Certified Reference Material

National Research Council Canada | Conseil national de recherches Canada

DOLT-3

Dogfish Liver Certified Reference Material for Trace Metals

The following table shows those elements for which certified values have been established for this dogfish (*Squalus acanthias*) liver reference material. Certified values are based on unweighted mean results from data 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 determined 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} encompasses every aspect that reasonably contributes to the uncertainty of the measurand [2,3]. A coverage factor of 2 was applied for all elements. The table below lists certifed values for DOLT-3.

TRACE ELEMENTS (milligram/kilogram)

Arsenic (d,g,h)	10.2	±	0.5
Cadmium (d,f,g,i,p)	19.4	±	0.6
Copper (d,i,p)	31.2	±	1.0
Iron (d,f,i)	1484	±	57
Lead (d,g,p)	0.319	±	0.045
Mercury (d,c,p)	3.37	±	0.14
Nickel (g,i,p)	2.72	±	0.35
Selenium (g,h,j)	7.06	±	0.48
Silver (f,g,i,p)	1.20	±	0.07
Zinc (d,i,p)	86.6	±	2.4

Coding

The coding refers only to the instrumental method of analyte determination.

c - Cold vapour atomic absorption spectrometry.
d - Inductively coupled plasma mass spectrometry
f - Flame atomic absorption spectrometry.
g - Electrothermal vaporization atomic absorption spectrometry (ETAAS).
h - Hydride generation atomic absorption spectrometry.
i - Inductively coupled plasma atomic emission spectrometry.
j- Hydride generation atomic fluorescence 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 used for the analysis of marine fauna and materials with a similar matrix.

Storage and Sampling

This material should be kept tightly closed in the original bottle and should be stored in a cool location, away from any significant radiation sources such as ultraviolet lamps and sunlight. The bottle should be well mixed by rotation and shaking prior to use, and tightly closed immediately thereafter.

Instructions for Drying

DOLT-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.

Stability

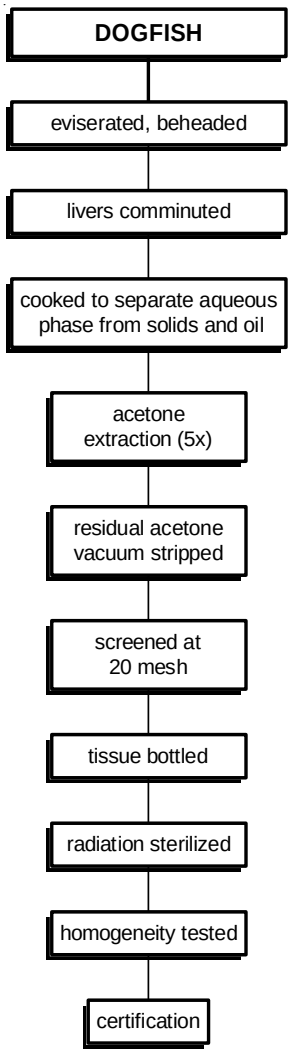
The predecessor CRM, DOLT-2, has been periodically analyzed for more than nine years and found to be both physically and chemically stable over this time interval. We expect similar behaviour from DOLT-3. The stability of this CRM will continue to be monitored and customers will be notified if any significant irregularity occurs prior to the expiry date.

Expiry

Based on sample stability noted above, the certified values for DOLT-3 are considered valid until September, 2011, provided the CRM is handled and stored in accordance with instructions herein.

Preparation of DOLT-3

This reference material was processed at the Guelph Food Technology Center, Guelph Ontario. The preparation sequence is illustrated below.



Information values

Due to the scatter of results, a certified value for Cr was not calculated. A lack of independent values precluded the certification of Sn and methylmercury. Information values for these analytes are given below.

Al	25	mg/kg
Cr	3.5	mg/kg
Sn	0.4	mg/kg
CH_3Hg (as Hg)	1.7	mg/kg

Certified value

DOLT-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 NRC [4]. The predecessor CRM DOLT-2 was provided as a quality control sample. Data generated at NRC was 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. Various dissolution procedures were utilized including closed vessel with microwave heating and open vessel digestion on a hot plate. Laboratories used HNO_3 or a combination of H_2O_2 and $HNO_{3,}$, although several participants included HF or HCl in the acid mixture.

Data was returned to NRC for evaluation. The results from a select sub-group of participants were used for the certification of DOLT-3. These laboratories were selected based on their performance history in previous intercomparisons. As well, if a laboratory did not submit satisfactory results for DOLT-2 their data for DOLT-3 were rejected.

The certified values were calculated from the unweighted means of the results of the participating laboratories. [5,6] Data were first examined for outliers using the Grubb's Test; no outliers of means were detected.

New guidelines for CRM producers suggest all sources relevant to the user of the material should contribute to the uncertainty of the certified value [2-4]. Included in the overall uncertainty estimate are uncertainties in the batch characterisation (μ_{char}), uncertainties related to possible between-bottle variation (μ_{hom}) as well as instability derived from effects relating to long-term storage and transport (μ_{stab}). Expressed as standard uncertainties these components can be combined as:

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

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

Characterisation

The characterisation uncertainties (μ_{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 [6].

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

Homogeneity

The homogeneity components of the uncertainty in the certified values were derived according to the recommendation of an international study group [7]. The material was tested for homogeneity at NRC using ETAAS. Results from triplicate sub-samples (0.150 g) from ten bottles were evaluated using ANOVA.

For Cd, Ni, Al, Pb and Zn, the inhomogeneity contribution to uncertainty, μ_{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, for As, Cu, Fe, Hg, Se and Ag, 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.

In these cases, μ_{hom} was calculated according to:

$$\mu_{hom} = \sqrt{\frac{s_{meas}}{n}} \qquad (4)$$

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

As previously discussed, based on NRC's experience with similar materials, uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Table 2. Statistical Data for DOLT-3

	components for μ_{char}, (mg/kg)			data sets	μ_{char}, (mg/kg)	μ_{hom}, (mg/kg)
	S_L	S_w	s of means			
As	0.62	0.26	0.64	12	0.18	0.14
Cd	0.8	0.34	0.82	16	0.21	0.23
Cu	1.59	0.78	1.63	16	0.41	0.24
Fe	59	26	61	13	17	23
Pb	0.036	0.015	0.037	12	0.011	0.02
Hg	0.149	0.09	0.158	14	0.042	0.058
Ni	0.27	0.15	0.29	13	0.08	0.08
Se	0.59	0.44	0.64	9	0.22	0.11
Ag	0.1	0.07	0.107	13	0.029	0.016
Zn	3.9	1.3	3.9	15	1	0.6

s_L - the between laboratory standard deviation from the laboratory intercomparison
s_w - the within laboratory standard deviation from the laboratory intercomparison

Criteria for acceptance

The property values reported in this certificate are the best estimates of the true values that can be obtained, based on the certification exercise. It is the responsibility of the analyst to assess the appropriateness of this CRM for purpose and interpret their own analytical results [8].

The user may assess laboratory bias from the difference between the calculated mean value of replicate measurements (x) and the certified value (μ): x-μ. According to ISO Guide 33: Uses of Certified Reference Materials, the criteria for acceptance is:

$$-a_2 - 2\sigma_D \le \bar{x} - \mu \le a_1 + 2\sigma_D \qquad (5)$$

where a_1 and a_2 are adjustment values chosen by the laboratory according to economic or technical limitations or requirements and σ_D is the standard deviation associated with the measurement process. The value of σ_D can be calculated from the user's laboratory quality control data and may be estimated from two components, as shown in equation 6:

$$\sigma_D = \sqrt{s_b^2 + \frac{s_w^2}{n}} \qquad (6)$$

where s_b is the between-laboratory standard deviation component associated with the measurement process (ideally this should include the long-term standard deviation of the user's method or, alternatively, s_L from Table 2), s_w the within-laboratory standard deviation (or repeatability standard deviation) and n the number of replicate analyses made of the reference material. Alternative methods for calculating s_b are discussed in reference 8.

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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://www.cm.inms.nrc.ca will contain any new information.

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Visit our web site at
http://www.cm.inms.nrc.ca

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