-1}$ and

$$\tau^2 = \max\left(0, \frac{Q-(N-1)}{\sum u_i^{-2} - \sum u_i^{-4} / \sum u_i^{-2}}\right) \quad (6)$$

Here, N is the number of participating laboratories, $Q = \sum u_i^{-2}(x_i - \bar{x})^2$ and $\bar{x}$ is the weighted mean of the results reported by individual laboratories, $\bar{x} = \sum(u_i^{-2} x_i) / \sum u_i^{-2}$.

The uncertainty of the certified mass fraction value, u_{CRM}, accounts for all sources of uncertainties from the characterization of the batch, u_{char}, between-bottle variation in the mass fraction values due to inhomogeneity, u_{hom}, and the uncertainty related to possible inconsistencies between the various measurement methods or between the individual laboratories ($u_{methods}$):

$$u^2_c = u^2_{char} + u^2_{hom} + u^2_{methods} \quad (7)$$

Based on our experience of monitoring the NRC seawater CRMs of previous generations, the chemical instability of the analytes in the seawater is deemed insignificant. The uncertainty due to inhomogeneity in the property values is typically assessed using the ANOVA. This relies, for example, on a standard $N \times M$ experimental design of N CRM units, each analyzed in M replicates. In our case, we have performed the analysis of N CRM units with each measurement having its associated measurement uncertainty. Applying random effects model to such data set, we extracted the uncertainty due to between-unit inhomogeneity from the variance estimate of the random effect.

Certified or reference values and uncertainties for trace metals in two new CRMs are listed in Table 3.

Table 3. Certified or Reference Values and Uncertainty Components for NASS-7 and CASS-6, µg kg^{-1}

Element	NASS-7					
	Assigned value	u_{char}	u_{hom}	u_{method}	u_c	U_{CRM} (k=2)
B (Certified)	3670	50	30	0	60	120
Cd (Certified)	0.0157	0.0004	0.0003	0.0006	0.0008	0.0016
Co (Certified)	0.0143	0.0006	0.0003	0.0000	0.0007	0.0014
Cu (Certified)	0.195	0.006	0.003	0.003	0.007	0.014
Fe (Certified)	0.344	0.011	0.000	0.007	0.013	0.026
Pb (Certified)	0.0025	0.0002	0.0003	0.0000	0.0004	0.0008
Mn (Certified)	0.74	0.02	0.02	0.01	0.03	0.06
Mo (Certified)	9.10	0.15	0.13	0.00	0.20	0.40
Ni (Certified)	0.243	0.005	0.007	0.000	0.009	0.018
U (Certified)	2.81	0.06	0.05	0.00	0.08	0.16
Zn (Certified)	0.41	0.03	0.02	0.00	0.04	0.08
As (Reference)	1.23	0.03	0.01	0.01	0.03	0.06
Cr (Reference)	0.105	0.004	0.006	0.004	0.008	0.016
V (Reference)	1.27	0.03	0.00	0.02	0.08	0.16
Element	**CASS-6**					
	Assigned value	u_{char}	u_{hom}	u_{method}	u_c	U_{CRM} (k=2)
B (Certified)	4010	50	10	0	50	100
Cd (Certified)	0.0213	0.0008	0.0003	0.0000	0.0009	0.0018
Co (Certified)	0.0659	0.0022	0.0014	0.0000	0.0026	0.0052
Cu (Certified)	0.520	0.012	0.008	0.008	0.016	0.032
Fe (Certified)	1.53	0.04	0.05	0.01	0.06	0.12
Pb (Certified)	0.0104	0.0008	0.0018	0.0000	0.0020	0.0040
Mn (Certified)	2.18	0.06	0.01	0.00	0.06	0.12
Mo (Certified)	8.96	0.24	0.09	0.00	0.26	0.52
Ni (Certified)	0.410	0.012	0.014	0.008	0.020	0.040
U (Certified)	2.86	0.19	0.01	0.08	0.21	0.42
Zn (Certified)	1.24	0.07	0.05	0.00	0.09	0.18
As (Reference)	1.02	0.05	0.01	0.00	0.05	0.10

Cr (Reference)	0.098	0.005	0.006	0.002	0.008	0.016
V (Reference)	0.49	0.01	0.02	0.06	0.06	0.12

Conclusion

The determination of metals at trace levels in seawater still presents a challenge, as it requires contamination-free sample preparation and analysis. In addition to matrix separation for the determination of trace metals, HR-ICPMS and QQQ-ICPMS have played important roles in obtaining interferences free measurements to achieve final accurate results. Overall, this inter-laboratory comparison for the trace metals in seawater was successful, as indicated by the observation that results from the majority of laboratories were in close agreement, demonstrating these laboratories' measurement capabilities for the accurate determination of trace metals in seawater matrices. As a result of this comparison, certified/reference values were successfully assigned for a total of 14 elements in NRC seawater Certified Reference Materials NASS-7 and CASS-6, suitable for the validation of methods used for seawater analysis.

Declarations of interest

Authors declare no conflict of interest.

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Graphical abstract: