1) Silicates

a) Scope and Application

i) This method provides a procedure for the determination of dissolved silicate concentrations normally found in surface and saline waters, domestic and industrial wastes.

ii) The method detection limit (MDL) is determined on a yearly basis. This MDL is defined as the student t times the standard deviation of at least seven replicates of a low level estuarine The range is determined by the instrument used, its configuration, and the standard curve that is used.

iii) This method should be used by analysts experienced in the use of automated colorimetric analyses, matrix interferences and procedures for their correction. Analyst training and/or a demonstration of capability should be documented.

b) Summary of Method

i) This method is an automated colorimetric method for the analysis of silcate concentration. Silicomolybdate and ascorbic acid are added to a filtered sample under acidic conditions to produce a molybdenum blue color complex. The color produced is proportional to the silicate concentration present in the sample.

c) Interferences

i) Interference from phosphate may be suppressed by adding oxalic acid.

ii) Hydrogen sulfide, depending on the method of analysis, may be removed by either boiling prior to analysis, by oxidation with bromine or stripping with nitrogen gas after acidification.

iii) Turbidity interference is corrected by filtration of samples.

iv) Large amounts of iron interfere with analysis.

v) Refractive Index interferences should be corrected for when analyzing estuarine/coastal samples. Alternatively, match the salinity of the calibration standards to the salinity of the samples.

d) Apparatus and Materials

i) Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube or recorder or computer based data system.

Comment [csj1]: Don't see this anywhere in the SOPs.?

Deleted: Flow injection or discrete analysis may also be used.

ii) Low silica glassware and plastic: 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 rinsing with reagent water. Some laboratories use critical cleaning liquid detergents instead of or before acid rinsing. A laboratory's glassware cleaning method will be considered sufficient if all quality control samples are within the expected ranges.

e) Reagents

i) 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 chemical s needed for the reaction will be listed, but not the specific amounts.

Comment [csj2]: ?

Deleted: If continuous flow is being utilized an appropriate surfactant like Brij is added to one or more of the reagents

(1) Oxalic Acid, Ascorbic Acid and Hydrogen Sulfide.

(2) Color Reagent: Ammonium Molybdate.

(3) Refractive Reagent: Use if necessary.

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Deleted: Should be made the same as the Color Reagent, omitting the sulfanilamide and N-1 napthylethylenediamine dihydrochloride

(4) Stock Silica Solution: A laboratory prepared or purchased stock standard can be used. If the stock standard is prepared in the laboratory, a purchased stock standard should be used as a calibration check standard.

ii) Reagent water: see Chapter VI, Section 4.2.

iii) Artificial Sea Water (ASW): see Chapter VI, Section 4.3. This can be used for the matrix at an appropriate salinity for the samples being analyzed.

Deleted: If precipitation occurs eliminate the magnesium sulfate.

iiv) Prepare a series of standards by diluting suitable volumes with reagent or ASW water. Prepare these 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. In Chesapeake Bay Tidal Laboratories the range can be as low as 0.001to 0.040 mg N/L for samples near the Bay mouth, to as high as 0.03 – 0.30 mg N/L when very high nitrite samples are encountered.

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v) Saline silica standards: When analyzing samples of varying salinities, it is also recommended that standards be prepared in a series of salinities in order to quantify the "salt error," the shift in the colorimetric response of silicate due to the change in the ionic strength of the solution.

f) Sample Handling

i) Samples are filtered in the field through a 0.7 um GF/F and the filtrate is captured in a HDPE bottle. Samples may be stored up to 28 days at 4 ± 2°C.

g) Procedure

i) Calibration: Standard curve(s) to bracket the concentration of expected samples should be analyzed.

ii) Sample analysis

(1) Equilibrate the samples to room temperature.

(2) Allow both colorimeter and recorder to warm up for 30 minutes or the specific instrument recommendation. Obtain a steady instrument state that is necessary for the instrument to be ready to collect data.

(3) Use a sampling rate which ensures reliable results.

(4) Analytical sequence: The samples and associated QC samples and standards should be run according to the following sequence.

(a) Five calibration standards with concentration within the linear range of the test.

(b) Two method blanks.

(c) Ten CBP samples.

(d) One matrix spike sample.

(e) One medium concentration calibration standard.

(f) One method blank.

(g) Steps 5.7.2.4.3 - 5.7.2.4.6 are repeated until samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

(h) One high concentration calibration standard.

(i) One medium concentration calibration standard.

(j) One low concentration calibration standard.

(5) 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 sample run.

iii) 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 and their corresponding peak heights are the dependent variable.

(2) Refractive Index Correction For Estuarine/Coastal Systems is optional. shall be performed in accordance with procedures described in Section 6.7.3.2

Comment [csj3]: EPA method 366 indicates this is optional.

(3) Correction for Salt Error in Estuarine/Coastal Samples shall be performed in accordance with procedures described in Section 6.7.3.3

Comment [csj4]: Is this still necessary? Don't instruments correct for matrix now when you run the saline blanks?

(4) Results should be reported in mg N/L.

h) Quality Control

i) Method detection limits (MDL): Method detection limits should be established using the ~~guidelines~~ procedures in Chapter VI, Section C.8.

ii) Calibration

(1) Linear calibration range: Calibration standards should bracket the range of CBP samples.

(2) Correlation coefficient: The correlation coefficient must be 0.995 or better for the calibration curve to be used.

iii) Method Blank: see Chapter VI, Section C.6.1.

iv) Matrix spike sample: see Chapter VI, Section C.6.4.

v) Laboratory duplicate: see Chapter VI, Section C.6.3.

vi) Reference materials: The laboratory must analyze a standard reference material or proficiency testing samples at least once a year, as available.

Proposed Summary Table: (Based on DCLS Tidal Acceptance limits)

QC INDICATOR	**ACCEPTANCE/ ACTION LIMITS**	**ACTION**	**FREQUENCY (BATCH)**
Correlation Coefficient	≥ 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.
LCS/QCS	± 10%	If QCS value is outside ± 10% of the target value, reject the run, correct the problem and rerun samples.	Beginning of run following the ICV.
ICV	± 10%	Recalibrate if outside acceptance limits.	Beginning of run following standard curve.
CCV	± 10%	If outside 10%, correct the problem. Rerun all samples following the last in-control CCV.	After every 10 samples and at end of batch
Method Blank	≤ 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 the ICV, after every 10 samples following the CCV and at the end of the run.
Method Quantitation Limit (MQL): The concentration of the lowest standard.		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 Sample Matrix Spike	± 10%	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 samples
Laboratory Duplicate	± 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 samples.

5.9 References

(a) EPA 1997. "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), Sept, 1997. Method 366.0, Rev. 1.0.

(b) EPA 1997. "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,

(c) 1989. "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 United States Geological Survey, Book 5, Chapter A1 Edited by Marvin J. Fishman and Linda C. Friedman. Method ID: I-2700-85.

Do not think we want a specific schematic. Every instrument is different

From the **Thursday, September 23, 2010 Federal Register 40 CFR Part 136:**

7. Add new § 136.7 to part 136 to read as follows:

§ 136.7 Quality assurance and quality control.

(a) Twelve essential Quality Control checks and acceptable abbreviations are:

(1) Demonstration of Capability (DOC);
(2) Method Detection Limit (MDL);
(3) Laboratory reagent blank (LRB), also referred to as method blank;
(4) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);
(5) Matrix spike, matrix spike duplicate, or laboratory fortified blank duplicate (LFBD) for suspected difficult matrices;
(6) Internal standards, surrogate standards (for organic analysis) or tracers (for radiochemistry);
(7) Calibration (initial and continuing), initial and continuing performance (ICP) solution also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);
(8) Control charts (or other trend analyses of quality control results);
(9) Corrective action (root cause analyses);
(10) QC acceptance criteria;
(11) Definitions of a batch (preparation and analytical); and
(12) Specify a minimum frequency for conducting these QC checks.

(b) These twelve quality control checks must be clearly documented in the written method along with a performance specification or description for each of the twelve quality control checks.