National Research Council Canada

Conseil national de recherches Canada

MOOS-1

Seawater Certified Reference Material for Nutrients

This reference material is primarily intended for use in the calibration of procedures and the development of methods used for the analysis of nutrients in seawater.

The following table shows those elements for which certified values have been established for MOOS-1.

Nutrient
(micromole/liter)

Orthophosphate	1.56	± 0.07
Silicate	26.0	± 1.0
Nitrite	3.06	± 0.15
Nitrite and Nitrate	23.7	± 0.9

Certified values are based on unweighted mean results from data submitted by laboratories participating in an annual intercomparison for the determination of nutrients, as well as results from NRC obtained by two independent analytical methods. 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}) and stability (u_{stab}).

It is intended that U_{CRM} encompass every aspect that reasonably contributes to the uncertainty of the measurand [2,3]. A coverage factor of 2 was applied for all analytes.

NRC · CNRC

Storage and Sampling

This material should be stored in the original bottle in a refrigerator (4°C), although samples stored at +20°C or +40°C for two month periods have not undergone detectable changes.

Once opened, contamination may cause changes in the analytes. Care should be taken if it is intended to remove only a portion of the sample and store the remainder for use at a later date. The bottle should be opened for the minimal period in a clean area and otherwise remain tightly closed.

Collection of Water for MOOS-1

MOOS-1 was collected at Lat. 47.062833 °N, Long. 59.982333 °W, off the northern tip of Cape Breton Island, NS, Canada. The water was collected from a depth of about 200 meters using a rosette containing 22 Niskins, each of about 10L volume. The contents of each Niskin were transferred, using a peristaltic pump, through a 0.05 µm cartridge filter into 50L carboys. The water was homogenized in a 400L tank, bottled in 50 mL aliquots in 60 mL bottles, sealed, and irradiated. The water was collected June 24, bottled July 11 & 12, and irradiated July 16, 1996. It was later found that irradiation caused bottle to bottle inhomogeniety and a portion of the original sample was reblended and bottled on April 3, 2001, without subsequent irradiation.

Certified value

Guidelines for CRM producers suggest all sources relevant to the user of the material contribute to the uncertainty of the certified value [2,3]. Included in the overall uncertainty estimate are uncertainties associated with 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 short term transport (u_{stab}). Expressed as standard uncertainties, these components can be combined as:

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

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

Characterisation

MOOS-1 was analysed by a number of expert laboratories participating in an annual intercomparison for nutrients sponsored by the National Oceanic and Atmospheric Administration (NOAA) [4]. Data generated at NRC using two independent methods of analysis were also included in the pool of intercomparison results.

Laboratories were requested to provide duplicate results using an analytical method of their choice.

Data were returned to NRC for evaluation. The results from a select sub-group of participants were used for the certification of MOOS-1. These laboratories were selected based on their satisfactory performance history in a previous intercomparison.

The certified values were calculated from the unweighted means of the results of the participating laboratories [3,5-7]. Data were first examined for outliers using the Grubb's Test.

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 [6].

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

Table 2. Statistical Data for MOOS-1

Uncertainty components, micromole/liter	Orthophosphate	Silicate	Nitrite	Nitrite + Nitrate
from intercomparison				
S_L	0.096	1.6	0.116	0.57
S_w	0.011	0.20	0.025	0.21
s of means	0.096	1.6	0.118	0.59
data sets, p	14	14	14	14
u_{char}	0.026	0.43	0.032	0.16
u_{hom}	0.011	0.17	0.029	0.31
u_{stab}	0.018	0.18	0.054	0.28

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

Analytical Methods

For the determination of nutrients in MOOS-1, laboratories predominantly used methods based on the traditional colorimetric procedures of Strickland and Parsons [8] and Morris and Riley [9]. Recently, automated colorimetric methods have been prepared by the USEPA based on these principles [10-12].

Independent methods based on ion chromatrography for nitrite and nitrate, and ion exclusion chromatography inductively coupled plasma mass spectrometry for silicate and phosphate were developed at NRC to corroborate the colorimetric results.

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 standard colorimetric procedures. Results from triplicate sub-samples from ten bottles were evaluated using ANOVA.

The inhomogeneity contribution to uncertainty, u_{hom}, was set equal to the experimentally determined between-unit standard deviation ($s_{between}$), as the best estimate of the uncertainty due to homogeneity.

Stability

Uncertainty components for long and short term stability were evaluated. To determine possible uncertainty associated with transport or short term instability, samples of MOOS-1 were stored at $+40^{\circ}C$, $+20^{\circ}C$ and $-25^{\circ}C$ for one month. These samples were analysed at the same time as several bottles which had been stored under recommended conditions of $+4^{\circ}C$. No between bottle differences were observed, therefore the uncertainty component for short term stability was set to zero.

The uncertainty components related to the long term stability of this CRM were calculated according to the recommendations of an international study group [7]. The slope and uncertainty in the regression fit of the temporal stability data were used to calculate the values in Table 2, based on a projected 60 month lifetime.

MOOS-1 has been repetitively monitored since 1996 and found to be stable with respect to nutrient concentration over this period. 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,the certified values for MOOS-1 are considered valid until December, 2007, provided the CRM is handled and stored in accordance with instructions herein.

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 for purpose of this CRM and interpret their own analytical results [13].

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:

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

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 is the within-laboratory standard deviation (or repeatability standard deviation) and n is the number of replicate analyses made of the reference material. Alternative methods for calculating s_b are discussed in reference 13.

Acknowledgements

References

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Updates

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