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Standard Test Method ~~Methods~~ for Estimating the Permanganate Natural Oxidant Demand of Soil and Aquifer Solids¹

This standard is issued under the fixed designation D7262; 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.

^{ε1} NOTE—Reapproved with editorial changes in July 2016.

1. Scope*

1.1 ~~This test method covers~~ These test methods cover the estimation of the permanganate natural oxidant demand (PNOD) through the determination of the quantity of potassium permanganate (KMnO_4) that organic matter and other naturally occurring oxidizable species present in soil or aquifer solids will consume under specified conditions as a function of time. Oxidizable species may include organic constituents and oxidizable inorganic ions, such as ferrous iron and sulfides. The following test methods are included:

Test Method A—48-hour Permanganate Natural Oxidant Demand

Test Method B—Permanganate Natural Oxidant Demand Kinetics

Test Method C—Permanganate Total Oxidant Demand

1.2 ~~This test method is~~ These test methods are limited by the reagents employed to a permanganate natural oxidant demand (PNOD) of ~~60~~⁴⁰ g KMnO_4 per kg soil or aquifer solids after a period of 48 hours (~~Method A~~) (Methods A and C) or two weeks (Method B).

1.3 All observed and calculated values shall conform to the guidelines for significant digits and rounding established in Practice ~~D6026~~.

1.4 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 This standard does not purport to interpret the results of the data. It is the responsibility of the user of this standard to interpret the results obtained and to determine the applicability of these results prior to use.

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~~ safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ ~~This test method is~~ These test methods are under the jurisdiction of ASTM Committee D18 on Soil and Rock and ~~is~~ are the direct responsibility of Subcommittee D18.21 on Groundwater and Vadose Zone Investigations.

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*A Summary of Changes section appears at the end of this standard

2. Referenced Documents

2.1 ASTM Standards:²

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D1193 Specification for Reagent Water

D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction

D4753 Guide for Evaluating, Selecting, and Specifying Balances and Standard Masses for Use in Soil, Rock, and Construction Materials Testing

D6026 Practice for Using Significant Digits and Data Records in Geotechnical Data

D6051 Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities

D6169 Guide for Selection of Subsurface Soil and Rock Sampling Devices for Environmental and Geotechnical Investigations

D6282 Guide for Direct Push Soil Sampling for Environmental Site Characterizations

D6286 Guide for Selection of Drilling and Direct Push Methods for Geotechnical and Environmental Subsurface Site Characterization

2.2 Other Standards:³

APHA/AWWA/WEF Method 4500—KMnO₄ Standard Methods for the Examination of Water and Wastewater, 20th Ed. 1998

ANSI/AWWA B603-03 Standard for Permanganates

3. Terminology

3.1 For common definitions of technical terms in this standard, refer to Terminology D653.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *permanganate natural oxidant demand (PNOD_t)*—the mass of potassium permanganate consumed per mass of soil or aquifer solids as a function of time.

3.2.2 *maximum permanganate natural oxidant demand (PNOD_{max})*—the maximum mass of potassium permanganate consumed per mass of soil or aquifer solids over time.

3.2.3 *permanganate natural oxidant demand kinetics*—the rate at which potassium permanganate is consumed by soil or aquifer solids.

4. Summary of Test Method Methods

4.1 Many organic and reduced inorganic substances present in soil and aquifer solids can be oxidized by permanganate. A standard potassium permanganate solution is added to a specific amount of soil or aquifer solids and allowed to react for a period of 48 hours (Method A) (Methods A and C) or two weeks (Method B). The residual permanganate concentration is measured at prescribed sampling times and the difference in concentration is used to calculate the PNOD_t at that time.

4.2 Many organic and reduced inorganic substances present in soil and aquifer solids can be oxidized by permanganate. However, some organic compounds react slowly and may not be completely oxidized within the test period while others may resist oxidation altogether.

5. Significance and Use

5.1 ~~The test method is~~ Test methods A and B are used to estimate the permanganate natural oxidant demand exerted by the soil or aquifer solids by determining the quantity of potassium permanganate that is consumed by naturally occurring species as a function of time. Typically the measurement of PNOD. Test Method C is used to estimate the permanganate total oxidant demand exerted by soil, aquifer solids, chemical contaminants or any other reduced species by determining the quantity of potassium permanganate that is consumed by all components of the bulk aquifer as a function of time. Typically, the measurement of oxidant demand is used to screen potential sites for in situ chemical oxidation (ISCO) with permanganate (Test Method A) and Methods A and C) and provide information to aid in the design of remediation systems (Test Method B). Methods B and C).

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.

³ Available from American Water Works Association (AWWA), 6666 W. Quincy Ave., Denver, CO 80235, <http://www.awwa.org>.

5.2 While some oxidizable species react relatively quickly (that is, days to weeks), others react more slower (weeks to months). Consequently, the $PNOD_t$ is expected to be some fraction of the $PNOD_{max}$.

5.3 ~~Due~~ For ISCO injection applications, the $PNOD$ may overestimate the demand exerted due to mass transport related issues at the field-scale it is reasonable to assume that issues. For soil blending applications, the $PNOD_t$ measured using the test method may overestimate is a more accurate measure of the demand exerted during ISCO applications due to better mass to oxidant contact.

NOTE 1—The quality of the result produced by this standard is dependent on the competence of the personnel performing it, and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice **D3740** are generally considered capable of competent and objective testing/sampling/inspection/and so forth.

6. Interferences

6.1 Manganese oxides produced as a result of permanganate reduction may interfere with the analysis of permanganate (Method 4500-KMnO₄).

7. Apparatus

7.1 *Reactor Apparatus*—A 250-mL glass vial (borosilicate glass or equivalent) with an oxidant resistant screw cap is recommended. Zero headspace is not required.

7.2 *Apparatus for Drying Samples*—A laboratory oven vented to the outside and capable of delivering sufficient controlled heat to maintain a temperature of 105°C ($\pm 10^\circ\text{C}$).

7.3 *Balance Scales*—A balance having a minimum capacity of 100 g and meeting the requirements of Guide **D4753**, readable (with no estimation) to 0.1 % of the test mass or better.

7.4 *Drying Pan*—Capable of holding a minimum of 600 g of representative soil.

7.5 *Spatula*.

8. Hazards

8.1 When performing laboratory analysis and handling chemicals, safety is a critical component. For this procedure, contact lenses may not be worn. Recommended personal protective equipment (PPE) for this procedure includes rubber gloves, safety glasses or goggles and a lab coat or rubber apron.

8.2 In the event of any chemical spill, refer to the specific MSDS for a proper clean-up procedure. In the case of solid potassium permanganate, sweep the solid into a clean container and dispose according to state and local regulations. A potassium permanganate spill ~~should~~shall be diluted with water to less than 4 % strength, collected and disposed of in an approved manner. Paper or cloth towels ~~should~~shall not be used to clean any permanganate spill.

8.3 Excess permanganate solutions can also be neutralized by sodium thiosulfate, citric acid, or other reducing agents. Solution concentrations must be less than 4 % prior to addition of any reducing agent. Excess heat can be generated and there is a potential for an unwanted reaction.⁴

9. Sampling

9.1 Collect the sample(s) in accordance with Practices **D6051**, **D6169**, **D6282**, or **D6286**. A minimum of 600 grams of soil or aquifer solids is required from each sampling location.

⁴ Additional references on general laboratory safety and procedures can be found at: <http://www.ceet.niu.edu/labs/safety.html>, <http://keats.admin.virginia.edu/lsm/home.html>, and http://www.ehs.iupui.edu/ehs/prog_chemlabsafety.asp.

9.2 Samples can be preserved at 4°C for up to 28 days. However, it is the responsibility of the users of the test method to ensure the maximum holding time for their samples.

TEST METHOD A—48-HOUR PERMANGANATE NATURAL OXIDANT DEMAND

10. Scope

10.1 The test method is appropriate for the determination of the 48-hour permanganate natural oxidant demand of soil and aquifer solids. The test is designed to be used for site screening purposes only. Research has shown that a large percentage of the total permanganate natural oxidant demand can be expressed after a period of 48 hours. Consequently, this test method ~~should~~shall not be used to determine the mass of oxidant required for the treatment of hazardous waste sites being considered for ISCO with permanganate.

11. Summary of Test Method

11.1 The sample and permanganate solutions are analyzed for permanganate after a 48-hour reaction period.

12. Reagents and Materials

12.1 *Purity of Reagents*—Reagent grade chemicals shall be used.

12.2 *Purity of Water*—Reference to water shall be understood to mean reagent grade water that meets the purity specifications of Type I or Type II water according to Specification [D1193](#).

12.3 *Potassium Permanganate Stock Solution (20 000 mg/L)*—Dissolve 20.0 g of potassium permanganate (KMnO₄) in water and dilute to 1 L. Mix the stock solution for a minimum of two hours to make certain the KMnO₄ crystals have completely dissolved.

NOTE 2—In place of potassium permanganate, sodium permanganate can be used. However, since the concentration of a commercially available NaMnO₄ solution may vary, standardization is required. This may be accomplished using ANSI/AWWA B603-03.

13. Procedure

13.1 Dry each sample in the laboratory oven at 105°C (±10°C) for a period of 24 h.

13.2 Homogenize the dried sample by gently mixing by hand. If large stones or rocks are present they ~~should~~shall be removed prior to analysis using a No. 10 U.S. standard mesh sieve (2.00 mm).

13.3 Place 100 mL of 20 000 mg/L KMnO₄ stock solution in a 250 mL glass vial for the blank determination.

13.4 Place 50 g of dried sample in each of three 250 mL glass vials (each experiment is run in triplicate).

13.5 Place 100 mL of 20 000 mg/L KMnO₄ stock solution in each of the three 250 mL glass vials containing the dried sample. Seal each of the vials and invert once to mix the reagents. Store vials at room temperature (20-22°C).

13.6 Sample each vial at 48 hours by removing a 1 mL sample aliquot. A centrifuge or oxidant resistant filter (~~20 μm~~) ~~should~~shall be used to remove manganese oxides from the sample prior to analysis using Method 4500—KMnO₄.

14. Calculations

14.1 PNOD_t values are expressed in units of mass of potassium permanganate per mass of dry aquifer solids using the following equation:

$$PNOD_t = \frac{V([\text{KMnO}_4]_0 - [\text{KMnO}_4]_t)}{m_{\text{soil}}} \quad (1)$$

where:

- $PNOD_t$ = permanganate natural oxidant demand at time = t (g $KMnO_4$ /kg soil or aquifer solids),
 V = volume of the aqueous phase (L),
 $[KMnO_4]_0$ = initial potassium permanganate concentration (g/L),
 $[KMnO_4]_t$ = potassium permanganate concentration (g/L) at time = t, and
 m_{soil} = mass of dry soil or aquifer solids (kg).

15. Precision and Bias

15.1 *Precision*—Test data on precision is not presented due to the nature of the soil and aquifer solids used by this test method. It is either not feasible or too costly at this time to have ten or more laboratories participate in a round-robin testing program. Also, it is either not feasible or too costly to produce multiple specimens that have uniform physical properties. Any variation observed in the data is just as likely to be due to specimen variation as to operator or laboratory testing variation.

15.2 The Subcommittee D18.21 is seeking any data from the users of this test method that might be used to make a limited statement on precision.

15.3 *Bias*—There is no accepted reference value for this test method, therefore, bias cannot be determined.

TEST METHOD B—PERMANGANATE NATURAL OXIDANT DEMAND KINETICS

16. Scope

16.1 The test method is appropriate for the determination of the permanganate natural oxidant demand kinetics for soil and aquifer solids. A curve fitting software package can be used to determine best-fit curves and kinetic parameters for each data set using the independent first-order model described below. The curve fitting software can also be used to predict the $PNOD_{max}$ of the soil or aquifer solids based on the kinetic data.

17. Summary of Test Method

17.1 The sample and permanganate solutions are analyzed for permanganate after reaction periods of 1, 3, 7, 24, 48, 168, and 336 hours.

18. Apparatus

18.1 *Reactor Apparatus*—A 250-mL glass vial (Pyrex or equivalent) with an oxidant resistant screw cap is recommended. Zero headspace is not required.

18.2 *Apparatus for Drying Sample*—A laboratory oven capable of delivering sufficient controlled heat to maintain a temperature of 105°C ($\pm 10^\circ\text{C}$).

18.3 *Balances/Scales*—A balance having a minimum capacity of 100g and meeting the requirements of Guide [D4753](#), readable (with no estimation) to 0.1 % of the test mass or better.

18.4 *Drying Pan*—Capable of holding 600 g of representative soil.

18.5 *Spatula*.

19. Reagents and Materials

19.1 *Purity of Reagents*—Reagent grade chemicals shall be used.

19.2 *Purity of Water*—Reference to water shall be understood to mean reagent grade water that meets the purity specifications of Type I or Type II water according to Specification [D1193](#).