Comparability of Ocean Nutrient Data by KIOST Reference Material Series for nutrients (K-RMS)

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ABSTRACT

Dissolved nutrients in seawater are recognized as an essential biogeochemical factor for detecting global environmental changes. The importance of nutrient reference material for seawater has been increased greatly for the comparison of nutrient data, measured in different time and space in global ocean by various researchers with different levels in nutrient analysis skill. In this study, we described the homogeneity and stability of nutrient reference material for seawater using natural seawater, collected at a station of Shihwa Lake, at a coastal station near Uljin (surface water), and at a station over the Ulleung Basin (surface water and 1500 m depth water) and sterilized. Based on the homogeneity data, the nutrient reference materials have similar homogeneity compared to other nutrient reference materials. During 3-13 month period, there was no unidirectional trend of increase or decrease in nutrient concentration of newly developed nutrient reference material for seawater. However, a sustained measurement is required to check stability for longer period.

History of Reference Material Production in KIOST

Since 2010, KIOST has implemented "Standardization and quality control of oceanographic research and monitoring program" to improve the quality of the oceanographic observation data produced by KIOST. As part of the program, KIOST established facility for the production of reference materials including clean room (Class 1000) and clean hood(Class 100), and improved the analytical system

KIOST Nutrient Reference Material Production Facility

Clean Room

Semi-Automatic RM packer

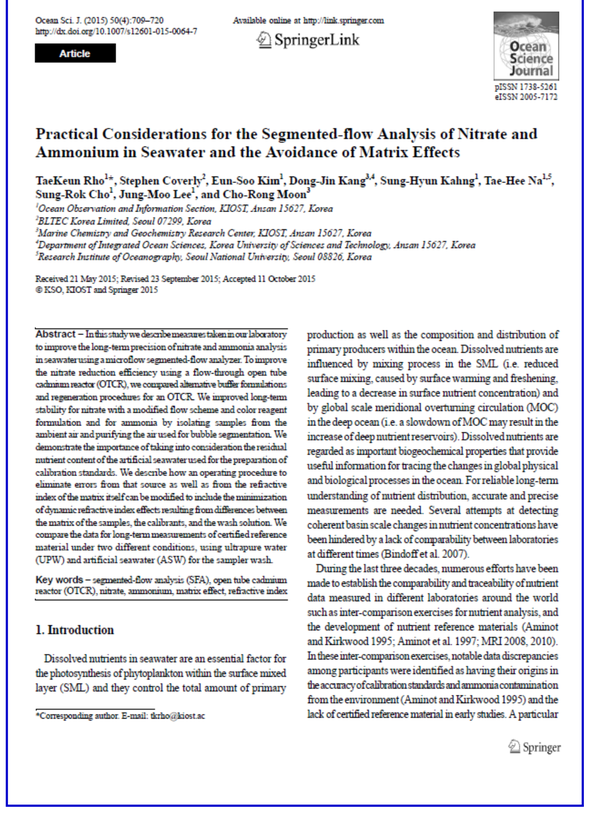
RM production

Autoclave container /rotating homogenizer

Autoclave

Nutrient Analytical Lab/Instruments

Improvement of Analytical System



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Practical Considerations for the Segmented-flow Analysis of Nitrate and Ammonium in Seawater and the Avoidance of Matrix Effects

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Abstract – In this study we describe measures taken in our laboratory to improve the long-term precision of nitrate and ammonia analysis in seawater using a microflow segmented-flow analyzer. To improve the nitrate reduction efficiency using a flow-through open tube cadmium reactor (OTCR), we compared alternative buffer formulations and regeneration procedures for an OTCR. We improved long-term stability for nitrate with a modified flow scheme and color reagent formulation and for ammonia by isolating samples from the ambient air and purifying the air used for bubble segmentation. We demonstrate the importance of taking into consideration the residual nutrient content of the artificial seawater used for the preparation of calibration standards. We describe how an operating procedure to eliminate errors from that source as well as from the refractive index of the matrix itself can be modified to include the minimization of dynamic refractive index effects resulting from differences between the matrix of the samples, the calibrants, and the wash solution. We compare the data for long-term measurements of certified reference material under two different conditions, using ultrapure water (UPW) and artificial seawater (ASW) for the sampler wash.

Key words – segmented-flow analysis (SFA), open tube cadmium reactor (OTCR), nitrate, ammonium, matrix effect, refractive index

1. Introduction

Dissolved nutrients in seawater are an essential factor for the photosynthesis of phytoplankton within the surface mixed layer (SML) and they control the total amount of primary production as well as the composition and distribution of primary producers within the ocean. Dissolved nutrients are influenced by mixing process in the SML (i.e. reduced surface mixing, caused by surface warming and freshening, leading to a decrease in surface nutrient concentration) and by global scale meridional overturning circulation (MOC) in the deep ocean (i.e. a slowdown of MOC may result in the increase of deep nutrient reservoirs). Dissolved nutrients are regarded as important biogeochemical properties that provide useful information for tracing the changes in global physical and biological processes in the ocean. For reliable long-term understanding of nutrient distribution, accurate and precise measurements are needed. Several attempts at detecting coherent basin scale changes in nutrient concentrations have been hindered by a lack of comparability between laboratories at different times (Bindoff et al. 2007).

During the last three decades, numerous efforts have been made to establish the comparability and traceability of nutrient data measured in different laboratories around the world such as inter-comparison exercises for nutrient analysis, and the development of nutrient reference materials (Aminot and Kirkwood 1995; Aminot et al. 1997; MRI 2008, 2010). In these inter-comparison exercises, notable data discrepancies among participants were identified as having their origins in the accuracy of calibration standards and ammonia contamination from the environment (Aminot and Kirkwood 1995) and the lack of certified reference material in early studies. A particular

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KIOST Nutrient Reference Material

K-RMS Homogeneity

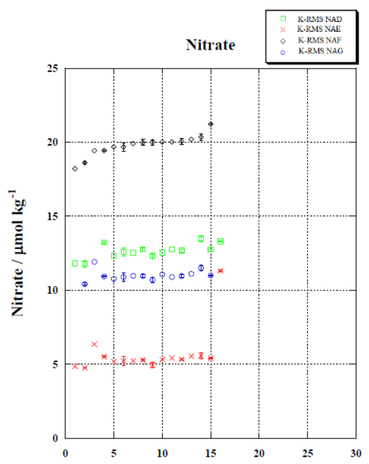
K-RMS (Salinity)		Nitrite (mmol kg^{-1})	Nitrate+Nitrite (mmol kg^{-1})	Ammonium (mmol kg^{-1})	Phosphate (mmol kg^{-1})	Silicate (mmol kg^{-1})
K-RMS NAD (28.140)	Average	0.6	13.34	5.97	0.462	14.13
	SD	0.05	0.07	0.19	0.005	0.02
	CV, %	0.67	0.51	3.2	1.06	0.19
K-RMS NAE (34.191)	Average	0.96	6.29	1.7	0.197	9.05
	SD	0.01	0.03	0.06	0.02	0.02
	CV, %	0.82	0.45	3.5	9.90	0.27
K-RMS NAF (34.000)	Average	0.61	20.51	1.22	1.641	78.83
	SD	0.020	0.08	0.11	0.02	0.1
	CV, %	3.19	0.40	9.4	1.01	0.13
K-RMS NAG (34.210)	Average	0.21	11.02	1.17	0.775	40.04
	SD	0.00	0.05	0.02	0.007	0.1
	CV, %	1.9	0.44	1.9	0.882	0.25

K-RMS Assigned Values

K-RMS (Salinity)		Nitrite (mmol kg^{-1})	Nitrate+Nitrite (mmol kg^{-1})	Ammonium (mmol kg^{-1})	Phosphate (mmol kg^{-1})	Silicate (mmol kg^{-1})
K-RMS NAD (28.140)	Average	0.56	13.34	5.97	0.457	14.13
	SD	0.09	0.36	0.19	0.026	0.05
	CV, %	10.8	2.71	3.20	5.79	0.36
K-RMS NAE (34.191)	Average	0.96	6.27	1.7	0.208	9.02
	SD	0.01	0.06	0.06	0.034	0.04
	CV, %	0.919	0.935	3.51	16.4	0.43
K-RMS NAF (34.000)	Average	0.60	20.51	1.22	1.641	78.54
	SD	0.02	0.24	0.117	0.036	0.38
	CV, %	3.73	1.16	9.36	2.20	0.49
K-RMS NAG (34.210)	Average	0.19	11.02	1.17	0.787	39.95
	SD	0.01	0.09	0.02	0.027	0.23
	CV, %	5.02	0.809	1.92	3.47	0.57

Results of IOCCP-JAMSTEC 2015 Inter-laboratory Calibration Exercise of a CRM for Nutrients in Seawater

During 2104 IOCCP/JAMSTEC co-organized inter-laboratory comparison study of nutrient reference material, 34 laboratories from 20 countries were voluntarily participated for the analysis of KIOST nutrient reference material (K-RMS). Results were submitted by 27 laboratories.



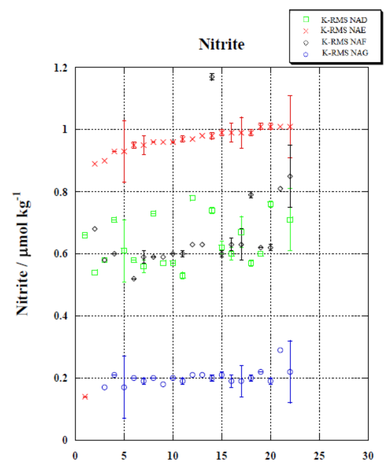


Figure KIOST 3. Nitrite results for KIOST RMs. Laboratories are ranked in order of concentrations reported for NAE.

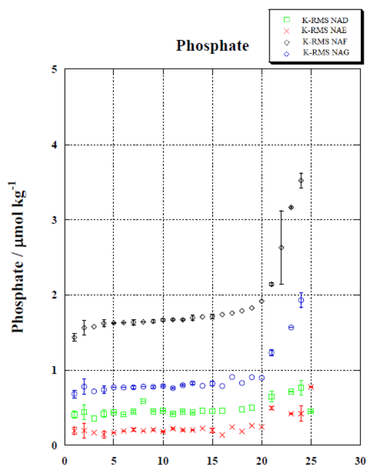


Figure KIOST 4. Phosphate results for KIOST RMs. Laboratories are ranked in order of concentrations reported for NAF.

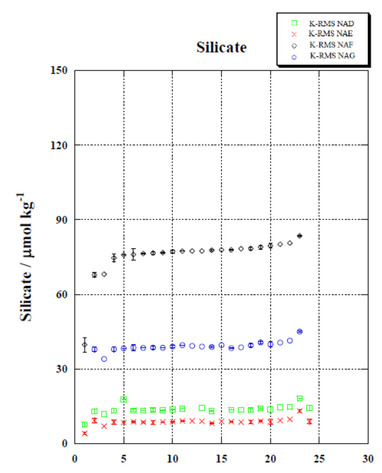


Figure KIOST 5. Silicate results for KIOST RMs. Laboratories are ranked in order of concentrations reported for NAF.

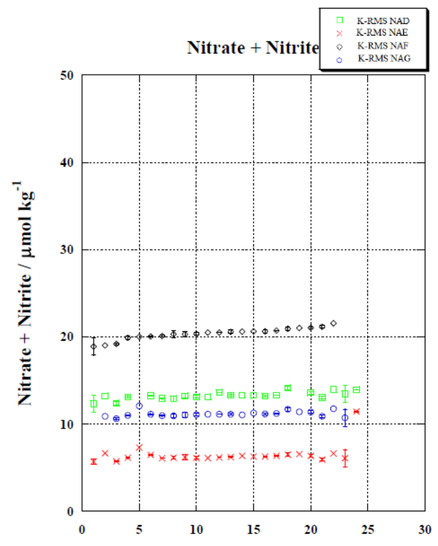
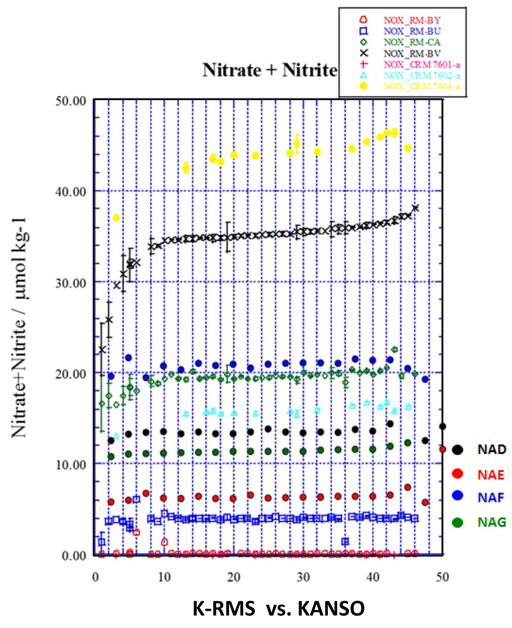


Figure KIOST 1. Nitrate+Nitrite results for KIOST RMs. Laboratories are ranked in order of concentrations reported for NAF.



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