

Chapter 12. The Determination of Reactive Silicate in Sea Water

Updated by: F. Howse (1997), A. Michaels, R. Dow and N. Bates (April 1991)
Prepared by: A. Michaels and R. Dow (October 1989)
Modified from: Strickland and Parsons (1968)

1.0 Scope and field of application

This procedure describes a method for the determination of reactive silicate in seawater. This method is suitable for the assay of oceanic concentrations between $0.1 \mu\text{mol l}^{-1}$ to $140 \mu\text{mol l}^{-1}$.

2.0 Definition

The silicate concentration of seawater is given in units of $\mu\text{mol kg}^{-1}$ in seawater.

3.0 Principle of Analysis

The determination of reactive silicate is based on the method of Strickland and Parson (1968). A seawater sample is allowed to react with ammonium molybdate under conditions which result in the formation of silicomolybdate, phosphomolybdate and arsenomolybdate complexes. A reducing agent of metol and oxalic acid is added and silicomolybdate is reduced to a silicomolybdous acid with a blue color, the absorbance of which is measured spectrophotometrically.

4.0 Apparatus

Spectrophotometer

5.0 Reagents

5.1 *Ammonium Molybdate reagent:* 4.0 g of reagent quality ammonium paramolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ is dissolved in 300 ml of Milli-Q water. 12.0 ml of concentrated HCl is added slowly while mixing. Milli-Q water is used to bring the volume up to 500 ml. This solution is stable for many months if stored refrigerated in a polyethylene bottle, but should be discarded if a white precipitate forms.

- 5.2 *Metol-sulphite solution:* 6g of anhydrous sodium sulphite, Na_2SO_3 , is dissolved in 500 ml of Milli-Q water, then 10 g of metol (*p*-methylaminophenol solution) is added. When the metol has dissolved, the solution is filtered through No.1 Whatman filter paper and stored in a tightly stoppered glass bottle. This solution should be replaced monthly.
- 5.3 *Oxalic acid solution:* 50 g of reagent grade oxalic acid dihydrate is shaken with 500 ml of Milli-Q water. The solution is stored in a glass bottle and decanted from the crystals for use. It is stable indefinitely.
- 5.4 *Sulfuric acid solution:* 250 ml of concentrated sulfuric acid is diluted to 500 ml with Milli-Q water and cooled. The solution is stored in a glass bottle.
- 5.5 *Reducing reagent:* 100 ml of metol-sulphite solution is mixed with 60 ml of oxalic acid solution. 60 ml of the 50% sulfuric acid solution is added and the solution made up to a volume of 300 ml with Milli-Q water. This reagent should be prepared as needed and used immediately.

6.0 Preparation for sampling

- 6.1 Samples are collected in 125ml polyethylene bottles. Contamination is a major problem with nutrient samples, especially near the surface where the ambient concentrations are low. All the nutrient bottles are rigorously cleaned before use. New bottles are soaked for 2-3 days in 5 % Aquet and tap water, rinsed with tap water, then soaked for 2-3 days in 10 % HCl. Bottles are then soaked overnight in Milli-Q water and rinsed 5-6 times with Milli-Q water. After bottles have been seasoned they are cleaned between uses by soaking overnight in 5 % detergent, transferred to 10 % HCl overnight, and rinsed 5-6 times with Milli-Q water.
- 6.2 Polycarbonate filter holders (Gelman) are used in the filtering of samples. Cleaning of these begins with an overnight soak in Aquet, followed by tap water rinsing, a soak in 5 % HCl for 1-2 hours, and 5-6 rinses with Milli-Q water.

7.0 Sampling

- 7.1 Samples for analysis of silicate are collected at 35 depths between the surface and 4200 m. A polycarbonate filter holder (Gelman) containing a $0.8 \mu\text{m}$ Nuclepore filter is connected to the OTE bottle with Tygon[®] tubing. The spigot is opened and samples are collected from the water that passes through the filter. Each bottle is rinsed three times and then filled just below the shoulder. Care must be taken to avoid over-

filling of samples to be frozen. The bottles are transferred to a freezer (- 20°C) and kept frozen until analysed.

7.2 Prolonged storage of samples is avoided.

8.0 Procedures

8.1 *Sample analysis*

- 8.1.1 Prior to analysis the samples are thawed and brought to a temperature of between 15° and 30°C. Once thawed, analysis should proceed as soon as possible.
- 8.1.2 All glassware should initially be washed in chromic-sulfuric acid and rinsed well with Milli-Q before and after each subsequent use.
- 8.1.3 Sample solutions should be stored at a temperature between 18° and 25°.
- 8.1.4 10 ml of the molybdate reagent is added to a dry 50 ml measuring cylinder fitted with a stopper.
- 8.1.5 25 ml of the sample is pipetted into the cylinder, which is then stoppered. The solutions are mixed and allowed to stand for 10 minutes.
- 8.1.6 The reducing reagent is added and mixed immediately to make the total volume 50 ml.
- 8.1.7 The solution is allowed to stand for 2–3 hours, then the extinction measured at a wavelength of 810 nm.

8.2 *Reagent blank determination*

- 8.2.1 The reagent blank is determined using open ocean surface seawater as a sample. The exact procedure outlined in section 8.1 is followed. A reagent blank should not exceed 0.01 on a 1 cm cell or 0.1 on a 10 cm cell and should be determined for each batch of samples.

8.3 *Standardization*

- 8.3.1 *Primary silicate standard:* 0.9403g dried Na_2SiF_6 is dissolved and made up to 1 liter with Milli-Q water. 1 ml = 5 μmol . It is stored in a dark polypropy-

lene bottle. Ultra pure sodium fluosilicate is difficult to obtain, as with nitrite. It may be advisable to compensate for these impurities.

- 8.3.2 Working standards of concentrations of 50, 25, 10 and 5 μM are prepared by diluting 10 ml, 5 ml, 2 ml and 1 ml of primary silicate standard respectively to 1000 ml in open ocean surface seawater. The exact procedure described in section 8.1 is carried out. These standards should be stored in plastic beakers and used within a few hours.

9.0 Calculation and expression of results

9.1 Standardization Factor, F

- 9.1.1 The absorbance of the reagent blanks is subtracted from the absorbance values of the standards. A linear regression of the silicate concentration and the corrected extinction values is performed. The slope of the line is the standardization factor, F . The value of F is typically 100. If a 10 cm cell is used, the F factor may be assumed to be equal to $0.1 \times F_{(1 \text{ cm})}$.
- 9.1.2 F is a function of the salinity of the seawater samples. Between salinities of 25 and 35, the variation may be neglected. The factor F_s at a salinity of S is related to F by:

$$F_s = \frac{F(1 + 0.003S)}{1.08}$$

This correction should be used when the salinity varies more than 10 from a value of 28.

- 9.2 The reactive silicate concentration is calculated by:

reactive silicate ($\mu\text{mol l}^{-1}$) = F • corrected extinction

Where:

F = standardization factor

Corrected absorbance = sample absorbance - blank absorbance

- 9.3 The units of $\mu\text{moles kg}^{-1}$ can be obtained by dividing the calculated silicate concentration by the density of the seawater at the time of analysis.

10.0 Notes

The silicate and molybdate must combine before the reducing agent is added. Ten minutes is allowed for this reaction. The reducing solution must be added within 30 minutes or else changes in the isomeric form of the silicomolybdate complex will occur.

The sample should be added to the acid molybdate solution instead of the reverse. This prevents unwanted isomeric forms of the silicomolybdate complex.

The time required for the full color development varies with the amount of silicate present in the sample. With a concentration of less than 50 μM , 1 hour is sufficient. For concentrations exceeding 75 μM at least 3 hours should be allowed.

11.0 References

Strickland, J.D.H., and Parsons, T.R. (1968). Determination of reactive silicate. In: *A Practical Handbook of Seawater Analysis*. Fisheries Research Board of Canada, Bulletin 167, 65–70.