





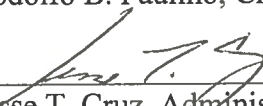
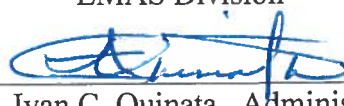
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Title: Silica, QuikChem 10-114-27-1-A
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**GUAM ENVIRONMENTAL PROTECTION AGENCY
 EMAS ANALYTICAL PROGRAM**

STANDARD OPERATING PROCEDURE

**DETERMINATION OF DISSOLVED SILICA IN WATER
 BY FLOW INJECTION ANALYSIS COLORIMETRY**

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1 SCOPE AND APPLICATION

- 1.1 This method covers the determination of silica in drinking water, ground water, surface waters, domestic and industrial wastewaters.
- 1.2 The applicable range is 0.20 to 2.00 mg/L SiO₂.
- 1.3 The quantitation limit for silica is 0.20 mg/L.

2 METHOD SUMMARY

- 2.1 Soluble silica reacts with molybdate under acidic conditions to form a yellow silicamolybdate complex. This complex is subsequently reduced with ANSA (1-amino-2-naphthol-4-sulfonic acid) and bisulfite to form a heteropoly blue complex which has an absorbance maximum at 820 nm.

3 INTERFERENCES

- 3.1 Phosphate and tannin interfere. Treatment with oxalic acid eliminates interference from phosphate and decreases interference from tannin.
- 3.2 Large amounts of iron or sulfides are interferences. Sulfides can be removed by boiling an acidified sample. Addition of disodium EDTA will eliminate the interference due to iron.
- 3.3 Silica contamination may be avoided by storing samples, standards, and reagents in plastic bottles. Avoid using glassware as much as possible.

4 DEFINITIONS

- 4.1 Analytical Sample – Any sample in which silica is being determined, excluding standards, method blanks, or QC reference samples.
- 4.2 Calibration Blank (CB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analyte.



- 4.3 Calibration Standard (CAL) – A solution prepared by diluting the primary stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 4.4 Field Reagent Blank (FRB) – An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if contamination is occurring in the field environment. Note: Field reagent blanks cannot be used for LD or LFM.
- 4.5 Field Duplicates (FD) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with the sample collection and storage as well as the laboratory procedures.
- 4.6 Instrument Performance Check (IPC) – A standard containing the analyte of interest that is used to verify the accuracy of analysis and monitor instrument drift. It is analyzed periodically through out an analysis sequence.
- 4.7 Calibration Verification (CV) solution: Initial (ICV) and Continuing Calibration Verification (CCV) solutions - A known value standard used to verify instrument performance during analysis. It is analyzed to verify that the initial calibration has not changed significantly during the analysis run. The CV fulfills the requirements of the IPC (4.6).
- 4.8 Laboratory Fortified Blank (LFB) – An aliquot of reagent water or other blank matrix to which known quantities of method analytes are added in the laboratory. The source of LFB must be independent of the calibration standards. LFB is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LFB also fulfills the requirements of the QCS (4.14).
- 4.9 Laboratory Fortified Sample Matrix (LFM) – An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 4.10 Laboratory Duplicate (LD) – An aliquot of sample prepared and analyzed separately with identical procedures. Analysis of the sample and LD indicates precision associated with the laboratory procedures, but not with sample collection, preservation or storage procedures.



- 4.11 Laboratory Reagent Blank (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly like a sample. The LRB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment.
- 4.12 Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.
- 4.13 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.
- 4.14 Quality Control Sample (QCS) – A standard containing orthophosphate that is used to verify the accuracy of the analysis. The method requires that the source of the QCS must be independent of the calibration standards and that the QCS be analyzed quarterly.
- 4.15 Quantitation Limit (QL) – The concentration at which confidence in the reported value requires no qualifying remarks. The QL, also called the practical quantitation limit (PQL) is approximately 5X the MDL and represents a practical and routinely achievable detection limit with a relatively good certainty that any reported value is reliable.
- 4.16 Stock Standard Solution (SSS) - A concentrated solution containing the method analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 4.17 Sample Delivery Group (SDG) – A group of twenty samples or less from the same case that is sent to the laboratory for analysis.

5 HEALTH AND SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your skin, wash thoroughly with soap and water. Contact your Supervisor or Health and Safety Coordinator to determine if additional treatment is required.



5.2 The following chemicals have the potential to be highly toxic or hazardous, for detailed explanations consult MSDS.

- 1) Sulfuric acid
- 2) 1-amino-2-naphthol-4-sulfonic acid (ANSA)
- 3) Oxalic acid

6 EQUIPMENT AND SUPPLIES

- 6.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.
- 6.2 Glassware – Class A volumetric flasks and plastic containers as required. Samples must be stored in plastic bottles.
- 6.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

- 6.3.1 Sampler
- 6.3.2 Multichannel proportioning pump
- 6.3.3 Reaction unit or manifold
- 6.3.4 Colorimetric detector
- 6.3.5 Data system
- 6.3.6 10 mm path length, 80 uL, glass flow cell

7 REAGENTS AND STANDARDS

7.1 Preparation of Reagents:

Use ASTM Type II water for all solutions.

7.1.1 Reagent 1. Ammonium Molybdate Solution

In a **500 mL** volumetric flask, dissolve **20.0 g ammonium molybdate tetrahydrate**, $((\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ in approximately **400 mL** water. Add **8.0 mL concentrated sulfuric acid** (H_2SO_4). Dilute to the mark. Stir and shake until dissolved. Store in plastic bottle and refrigerate. Prepare this reagent monthly and discard if precipitate or blue color is observed.

7.1.2 Reagent 2. Oxalic Acid Solution

In a **500 mL** volumetric flask, dissolve **50.0 g oxalic acid, dehydrate** ($\text{HO}_2\text{CCO}_2\text{H} \cdot 2\text{H}_2\text{O}$) in approximately **450 mL water**. Dilute to the mark. Invert to mix. Store in plastic bottle.

7.1.3 Reagent 3. ANSA Reducing Agent



In a **100 mL** volumetric flask, dissolve **2.0 g sodium sulfite** (Na_2SO_3) in approx. **80 mL water**. Add **0.25 g ANSA** (1-amino-2-naphthol-4-sulfonic acid). Dissolve and dilute to the mark. **(NOTE: The ANSA solid should be stored in the refrigerator)**. Prepare a second solution by dissolving **15 g sodium bisulfite** (NaHSO_3) in **300 mL water**. In a dark plastic container mix the two solutions. Add **4 mL glycerol**. Store in the refrigerator and discard when it becomes dark.

7.2 Preparation of Standards

7.2.1 **Stock Standards:** Stock standard solutions may be purchased as certified solutions or prepared from ACS grade materials and are stable for three months when stored in plastic and refrigerated at 4 °C.

7.2.2 Standard 1. Stock Standard 1000 mg SiO_2/L :

In a **500 mL** plastic volumetric flask, dissolve **1.565 g silicofluoride** ($(\text{Na}_2\text{SiF}_6)$) in about 400 mL water. Dilute to the mark and mix. When stored in plastic and refrigerated, this standard is valid up to three months. Alternatively, a commercially prepared standard can be obtained from a reputable supplier.

7.2.3 **Standard 1A. Working Standards** – Prepare fresh daily. The following calibration standards are prepared using Standard 1 (7.2.2), 1000 mg SiO_2/L and diluted with reagent water.

Calibration Standard	Volume of Stock Standard 1	Final volume
2.00 mg/L	200 uL	100 mL
1.00 mg/L, CV	100 uL	100 mL
0.50 mg/L	50 uL	100 mL
0.20 mg/L, QL	20 uL	100 mL
Blank	0 uL	100 mL

QCS (or LFB): 1.00 mg/L --- must be prepared from a second source stock standard.

8 SAMPLE HANDLING AND PRESERVATION

8.1 Samples should be collected in precleaned polyethylene bottles and refrigerated at 4°C until analyzed. Chemical preservation for silica is not recommended. Adding acid will precipitate silica. Freezing decreases silicate concentrations, especially at concentrations greater than 100 ug SiO_2/L . Samples may be held for 28 days.



- 8.2 Samples are received in the EMAS Laboratory by a laboratory staff. Sample IDs, dates and times of collection are verified against the chain-of-custody form. Samples are logged in using the Laboratory Information System (LIMS).

9 QUALITY CONTROL PROCEDURES

- 9.1 Guam EPA operates a formal quality control (QC) program. The QC program consists of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks, QCS samples and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

Initial Demonstration Proficiency – Each analyst must complete an initial demonstration of proficiency prior to analyzing samples following this method.

- 9.2.2 MDL – A method detection limit must be confirmed annually and must be $<1/2$ the QL or corrective action must be initiated.
- 9.2.3 QCS – a QCS must be prepared and analyzed when beginning the use of this method, on a quarterly basis or as required to meet data-quality needs. The source of the QCS must be independent of the calibration standards. The QCS verifies the calibration standards. Guam EPA Laboratory fulfills the requirements of the QCS with analysis of the LFB.
- 9.3 Routine Analytical Quality Control
- 9.3.1 The instrument must be calibrated with a blank and minimum of three standards. The correlation coefficient of the calibration curve must be ≥ 0.995 or the instrument must be recalibrated.
- 9.3.2 CV – The accuracy and stability of the calibration shall be verified by the periodic analysis of a CV standard. It must be analyzed at the beginning of an analytical run (the ICV), after every 10 analytical samples (the CCV), and at the end of an analytical run (the closing CCV). The CV solution should be prepared from the same standard stock solutions used to prepare the calibration standards.

The recovery of silica in the CV is calculated as follows:

$$\% R = \frac{M}{T} \times 100$$



Where

%R = percent recovery of the standard
M = measured concentration of silica, mg/L
T = true concentration of silica in the CV, mg/L

If the CV recovery exceeds the limits of 90 – 110%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable CV results must be reanalyzed.

- 9.3.3 CB (ICB/CCB) – The stability of the baseline must be monitored by analyzing a CB immediately after every CV standard. If the absolute value of the CB result equals or exceeds the QL, the analysis must be terminated. The cause of high CB result must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable CB results must be reanalyzed.
- 9.3.4 QL – The accuracy of the calibration at the reporting limit may be verified by the analysis of a QL standard. The QL should be analyzed at the beginning of each analytical run, prior to the analysis of environmental samples. The recovery of silica in the QL is calculated as follows:

$$\%R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard
M = measured concentration of silica, mg/L
T = true concentration of silica in the QL, mg/L

If the QL recovery exceeds the limits of 50 – 150%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all the samples analyzed after the out-of-control QL standard must be reanalyzed. If, after recalibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be re-prepared and the instrument recalibrated.

- 9.3.5 LRB – The laboratory must analyze at least one LRB daily or with each batch of 20 or fewer samples of the same matrix, whichever is more frequent. LRB data are used to assess contamination in the laboratory environment. LRB values that exceed the MDL indicate potential laboratory contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with affected samples, and reanalyzed.



- 9.3.6 LFB – A LFB must be prepared and analyzed with each batch of 20 or fewer samples. The LFB assures that the calibration standards used to calibrate are accurate. The LFB is the QCS. The recovery of silica in the LFB is calculated as follows:

$$\%R = \frac{\text{LFB}}{s} \times 100$$

Where

%R = percent recovery
LFB = measured concentration of silica in the LFB, mg/L
s = silica concentration in the LFB, mg/L

The recovery of silica in the LFB must be within the 90 – 110% limits. If the recovery exceeds the limits, the analysis system is judged to be out-of-control, and the source of the problem must be identified and resolved before continuing analyses.

- 9.3.7 LD – Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity.

One LD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LD for a batch containing 1-10 routine samples, 2 LDs for a batch containing 20 routine samples, etc.). Shake the sample selected as the LD, obtain a representative aliquot, and proceed with the sample preparation and analysis, treating the LD sample as a routine sample.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{(C_{ld} - C)}{(C_{ld} + C) / 2} \times 100$$

Where

RPD = relative percent difference
 C_{ld} = measured silica in the LD, mg/L
C = measured silica in the routine sample, mg/L

The relative percent difference (RPD) must be $\leq 20\%$ for samples with silica levels greater than or equal to 5X the QL. For other samples, the absolute difference between duplicate results must be less than the QL. If the control limits are exceeded, flag all associated analyte results. Document actions in the **Notes** section of the LIMS analytical results report.

- 9.3.8 LFM – The LFM is designed to provide information about the effect of sample matrix on the measurement system. One LFM must be prepared for every ten routine



- 1) Turn on the Lachat QuikChem 8000 FIA+ instrument and allow the colorimeter to warm up for about 30 minutes.
- 2) Set up the silica manifold.
- 3) Turn on the pump and set the speed to 35 RPM.
- 4) Download the silica method in the computer.
- 5) Pump reagent water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow system to equilibrate until a stable baseline is achieved. Don't forget to place the waste lines into the silica analysis waste container.

10.1.2 Calibration and Sample Analysis

- 1) Pour the four calibration standards and the blank into standard tubes and position them in decreasing order in the standards rack at the rear of the autosampler.
- 2) Load the analytical and QC samples into the samples rack using the sample tubes.
- 3) The usual sample loading sequence is listed in the following table:

Row	Sample ID	Cup #	Sample Type	Level
1	Cal Std 1	1	Cal Std	1
2	Cal Std 2	2	Cal Std	2
3	Cal Std 3	3	Cal Std	3
4	Cal Std 4	4	Cal Std	4
5	Blank	5	Cal Std	5
6	ICV	1	Unknown	0
7	ICB	2	Unknown	0
8	LFB (QCS)	3	Unknown	0
9	LRB	4	Unknown	0
10	Sample 1	5	Unknown	0
11	Sample 1 – LD	6	Unknown	0
12	Sample 1 – LFM	7	Unknown	0
13	Sample 2	8	Unknown	0
14	Sample 3	9	Unknown	0
15	Sample 4	10	Unknown	0
16	Sample 5	11	Unknown	0
17	Sample 6	12	Unknown	0
18	CCV1	13	Unknown	0



19	CCB1	14	Unknown	0
20	Sample 7	15	Unknown	0
21	Sample 8	16	Unknown	0
22	Sample 9	17	Unknown	0
23	Sample 10	18	Unknown	0
24	Sample 11	19	Unknown	0
25	Sample 11 – LD	20	Unknown	0
26	Sample 11 – LFM	21	Unknown	0
27	Sample 12	22	Unknown	0
28	Sample 13	23	Unknown	0
29	Sample 14	24	Unknown	0
30	CCV2	25	Unknown	0
31	CCB2	26	Unknown	0
32	Sample 15	27	Unknown	0
33	Sample 16	28	Unknown	0
34	Sample 17	29	Unknown	0
35	Sample 18	30	Unknown	0
36	Sample 19	31	Unknown	0
37	Sample 20	32	Unknown	0
38	CCV	33	Unknown	0
39	CCB	34	Unknown	0

- 3) Input the information required by the data system such as concentrations, replicates and quality control scheme.
- 4) Calibrate the instrument by injecting the working standards. The system will analyze the calibration standards and calculate a calibration curve prior to analyzing any of the samples. A correlation coefficient of ≥ 0.995 is the requirement for the calibration to pass. The system will now automatically analyze the samples loaded in the sample tray.

10.1.3 Post-analysis Review

- 1) QC Sample Results – Review the results for all QC samples for compliance with the criteria specified in Section 9. If results are not acceptable, take appropriate corrective action.
- 2) Off-scale Results – Review results for samples that exceed the calibration range. Samples having silica concentrations larger than the highest calibration standard must be diluted and reanalyzed.

10.1.4 Instrument Shutdown



- 1) At the end of the run with the pump still turned on, place the ammonia molybdate reagent, oxalic acid and ANSA transmission lines in to the NaOH-EDTA solution (Reagent 5 in Orthophosphate analysis, SOP # CH-01-02). Pump this solution for approximately 5 minutes. Then place these lines in reagent water and pump for at least 15 minutes.
- 2) After the 15 minute period, remove the reagent lines from the reagent water and allow the reagent lines to be purged of the reagent water. Observe the tubing on the manifold – when no liquid is apparent in the tubing the pump can be turned off. Cap all reagents, discard all samples and standards into the appropriate waste containers and turn the power off.

10.2 **Data Reduction and Reporting** – After set-up and calibration the software reports results for the analyzed solution in units of mg/L. No further calculations are necessary and values may be reported directly from the data system. All results should be reported using no more than three significant figures; however, no values of less significance than the MDL may be reported. Values less than the MDL should be reported as <MDL values. Values between the MDL and QL will be flagged as estimated (J flag).

10.2.1 Sample results are entered into the Laboratory Information Management System (LIMS) and analytical results are reported.

10.2.2 Before releasing the results, the laboratory conducts data verification and validation. This is done through peer review of the data and validation by another analyst. The QA Manager makes the final audit and validation prior to the release of the results.

11 DOCUMENTATION

Refer to Section 11 of SOP Determination of Orthophosphate in Water by FIA (Number: CH-01-02)

12 REFERENCES

12.1 QuikChem Method 10-114-27-1-A, Determination of Silica in Waters by Flow Injection Analysis, LACHAT Instruments, 13 Sep 2000.

12.2 Method 4500-SiO₂, Standard Methods for Examination of Water and Wastewater, 20th Edition, 1998.



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Attachment A

Deviation from Reference Method

- A. 1 The applicable range is 0.20 to 2.00 mg SiO₂/L.

