Designation: D7126 – 15

Standard Test Method for On-Line Colorimetric Measurement of Silica[1]

This standard is issued under the fixed designation D7126; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the on-line determination of soluble silica in water by colorimetric analysis using the molybdenum blue method, also known as the heteropoly blue method.

1.2 This test method is applicable for silica determination in water with silica concentrations within 0.5–5000 ppb (µg/L).

1.3 This test method covers the determination of soluble silica SiO_2 (silicon dioxide) or silicates in water. Soluble silica compounds are considered molybdate reactive silica. This test method does not cover the determination of colloidal or polymeric silica, which is considered non-molybdate reactive silica.

1.4 This test method does not cover the laboratory or grab sample measurement of silica in water. Refer to Test Method D859.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D859 Test Method for Silica in Water
D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D3864 Guide for On-Line Monitoring Systems for Water Analysis
D5540 Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129 and Practice D3864.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *heteropoly compound, n*—a compound in which groups of different elements are joined together by metal-metal bonds.

3.2.2 *metalloid, n*—an element which has properties that are intermediate between those of a metal and a nonmetal.

3.2.3 *photodetector, n*—a device for detecting and measuring the intensity of radiant energy.

4. Summary of Test Method

4.1 This test method describes the analysis of soluble silica by analyzing a sample from a continuous stream. This test method is based on the colorimetric determination of soluble silica by the formation and reduction of molybdosilicic acid. Reduced molybdosilicic acid forms a molybdenum blue complex. The optical absorbance of this complex is typically measured at 815 ± 10 nm. The absorbance is directly proportional to the concentration of silica in the sample.

4.2 This on-line test method requires reagents which are added sequentially with separate reaction periods. Each reaction must be allowed to go to completion before the next reagent is added.

5. Significance and Use

5.1 Silicon (Si), a metalloid, is the second most abundant element in the earth's crust. Various forms of silica (silicon dioxide SiO_2) are found in quartz, sand, and rocks. The degradation of these rocks results in silica found in natural waters. Silica in natural waters can be found as ionic silica, silicates, colloidal or suspended particles.

5.2 Elevated temperatures and pressure can cause silica in water to vaporize and form deposits or scale. Scale deposits of

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

silica will coat boilers and turbine blades used in power plants. The presence of silica scale affects the ability of metals to transfer heat. Silica needs to be removed when deionized water is used as a rinse for manufacturing wafers in the semiconductor industry.

5.3 Silica is commonly removed by demineralization using anion exchange resins, distillation, reverse osmosis or precipitation in a lime softening process. The on-line measurement of silica is the preferred method to laboratory analyses for industries trying to obtain and monitor ultra-pure water. Since silica is one of the first species to breakthrough anion exchange resins, on-line silica monitoring is frequently used to determine the need for regeneration of an anion or mixed resin bed.

6. Interferences

6.1 Colored and turbid samples and reagents may interfere in the colorimetric detection of silica. At low levels (ppb range) samples can be filtered to eliminate particles and suspended solids in solutions, however filtration is not recommended, because of the potential to introduce silica contamination. A blank (zero) absorption can be performed prior to the final absorption measurement to reduce interferences from turbidity and color.

6.2 Phosphate interferes in the colorimetric detection of silica by reacting with the molybdate compound used in the first reagent to form molybdophosphoric acid. Molybdophosphoric acid can be destroyed by the addition of tartaric, citric or oxalic acid after the molybdosilicic acid reaction has completed.

6.3 Sample temperature is a potential interferant in the determination of silica by this method. If the on-line instrument allows sufficient time for the sample and the reagents to equilibrate to a constant temperature, sample temperature will not interfere. At controlled, higher temperatures, the reaction sequence time period (typically 10–15 min) can be decreased to 5–10 min.

6.4 Glassware (which contains silica) will interfere and cause erroneously high results. Therefore, containers of plastic or other non-silica containing materials should be used for reagents, calibration standards, and instrument components.

6.5 If a batch style instrument will be used for on-line analysis, adequate rinsing in-between samples is necessary to avoid silica contamination from previous samples.

7. Apparatus

7.1 *Process Instrument:*

7.1.1 A spectrophotometer or colorimeter capable of accurately measuring absorbance values at 815 ± 10 nm is necessary. The instrument should be capable of analyzing a sample from an on-line process water stream by addition of the necessary reagents for the heteropoly blue method. The instrument should also be capable of adding a calibration standard automatically for recommended calibration of the on-line instrument. The instrument may provide alarms, relays, isolated analog, and digital outputs.

8. Reagents

8.1 *Purity of Water*—References to water that is used for reagent preparation, rinsing or dilution shall be understood to mean water that conforms to the quantitative specifications of Type II reagent water of Specification D1193.

8.2 *Silica Solution, Standard*—To prepare a silica standard solution, dissolve ACS reagent grade or better sodium metasilicate (Na_2SiO_3•$9H_2O$) and dilute with deionized water to volume, or use commercially prepared standards. Refer to the instrument manufacturers manual for the correct standard concentration to use. Standards and samples should not be frozen, which can result in lower soluble silica values.[3] Standards should be prepared at room temperature and stored at 4°C to maintain maximum stability.

8.3 *Silica Reagents*—The colorimetric analysis described in this method requires at least 3 reagents for the on-line determination of silica. The reagents necessary for this method are specific for the on-line instrument, colorimeter or spectrophotometer used. Refer to the instrument manufacturers recommended reagents. It is essential that the reagents used are matched to the analyzer. Either use reagents provided or prescribed by the manufacturer or validate the results obtained from any other reagent formulation. This validation must include validation of the calibration data.

NOTE 1—All reagents and calibration standards used in this test method should be stored in polyethylene, plastic or other non-silica containing bottles.

NOTE 2—The first reagent used is an acidified molybdate reagent which reacts with silica in the sample to form molybdosilicic acid. If phosphate is present in the sample, molybdophosphoric acid is also formed. The first reaction requires time to ensure all of the silica in the sample has time to react with the acidified molybdate reagent. The reaction time depends on the concentration of the reagent and sample temperature. The user should use the reaction time and temperature suggested by the reagent or instrument manufacturer, or both.

The second reagent destroys the molybdophosphoric acid formed in the first step. Phosphate interferes in the measurement of silica because the reduced product absorbs at the same wavelength as that of the reduction product of molybdosilicic acid.

The third reagent reduces the molybdosilicic acid formed in the first step. The reduced molybdenum complex forms the heteropoly blue compound and absorption of this molybdenum (heteropoly) blue complex is measured at 815 ± 10 nm.

9. Sampling

9.1 For sampling, refer to Practices D1066, D3370, and D5540, as applicable.

10. Calibration

10.1 The instrument should be calibrated using a silica standard solution prepared as described in 8.2 or by using commercial standards. The standard silica solution should be used as a calibration standard according to the instrument manufacturer's instructions for calibration. If using validated reagents other than those provided or prescribed by the

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[3] Clescari, L., Greenberg, A., Eaton, A., and Rice, E., (Eds), *Standard Methods for the Examination of Water and Wastewater*, 21st Edition, Washington, D.C.: American Public Health Association, 2005, pp. 4-117–4-123.

instrument manufacturer be sure to regenerate the calibration curve with these reagents.

11. Procedure

11.1 The instrument should be calibrated according to 10.1.

11.2 Prepare and connect the reagents according to manufacturer's instructions. Determine required sample flow as specified by the instrument manufacturer and measure flow rate if necessary. Switch the analyzer to automatic analysis mode for continuous on-line silica measurement.

11.3 Sample should be collected from a flowing stream and diverted into or through a reaction cell/vessel. Refer to Fig. 1. The volume of sample inside the reaction cell should encompass the light path from the emitting light source. Each reagent used in the analysis should be added into the reaction cell by a pump or liquid metering device. The appropriate reaction time required after each reagent addition should be allowed for by the instrument.

11.4 The light source from the on-line instrument should travel through the sample to a photodetector. In some instruments, the light is directed through the sample to a reflector. The reflected light then travels back through the sample to the photodetector to be measured at 815 ± 10 nm. Some instruments also take a second reference wavelength measurement at a wavelength out side the absorption band for silica (approximately 450 nm) An analog signal from the photodetector is passed to a microprocessor in the electronics assembly to be calculated as absorbance.

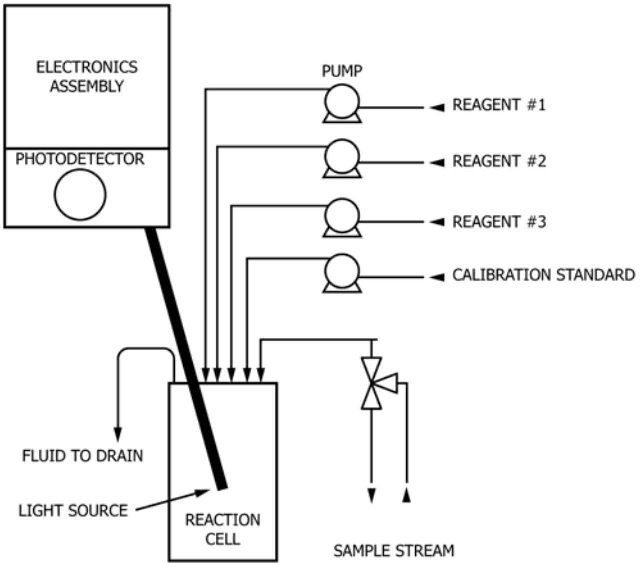

FIG. 1 Fluidics System of an On-Line Silica Instrument

12. Report

12.1 Report readings to the nearest 0.1 ppb (µg/L) Silica.

13. Quality Control

13.1 Instrument calibration must be performed according to the manufacturer's schedule and instructions.

13.2 Instrument calibration and blank readings must be checked whenever reagents or components in the optical path are changed. A calibration verification should be carried out on a sample of known silica concentration at a concentration different than that used for the instrument calibration.

13.3 The user should confirm that the unit is giving proper response using the sample matrix and operating under the environmental extremes of interest.

14. Precision and Bias

14.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D2777 since this test method is a continuous determination. This inability to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D2777.

14.2 The precision and bias of this method is expected to be similar to or better than the static method for silica determination (Practice D859), which uses similar chemistries. The on-line method is expected to improve the precision by minimizing contamination, operator involvement, and exposure to air, which can contain silica.

15. Keywords

15.1 colorimetric; on-line; process measurement; silica