National Research Council Canada
Conseil national de recherches Canada

Certified Reference Material

DORM-3

Fish Protein Certified Reference Material for Trace Metals

The following table shows those elements for which certified values have been established for this reference material. Certified values are based on unweighted mean results from data generated at NRCC as well as results submitted by laboratories participating in an annual intercomparison. 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 ISO Guide [1] and k is the coverage factor. The value of u_c is calculated from the combined uncertainties of the various methods (u_{char}) as well as uncertainties associated with homogeneity (u_{hom}).

It is intended that U_{CRM} accounts for every aspect that reasonably contributes to the uncertainty of the measurand [2]. A coverage factor of 2 was applied for all elements. The table below lists certified values for DORM-3 expressed on a dry mass basis.

TRACE ELEMENTS (milligram/kilogram)

Arsenic (d,g,h)	6.88	±	0.30
Cadmium (d,g,i,p)	0.290	±	0.020
Copper (d,i,p)	15.5	±	0.63
Chromium (d,g,i)	1.89	±	0.17
Iron (d,i)	347	±	20
Lead (d,g,p)	0.395	±	0.050
Mercury (c,d,p)	0.409	±	0.027
Nickel (d,g,i,p)	1.28	±	0.24
Tin (d,p)	0.066	±	0.012
Zinc (d,i,p)	51.3	±	3.1

Coding

The coding refers only to the instrumental method used for quantitation.

c - Cold vapour atomic absorption spectrometry.
d - Inductively coupled plasma mass spectrometry.
g - Electrothermal vaporization atomic absorption spectrometry.
h - Hydride generation atomic absorption, fluorescence or emission spectrometry.
i - Inductively coupled plasma atomic emission spectrometry.
p - Isotope dilution inductively coupled plasma mass spectrometry.

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Intended Use

This reference material is primarily intended for use in the calibration of procedures and the development of methods for the analysis of marine fauna and materials of similar matrix.

Storage and Sampling

This material should be stored in a cool and dark location. Prior to use, the bottle should be rotated and shaken to ensure the contents are well mixed. The bottle should be tightly closed thereafter. Certified values are based on a minimum 0.250 g sub-sample from the bottle.

Instructions for Drying

Determination of dry mass should be performed on a separate sample to avoid contamination. DORM-3 can be dried to constant weight 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.

Expiry

Based on sample stability noted on page 3, the certified values for DORM-3 are considered valid until September, 2016, provided the CRM is handled and stored in accordance with instructions herein.

Preparation of DORM-3

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, Québec.

Information values

Due to the scatter of results, certified values for Ag and Se were not calculated. A lack of independent values precluded the determination of a certified value for Al and Mn. Information values for these analytes are thus given below.

Ag	0.04	mg/kg
Se	3.3	mg/kg
Al	1700	mg/kg
Mn	4.6	mg/kg

Updates

It is anticipated that as more data become available, the established values may be updated and reliable values assigned to more elements. Our web site at http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_e.html will contain any new information.

Uncertainties

The uncertainties associated with the various methods (u_{char}) as well as uncertainties associated with homogeneity (u_{hom}) are listed in Table 2. The principles used to calculate these values are described on page 3.

Table 2. Statistical Data for DORM-3

	data sets	u_{char}, (mg/kg)	u_{hom}, (mg/kg)
As	6	0.05	0.14
Cd	8	0.006	0.008
Cu	7	0.20	0.26
Cr	5	0.04	0.07
Fe	5	5	9
Pb	5	0.015	0.020
Hg	4	0.006	0.012
Ni	6	0.08	0.08
Sn	5	0.004	0.005
Zn	7	1.1	1.0

Certified value

DORM-3 was provided as an unknown sample to a group of laboratories participating in an annual intercomparison for trace metals in marine samples sponsored by NRCC [3]. Data generated by NRCC were also included in the pool of intercomparison results.

Laboratories were requested to provide triplicate dry weight values using an analytical method of choice based on total digestion of the sample.

Data were returned to NRCC for evaluation. The results from a select sub-group of participants were used for the certification of DORM-3. Such laboratories were selected based on their performance history in previous intercomparisons. NIST SRM 2976, Mussel Tissue served as a quality control sample.

The certified values were calculated from the unweighted means of the results of the selected laboratories [4]. Data were first examined for outliers using the Dixon and Grubb's Tests. Testing of variances was conducted using the Cochran and Bartletts Tests.

Included in the overall uncertainty estimate are uncertainties in the batch characterisation (u_{char}), uncertainties related to possible between-bottle variation (u_{hom}) as well as instability derived from effects relating to long-term storage and transport (u_{stab}). Expressed as standard uncertainties these components can be combined as:

$$u^2_{c(CRM)} = u^2_{char} + u^2_{hom} + u^2_{stab} \qquad (1)$$

Results for the various statistics used to calculate the certified values are shown in Table 2.

Characterisation

The characterisation uncertainties (u_{char}) were calculated in accordance with equation 2, where s is the standard deviation of the means and p is the number of mean results included in the calculation [4].

$$u_{char} = \frac{s}{\sqrt{p}} \qquad (2)$$

Homogeneity

The homogeneity components of the uncertainties in the certified values were derived according to the recommendation of an international study group [4]. The material was tested for homogeneity at NRCC using ICP-MS. Results from sub-samples (0.250 g) from twelve bottles were evaluated using ANOVA.

In certain situations the inhomogeneity contribution to uncertainty, u_{hom} , was set to the experimentally determined between-unit standard deviation ($s_{between}$) as the best estimate of the uncertainty due to between-unit heterogeneity. However, if the situation depicted in equation 3 occurred:

$$s^2_{between} < \frac{s^2_{meas}}{n} \qquad (3)$$

where s_{meas} is the repeatability standard deviation for the method used in the homogeneity assessment and n is the number of replicates per unit, then u_{hom} was calculated according to:

$$u_{hom} = \sqrt{\frac{s^2_{meas}}{n}} \qquad (4)$$

It is recognized that this is not an ideal situation, as it represents a worst case scenario by suggesting the homogeneity could be as poor as the precision of the measurement technique selected for homogeneity assessment.

Stability

The predecessor CRM, DORM-2, 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-3. The stability of this CRM will continue to be monitored and customers will be notified if any significant irregularity occurs prior to the expiry date. Uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

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[1] Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st ed. ISO, Geneva, Switzerland (1993).

[2] J. Pauwels, A. van der Veen, A. Lamberty, H. Schimmel, Evaluation of uncertainty of reference materials.
Accred Qual Assur (2000) 5:95-99.

[3] S. Willie, Fifteenth Intercomparison for Trace Elements in Marine Sediments and Biological Tissues, NRC No. 46670, June 2004.

[4] S.L.R. Ellison, S.Burke, R.F.Walker, K. Heydorn, M.Månsson, J.Pauwels, W.Wegscheider, B.te Nijenhuis, Uncertainty for reference materials certified by interlaboratory study.
Accred Qual Assur (2001) 6:274–277.

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The results listed in this certificate are traceable to the SI through gravimetrically prepared standards of established purity and international measurement intercomparisons. As such, they serve as suitable reference materials for laboratory quality assurance programs, as outlined in ISO/IEC 17025. This CRM is registered at the Bureau International des Poids et Mesures (BIPM) in Appendix C of the Comité International des Poids et Mesures database listing Calibration and Measurement Capabilities accepted by signatories to the Mutual Recognition Arrangement of the Metre Convention.

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