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2006 Inter-laboratory Comparison Study for Reference Material for Nutrients in Seawater

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栄養塩測定用海水組成標準の2006年国際共同実験報告

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Preface

The history of the analysis of nutrients in seawater is long. Nutrients and total inorganic carbon have been the major observational variables in various international global ocean observation expeditions, such as the Geochemical Ocean Sections Study and the World Ocean Circulation Experiment (WOCE). Observation of the natural variability of nutrients and inorganic carbon in the world's oceans, and investigation of temporal and spatial changes due to the oceans' response to climate change and increasing carbon dioxide in the atmosphere, continue to be important topics of oceanographic research. To address the need for highly accurate and precise data regarding the effects of climate change on nutrient concentrations, the WOCE Hydrographic Program office proposed criteria for the precision and accuracy of nutrient analysis in early 1990. However, attaining these criteria was not possible, owing to the lack of an accepted standard or reference materials for nutrients in seawater that was applicable to the Pacific Ocean, where the maximum nutrient concentrations are greater than in the Atlantic and Indian Oceans. Current knowledge about the variability of nutrient concentrations in seawater is limited because the variation is very small. Therefore we need traceability and comparability of the nutrients data as well as high accuracy and high precision of them.

The Geochemical Research Department of the Meteorological Research Institute (MRI) of Japan started to develop seawater-based reference materials for nutrient analysis about ten years ago. This research continues today as part of the "Observational Study on the Variability of the Carbon Cycle in the Ocean, I (2004–2006) and II (2007–2008)". A major goal of this research is the development of standard materials for the analysis of nutrients in seawater that satisfy the requirements for oceanographic research. The MRI research comprises three parts: the development of seawater-based reference materials, the conducting of global inter-laboratory comparison study to use and test the reference materials, and the practical use of the reference materials on board the R/V *Mirai* of Japan Agency for Marine-Earth Science and Technology (JAMSTEC) during a series of research voyages. We are now progressing towards having seawater-based nutrient reference materials with stability and homogeneity that are sufficient to satisfy our present requirements. To establish a standard material for nutrient analysis in seawater, an inter-laboratory comparison study in the world is an important step.

This technical report summarizes results of the second inter-calibration exercise conducted by MRI, in which 52 laboratories participated.

Katsumi Hirose

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序文

海水中の栄養塩の分析は長い歴史がある。海水栄養塩分析の海洋学的目的の一つは、海水中の栄養塩濃度の自然変動、及びそれに関連して大気中の二酸化炭素の増大やその結果引き起こされる気候変動に応答した海洋の栄養塩の変動を検出することにある。事実、過去にGEOSECSやWOCE等の時代を画するような世界的プロジェクト研究が実施されてきたが、この中で海水中の栄養塩は重要な測定項目として取り上げられてきた。特に、1990年代に実施されたWOCEでは、海洋における栄養塩の変動を検出するため必要とされる分析精度や確度についての目標値が提案された。しかし、最近まで海水中の栄養塩の分析では、提案された基準（特に、確度）を満足することができていない。その主要な原因は、海水中の栄養塩の分析に関して、基準を満足させるための標準物質ないし参照物質が提供されなかったためである。そのため、現在に至るも海洋における栄養塩の変動に関する知識は限られている。従って、変動を検出するためには、高精度であるばかりでなく追跡可能性（トレーサビリティ）や比較可能性（コンパラビリティ）のある栄養塩データを得るために必要な標準物質ないし参照物質の確立が求められている。

1990年代の中頃より、気象研究所地球化学研究部（青山）では、海水をベースにした栄養塩の参照物質を作成する研究を始めた。この数年間は、融合型経常研究「海洋における炭素循環の変動に関する観測的研究I（平成16～18年度）及びⅡ（平成19～20年度）」の一部としてこの研究が進められている。主要な目標は、海水中の栄養塩分析に関して海洋学的要求を満たした標準物質システムを構築することである。この研究は、1：海水ベースの栄養塩参照物質の開発、2：参照物質とするための国際比較実験の実施、3：観測船「みらい」の船上での栄養塩分析における参照物質の実用試験からなる。現在、栄養塩参照物質の開発に関して、この条件を満たし安定でしかも均一な海水ベースの参照物質を作成しつつある。この標準物質システム構築の過程で、必要な一歩として、この国際的な相互比較実験がある。

この技術報告では、52機関の参加で得られた第2回国際相互比較実験の結果が取りまとめられている。

地球化学研究部長　　廣瀬勝己

Abstract

Autoclaved natural seawater collected in the North Pacific Ocean was used as a reference material for analysing nutrient concentrations in seawater during an inter-laboratory comparison study conducted in 2006; this study was a follow-up to a similar but smaller study conducted in 2003. Homogeneity of sample #2 was confirmed by the repeatability of the nutrient concentration measurements and those interms of one sigma of standand deviation are: 0.2%, 0.3%, and 0.2% for nitrate, phosphate and silicate, respectively. Sets of six samples with concentration ranges of 0.1–42.4 μmol kg^{-1} for nitrate, 0.0–0.6 μmol kg^{-1} for nitrite, 0.0–3.0 μmol kg^{-1} for phosphate, and 1.7–156.1 μmol kg^{-1} for silicate were analysed. A set of samples was distributed to each of 55 laboratories around the globe (20 countries), and results were returned by 52 of those laboratories (19 countries).

Analytical precisions reported by the participating laboratories for all deteminands were generally lower, by at least 50%, than the consensus standard deviations of the reported concentrations. The consensus standard deviations for sample #2 for all determinands were 5 to 10 times as large as the homogeneities of sample #2 for all determinands. In some laboratories, the non-linearity of the calibration curve was not treated effectively.

Our results indicate that variability in the in-house standards of the participating laboratories and the handling of the non-linearity of the calibration curve of the participating laboratories were the primary sources of inter-laboratory discrepancies. The results confirm that a certified reference material for nutrients in seawater and a common method for measuring nutrient concentrations are essential for the improvement of the global comparability of nutrient data in the world’s oceans.

要旨

栄養塩測定用海水組成標準の2006年国際共同実験が行われた、この国際共同実験では、オートクレーブで滅菌処理された天然海水が試料として用いられた。これらの試料は、栄養塩測定用海水組成標準の2003年国際共同実験で用いられたものと同様に処理されたものである。試料の均一性は、硝酸塩において0.2%、リン酸塩において0.3%、ケイ酸塩において0.2%であった。六本一組で用いられた試料の濃度範囲は、硝酸塩が0.1 – 42.4 μmol kg^{-1} , 亜硝酸塩が0.0 – 0.6 μmol kg^{-1} , リン酸塩が 0.0 – 3.0 μmol kg^{-1} , ケイ酸塩で1.7 – 156.1 μmol kg^{-1} である。20カ国55機関に試料が送付され、19カ国52機関から結果が報告された。

各機関から報告された全分析項目の分析繰り返し精度は、報告された値のコンセンサス（合意）濃度の標準偏差（1シグマ）の半分あるいはそれ以下という値であった。試料番号2について、報告された濃度から導かれたコンセンサス（合意）濃度の標準偏差（1シグマ）は、全分析項目において試料の均一性の5倍から10倍の大きさであった。また、いくつかの機関において分析時に検量線の非直線性を十分に考慮していないことが見出された。

これらの結果は、各機関における栄養塩分析用標準液の違いと分析時における検量線の非直線性の扱い方の違いが、各機関相互の栄養塩濃度の報告値の違いの主たる原因であることを示している。従って、認証標準物質の使用と栄養塩分析における手法の共通化が、全海洋での栄養塩データの追跡可能性（トレーサビリティ）と比較可能性（コンパラビリティ）を確立するために重要である。

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