

Certificate of Analysis

Certified Reference Material

NASS-7

Seawater Certified Reference Material for Trace Metals and other Constituents

The following tables show those constituents for which certified, reference and information values have been established for this seawater certified reference material (CRM).

The expanded uncertainty (U_{CRM}) in the certified value is equal to $U = ku_c$ where u_c is the combined standard uncertainty calculated according to the JCGM Guide [1] and k is the coverage factor. A coverage factor of two (2) was applied for all elements. It is intended that U_{CRM} accounts for every aspect that reasonably contributes to the uncertainty of the measurement. The density of NASS-7 is 1.021 g/mL at 21 °C.

Table 1: Certified quantity values and expanded uncertainties for NASS-7

Element	Mass fraction, μg/kg	Mass concentration, μg/L	International recognition of measurement capability (CMC)	
boron (a,b)	3670 ± 120	3750 ± 120	-	
cadmium (a,b,c)	0.0157 ± 0.0016	0.0161 ± 0.0016	<u>TEW20</u>	
cobalt (b,c)	0.0143 ± 0.0014	0.0146 ± 0.0014	<u>TEW22</u>	
copper (a,b,c)	0.195 ± 0.014	0.199 ± 0.014	TEW23	
iron (a,c)	0.344 ± 0.026	0.351 ± 0.026	TEW24	
manganese (b,c)	0.74 ± 0.06	0.75 ± 0.06	TEW26	
molybdenum (a,b,c)	9.10 ± 0.40	9.29 ± 0.40	TEW27	
nickel (a,b,c)	0.243 ± 0.018	0.248 ± 0.018	TEW28	
lead (a,b,c)	0.0025 ± 0.0008	0.0026 ± 0.0008	TEW25	
uranium (a,b,c)	2.81 ± 0.16	2.87 ± 0.16	_	
zinc (a,b,c)	0.41 ± 0.08	0.42 ± 0.08	<u>TEW30</u>	

Table 2: Reference quantity values and expanded uncertainty for NASS-7

Element	Mass fraction, μg/kg	Mass concentration, μg/L	International recognition of measurement capability (CMC)
arsenic (b,c)	1.23 ± 0.06	1.26 ± 0.06	<u>TEW19</u>
chromium (a,c)	0.105 ± 0.016	0.107 ± 0.016	<u>TEW21</u>
vanadium (b,c)	1.27 ± 0.08	1.30 ± 0.08	TEW29



NRC **NASS-7** 2/7

Table 3: Information values for NASS-7

Element	Mass fraction, μg/kg	Mass concentration, μg/L
lanthanum (c)	0.006	0.006
cerium (c)	0.003	0.003
praseodymium (c)	0.002	0.002
neodymium (c)	0.003	0.003
samarium (c)	0.002	0.002
europium (c)	0.0006	0.0006
gadolinium (c)	0.0014	0.0014
terbium (c)	0.0003	0.0003
dysprosium	0.0013	0.0013
holmium (c)	0.0010	0.0010
erbium (c)	0.0012	0.0012
thulium (c)	0.000 11	0.000 11
ytterbium (c)	0.0010	0.0010
lutetium (c)	0.0002	0.0002

Table 3 (continued): Information values for NASS-7

Compound	Mass fraction, μg/kg	Mass concentration, μg/L	
inorganic arsenic (d)	0.83	0.85	
monomethylarsenic (as As) (d)	0.018	0.019	
dimethylarsenic (as As) (d)	0.190	0.190	
trimethylarsenic (as As) (d)	0.013	0.013	

Coding

The coding refers to the instrumental method of analyte determination.

- a Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS)
- **b** Standard addition inductively coupled plasma mass spectrometry (SA-ICP-MS)
- c Inductively coupled plasma mass spectrometry (ICP-MS)
- d Hydride generation cryo-trapping ICP-MS

International recognition of measurement capability

The measurement capabilities supporting these results are registered at the Calibration and Measurement Capabilities (CMC) database of the Bureau international des poids et mesures (BIPM) indicating recognition of the measurement certificates by National Metrology Institutes (NMIs) participating in the Mutual Recognition Arrangement (MRA) with the corresponding identifiers. List of all registered measurement capabilities in water matrix could be found in the BIPM database at https://www.bipm.org/kcdb/.



NRC NASS-7

Certified values

Certified values are considered to be those for which the National Research Council Canada (NRC) has the highest confidence in accuracy and that all known and suspected sources of bias have been taken into account and are reflected in the stated expanded uncertainties. Certified values are the best estimate of the true value and uncertainty (Table 1).

Reference values

Reference values are non-certified values for which insufficient data are available to provide a comprehensive estimate of uncertainty to permit their full certification (Table 2).

Information values

Information values are those for which insufficient data are available to provide any estimate of uncertainty (Table 3).

Intended use

This certified reference material is primarily intended for use in the calibration of procedures and the development of methods used for the analysis of seawater for trace metals. A minimum sample volume of 10 mL is recommended.

Storage and sampling

It is recommended that the material be stored at nominal temperature of +4 °C temperature under typical refrigerator conditions. Material shall not be frozen. The bottles should be opened only in a clean area with precautions taken against contamination during sampling.

Preparation of material

The water was collected August 2014 in the North Atlantic at a depth of 10 m, off the continental shelf east of Halifax, NS, Canada (44°16.96'N, 63°19.68'W). The sample was peristaltically pumped through cleaned polyethylene lined ethyl vinyl acetate tubing and 0.45 µm acrylic copolymer filters. It was acidified to pH 1.6 with ultrapure nitric acid during its immediate transfer to 50-litre acid leached polypropylene carboys previously conditioned with ultrapure water acidified to pH 1.6. In a cleanroom at NRC the seawater was later refiltered through 0.2 µm acrylic copolymer filters, homogenized in a precleaned polyethylene tank and bottled in cleaned 500 mL polyethylene bottles. The bottled water was gamma irradiated to a minimum dose of 25 kGy at the Canadian Irradiation Centre, Laval, Quebec, to inhibit any bacterial action.

Stability

The predecessor CRMs have been periodically analyzed for more than 10 years and found to be stable with respect to total trace metal concentration over this interval. Uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Homogeneity

The material was tested for homogeneity at NRC using ICP-MS. Results from sub-samples (10 mL) were evaluated using ANOVA and/or the DerSimonian-Laird random effects model and included in the calculation of the certified values [2].



NRC **NASS-7** 4/7

Uncertainty

Included in the overall combined uncertainty estimate (u_c) are uncertainties in the batch characterization (u_{char}) , uncertainties related to possible between-bottle variation (u_{hom}) , and uncertainties related to inconsistency between the various measurement methods (u_{method}) . The latter is estimated as the heterogeneity in the random effects model fitted to the results of individual methods, also known as the dark uncertainty [3,4]. Expressed as standard uncertainties, these components are listed in Table 4.

Element	υ _c , μg/kg	υ _{char} , μg/kg	υ _{hom} , μg/kg	<i>u</i> _{method} , μg/kg
boron	60	50	30	0
cadmium	0.0008	0.0004	0.0003	0.0006
cobalt	0.0007	0.0006	0.0003	0.0000
copper	0.007	0.006	0.003	0.003
iron	0.013	0.011	0.000	0.007
manganese	0.03	0.02	0.02	0.01
molybdenum	0.20	0.15	0.13	0.00
nickel	0.009	0.005	0.007	0.000
lead	0.0004	0.0002	0.0003	0.0000
uranium	0.08	0.06	0.05	0.00
zinc	0.04	0.03	0.02	0.00

Table 4: Uncertainty components for NASS-7

Table 4 (continued): Uncertainty components for NASS-7

Element	<i>u</i> _c , μg/kg	υ _{char} , μg/kg	υ _{hom} , μg/kg	<i>u</i> _{method} , μg/kg
arsenic	0.03	0.03	0.01	0.01
chromium	0.008	0.004	0.006	0.004
vanadium	0.04	0.03	0.00	0.02

Metrological traceability

Results presented in this certificate are traceable to the SI through gravimetrically prepared standards of established purity, CRMs and international measurement intercomparisons. As such, NASS-7 serves as suitable reference material for laboratory quality assurance programs, as outlined in ISO/IEC 17025.

Quality Management System (ISO 17034, ISO/IEC 17025)

This material was produced in compliance with the NRC Metrology Quality Management System, which conforms to the requirements of ISO 17034 and ISO/IEC 17025. The Metrology Quality Management System supporting NRC Calibration and Measurement Capabilities, as listed in the Bureau international des poids et mesures (BIPM) Key Comparison Database (kcdb.bipm.org/), has been reviewed and approved under the authority of the Inter-American Metrology System



NRC **NASS-7** 5/7

(SIM) and found to be in compliance with the expectations of the *Comité international des poids et mesures* (CIPM) Mutual Recognition Arrangement. The SIM approval is available upon request.

Updates

Users should ensure that the certificate they have is current. Our website at www.nrc.gc.ca/crm will contain any new information.

References

- 1. Evaluation of measurement data: Guide to the expression of uncertainty in measurement JCGM100:2008
- 2. R. DerSimonian, N. Laird (1986) Meta-analysis in clinical trials. Controlled Clinical Trials 7: 177-188. 3. A. Possolo, B. Toman (2007) Assessment of measurement uncertainty via observation equations. Metrologia, 44: 464-475.
- 4. M. Thompson, S.L.R Ellison (2011) Dark uncertainty. Accreditation and Quality Assurance, 16: 483-487.

Cited by

A list of scientific publications citing NASS-7 CRM can be found at doi.org/10.4224/crm.2016.nass-7

Authorship

The following NRC staff members contributed to the production and certification of NASS-7: Kenny Nadeau, Christine Brophy, Lu Yang, Patricia Grinberg, Indumathi Pihillagawa Gedara, Juris Meija, Enea Pagliano, Garnet McRae, and Zoltan Mester.

Acknowledgements

The following NRC staff members are gratefully acknowledged: Jennifer Bates, Michelle Chartrand, Joe Lam, Paulette Maxwell, Jeremy Melanson, Phuong Mai Le, Ralph Sturgeon, and Anthony Windust.

The cooperation of the following is gratefully acknowledged:

Donald J. Belliveau, Fisheries and Oceans Canada, Bedford Institute of Oceanography, Dartmouth, NS, Canada

Rick Starr and Charles Hamilton, Canadian Coast Guard, Dartmouth, NS, Canada

Prof. Dr. Marco Grotti and Dr. Francisco Ardini, University of Genoa, Genova, Italy

Prof. Dr. Christian Schlosser and Prof. Eric Achterberg, GEOMAR, Helmholtz Centre for Ocean Research, Kiel, Germany

Prof. Dr. Yoshiki Sohrin, Institute for Chemical Research, Kyoto University, Kyoto, Japan

Prof. Dr. Peter Croot, School of Natural Sciences, National University of Ireland Galway, Galway, Ireland

Prof. Jingfeng Wu, Rosentiel School of Marine and Atmospheric science, University of Miami, Miami, FL, USA

Dr. Michael Ellwood, Research School of Earth Sciences, Australian National University, Canberra, Australia

Dr. Clara Turetta, Institute for the Dynamics of Environmental Processes, National Research Council of Italy, Venice, Italy



NRC NASS-7 6/7

Prof. Dr. Ana Aguilar-Islas, School of Fisheries and Ocean Sciences, University of Alaska Fairbanks, Fairbanks, Alaska, USA

Dr. Geraldine Sarthou, Laboratorie des sciences de l'environment marin, Univ. Brest, France Dr. Tomas Matousek, Institute of Analytical Chemistry of the Czech Academy of Sciences, Prague, Czech Republic

Dr. Alessandro D'Ulivo, Istituto di Chimica dei Composti Organometallici, Pisa, Italy Ing. Steven Crum, Quasimeme Laboratory Performance Studies, Wageningen, The Netherlands Dr. Rembert Breidenbach, Rijkswaterstaat Centrale Informatie Voorziening, Rotterdam, The Netherlands

Dr. Daniela Berto, ISPRA- Italian National Institute for Environmental Protection and Research, Chioggia, Italy

Citation

Nadeau K, Brophy C, Yang L, Grinberg P, Gedara I P, Meija J, Pagliano E, McRae G, and Mester Z. NASS-7 Seawater Certified Reference Material for Trace Metals and other Constituents. Ottawa: National Research Council Canada; 2016.

Available from: doi.org/10.4224/crm.2016.nass-7



NRC **NASS-7** 7/7

NASS-7

Date of Issue: February 2016
Date of Expiry: December 2024

Revised: January 2017 (inorganic arsenic), August 2018 (date of expiry extended), December

2019 (storage and sampling, stability, uncertainty sections and editorial update)

Approved by:

Zoltan Mester, Ph. D.

Team Leader, Inorganic Chemical Metrology

NRC Metrology

This Certificate is only valid if the corresponding material was obtained directly from the NRC or an Authorized Reseller.

Comments, information and inquiries should be addressed to:

National Research Council Canada Metrology 1200 Montreal Road Building M36, Room 1029 Ottawa, Ontario K1A 0R6

Telephone: 613-993-2359

Fax: 613-993-8915

Email: CRM-MRCOttawa@nrc-cnrc.gc.ca



