

## A new SI traceable silicon standard solution for certification of nutrients CRM and measurement of silicate in seawater

\*Michio Aoyama<sup>1,2</sup>, Chikako Cheong<sup>3</sup>, Tsutomu Miura<sup>3</sup>, Takeshi Fujii<sup>4</sup>, Hitoshi Mitsuda<sup>4</sup>, Tomomi Sone<sup>5</sup>, Hiroshi Uchida<sup>1</sup>, Akihiko Murata<sup>1</sup>

1. RIGC, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2. Faculty of Life and Environmental Sciences, University of Tsukuba, 3. National Institute of Advanced Industrial Science and Technology (AIST), National Metrological Institute of Japan (NMIJ), 4. Laboratory for Instrumentation and Analysis, KANSO CO., LTD. , 5. MARINE WORKS JAPAN LTD.

A new SI traceable silicon standard solution for certification of nutrients CRM and measurement of silicate in seawater was established. This standard solution was produced by a dissolution technique with an alkaline solution. A 2.14 g sample of silicon dioxide of which purity is 99.999 % was placed in a platinum crucible and fused with 3.90 g of sodium carbonate of which purity is also 99.999 %. A fusion reaction was conducted at 1150 deg. C for one hour at JAMSTEC. Then a silicon standard solution having a mass fraction of 1000 mg Si kg<sup>-1</sup> was prepared. The mass fraction of Si in the produced solution was calibrated based on NMIJ CRM 3645-a Si standard solution by a technology consulting system of AIST, and this value is traceable to the International System of Units. For an example, a nominal mass fraction of lot. exp64 solution prepared in June 2019 was 999.3 mg Si kg<sup>-1</sup> and certified mass fraction of this solution was 999.3 mg Si kg<sup>-1</sup> ±2.8 mg Si kg<sup>-1</sup>. The expanded uncertainty is 0.3 %, which is better than the 0.5 % of NIST and Merck silicon standard solutions. As a standard solution, homogeneity and long term stability are essential. The initial homogeneity measurement result (for solution exp64) was better than 0.1 %, which indicates that the homogeneity is sufficiently good. It is presumed that the long term stability might be theoretically good for a long period from a view of the chemical composition. In fact, no change in concentration has been observed in the results of a storage experiment for about six months. Traditionally, Merck silicon standard solution SiO<sub>2</sub> in NaOH 0.5 mol/l 1000 mg/l Si Certipur® which is traceable to SRM 3150 from NIST have been used to certify silicate concentration in KANSO CRM and JAMSTEC-SCOR CRM for nutrient in seawater and also used to measure silicate concentration of silicate in seawater samples in some of the laboratories in the world. However, Merck silicon standard solution showed significant variability up to ±0.5 % during these 15 years. This fact was confirmed by lot-to-lot comparisons of Merck silicon standard solutions itself and comparisons between the nutrients CRMs and the Merck solutions. Although the variability was within the uncertainty range of Merck certified values, it is not acceptable now from a view point of ocean science and study of climate change. For this reason, we developed a more stable silicon standard solutions by self-manufacturing, and NMIJ certified these solutions. The new SI traceable silicon standard solution is targeted for use in the certification of nutrient CRM and for use of silicate measurement in seawater worldwide.

Keywords: silicon standard solution, seawater, silicate, SI traceable, certified reference material