National Research Council Canada | Conseil national de recherches Canada

Certificate of Analysis

Certified Reference Material

PACS-3

Marine Sediment Certified Reference Material for total and extractable metal content

PACS-3 is a marine Sediment Certified Reference Material (CRM) from the National Research Council Canada (NRC) for total and extractable metal content. A unit of PACS-3 consists of approximately 50 grams of marine sediment. This material is intended for use in the calibration of procedures and the development of methods for the determination of trace metals and matrix constituents in marine sediments and materials with similar matrices.

The following tables show those constituents for which certified, reference and information values have been established for this RM. 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 which corresponds to approximately 95 % confidence. It is intended that U_{CRM} accounts for every aspect that reasonably contributes to the uncertainty of the measurement. All listed values are expressed on a dry mass basis.

Table 1: Mass fractions and expanded uncertainty (*k*=2) for total metals in PACS-3

Element/ Substance	Mass fraction, mg/kg	Type	International recognition of measurement capability (CMC)
aluminium (c,d)	65 800 ± 1200	certified	MES24
antimony (a,c)	14.7 ± 2.2	certified	TES01
arsenic (b,c)	30.3 ± 2.4	certified	TES02
beryllium (b)	1.06 ± 0.12	certified	TES03
cadmium (a)	2.23 ± 0.16	certified	TES04
calcium (c,d)	18 900 ± 1200	certified	MES25
chromium (a,c)	90.6 ± 4.0	certified	TES05
cobalt (b)	12.1	information	TES06
copper (a,c)	326 ± 10	certified	TES07
iron (c,d)	41 060 ± 640	certified	MES26
lead (a,c)	188.0 ± 7.4	certified	TES08
lithium (a,c)	31.9 ± 4.2	certified	TES09
magnesium (c,d)	14 020 ± 580	certified	MES28
manganese (b,c)	432 ± 16	certified	TES10
mercury (a)	2.98 ± 0.36	certified	TES11
molybdenum (a)	5.9	information	TES12
nickel (a,c)	39.5 ± 2.2	certified	TES13

Element/ Substance	Mass fraction, mg/kg	Type	International recognition of measurement capability (CMC)
phosphorus (c,d)	937 ± 44	certified	MES30
potassium (c,d)	12 530 ± 400	certified	MES27
silicon (d)	261 000 ± 34 000	certified	MES33
silver (a)	1.10 ± 0.08	reference	TES15
sodium (c)	35 200 ± 3400	certified	MES29
strontium (a,c)	267 ± 10	certified	TES16
sulfur (d)	11 700 ± 4400	certified	MES31
tin (a,c)	22.0 ± 2.2	certified	TES18
titanium (c,d)	4420 ± 180	certified	MES32
uranium (a)	2.6	information	--
vanadium (b,c)	129 ± 8	certified	TES19
zinc (a,c)	376 ± 12	certified	TES20
monobutyltin (as Sn) (e,f)	1.47 ± 0.22	certified	TEOMS03
dibutyltin (as Sn) (e,f)	0.631 ± 0.038	certified	TEOMS02
tributyltin (as Sn) (e,f)	0.43 ± 0.06	certified	TEOMS01

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 (ICP-MS)
- **c** Standard addition inductively-coupled plasma atomic emission spectroscopy (ICP-AES)
- **d** Fusion X-ray fluorescence spectroscopy (XRF)
- **e** Isotope dilution gas chromatography ICP-MS (ID-GC-ICP-MS)
- **f** Isotope dilution gas chromatography mass spectrometry (ID-GC-MS)

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

Element	BCR step 1, mg/kg	BCR step 2, mg/kg	BCR step 3, mg/kg	BCR Residue, mg/kg
aluminium	198 ± 61	1933 ± 205	2736 ± 266	53 358 ± 4401
antimony	0.283 ± 0.139	0.164 ± 0.023	0.102 ± 0.013	9.70 ± 1.92
arsenic	1.83 ± 0.43	9.41 ± 0.97	4.58 ± 0.39	13.4 ± 0.7
beryllium	0.071 ± 0.022	0.131 ± 0.037	0.078 ± 0.036	0.538 ± 0.034
calcium	3427 ± 35	1783 ± 34	387 ± 127	13 031 ± 1189
cadmium	1.56 ± 0.16	0.378 ± 0.052	0.050 ± 0.009	0.361 ± 0.071
chromium	0.906 ± 0.093	5.47 ± 0.81	17.6 ± 0.3	51.7 ± 4.2

Element	**BCR step 1, mg/kg**	**BCR step 2, mg/kg**	**BCR step 3, mg/kg**	**BCR residue, mg/kg**
cobalt	0.835 ± 0.018	1.41 ± 0.12	1.84 ± 0.58	11.0 ± 0.08
copper	56.0 ± 7.7	69.8 ± 6.6	124 ± 16	28.5 ± 0.4
iron	696 ± 71	6190 ± 463	5314 ± 475	23 291 ± 6583
lead	16.8 ± 1.8	122 ± 9	9.48 ± 4.50	28.3 ± 4.6
lithium	2.04 ± 0.61	4.94 ± 0.58	4.09 ± 2.25	16.8 ± 0.6
magnesium	2725 ± 227	973 ± 59	1513 ± 5	8300 ± 836
manganese	18.9 ± 1.8	30.2 ± 1.3	43.8 ± 6.1	277 ± 24
molybdenum	0.080 ± 0.076	0.178 ± 0.08	0.740 ± 0.195	3.74 ± 0.22
nickel	3.30 ± 0.32	3.93 ± 0.49	7.02 ± 0.65	20.4 ± 1.6
potassium	1267 ± 29	549 ± 130	168 ± 30	9753 ± 566
phosphorus	13.5 ± 1.3	588 ± 38	143 ± 14	229 ± 14
selenium	0.026 ± 0.010	0.033 ± 0.002	1.05 ± 0.25	0.067 ± 0.012
sodium	18243 ± 197	473 ± 22	155 ± 15	13 552 ± 1988
strontium	30.9 ± 2.9476	18.7 ± 5	3.86 ± 0.38	222 ± 33
sulfur	2889 ± 35	169 ± 9	8044 ± 286	570 ± 66
thallium	0.027 ± 0.003	0.116 ± 0.008	0.092 ± 0.013	0.285 ± 0.044
tin	0.118 ± 0.032	0.268 ± 0.070	0.215 ± 0.041	16.5 ± 2.3
uranium	0.137 ± 0.035	0.246 ± 0.063	1.17 ± 0.31	0.841 ± 0.160
vanadium	3.95 ± 0.50	22.3 ± 1.2	6.27 ± 1.21	80.2 ± 5.0
zinc	204 ± 2	89.8 ± 6.7	36.8 ± 6.5	51.2 ± 3.5

*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 PACS-3*

Element	**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	0.046 ± 0.016	0.223 ± 0.009	0.442 ± 0.399	0.079 ± 0.049	13.0 ± 1.3
arsenic	0.093 ± 0.034	0.363 ± 0.016	10.0 ± 0.2	1.87 ± 0.25	18.5 ± 3.9
beryllium	<0.004	0.032 ± 0.004	0.176 ± 0.05	0.030 ± 0.002	0.750 ± 0.035
cadmium	<0.02	1.18 ± 0.33	0.910 ± 0.356	0.085 ± 0.078	0.098 ± 0.06
chromium	0.133 ± 0.056	0.917 ± 0.213	20.8 ± 2.3	11.6 ± 1.9	66.1 ± 8.5

Element	Tessier step 1, mg/kg	Tessier step 2, mg/kg	Tessier step 3, mg/kg	Tessier step 4, mg/kg	Tessier residue, mg/kg
copper	4.15 ± 0.83	27.8 ± 7.5	20.6 ± 4.2	223 ± 21	42.2 ± 5.3
iron	4.05 ± 3.31	340 ± 214	7353 ± 421	4907 ± 539	24 482 ± 327
lead	0.919 ± 0.330	37.5 ± 12.3	118 ± 26	22.9 ± 2.4	36.1 ± 8.2
lithium	0.518 ± 0.012	0.277 ± 0.083	7.76 ± 0.88	2.37 ± 0.03	19.3 ± 4.9
manganese	2.33 ± 0.27	6.55 ± 1.31	49.3 ± 8.0	38.2 ± 1.3	299 ± 39
nickel	0.247 ± 0.080	1.40 ± 0.07	10.6 ± 2.5	4.55 ± 0.73	24.7 ± 4.2
selenium	0.024 ± 0.008	0.039 ± 0.011	<0.02	0.888 ± 0.254	0.232 ± 0.005
strontium	28.1 ± 2.5	11.3 ± 1.9	15.1 ± 1.2	4.08 ± 0.28	174 ± 103
tin	<0.01	<0.01	1.89 ± 0.10	<0.01	24.4 ± 7.9
uranium	<0.01	0.584 ± 0.047	0.555 ± 0.211	0.328 ± 0.284	1.17 ± 0.27
vanadium	0.273 ± 0.310	0.591 ± 0.207	38.3 ± 5.5	4.14 ± 0.48	95.9 ± 19.1
zinc	17.2 ± 1.2	140 ± 19	168 ± 38	33.4 ± 3.4	72.0 ± 10.2

*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 water 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 primarily intended for use in the calibration of procedures and the development of methods for the determination of trace and matrix constituents for total and extractable metal content in marine sediments and materials with similar matrices. A minimum sample mass of 250 mg is recommended.

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 which serves as an impermeable barrier to mercury vapour. Under conditions of high ambient levels of mercury vapour, mercury is able to penetrate the plastic cap of the bottle, thereby potentially contaminating the contents. The bottle contents should be well mixed by rotation and shaking prior to use, and tightly closed immediately thereafter. Certified values are based on a minimum 250 mg sub-sample from the bottle. To ensure the stability of the butyltin compounds in PACS-3, it is necessary to store the material at a temperature of 4 ^{o}C or lower.

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 moisture content in PACS-3 is approx. 0.02 g/g.

Preparation of material

PACS-3 was collected from Esquimalt harbour, B.C. All were freeze dried, screened to pass a No. 120 (125 µm) screen, blended and bottled by Institute 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 by Nordion Gamma Centre of Excellence (Laval, QC, Canada) to minimize any effects from biological activity.

Stability

The predecessor CRM, PACS-2, 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 PACS-3. Uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Homogeneity

PACS-3 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

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 mass fraction of total metals in PACS-3

Element	u_c, mg/kg	u_{char}, mg/kg	u_{hom}, mg/kg	u_{method}, mg/kg
aluminium	600	500	300	0
antimony	1.1	1.0	0.4	0.0
arsenic	1.2	1.0	0.6	0.0
beryllium	0.06	0.04	0.05	0.00
cadmium	0.08	0.07	0.03	0.00
calcium	600	600	100	0
chromium	2.0	1.4	1.4	0.0
copper	5	4	3	0
iron	320	180	270	0
lead	3.7	2.3	2.9	0.0
lithium	2.1	0.6	0.7	1.9
magnesium	290	280	80	0
manganese	8	5	1	6
mercury	0.18	0.16	0.09	0.00
nickel	1.1	0.8	0.8	0.0
phosphorus	22	22	3	0
potassium	200	100	80	160
silicon	17 000	17 000	1000	0
silver	0.04	0.01	0.04	0.00
sodium	17 000	1700	400	0
strontium	5	2	4	3
sulfur	2200	2200	100	0
tin	1.1	1.0	0.5	0.0
titanium	90	90	30	0
vanadium	4	4	1	0
zinc	6	5	4	0
monobutyltin (as Sn)	0.11	0.04	0.10	0.00
dibutyltin (as Sn)	0.019	0.014	0.013	0.000
tributyltin (as Sn)	0.03	0.02	0.02	0.00

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, PACS-3 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

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. Kumkrong P, Mercier PHJ, Pihilligawa IG , Mihai O, Tyo DD, Cindy J, Kingston DM, Mester Z (2021) Determination of 27 metals in HISS-1, MESS-4 and PACS-3 marine sediment certified reference materials by the BCR sequential extraction. *Talanta*, 221: 121543 https://doi.org/10.1016/j.talanta.2020.121543
3. Kumkrong P, Mihai O, Mercier PHJ, Pihilligawa IG, Tyo DD, Mester Z (2021) Tessier sequential extraction on 17 elements from three marine sediment certified reference materials (HISS-1, MESS-4, and PACS-3). *Analytical and Bioanalytical Chemistry* 413: 1047-1057 https://doi.org/10.1007/s00216-020-03063-z
4. DerSimonian R, Laird N (1986) Meta-analysis in clinical trials. *Controlled Clinical Trials*, 7: 177-188. https://doi.org/10.1016/0197-2456(86)90046-2
5. Possolo A, Toman B (2007) Assessment of measurement uncertainty via observation equations. *Metrologia*, 44: 464-475. https://doi.org/10.1088/0026-1394/44/6/005
6. Thompson M, Ellison SLR (2011) Dark uncertainty. *Accreditation and Quality Assurance*, 16: 483-487. https://doi.org/10.1007/s00769-011-0803-0

Cited by

A list of scientific publications citing PACS-3 RM can be found at doi.org/10.4224/crm.2013.pacs-3.

Authorship

Scott Willie[1], Victor Boyko[1], Christine. Brophy[1], Vincent Clancy[1], Indu Gedara Pihillagawa[1], Patricia Grinberg[1], Paramee Kumkrong[1], Patrick H.J. Mercier[1], Ovi Mihai[1], Daniel D. Tyo[1], Cindy Jiang[1], David M. Kingston[1], Paulette Maxwell[1], Juris Meija[1], Zoltan Mester[1], Ralph Sturgeon[1], Lu Yang[1].

[1] National Research Council Canada, 1200 Montreal Rd, Ottawa ON K1A 0R6, Canada

Citation

Willie S, Boyko V, Brophy C, Clancy V, et al. PACS-3: Marine Sediment Certified Reference Material for total and extractable Metal content. Ottawa: National Research Council Canada; 2013. Available from: doi.org/10.4224/crm.2013.pacs-3.

PACS-3

Date of issue: October 2013
Date of expiry: October 2033
Revised: April 2015, March 2016 (editorial update), May 2018 (date of expiry extended), June 2021 (values related to Tessier and BCR extraction added, date of expiry extended, 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.

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

Canada