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Standard Test Method for On-Line Colorimetric Measurement of Silica¹

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 ($\mu\text{g/L}$).

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~~

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 ~~D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits~~

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

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

3.2.3 ~~photodetector~~ 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 molybdsilicic acid. Reduced molybdsilicic 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.

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 of Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water. Water. Current edition approved March Dec. 1, 2006; 2010. Published March 2011. Originally approved in 2006 as D7126-06. DOI: 10.1520/D7126-106.

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.

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 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, 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*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the purity specifications of Type I or Type II water, presented in—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 ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) 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. (1) 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 and/or instrument manufacturer.

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.