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Certificate of Analysis

Certified Reference Material

DORM-4

Fish Protein 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 fish protein 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. All listed values are expressed on a dry mass basis

Table 1: Certified quantity values and expanded uncertainty for DORM-4

Element	Mass fraction, mg/kg	International recognition of measurement capability (CMC)
arsenic (b,d,f)	6.87 ± 0.44	MEF-14
cadmium (a,d)	0.299 ± 0.018	MEF-16
calcium (d,e)	2360 ± 140	MEF-17
chromium (a,d,e)	1.87 ± 0.18	MEF-18
copper (a,d,e)	15.7 ± 0.46	MEF-20
iron (a,d)	343 ± 20	MEF-21
lead (a,b,d)	0.404 ± 0.062	MEF-22
magnesium (d,e)	910 ± 80	MEF-23
manganese (b,d,e)	3.17 ± 0.26	MEF-24
mercury (a,c,g)	0.412 ± 0.036	MEF-25
nickel (a)	1.34 ± 0.14	MEF-28
potassium (d,e)	15 500 ± 1000	MEF-29
selenium (a,d,f)	3.45 ± 0.40	MEF-30
silver (a,d)	0.0252 ± 0.0050	MEF-31
strontium (d,e)	10.1 ± 0.8	MEF-33
vanadium (d,e)	1.57 ± 0.14	MEF-34
zinc (a,d)	51.6 ± 2.8	MEF-35

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Table 1 (continued): Certified quantity values and expanded uncertainty for DORM-4

Substance	Mass fraction, mg/kg	International recognition of measurement capability (CMC)
arsenobetaine (as As) (h,i)	3.95 ± 0.36	MEF-15
methylmercury (as Hg) (j,k)	0.355 ± 0.028	MEF-26

Table 2: Reference values and expanded uncertainty for DORM-4

Element	Mass fraction, mg/kg	International recognition of measurement capability (CMC)
aluminium (b,d,e)	1280 ± 340 *	MEF-13
sodium (d,e)	14 000 ± 2400	MEF-32
tin (a,d)	0.061 ± 0.018	--

* Note: The mass fraction of aluminium is obtained without the use of hydrofluoric acid.

Table 3: Information values for DORM-4

Element	Mass fraction, mg/kg	International recognition of measurement capability (CMC)
cobalt (d)	0.25	MEF-19
lithium (d)	1.21	--
molybdenum (d)	0.29	MEF-27
phosphorus (d)	8 000	--
uranium (d)	0.050	--

Table 3 (continued): Information values for DORM-4

Substance	Mass fraction, mg/kg (as Sn)	International recognition of measurement capability (CMC)
monobutyltin (j)	< 0.05	--
dibutyltin (j)	< 0.005	--
tributyltin (j)	< 0.005	--

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 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 (ICP-AES)
f Hydride generation graphite furnace atomic absorption spectroscopy
g Cold-vapour atomic absorption spectroscopy (CV-AAS)
h Standard addition liquid chromatography ICP-MS (LC-ICP-MS)
i Isotope dilution liquid chromatography Orbtrap mass spectrometry
j Isotope dilution gas chromatography ICP-MS (ID-GC-ICP-MS)
k Isotope dilution gas chromatography mass spectrometry (ID-GC-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. 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 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 mean and uncertainty (Table 1).

Reference values

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

Instructions for drying

Although initially free from moisture following the freeze drying, the materials have adsorbed moisture during subsequent operations. A separate sample aliquot should be dried to a constant mass to obtain moisture content. DORM-4 can be dried to constant mass by: (1) drying at reduced pressure (e.g., 50 mm Hg) at room temperature in a vacuum desiccator over magnesium perchlorate for 24 hours; (2) vacuum drying (about 0.5 mm Hg) at room temperature for 24 hours.

Preparation of material

This reference material was prepared from a fish protein homogenate. A uniform material was produced using an enzyme hydrolysis procedure subsequent to removal of the bones and the majority of the oil. The protein hydrolysate was spray dried, sieved to pass a 297 µm screen, blended and bottled. After bottling the material was sterilized by subjecting it to a minimum dose of 25 kGy gamma irradiation at the Canadian Irradiation Centre, Laval, Quebec.

Stability

The predecessor CRM, DORM-3, has been periodically analyzed for more than nine years and found to be both physically and chemically stable over this time interval. We expect similar results for DORM-4. 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 (250 mg) from thirty bottles were evaluated using ANOVA and/or the DerSimonian-Laird random effects model and included in the calculation of the certified values [2].

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}). Expressed as standard uncertainties, these components are listed in Table 4.

Table 4: Uncertainty Components for DORM-4

Element	u_c, mg/kg	u_{char}, mg/kg	u_{hom}, mg/kg	u_{method}, mg/kg
arsenic	0.22	0.11	0.19	0.00
cadmium	0.009	0.005	0.007	0.000
calcium	70	30	60	0
chromium	0.09	0.05	0.08	0.00
copper	0.23	0.07	0.22	0.00
iron	10	5	9	0
lead	0.031	0.007	0.030	0.000
magnesium	40	40	20	0
manganese	0.13	0.09	0.10	0.00
mercury	0.018	0.009	0.016	0.000
nickel	0.07	0.05	0.05	0.00
potassium	500	300	400	0
selenium	0.20	0.10	0.17	0.00
silver	0.0025	0.0014	0.0020	0.0004
strontium	0.4	0.3	0.3	0.0
vanadium	0.07	0.07	0.01	0.0
zinc	1.4	0.8	1.1	0.0

Table 4 (continued): Uncertainty Components for DORM-4

Substance	u_c, mg/kg	u_{char}, mg/kg	u_{hom}, mg/kg	u_{method}, mg/kg
arsenobetaine (as As)	0.18	0.17	0.05	0.00
methylmercury (as Hg)	0.014	0.007	0.012	0.000

Table 4 (continued): Uncertainty Components for DORM-4

Element	u_c, mg/kg	u_{char}, mg/kg	u_{hom}, mg/kg	u_{method}, mg/kg
aluminium	170	40	50	160
sodium	1200	200	200	1200
tin	0.009	0.003	0.004	0.007

Metrological traceability

Results presented in this certificate are traceable to the SI through gravimetrically prepared standards of established purity and international measurement intercomparisons. As such,

DORM-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

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

Authorship

The following staff members of the NRC contributed to the production and certification of DORM-4: S. Willie, C. Brophy, V. Clancy, I.P. Gedara, J. Lam, P. Maxwell, P. McCooeye, P. Grinberg, J. Meija, Z. Mester, R. Sturgeon, and L. Yang.

DORM-4

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Approved by:

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NRC Metrology

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

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