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Title TECHNICAL OPERATING PROCEDURE FOR SPECTROPHOTOMETRIC DETERMINATION OF ALUMINUM

EFFECTIVITY AND APPROVAL

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

Page No.	Change	Date Effective
All	0	03/04/91

Supersedes Procedure No. None

Approvals

Written By	Date	Technical Review	Date
James D. Purby	3/1/91	R J Pabalan	3/6/91
Quality Assurance	**Date**	**Cognizant Director**	**Date**
R D Brient	3/4/91		3/11/91

CNWRA Form TOP-1

TOP-013
TECHNICAL OPERATING PROCEDURE FOR
SPECTROPHOTOMETRIC DETERMINATION OF ALUMINUM

1. PURPOSE

The purpose of this procedure is to describe a general method for the spectrophotometric determination of aluminum 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 from 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 maintainance 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

(3) Volumetric flasks, volumetric pipettes, burets, beakers, and other necessary glassware. All glassware shall be treated

with 10% HNO_3 (section 7.9) and rinsed with aluminum-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% HNO_3 (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) Porcelain dishes

(9) Titrating assembly and stand

(10) 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 possilbe. Some chemicals may not be available in A.C.S. grade and a certified grade such as Fisher Certified Grade may be used.

(1) Aluminum metal

(2) Hydrochloric acid (HCl)

(3) Sulfuric acid (H_2SO_4)

(4) Ascorbic acid ($C_6H_8O_6$)

(5) Sodium acetate ($NaC_2H_3O_2 + 3H_2O$)

(6) Acetic acid, glacial (CH_3COOH)

(7) Eriochrome cyanine R ($C_{23}H_{15}Na_3O_9S$)

(8) Methyl orange solution

(9) EDTA (disodium ethylenediamine tetraacetate; $Na_2C_{10}H_{14}O_8N_2 + 2H_2O$)

(10) Nitric acid (HNO_3)

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., "500 ppm Aluminum Stock 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 or weight 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 aluminum, and aluminum-free high purity water (about 17-18 megohm-cm resistivity).

7.1 Stock Aluminum Solution

Dissolve 500.0 mg aluminum metal in 10 ml concentrated HCl in a 1L volumetric flask by heating gently. Dilute to 1L with water. Transfer solution to a 1L plastic bottle and label.

7.2 Standard Aluminum Solution

Dilute 10 ml stock aluminum solution to 1L with water in a 1L volumetric flask (1.00 ml = 5.00 ug Al). Stopper flask and label. Prepare daily or as needed.

7.3 Sulfuric Acid, H_2SO_4, 0.02N

Add 0.28 ml concentrated H_2SO_4 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.

7.4 Ascorbic Acid Solution

Dissolve 0.10 g ascorbic acid in water and make up to 100 ml in a 100 ml volumetric flask. Stopper flask and label. Prepare daily or as needed.

7.5 Buffer Reagent

Dissolve 136 g sodium acetate in 800 ml water in a 1L volumetric flask. Dilute 5.8 ml glacial acetic acid to 100 ml with water in a 100 ml volumetric flask. Add 40 ml acetic acid solution to the sodium acetate solution and dilute to 1L with water. Transfer solution to a 1L plastic bottle and label.

7.6 Stock Dye Solution

Dissolve 150 mg of Eriochrome cyanine R in about 50 ml water in a 100 ml glass beaker. Dilute 5 ml glacial acetic acid to 10 ml with water in a 10 ml volumetric flask. Adjust pH of the Eriochrome cyanine R solution to about 2.9 with the acetic acid solution added dropwise (approximately 2 ml is required). Transfer Eriochrome cyanine solution to a 100 ml volumetric flask and dilute with water to 100 ml. Transfer solution to a 100 ml plastic bottle and label. Stock dye solutions are stable for up to a year.

7.7 Working Dye Solution

Dilute 10 ml of stock dye solution to 100 ml in a volumetric flask with water. Transfer solution to a 100 ml plastic bottle and label. Working dye solutions are stable for at least 6 months.

7.8 EDTA, 0.01M

Dissolve 3.7 g EDTA in a 1L volumetric flask with water and dilute to 1L with water. Transfer solution to a 1L plastic bottle and label.

7.9 Acid Bath, 10% HNO_3

Add 2L concentrated HNO_3 to 18L water in an 18 gallon rubber tub. All glassware and plasticware shall be bathed and rinsed before use in this acid bath.

8. PROCEDURE

Eriochrome cyanine R dye produces a red to pink complex with aluminum in dilute aqueous solutions buffered to a pH of 6.0. Maximum aborption is exhibited by this complex at a wavelength of 535 nm. The minimum aluminum concentration detectable by this method is approximately 6 ug/L. The optimum concentration range determined by this method lies between 20 and 300 ug/L but can be extended upward by sample dilution.

8.1 Preparation of Calibration Curve

(1) Prepare a series of aluminum standards from 0 to 300 ug/L based on a 50 ml sample by accurately pipetting calculated volumes of standard aluminum solution (5 ug Al/ml) into 50 ml volumetric flasks. Add water to a total volume of approximately 25 ml.

(2) Add 1 ml 0.02N H_2SO_4 to each standard using a volumetric pipette and mix.

(3) Add 1 ml ascorbic acid solution to each standard using a volumetric pipette and mix.

(4) Add 10 ml buffer reagent to each standard using a volumetric pipette and mix.

(5) Add 5 ml of working dye solution to each standard using a volumetric pipette and mix.

(6) Immediately make each standard up to 50 ml with water, mix, and let stand for 5 to 10 minutes.

(7) Transfer 2 to 3 ml of each standard solution to a spectrophotometric cell.

(8) Set spectrophotometer to a wavelength of 535 nm and adjust spectrophotometer to zero absorbance with the standard containing no aluminum.

(9) 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.

8.2 Treatment to compensate for color and turbidity

If the sample is cloudy or turbid, include this step, otherwise proceed to 8.3.

(1) Filter sample through a 0.2 um membrane filter.

(2) Place 25 ml sample, or a portion diluted to 25 ml, in a porcelain dish using a volumetric pipette. Add 2 drops of methyl orange indicator using a glass medicene dropper and titrate with 0.02N H_2SO_4 using a 25 ml volumetric buret to a faint pink color. Record amount of 0.02N H_2SO_4 added and discard sample.

(3) Place two similar 25 ml samples into 50 ml volumetric flasks using volumetric pipettes and add the same amount of 0.02N H_2SO_4 used in the titration and 1 ml in excess using volumetric pipettes.

(4) To one sample from (3) add 1 ml EDTA solution using a volumetric pipette. This sample will serve as a blank by complexing any aluminum present and compensating for color and turbidity.

(5) To both samples from (3) add 1 ml ascorbic acid solution using volumetric pipettes and mix.

(6) To both samples add 10 ml buffer reagent using volumetric pipettes and mix.

(7) To both samples add 5 ml working dye reagent using volumetric pipettes and mix.

(8) Immediately make up both samples to 50 ml with water, mix, and let stand 5 to 10 minutes.

(9) Transfer 2 to 3 ml of each sample to a spectrophotometer cell.

(10) Adjust spectrophotometer to zero absorbance using the EDTA blank solution.

(11) Determine the concentration of the sample by performing step 8.3.9.

8.3 Sample measurement

(1) Filter sample through a 0.2 um membrane filter.

(2) Place sample into a 50 ml volumetric flask and add water to a total volume of approximately 25 ml.

(3) Add 1 ml 0.02N H_2SO_4 using a volumetric pipette and mix.

(4) Add 1 ml ascorbic acid solution using a volumetric pipette and mix.

(5) Add 10 ml buffer reagent using a volumetric pipette and mix.

(6) Add 5 ml of working dye solution using a volumetric pipette and mix.

(7) Immediately make up to 50 ml with water, mix, and let stand for 5 to 10 minutes.

(8) Transfer 2 to 3 ml of the sample solution to a spectrophotometric cell.

(9) Determine the concentration of the sample by either,

(a) Reading the absorbance of the sample and determining aluminum concentration from the standard curve prepared in 8.1(9a) 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(9b).

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

Shull, K. E. and Guthan, G. R., 1967. Rapid modified Eriochrome cyanine R method for determination of aluminum in water. Journal American Water Works Association, Vol. 59, p. 1456.

Standard Methods for the Examination of Water and Wastewater, 16th Editiion, p. 183, Method 306B, (1985).