Comparability of oceanic nutrient data: Methods of certified reference material (CRM) production and certification for reference materials for nutrients in seawater (RMNS).

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Abstract
KANSO CO., LTD. (KANSO) started the production of reference materials for nutrients in seawater (RMNS) in 2003. RMNSs were used in the 2003, 2006, 2008, and 2012 global inter-laboratory comparison studies conducted by the International Ocean Carbon Coordination Project (IOCCP) and the International Ocean Carbon Coordination Project (IOCCP). In 2015, the IOCCP started the production of CRMs as one of the candidates to be used as common reference materials for all laboratories to improve the comparability of oceanic nutrient data. RMNSs are produced by only natural seawater. The production method involves filtration of collected seawater and air-stable but reactive chambers of which inside is electro-polished. After the seawater has been autoclaved, 90-mL aliquots are transferred into UV-sterilized polypropylene bottles in a clean room. The bottles are hermetically sealed in aluminum-film bag which has excellent barrier properties for suppressing long-term water evaporation. Nutrient concentration levels of RMNSs range from low nutrient seawater in subtropical surface water to highest deep Pacific seawater. A range of nutrient levels is achieved by mixing collected natural seawaters of different nutrient concentrations at various mixing ratio.

Source seawater is filtered (0.45 μm).

Mixed seawater is autoclaved twice in a 320-L stainless-steel reaction chamber at 121°C for 2h.

Polypropylene bottles (100 mL) are UV-sterilized.

Bottled in a clean room (ca. 90-mL aliquot per bottle).

Packaged into hermetically-sealed aluminum-film bag

Certification
From 2015, to increase reliability in the certified values, the values have become the arithmetic means of independently measured concentrations by JAMSTEC and KANSO. From 2015, the certified values have been obtained by measuring 30 bottles in duplicates using gas-segmented continuous flow analyzer (QuAAtro 2-HR, SEAL Analytical, UK).

The production of RMNS is Maximum of 250 bottles produced per one lot.

Validity of certification
When conducting measurement for certification, KANSO CRMs and NMIJ CRMs were also measured. Table 1 shows the values are in good agreement and are within expanded uncertainty (k = 2) of each certified value.

Table 1 KANSO CRMs and NMIJ CRMs measured results

<table>
<thead>
<tr>
<th>Source</th>
<th>Measured Value</th>
<th>Measured Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>5.49 ± 0.13</td>
<td>0.13 μmol/kg</td>
</tr>
<tr>
<td>Silicate</td>
<td>161.0 ± 0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Phosphate</td>
<td>35.9 ± 0.1</td>
<td>0.13 μmol/kg</td>
</tr>
</tbody>
</table>

Figure 1 Independently obtained nitrate, silicate, and phosphate concentrations by JAMSTEC and KANSO

Uncertainty calculation
Uncertainties of certified values were calculated using equation 1. Each uncertainty component is described in Table 2. An example, calculated results for Lot CD nitrate is shown.

Equation 1 Calculation formula for uncertainty determination

\[ u_{\text{total}} = u_{\text{expanded}} = \left( u_{\text{traceability}}^2 + u_{\text{traceability}}^2 + \ldots \right)^{1/2} \]

Table 2 Uncertainty of Nitrate (Lot CD: 5.50±0.05 μmol/kg)

<table>
<thead>
<tr>
<th>Uncertainty Source</th>
<th>Percentage Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traceability</td>
<td>99.5</td>
</tr>
<tr>
<td>Traceability</td>
<td>99.5</td>
</tr>
<tr>
<td>Traceability</td>
<td>99.5</td>
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</tbody>
</table>

Conclusion
Uncertainties of certified values were calculated using equation 1. Each uncertainty component is described in Table 2. An example, calculated results for Lot CD nitrate is shown. Major uncertainty components will differ based on the type of determinands and concentration measured for certification.

References