Silicates

Scope and Application

* 1. This method describes the determination of dissolved silicate, mainly in the form of silicic acid found in estuarine and/or coastal waters.
  2. In Chesapeake Bay Tidal Laboratories the applicable range can be as low as 0.001 to 0.004 mg Si/L for samples near the Bay mouth, to as high as 0.03 to 0.30 mg Si/L when very high nitrite samples are encountered.
  3. The method detection limits (MDL) are determined on a yearly basis, and should be established using the guidelines in Chapter VI, Section C.
  4. This method should be used by analysts experienced in the use of colorimetric analyses, matrix interferences and procedures for their correction. Analyst training and/or a demonstration of capability should be documented.
  5. The reaction chemistry described may be used with a continuous flow automated analytical system.

Summary of Method

* 1. In this method the silicate in the samples reacts with ammonium molybdate under acidic conditions to form-molybdosilicic acid. This complex is then reduced by ascorbic acid to form molybdenum blue that is measured at 660 nm. The color is proportional to the silicate concentrations present in the sample. The colorimetric procedure conforms to EPA Method 366.0 (1997).

Interferences

1. Sample turbidity should be removed by filtration prior to analysis.
2. Interference from phosphate may be suppressed by adding oxalic acid.
3. Hydrogen sulfide may be removed by either boiling prior to analysis, by oxidation with bromine or stripping with nitrogen gas after acidification.
4. Large amounts of iron interfere with analysis.
5. The difference in refractive index of seawater and reagent water should be corrected for when analyzing estuarine/coastal samples. Alternatively, match the salinity of the calibration standards to the salinity of the samples.

Apparatus and Materials

1. Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube or recorder or computer based data system.
2. Plastic containers should be utilized for the analysis of silica. Any glassware used in the analysis must be low in silica to avoid sample reagent contamination. Wash with 10% HCl and thoroughly rinse with reagent water has been found to be effective. A laboratory’s glassware cleaning method will be considered sufficient if all quality control samples are within the expected ranges.

Reagents

1. Stock reagent solutions: The specific recipe for these reagents is generally instrument dependent, and may change due to the concentration of the samples being analyzed. In this SOP the chemicals needed for the reaction will be listed, but not the specific amounts.
   * 1. Ammonium Molybdate Solution: This reagent is prepared by dissolving ammonium molybdate tetrahydrate in reagent water. The solution is stored in plastic containers for up to three months at 4 ± 2°C.
2. Calibration standards: Laboratories may purchase or prepare stock and working standards. The calibration check standard must be purchased or made from a second source.
   * 1. Stock Silicate Solution: Sodium hexafluorosilicate is dried overnight at 105 ± 2°C. To prepare the stock solution, 0.6696 g is dissolved in 1000 mL reagent water. The solution is stable for one year when stored at 4 ± 2°C.
     2. Prepare a series of standards by diluting suitable volumes of stock silicate solutions with reagent water or low nutrient seawater. Prepare working standards daily. When working with samples of known salinity it is recommended that the standard curve concentrations be prepared in substitute ocean water diluted to that salinity and that the sampler wash solution also be substitute ocean water diluted to that salinity. When analyzing samples of varying salinities, it is recommended that the standard curve be prepared in reagent water and refractive index corrections be made to the sample concentrations. Standards should bracket the expected concentration of the samples, and not exceed two orders of magnitude. At least five calibration standards with equal increments in concentration should be used to construct the calibration curve.



1. Reagent water: Refer to Chapter VI, Section 4.2.
2. Artificial seawater (ASW): Refer to Chapter VI, Section 4.3. This can be used for the matrix at an appropriate salinity for the samples being analyzed.

Sample Handling

1. Samples must be filtered using a 0.7 µm glass fiber filter as soon as possible after collection, preferably on the field, and stored in HDPE bottles.
2. Samples may be stored at 4 ± 2°C for up to 28 days.

Procedure

1. Equilibrate the samples to room temperature.
2. Allow both the colorimeter and recorder to warm up, and obtain a stable baseline with reagent water running through the sample line.
3. Use a sampling rate that ensures reliable results.
4. Switch the sample line from reagent water to sampler and begin analysis, starting with the standards in order of decreasing concentration.
5. Subtract the blank background response from the standards before preparing the standard curve.
6. Record the stabilized potential of each unknown sample and convert the potential reading to the phosphorous concentration using the standard curve.
7. If a low concentration sample peak follows a high concentration sample peak, a certain amount of carryover can be expected. It is recommended that if there is not a clearly defined low concentration peak, that the sample be reanalyzed at the end of the run.

Calculations

1. Silicate concentrations are calculated from the linear regression obtained from the standard curve in which the concentrations of the standards are entered as the independent variable (x-axis) and the corresponding peak heights as the dependent variable (y-axis).
2. Refractive index correction for estuarine/coastal systems is optional, and shall be performed in accordance with procedures described in Section 6.7.3.2.
3. A correction of salt error in estuarine/coastal samples shall be performed in accordance with procedures described in Section 6.7.3.3.
4. Results should be reported in units of mg Si/L.

Quality Control

1. Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter VI, Section C.
2. Reference materials: The laboratory must analyze a standard reference material or profieciency testing samples at least once a year, as available.
3. Additional quality control parameters are listed in the table below.

Summary of acceptance and corrective actions for particulate phosphorous QC parameters

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| --- | --- | --- | --- |
| **INDICATOR** | **ACCEPTANCE/ACTION LIMITS** | **ACTION** | **FREQUENCY (BATCH)** |
| Correlation Coefficient (r) | r ≥ 0.995 | If < 0.995, evaluate data points of the calibration curve. If any data point is outside established limits, reject as outlier. | 1 per batch if acceptable. |



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| --- | --- | --- | --- |
| ICV | ± 10% | Recalibrate if outside acceptance limits. | Beginning of run following standard curve. |
| QCS | ± 10% (EPA 1993)  ± 3s (NELAC) | If QCS value is outside ± 10% of the QCS concentration, reject the run, correct the problem and rerun samples. |  |
| CCV | ± 10% | If outside 10%, correct the problem. Rerun all samples following the last in-control CCV. | After every 10-20 samples and at end of batch |
| Method Blank/Laboratory Reagent Blank (LRB) | ≤ Method Quantitation Limit | If the LRB exceeds the quantitation limit, results are suspect. Rerun the LRB. If the concentration still exceeds the quantitation limit, reject or qualify the data, or raise the quantitation limit. | Following ICV, after every 10-20 samples and at the end of the run. |
| Method Quantitation Limit (MQL) check standard | Within +3s of average MQL check standard output?  ±30% ? | When the value is outside the predetermined limit and the ICV is acceptable, reanalyze the sample. If the reanalysis is unacceptable, increase the concentration and reanalyze. If this higher concentration meets the acceptance criteria, raise the reporting limit for the batch. | Beginning of run following the LRB |
| Laboratory Fortified Matrix Spike Sample | ± 20% | If the recovery of any analyte falls outside the designated acceptance limits and the QCS is in control, the recovery problem is judged matrix induced. Repeat the LFM and if the sample results are again outside the acceptable recovery range, the sample should be reported with a “matrix induced bias” qualifier. | After every 10-20 samples |
| Laboratory Duplicate Sample | ± 20% | If the RPD fails to meet the acceptance limits, the samples should be reanalyzed. If the RPD again fails to meet the acceptance limits, the sample must be reported with a qualifier identifying the sample analysis result as not having acceptable RPD for duplicate analysis. | After every 10-20 samples |

References

1. US Environmental Protection Agency, “Determination of Dissolved Silicate in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis”, in Methods for Determination of Chemical Substances in Marine and Estuarine Matrices – 2nd Edition (EPA/600/R-97/072). Sep 1997, Method 366.0.
2. US Environmental Protection Agency, “Determination of Dissolved Silicate in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis”, in Methods for the Chemical Analysis of Water and Wastes (MCAWW) (EPA/600/4-79/020). 1971, Method 370.1.
3. “Silica, colorimetric, molybdate blue, automated-segmented flow” in Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey Method ID I-2700-85. Edited by Marvin J. Fishman and Linda Friedman, 1989.
4. EPA Code of Federal Regulations 40, chapter 1, subchapter D, part 136.