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Standard Test Method for Estimating the Permanganate Natural Oxidant Demand of Soil and Aquifer Solids[1]

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.

ε^1 NOTE—Reapproved with editorial changes in July 2016.

1. Scope*

1.1 This test method covers 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

1.2 This test method is limited by the reagents employed to a permanganate natural oxidant demand (PNOD) of 60 g $KMnO_4$ per kg soil or aquifer solids after a period of 48 hours (Method A) 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 practices and determine the applicability of regulatory limitations prior to use.*

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 in Geotechnical Data
D6051 Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities
D6169 Guide for Selection of Soil and Rock Sampling Devices Used With Drill Rigs for Environmental Investigations
D6282 Guide for Direct Push Soil Sampling for Environmental Site Characterizations
D6286 Guide for Selection of Drilling Methods for Environmental Site Characterization

2.2 *Other Standards:*[3]

Method 4500—$KMnO_4$ 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.

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

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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.

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

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

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

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) 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 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 is used to screen potential sites for in situ chemical oxidation (ISCO) with permanganate (Test Method A) and provide information to aid in the design of remediation systems (Test Method B).

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 to mass transport related issues at the field-scale it is reasonable to assume that the $PNOD_t$ measured using the test method may overestimate the demand exerted during ISCO applications.

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-$KMnO_4$).

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 capable of delivering sufficient controlled heat to maintain a temperature of 105°C (±10°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.

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 be diluted with water to less than 4 % strength, collected and disposed of in an approved manner. Paper or cloth towels should 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.

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 not be used to determine the mass of oxidant

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[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.

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 ($KMnO_4$) in water and dilute to 1 L. Mix the stock solution for a minimum of two hours to make certain the $KMnO_4$ crystals have completely dissolved.

NOTE 2—In place of potassium permanganate, sodium permanganate can be used. However, since the concentration of a commercially available $NaMnO_4$ 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 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 $KMnO_4$ 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 $KMnO_4$ 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 be used to remove manganese oxides from the sample prior to analysis using Method 4500—$KMnO_4$.

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:

$$PNOD_t = \frac{V([KMnO_4]_0 - [KMnO_4]_t)}{m_{soil}} \qquad (1)$$

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),
$[KMnO_4]_1$ = 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 (±10°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.

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.

19.3 *Potassium Permanganate Stock Solution (30 000 mg/L)*—Dissolve 30.0 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L. Mix the stock solution for a minimum of two hours to make certain the $KMnO_4$ crystals have completely dissolved.

19.4 *Potassium Permanganate Stock Solution (20 000 mg/L)*—Dilute 333.3 mL of 30 000 mg/L potassium permanganate stock solution to 500 mL.

19.5 *Potassium Permanganate Stock Solution (10 000 mg/L)*—P – Dilute 166.7 mL of 30 000 mg/L potassium permanganate stock solution to 500 mL.

20. Procedure

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

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

20.3 Place 100 mL of 30 000 mg/L $KMnO_4$ stock solution in a 250 mL glass vial for the blank determination.

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

20.5 Place 100 mL of 30 000 mg/L $KMnO_4$ 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).

20.6 Sample each vial at 48 hours by removing a 1 mL sample aliquot. A centrifuge or oxidant resistant filter (20 µm) should be used to remove manganese oxides from the sample prior to analysis using Method 4500—$KMnO_4$.

20.7 Repeat 20.3 through 20.6 using the 20 000 and 10 000 mg/L $KMnO_4$ stock solutions.

21. Calculations

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

$$PNOD_t = \frac{V([KMnO_4]_0 - [KMnO_4]_t)}{m_{soil}} \tag{2}$$

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),
$[KMnO_4]_1$ = potassium permanganate concentration (g/L) at time = t, and
m_{soil} = mass of dry soil or aquifer solids (kg).

21.2 Permanganate concentration tends to decrease rapidly within the first 48 hours and more slowly thereafter. The independent first-order kinetic rate expression shown in Eq 3, with fast and slow reaction rate constants, can be used to model permanganate decay over time.

$$\frac{d[KMnO_4]}{dt} = -k_f a[KMnO_{4f}] - k_s b[KMnO_{4s}] \tag{3}$$

where:

$[KMnO_{4f}]$ = the concentration of $KMnO_4$ involved in the fast reactions,
$[KMnO_{4s}]$ = the concentration of $KMnO_4$ involved in the slow reactions,
k_f = the first-order reaction rate constant representing the fast reactions (s^{-1}),
k_s = the first-order reaction rate constant representing the slow reactions (s^{-1}),
a = the fraction of $KMnO_4$ involved in the fast reactions, and
b = the fraction of the $KMnO_4$ involved in the slow reactions.

A curve fitting software package should be used to determine best-fit curves and kinetic parameters for each data set using the independent first-order model. The curve fitting software can also be used to predict the $PNOD_{max}$ based on the kinetic data.

22. Precision and Bias

22.1 *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.

22.2 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.

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

23. Keywords

23.1 Permanganate natural oxidant demand; *in situ* chemical oxidation; potassium permanganate

SUMMARY OF CHANGES

In accordance with Committee D18 policy, this section identifies the location of changes to this standard since the last edition (2010) that may impact the use of this standard. (July 15, 2016)

(1) Reapproved with editorial corrections to measurement abbreviations.

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