

**CENTER FOR NUCLEAR WASTE
REGULATORY ANALYSES**

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Title TECHNICAL OPERATING PROCEDURE FOR SPECTROPHOTOMETRIC DETERMINATION OF SILICA

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on 03/04/91. This procedure consists of the pages and changes listed below.

<u>Page No.</u>	<u>Change</u>	<u>Date Effective</u>
ALL	-	03/04/91

Supersedes Procedure No. None

Approvals

Written By <i>James D. Luby</i>	Date <u>3/1/91</u>	Technical Review <i>M. J. Sabolew</i>	Date <u>3/1/91</u>
Quality Assurance <i>Robert Burt</i>	Date <u>3/4/91</u>	Cognizant Director <i>[Signature]</i>	Date <u>3/1/91</u>

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TOP-014
TECHNICAL OPERATING PROCEDURE FOR
SPECTROPHOTOMETRIC DETERMINATION OF SILICA

1. PURPOSE

The purpose of this procedure is to describe a general method for the spectrophotometric determination of silica (SiO₂) in aqueous solutions. This procedure will be used for aqueous solutions generated by geochemical experiments involving silicate minerals (e.g., zeolites and feldspars) but may also be used for analyses of water samples collected from laboratory experiments or in the field. This procedure implements the requirements of CQAM Section 3.

2. APPLICABLE DOCUMENT

The following document forms a part of this procedure, as applicable:

Operator's Manual for Milton Roy Spectronic 1201
Spectrophotometer (1988)

3. RESPONSIBILITY

- (1) The Geosciences Element Manager shall be responsible for the development and maintenance of this procedure.
- (2) The cognizant Principal Investigator shall be responsible for the implementation of this procedure.
- (3) Personnel performing tasks described in this procedure are responsible for complying with its requirements.

4. EQUIPMENT

- (1) Milton Roy Spectronic 1201 Spectrophotometer with microprocessor-controlled functions and features including a linear curve fit test mode or equivalent.
- (2) Spectrophotometer cells, 1 cm light paths

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- (3) Volumetric flasks, volumetric pipettes, burets, beakers, and other necessary glassware. All glassware shall be treated with 10% HNO₃ (section 7.9) and rinsed with silica-free high purity water prior to use to avoid errors caused by materials adsorbed on the glass.
- (4) Analytical balance accurate to within 0.1 mg (calibrated biannually)
- (5) Plastic bottles (polyethylene or polypropylene). Bottles shall be treated with 10% HNO₃ (section 7.9) and dried prior to use to avoid contamination.
- (6) Hot plate
- (7) pH meter calibrated before use with appropriate buffer solutions and accurate to within 0.1 pH unit
- (8) Nessler tubes, matched, 50 ml, tall form
- (9) Steam bath
- (10) Teflon dishes
- (11) 0.2 um membrane filters

5. CHEMICALS

Chemicals used to prepare solutions in accordance with this procedure shall meet the purity requirements as specified by American Chemical Society Standards (Certified A.C.S. or Reagent A.C.S.) if possible. Some chemicals may not be available in A.C.S. grade and a certified grade such as Fisher Certified Grade may be used.

- (1) Sodium bicarbonate (NaHCO₃)
- (2) Hydrochloric acid (HCl)
- (3) Sulfuric acid (H₂SO₄)
- (4) Ammonium molybdate ((NH₄)₆Mo₇O₂₄ + 4H₂O)
- (5) Oxalic acid (H₂C₂O₄ + H₂O)

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- (6) Sodium hydroxide (NaOH)
- (7) Silica standard (1 ml = 1 mg SiO₂)
- (8) 1-amino-2-naphthol-4-sulfonic acid (C₁₀H₉NO₄S)
- (9) Sodium sulfite (Na₂SO₃)
- (10) Sodium bisulfite (NaHSO₃)
- (11) Nitric acid (HNO₃)

6. IDENTIFICATION AND DESCRIPTION OF SOLUTIONS

Solutions prepared for use in this procedure shall be identified on a label that includes the following:

- (1) Description of the solution (e.g., "Oxalic Acid Solution") that includes the scientific notebook number and page number on which the preparation of the solution has been recorded (for example "GC-03/12").
- (2) Preparation date
- (3) Expiration date, if applicable

Preparation and identification of solutions shall be described in the scientific notebook. The lot number and actual concentration of each chemical used to prepare a given solution shall be included in the scientific notebook entry.

7. PREPARATION OF SOLUTIONS

Solutions are prepared using chemicals low in silica and silica-free high purity water (about 17-18 megohm-cm resistivity).

7.1 Sulfuric Acid, H₂SO₄, 1N

Add 14 ml concentrated H₂SO₄ to at least 350 ml water in a 500 ml volumetric flask and dilute to 500 ml with water. Transfer solution to a 500 ml plastic bottle and label.

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7.2 Hydrochloric Acid, HCl, 1+1

Add 250 ml concentrated HCl to 250 ml water in a volumetric flask. Transfer solution to a 500 ml plastic bottle and label.

7.3 Sodium Hydroxide, NaOH, 6M

Dissolve 120 g NaOH in water and make up to 500 ml in a 500 ml plastic beaker. Transfer solution to a 500 ml plastic bottle and label.

7.4 Ammonium Molybdate Reagent

Place 10 g ammonium molybdate in water in a 100 ml volumetric beaker. Dissolve by stirring and gently warming. Dilute to 100 ml. Filter if necessary. Adjust solution to pH 7 to 8 with 6M NaOH added dropwise. Transfer solution to a 250 ml plastic bottle and label.

7.5 Oxalic Acid Solution

Dissolve 7.5 g oxalic acid in water in a 100 ml volumetric flask and dilute to the mark. Transfer solution to a 250 ml plastic bottle and label.

7.6 Standard Silica Solution, 1ml = 10ug SiO₂

Dilute 10 ml silica standard (1ml = 1mg SiO₂) to 1L with water in a 1L volumetric flask. Transfer solution to a 1L plastic bottle and label.

7.7 Standard Silica Solution, 1ml = 100ug SiO₂

Dilute 10 ml silica standard (1ml = 1mg SiO₂) to 100 ml with water in a 100 ml volumetric flask. Transfer solution to a 250 ml plastic bottle and label.

7.8 Reducing agent

Dissolve 500 mg of 1-amino-2-naphthol-4-sulfonic acid and 1 g Na₂SO₃ in 50 ml water with gentle warming if necessary. Dissolve 30 g NaHSO₃ in 150 ml water. Mix

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these two solutions. Filter into a 250 ml plastic bottle and label. Refrigerate and avoid exposure to light. Discard solution when it darkens.

7.9 Acid bath, 10% HNO₃

Add 2L concentrated HNO₃ to 18L water in a 18 gallon rubber tub and store under fume hood. All glassware and plasticware shall be treated before use by bathing and rinsing in this acid bath.

8. PROCEDURE

8.1 Molybdosilicate Method

Ammonium molybdate in aqueous solution at a pH of about 1.2 reacts with silica and forms a greenish-yellow color complex proportional to the concentration of "molybdate-reactive" silica in the sample. The optimum absorption wavelength for measuring the color complex spectrophotometrically is 410 nm. The minimum silica concentration detectable by this method is about 1 mg/L. The optimum concentration range determined by this method lies between 2 and 25 mg/L.

8.1.1 Preparation of calibration curve

- (1) Prepare a series of silica standards from 0 to 25 mg/L based on a 55 ml sample by accurately pipetting calculated volumes of standard silica solution (1 ml = 100 ug SiO₂) into 50 ml Nessler tubes. If digestion (8.1.2) is used, add to each standard 200 mg NaHCO₃ and 2.4 ml 1N H₂SO₄, to compensate for silica introduced by these reagents and for the effect of the salt on color intensity. Add water to a total volume of 50 ml.
- (2) Add rapidly to each standard 1 ml of 1+1 HCl and 2 ml ammonium molybdate reagent using volumetric pipettes. Mix by inverting at least 6 times.

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- (3) Let stand for 5 to 10 minutes.
- (4) Add 2 ml oxalic acid solution to each standard using a volumetric pipette and mix thoroughly.
- (5) After 2 minutes but before 15 minutes from the addition of the oxalic acid solution, transfer 2 to 3 ml of each standard to a spectrophotometer cell.
- (6) Set spectrophotometer to a wavelength of 410 nm and adjust spectrophotometer to zero absorbance with water.
- (7) Construct a standard curve by either,
 - (a) Reading the absorbance of each standard on the spectrophotometer and plotting absorbance values versus the concentration of each standard or,
 - (b) Performing a linear curve fit test as described in Section 4.6.2 of the Operator's Manual for the Milton Roy Spectronic 1201 Spectrophotometer. If this technique is used the spectrophotometer measures the absorbance and prompts the operator for the concentration of each standard. When the spectrophotometer has the data for all standards, it mathematically constructs a standard curve using the absorbance and concentration of each standard. It then calculates slope and intercept values for the standard curve.

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8.1.2 Digestion

If molybdate unreactive silica (e.g., complex ions containing silica) is present and its inclusion in the analysis is desired, include this step, otherwise proceed to 8.1.3.

- (1) Filter sample through a 0.2 um membrane filter.
- (2) Place 50 ml sample, or a smaller sample portion diluted to 50 ml, in a 100 ml teflon dish using a volumetric pipette.
- (3) Add 200 mg NaHCO_3 and digest on a steam bath for 1 hour. Cool.
- (4) Add slowly and with stirring 2.4 ml 1N H_2SO_4 using volumetric pipettes.
- (5) Immediately transfer to a 50 ml Nessler tube, dilute to the mark with water and proceed to 8.1.3 without delay.

8.1.3 Color development and measurement

- (1) Filter sample through a 0.2 um membrane filter.
- (2) Place 50 ml sample, or a smaller sample portion diluted to 50 ml, in a Nessler tube using a volumetric pipette.
- (3) Add rapidly 1 ml of 1+1 HCl and 2 ml ammonium molybdate reagent using volumetric pipettes. Mix by inverting at least 6 times.
- (4) Let stand for 5 to 10 minutes.
- (5) Add 2 ml oxalic acid solution using a volumetric pipette and mix thoroughly.

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- (6) After 2 minutes but before 15 minutes from the addition of the oxalic acid solution, transfer 2 to 3 ml of sample to a spectrophotometer cell.
- (7) Determine the concentration of the sample at 410 nm by either,
 - (a) Reading the absorbance of the sample and determining silica concentration from the standard curve prepared in 8.1.1(7a) or,
 - (b) Measuring the absorbance of the sample using the spectrophotometer's linear curve fit test as described in Section 4.6.2 of the Operator's Manual for the Milton Roy Spectronic 1201 Spectrophotometer. After measuring the absorbance of the sample the spectrophotometer will automatically determine the concentration of the sample using the slope and intercept values calculated in 8.1.1(7b).

8.2 Heteropoly Blue Method

In a low concentration modification of the molybdosilicate method, the yellow molybdosilicic acid color is reduced by 1-amino-2-naphthol-4-sulfonic acid to a more intense heteropoly blue that exhibits maximum absorption at a wavelength of 815 nm. The minimum silica concentration detectable by this method is about 20 ug/L and the optimum concentration range lies between 50 ug/L and 2.5 mg/L.

8.2.1 Preparation of calibration curve

- (1) Prepare a series of silica standards from 0 to 2.5 mg/L based on a 57 ml sample by accurately pipetting calculated volumes of standard silica solution (1 ml = 10 ug SiO₂) into 50 ml Nessler tubes. If

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digestion (8.2.2) is used, add to each standard 200 mg NaHCO_3 and 2.4 ml 1N H_2SO_4 . Add water to a total volume of 50 ml.

- (2) Perform steps 8.1.1(2) thru 8.1.1(4).
- (3) At least 2, but not more than 15 minutes after oxalic acid addition, add 2 ml reducing agent to each standard using a volumetric pipette and mix thoroughly.
- (4) After 5 minutes, transfer 2 to 3 ml of each standard to a spectrophotometer cell.
- (5) Set spectrophotometer to a wavelength of 815 nm and adjust spectrophotometer to zero absorbance with water.
- (6) Construct a standard curve by performing step 8.1.1(7).

8.2.2 Digestion

If molybdate unreactive silica is present and its inclusion in the analysis is desired, include this step, otherwise proceed to 8.2.3.

- (1) Perform steps 8.1.2(1) thru 8.1.2(4).
- (2) Immediately transfer sample solution to a 50 ml Nessler tube, dilute to the mark with water and proceed to 8.2.3 without delay.

8.2.3 Color development and measurement

- (1) Perform steps 8.1.3(1) thru 8.1.3(5).
- (2) At least 2, but not more than 15 minutes after oxalic acid addition, add 2 ml reducing agent using a volumetric pipette and mix thoroughly.
- (3) After 5 minutes, transfer 2 to 3 ml of sample to a spectrophotometer cell.

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- (4) Determine the concentration of the sample at 815 nm from the standard curve constructed in 8.2.1(6).

9. RECORDS

The scientific notebook shall be used to record results of this procedure and shall contain the following:

- (1) Date of activity
- (2) Initials of individual(s) performing the task
- (3) Description of work performed, e.g., preparation of calibration curve
- (4) Equipment, materials, chemicals, or solutions used
- (5) Methods or procedures used, including any modification of established procedures
- (6) Results

Scientific notebooks shall be maintained as QA records in accordance with CQAM Section 17.

10. BIBLIOGRAPHY

Fanning, K. A. and Pilson, M. E. Q., 1973. On the spectrophotometric determination of dissolved silica in natural waters. Analytical Chemistry, Vol. 45, p. 136.

Standard Methods for the Examination of Water and Wastewater, 16th Edition, p. 457, Methods 425C and 425D, (1985).