National Research Council Canada | Conseil national de recherches Canada

Certificate of Analysis

Certified Reference Material

MESS-4

Marine Sediment Certified Reference Material for total and extractable metal content

MESS-4 is a marine sediment Certified Reference Material (CRM) from the National Research Council Canada (NRC) with information on total and extractable metal content. A unit of MESS-4 consists of approximately 50 grams of marine sediment.

The following tables show the certified, reference and information values established for MESS-4. The expanded uncertainties associated with the certified and reference values were calculated according to the JCGM Guide [1] and correspond to approx. 95 % confidence (k = 2). All listed values are expressed on a dry mass basis.

Table 1: Mass fractions and expanded uncertainty (k=2) for total metals in MESS-4

Analyte	Mass fraction, mg/kg	Type of value	International recognition of measurement capability (CMC)
aluminium (c,d,e,h)	79 100 ± 2000	certified	MES24
antimony (a,d,g)	1.07 ± 0.16	certified	TES01
arsenic (b,e,d,g)	21.7 ± 2.8	certified	TES02
barium (d,g)	920	information	MYC01
beryllium (b,c,d)	2.09 ± 0.28	certified	TES03
bismuth (d)	2.7	information	MYC02
bromine (g)	60	information	--
caesium (d,g)	10	information	--
cadmium (a,d)	0.28 ± 0.04	certified	TES04
calcium (c,d,e,h)	13 100 ± 600	certified	MES25
carbon (i)	17 900	information	--
cerium (d,g)	72	information	MYC03
chlorine (g,h)	13 100 ± 4400	certified	--
chromium (a,d,e,g)	94.3 ± 1.8	certified	TES05
cobalt (b,d,g)	13.0 ± 0.8	certified	TES06
copper (a,c,d,e)	32.9 ± 1.8	certified	TES07
dibutyltin (as Sn) (e,f)	< 0.005	information	TEOMS02
europium (g)	1.3	information	MYC06
gallium (d)	18	information	MYC08
germanium (d)	0.16	information	MYC09
hafnium (d,g)	3.0	information	--
indium (d)	0.10	information	MYC11

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Analyte	Mass fraction, mg/kg	Type of value	International recognition of measurement capability (CMC)
iron (d,e,g,h)	37 900 ± 1600	certified	MES26
lanthanum (d,g)	35	information	MYC12
lead (a,c,d,e)	21.5 ± 1.2	certified	TES08
lithium (a,c,d,e)	65.3 ± 6.8	certified	TES09
lutetium (g)	0.11	information	--
magnesium (c,d,e,h)	15 800 ± 1200	certified	MES28
manganese (b,c,d,e)	298 ± 14	certified	TES10
mercury (a,f)	0.09 ± 0.04	reference	TES11
molybdenum (a,c,d)	2.53 ± 0.12	reference	TES12
monobutyltin (as Sn)	< 0.05	information	TEOMS03
neodymium (g)	42	information	MYC14
nickel (a,c,d,e)	42.8 ± 1.6	certified	TES13
niobium (d)	12	information	MYC15
phosphorus (c,d,h)	1040 ± 160	certified	MES30
potassium (c,d,e,h)	23 800 ± 1000	certified	MES27
rhenium (d)	0.004	information	MYC18
rubidium (d,g)	180	information	MYC17
samarium (g)	5.5	information	MYC19
scandium (d,g)	13.4	information	MYC20
selenium (a,d)	1.5	information	TES14
silicon (c,h)	278 000 ± 20	certified	MES33
silver (a,c,d)	0.161 ± 0.024	certified	TES15
sodium (d,e,g)	12 600 ± 800	certified	MES29
strontium (a,c,d,e)	132 ± 8	certified	TES16
sulfur (c,d,h,i)	1580 ± 200	certified	MES31
tantalum (d)	1	information	MYC21
tellurium (d)	0.1	information	MYC22
thallium (a,d)	0.85 ± 0.10	certified	TES17
thorium (d,g)	12	information	--
tin (a,d,g)	2.35 ± 0.12	certified	TES18
titanium (c,d,e,h)	3840 ± 220	certified	MES32
tributyltin (as Sn) (e,f)	< 0.005	information	TEOMS01
tungsten (d)	1.3	information	MYC25
uranium (a,d,g)	3.4 ± 0.4	certified	--
vanadium (b,c,d,e)	216 ± 8	certified	TES19
ytterbium (g)	2	information	MYC26
yttrium (d,g)	20	information	MYC27
zinc (a,c,d,e)	147 ± 6	certified	TES20
zirconium (d)	96	information	MYC28

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** Inductively-coupled plasma atomic emission spectroscopy (ICP-AES)
- **e** Standard addition inductively-coupled plasma atomic emission spectroscopy (SA-ICP-AES)
- **f** Cold-vapour atomic absorption spectroscopy (CV-AAS)
- **g** Instrumental Neutron Activation Analysis (INAA)
- **h** Fusion X-ray fluorescence spectroscopy (XRF)
- **i** Combustion infrared spectroscopy (LECO)
- **j** Isotope dilution gas chromatography ICP-MS (ID-GC-ICP-MS)
- **k** Thermal decomposition atomic absorption spectroscopy (TD-AAS)

Table 2: Reference values and expanded uncertainty (*k*=2) for extractable mass fraction based on BCR sequential extraction [2] in MESS-4*

Analyte	BCR step 1, mg/kg	BCR step 2, mg/kg	BCR step 3, mg/kg	BCR Residue, mg/kg
aluminium	140 ± 73	1315 ± 3	1204 ± 628	59 762 ± 12 617
antimony	0.037 ± 0.030	0.016 ± 0.001	0.003 ± 0.002	0.980 ± 0.434
arsenic	0.687 ± 0.121	3.52 ± 0.79	1.17 ± 0.28	15.9 ± 1.7
beryllium	0.132 ± 0.087	0.334 ± 0.053	0.148 ± 0.067	1.19 ± 0.12
cadmium	0.140 ± 0.015	0.045 ± 0.013	0.043 ± 0.023	0.068 ± 0.002
calcium	11 000 ± 280	1994 ± 12	186 ± 32	814 ± 424
chromium	0.305 ± 0.072	1.98 ± 0.23	3.86 ± 0.67	80.5 ± 8.0
cobalt	1.05 ± 0.08	2.61 ± 0.15	1.84 ± 0.04	10.0 ± 0.2
copper	2.01 ± 0.24	6.76 ± 0.88	9.41 ± 2.31	12.3 ± 2.7
iron	599 ± 92	6632 ± 1005	1837 ± 973	22 729 ± 704
lead	0.688 ± 0.268	11.4 ± 0.4	0.663 ± 0.425	7.37 ± 1.56
lithium	2.45 ± 1.8	3.43 ± 1.48	6.61 ± 5.34	46.3 ± 5.4
magnesium	5947 ± 691	921 ± 1	562 ± 178	6659 ± 1461
manganese	109 ± 9	45.6 ± 2.1	23.0 ± 3.9	113 ± 8
molybdenum	0.015 ± 0.019	0.028 ± 0.002	0.064 ± 0.071	2.24 ± 0.83
nickel	2.09 ± 0.35	5.70 ± 0.49	10.1 ± 1.8	20.8 ± 1.7
phosphorus	6.46 ± 1.34	543 ± 81	88.5 ± 6.0	462 ± 12
potassium	1302 ± 92	614 ± 99	262 ± 37	18 210 ± 2895
selenium	0.038 ± 0.024	0.027 ± 0.011	0.870 ± 0.232	0.251 ± 0.175
sodium	9057 ± 282	129 ± 30	39.7 ± 2.7	3669 ± 252
strontium	24.1 ± 3.8	14.0 ± 3.2	2.88 ± 0.46	85.8 ± 0.2
sulfur	679 ± 19	48.4 ± 9.3	565 ± 47	152 ± 60

Analyte	BCR step 1, mg/kg	BCR step 2, mg/kg	BCR step 3, mg/kg	BCR Residue, mg/kg
thallium	0.003 ± 0.001	0.022 ± 0.002	0.023 ± 0.003	0.745 ± 0.232
tin	<0.01	<0.01	0.015 ± 0.004	1.89 ± 0.05
uranium	0.121 ± 0.034	0.238 ± 0.144	0.593 ± 0.093	1.64 ± 0.04
vanadium	0.370 ± 0.175	18.1 ± 1.2	3.59 ± 1.72	176 ± 9
zinc	17.9 ± 0.4	29.4 ± 2.0	22.1 ± 4.9	74.7 ± 6.6

*BCR step 1: exchangeable fraction; BCR step 2: reducible fraction, BCR step 3: oxidizable fraction, BCR residue: residue from step 3. Full report and data from ref [2].

Table 3: Reference values and expanded uncertainty (*k*=2) for extractable mass fraction based on Tessier sequential extraction [3] in MESS-4*

Analyte	Tessier step 1, mg/kg	Tessier step 2, mg/kg	Tessier step 3, mg/kg	Tessier step 4, mg/kg	Tessier Residue, mg/kg
antimony	0.020 ± 0.016	0.028 ± 0.002	0.011 ± 0.007	<0.01	1.11 ± 0.18
arsenic	0.102 ± 0.014	0.257 ± 0.050	2.57 ± 0.27	0.264 ± 0.060	18 ± 3.7
beryllium	<0.004	0.041 ± 0.024	0.472 ± 0.180	0.07 ± 0.01	1.72 ± 0.13
cadmium	<0.02	0.080 ± 0.025	0.049 ± 0.035	0.04 ± 0.072	0.072 ± 0.059
chromium	0.005 ± 0.001	0.159 ± 0.030	3.55 ± 0.69	1.84 ± 0.40	89.0 ± 10.4
copper	0.463 ± 0.015	1.44 ± 0.295	4.42 ± 0.27	7.13 ± 0.93	20.9 ± 2.7
iron	4.26 ± 1.23	327 ± 31	6152 ± 235	508 ± 108	27 826 ± 6756
lead	0.014 ± 0.006	2.50 ± 0.34	8.33 ± 1.88	0.271 ± 0.025	10.2 ± 2.7
lithium	0.403 ± 0.086	0.486 ± 0.022	6.80 ± 1.51	2.35 ± 0.28	48.6 ± 7.7
manganese	2.95 ± 0.26	75.7 ± 7.1	71.5 ± 10.4	11.4 ± 0.24	111 ± 16
nickel	0.055 ± 0.009	0.829 ± 0.067	12.3 ± 3.3	5.82 ± 0.89	26.8 ± 4.6
selenium	0.025 ± 0.005	0.205 ± 0.138	0.099 ± 0.184	0.526 ± 0.125	0.219 ± 0.08
strontium	14.4 ± 0.2	10.7 ± 1.7	10.7 ± 2.0	2.38 ± 0.38	85.4 ± 13.3
tin	<0.01	<0.01	<0.01	<0.01	3.23 ± 0.48
uranium	0.055± 0.003	0.237 ± 0.0312	0.353 ± 0.224	0.162 ± 0.004	2.28 ± 0.93
vanadium	0.276 ± 0.044	0.471 ± 0.121	21.9 ± 2.3	0.764 ± 0.205	199 ± 25
zinc	0.101 ± 0.044	11.7 ± 0.5	49.4 ± 10.4	13.6 ± 2.1	81.8 ± 8.1

*Tessier step 1: exchangeable fraction; Tessier step 2: carbonate bound fraction; Tessier step 3: Fe-Mn oxide bound fraction; Tessier step 4: organic matter and sulfide bound fraction, Tessier residue: residue from step 4. Full report and data from ref [3].

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. Lists of all registered measurement capabilities in a sediment matrix can be found in the BIPM database at https://www.bipm.org/kcdb/.

Certified values

Certified values are considered to be those for which the 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.

Reference values

Reference values are those for which insufficient data are available to provide a comprehensive estimate of uncertainty.

Information values

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

Intended use

This reference material is intended for use in the method development, validation, and quality control for the analysis of trace and matrix constituents for total and extractable metal content in marine sediments and materials with similar matrices.

Storage and sampling

It is recommended that the material be stored in a cool, clean location. Each bottle is packaged in a trilaminate foil pouch.

Prior to use, the bottle contents should be well mixed, and tightly closed immediately thereafter. Certified values are based on a minimum 250 mg sub-sample.

Instructions for drying

Although initially free from moisture following the freeze drying, the materials have adsorbed moisture during subsequent operations. A designated sample aliquot should be dried to a constant mass for moisture determination. Drying for several hours at 105 ^{o}C is recommended as a relatively simple method to achieve a dry mass for most purposes. The estimated moisture content of MESS-4 is approximately 0.019 g/g.

Preparation of material

MESS-4 was collected from Beufort Sea (Arctic Canada), freeze-dried, screened to pass a No. 120 (125 µm) screen, blended and bottled by NRC staff using the facilities of the Canada Centre for Mineral and Energy Technology in Ottawa. After bottling, the samples were radiation sterilized with a minimum dose of 25 kGy to minimize any effects from biological activity.

Stability

The predecessor CRM, MESS-3, has been periodically analyzed for more than ten years and found to be both physically and chemically stable over this time interval. We expect similar results for MESS-4. Uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Homogeneity

MESS-4 was tested for homogeneity at NRC. Results from sub-samples (250 mg) were evaluated using the DerSimonian-Laird random effects model and included in the calculation of the certified values [4].

Uncertainty

Evaluation of the uncertainty associated with certified and reference values was carried out. 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 [5,6]. Expressed as standard uncertainties, these components are listed in Table 4.

Table 4: Uncertainty Components for total mass fraction of total metals in MESS-4

Analyte	u_c, mg/kg	u_{char}, mg/kg	u_{hom}, mg/kg	u_{method}, mg/kg
aluminium	1000	600	800	0
antimony	0.08	0.08	0.02	0.00
arsenic	1.4	1.0	1.0	0.0
beryllium	0.14	0.06	0.13	0.00
cadmium	0.02	0.02	0.01	0.00
calcium	300	300	100	0
chlorine	2200	600	1200	1700
chromium	0.9	0.6	0.7	0.0
cobalt	0.4	0.2	0.3	0.0
copper	0.9	0.7	0.5	0.0
iron	800	400	700	0
lead	0.6	0.5	0.3	0.0
lithium	3.4	0.9	0.6	3.2
magnesium	600	400	0	400
manganese	7	6	4	0
nickel	0.8	0.6	0.6	0.0
phosphorus	80	50	30	50
potassium	500	380	320	0
silicon	10 000	10 000	3000	0
silver	0.012	0.012	0.003	0.000
sodium	400	400	100	0
strontium	4	3	2	0
sulfur	100	60	50	70
thallium	0.05	0.05	0.00	0.00
tin	0.06	0.04	0.05	0.00

Analyte	u_c, mg/kg	u_{char}, mg/kg	u_{hom}, mg/kg	u_{method}, mg/kg
titanium	110	80	80	0
uranium	0.2	0.2	0.0	0.0
vanadium	4	3	2	0
zinc	3	2	2	0.0

Metrological traceability

Results presented in this certificate are traceable to the SI through CRMs produced by National Metrology Institutes and gravimetrically prepared standards of established purity. As such, MESS-4 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 (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

For updates please refer to doi.org/10.4224/crm.2014.mess-4

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Cited by

A list of scientific publications citing MESS-4 can be found at doi.org/10.4224/crm.2014.mess-4.

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MESS-4

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

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