

Standard Test Method for Determining the Permanganate Soil Oxidant Demand (Screening Phase, PSOD-1)

1. Scope

1.1 This test method is used to screen soil for oxidant demand, when soils are to be treated with sodium or potassium permanganate for soils and groundwater remediation. The oxidant demand test is performed to measure the amount of permanganate reagent that will be consumed by oxidizable species in a soil or a soil and groundwater mixture in the course of treatment to destroy chemical contaminants. This information is used along with contaminant concentrations to determine the permanganate dosing requirements for a treatment zone.

1.2 This test method is a smaller scale bench test used as the first step in evaluating treatment dosage. A second level screening test (e.g PSOD-2 being developed) may be performed on a larger more global scale for more accurate determination of treatment dosage.

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

1.4 All observed and calculated values shall conform to the guidelines for significant digits and rounding established in Practice D 6026.

1.5 This proposed 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 to determine the applicability of regulatory limitations prior to use(section 9 has some considerations for lab safety).

2. Referenced Documents

2.1 *ASTM Standards:*

D 6051-96 Standard Guide for Composting Sampling and Field Subsampling for Environmental Waste Management Activities, 2001.

D 2216-98 Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D 4753, Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing.

D 6286-98 Standard Guide for Selection of Drilling Methods for Environmental Site Characterization

D 6282-98(2005) Standard Guide for Direct Push Soil Sampling for Environmental Site Characterizations

D 6169-98(2005) Standard Guide for Selection of Soil and Rock Sampling Devices Used With Drill Rigs for Environmental Investigations

D 6724-04 Standard Guide for Installation of Direct Push Ground Water Monitoring Wells

D 6001-05 Standard Guide for Direct-Push Water Sampling for Geoenvironmental Investigations

D 6026-01 Standard Practice for Using Significant Digits in Geotechnical Data.

D 3740 - Practice for Minimum Requirements for Agencies Engaged in the Testing of Soil and Rock as Used In Design and Construction.

D 5092 Practice for design and Installation of Ground water Monitoring Wells in Aquifers

2.2 *Other Standards:*

Method 4500- KMnO_4 , Standard Methods for the Examination of Water and Wastewater, 20th Ed. 1998 Prepared and Published Jointly by the American Public Health Association, American Water Works Association, and the Water Environment Federation

3. Terminology

3.1 *Definitions:*

3.1.1 Definitions of Term Specific to This Standard:

3.1.1.1 Permanganate Soil Oxidant Demand (PSOD) – The amount of oxidant consumed by soil or soil and groundwater when exposed to permanganate.

4. Summary of Test Method

4.1 A known amount of permanganate is added to a specific amount of soil and water and allowed to react for a predetermined amount of time. After the reaction period, the residual permanganate is measured and the difference from the initial amount is the PSOD-T1.

5. Significance and Use

5.1 In the area of site remediation, In Situ Chemical Oxidation (ISCO) is becoming a widely used technology. ISCO using permanganate, as well as other technologies such as persulfate, is an emerging groundwater remediation technology for the treatment of common chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE), naphthalene, and pyrene. The key benefit of the ISCO technology is that it provides significantly enhanced destruction of target contaminants (complete mineralization to carbon dioxide and water is the desired endpoint of an ISCO process) within a relatively short period of time (i.e., months) by comparison with

standard pump & treat approaches that require decades to restore groundwater quality. A key benefit of the ISCO approach is that it can accelerate the dissolution of dense nonaqueous phase liquids (DNAPLs) by order(s) of magnitude, which is expected to reduce the time and cost for source remediation by a comparable factor.

5.2 Potassium or sodium permanganate (KMnO_4 , NaMnO_4) is frequently chosen as the oxidant. Unlike other in-situ oxidants, soils with a high carbonate or bicarbonate content will have no impact on permanganate's ability to oxidize TCE/PCE or other compounds. Also, contaminants in the soil will not lead to the exothermic decomposition of the oxidant and release some of the reagents oxidizing power as gaseous oxygen. With proper training, handling permanganate is relatively safe and the use of permanganate as the ISCO oxidant is compatible with post-treatment biological processes.

5.3 In order to properly size and design a full-scale treatment process, all potential reactions that may consume the oxidant should be determined. However, due to the non-homogeneity and unknown components of most soils, the determinations of specific reactions are not possible. A more global test is required that will determine the oxidant demand of all species present in the site soil and associated groundwater.

5.4 Sodium or potassium permanganate will not only oxidize target organic contaminants in groundwater and soil, but will also oxidize natural organic and inorganic material in these matrices. The oxidant demand test is performed to measure the amount of permanganate reagent that will be consumed by oxidizable species in a soil or a soil and groundwater mixture in the course of treatment to destroy chemical contaminants. This information is used along with contaminant concentrations to determine the permanganate dosing requirements for a treatment zone.

5.5 The Permanganate Soil Oxidant Demand Tier 1 (PSOD-T1) is a preliminary screening tool that is rapid and inexpensive to perform. It is intended to provide general information on the amount of permanganate (potassium or sodium) that could be consumed by natural materials (organic and inorganic) and any contaminants of concern (COC) in soils/groundwater at a potential remediation site. Its value is in providing a first estimate of the amount of permanganate that may be needed at a site to assist with determining the economic viability of this technology. This procedure provides Tier 1 screening information. It is not intended to provide specific engineering data required for full-scale implementation. Additional bench scale testing, pilot studies, and/or soil & groundwater samples and analysis may be required prior to any full-scale implementation. This procedure does not address where to obtain representative samples or provide information to design an optimized sampling plan to achieve specific data quality objectives. A more comprehensive study (e.g PSOD-T2 in development) is recommended to obtain the detailed information required for full-scale design and evaluation.

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 D 3740 are generally considered capable of competent and objective testing/sampling/inspection/etc. Users of this standard are cautioned that compliance with Practice D 3740 does not in itself assure reliable results. Reliable results depend on many factors; Practice D 3740 provides a means of evaluating some of those factors.

6. Interferences

6.1 Sampling - Soil and groundwater samples should be preserved for transportation and tested promptly. Soil and groundwater samples exposed to air and drying may undergo physical and chemical changes with time, such as oxidation and reduction reactions.

6.2 Temperature - Tests are to be conducted at room temperature. Exposure to high heat or cold temperatures may alter oxidant demand.

7. Apparatus

7.1 Reactor material: A 250 mL glass vial, bottle, or jar with an oxidant resistant screw cap is recommended. Zero headspace is not required.

7.2 Balances/Scales - A Balance having a minimum capacity of 500g and meeting the requirements of Guide D 4573 readable (with no estimation) to 0.1% of the test mass or better.

7.3 Balances/Scales - A Balance having a minimum capacity of 50g and meeting the requirements of Guide D 4573 readable (with no estimation) to 0.1% of the test mass or better.

8. Reagents and Materials

8.1 Potassium Permanganate Stock Solution - Prepare a stock potassium permanganate dosing solution having a concentration of 30,000 mg/L (3.0 % as KMnO_4) by dissolving 30.6 grams of solid KMnO_4 (minimum 98% assay) into 1 liter of distilled or deionized water. Mix for a minimum of 1 hour to make sure the permanganate has completely dissolved. Check the concentration of the solution using Standard Method 4500 KMnO_4 . Weigh KMnO_4 to the nearest 0.01 gm.

8.2 Sodium Permanganate Stock Solution - Prepare a stock sodium permanganate dosing solution having a concentration of 30,000 mg/L (3.0 % as NaMnO_4) by dissolving 75.0 grams of liquid NaMnO_4 (minimum 40% as NaMnO_4) into 1 liter of distilled or deionized water. Stock solutions of 15,000 and 3,000 mg/L can be made by adding 37.5 and 7.50 grams of liquid NaMnO_4 respectively to 1 liter of distilled or deionized water. Check the concentration using

Standard Method 4500 KMnO_4 and adjust the determined concentration by 0.89 to take into account the difference in the molecular weight of KMnO_4 and NaMnO_4 . Weigh NaMnO_4 to the nearest 0.01 gm.

9. Hazards

9.1 When performing laboratory analysis and handling chemicals, safety is a critical component. For this procedure, contact lenses may not be worn. Personal Protective Equipment (PPE) that must be worn for this procedure includes rubber gloves, safety glasses or goggles and a lab coat or rubber apron.

9.2 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 liquid potassium or sodium 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.

9.3 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.

9.4 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>

http://www.ehs.iupui.edu/ehs/prog_chemlabsafety.asp

10. Sampling, Test Specimens, and Test Units

10.1 Soil Sample - A minimum of 250 grams of soil are required for each PSOD Tier 1 test.

Representative soil samples from the treatment zone are taken using a variety of methods.

Discrete or composite soil samples (D6051) can be taken. Geotechnical type soil samplers are described in D 6169. These samplers often require the use of a drilling rig (D 6286). Direct push soil samplers (D 6282) are often used for ground water quality studies.

10.1.1 For this screening test, sample preservation (e.g. cooling at 4° C) is required during transport and storage.

10.1.2 Analysis sample size: A minimum of 50 grams of soil is recommended for each analysis. For this procedure using three (3) concentrations of permanganate, a minimum of 200 grams will be required. No multiple testing is performed.

10.2 Make up water: If site ground water is available, it should be used. If site groundwater is not provided or available, de-ionized (DI) or distilled water can be substituted and should be noted in the report. It should be noted that the effects of contaminants in the site groundwater usually will not significantly impact the test results. The concentrations of materials in the soil that will react with permanganate is the major contributing factor.

10.2.1 Ground water samples can be obtained from ground water monitoring wells (D-5092) or via Direct Push water sampling (D 6001) or Direct Push Wells (D6724). The water sample should be representative of the treatment zone and should be the same ground water that is present at the soils sampling locations.

11 Calibration and Standardization

11.1 Soil to water ratio: It is recommended that a ratio of 1:2 (w:w wet basis) be used for the test. If the soil is primarily clay this ratio can be increased to 1:4 to improve the contact between the soil and the permanganate. The total amount of water includes both the make up water and the permanganate dosing solution.

11.2 Oxidant dose: It is recommended that three (3) dose levels of permanganate be used for the PSOD-T1. Recommended levels are low (3.0 g/kg), medium (15.0 g/kg), and high (30.0 g/kg) permanganate. Higher levels can and may be required by the specific characteristics of the soil. Note that in the following calculations and examples, potassium permanganate is used as the oxidant.

11.2.1 Oxidant dose calculation - Determine the target dose of permanganate (g KMnO_4 /kg of soil) from Equation 1.

$$\text{Eqn. 1 } [\text{KMnO}_4 \text{ dose (g/Kg)}] = (V \times C \times 0.001) / W_s$$

Where

V = Volume of the permanganate dosing solution added in mL to the soil/water reactor

C = Concentration of the permanganate dosing solution in mg/L

W_s = Weight of the soil in grams. Report both wet and dried weight

11.2.2 Example: The stock permanganate dosing solution has a concentration of 30,000 mg/L (30.g/L as KMnO_4). To a 50 gram soil sample containing 10% moisture, Table 1 illustrates the amount of dosing solution required to reach the target doses. It also shows the actual dose when the moisture content of the soil is taken into account. The total volume of water remains constant at 100 mL (total volume of water includes make-up water and the permanganate dosing solution). Sodium permanganate (NaMnO_4) can also be used in the calculations.

Table 1. Permanganate Dosing Concentrations*

Test Number	Volume (V) of KMnO ₄ Dosing Solution (mL)	Total Volume (V _t) of Make-up Water (mL)	Target KMnO ₄ Dosage (g KMnO ₄ /Kg Soil Dry)	Actual KMnO ₄ Dose with Soil Moisture [KMnO ₄] _{t0} (g KMnO ₄ /Kg Soil)
1	5.0	95.0	3.0	3.3
2	25.0	75.0	15.0	16.7
3	50.0	50.0	30.0	33.3

* In this Example, the stock KMnO₄ dosing solution is 30.0 g/L and the soil moisture is 10%

11.2.3 In this example, the concentration of the KMnO₄ dosing solution is 30.0 g/L. The volume of the dosing solution required to obtain a target soil dose of 3 g/Kg can be found by rearranging Equation 1 to solve for V as shown below:

$$V \text{ (mL)} = \{[\text{KMnO}_4 \text{ dose (g/Kg)} \times W_s \text{ (g)}]\} / \{C \text{ (mg/L)} \times 0.001\}$$

With the desired soil target dose of 3 g/Kg, the volume V of dosing solution can be calculated as:

$$V \text{ (mL)} = \{[3 \text{ (g/Kg)} \times 50 \text{ g}]\} / \{30,000 \text{ (mg/L)} \times 0.001\}$$

$$V \text{ (mL)} = 5$$

11.2.4 To take into account the soil moisture content, the target dose will be modified according to Equation 2 where [KMnO₄]_{t0} is the actual KMnO₄ dose that will be applied to the soil.

$$\text{Eqn 2} \quad [\text{KMnO}_4]_{t0} = [\text{Target Dosage}] / (1 - \% \text{Moisture})$$

In the example above the soil contained 10% moisture so the [KMnO₄]_{t0} dose, based on a target value of 3.0 g/Kg would be:

$$[\text{KMnO}_4]_{t_0} = 3.0 \text{ g/Kg}/(1 - 0.10)$$

$$[\text{KMnO}_4]_{t_0} = 3.30 \text{ g/Kg}$$

12 Conditioning

12.1 Soil Sample drying: The sample should be used “as is” without any drying. The PSOD-T1 will be reported as mass of permanganate to a wet and dry weight of soil basis. The moisture content for each soil sample can be determined using ASTM Method D 2216-98. If this method is not used, detailed information on the drying conditions must be included. The soil specimen can be split from the wet sample by progressive piling and quartering the sample.

12.2 Soil preparation: If there are large stones or rocks, they should be removed prior to testing. The remaining sample should be well mixed and the best representative sample obtained for testing. A number of alternatives for soil homogenization and composting are given (D6051-96).

13 Procedure

13.1 From the bulk soil site sample, obtain four (4) representative 50 g samples. Weigh specimens to the nearest 0.1 gm. Three will be used “as is” for the PSOD-T1, the other will be used to determine the moisture content.

13.2 Place each sample into a 250 mL glass reactor.

13.3 Dose each with the proper amount of permanganate solution and water (see 11.2.1) to achieve an initial target concentration of low (3.0 g/kg), medium (15.0 g/kg), and high (30.0 g/kg).

13.4 Invert each reactor once and allow to remain at room temperature for the remainder of the test.

13.5 Invert the reactors twice a day for 2 days (48 hrs).

13.6 Determine the moisture of the soil (use control sample) using Method D2216.

13.7 Measure the residual permanganate concentration at 48 hours (Standard Method 4500 KMnO_4) and report the residual KMnO_4 concentration in g/Kg. In some cases the resulting solution may be cloudy or contain a suspension of solids. A centrifuge or an oxidant resistant filter can be used to clarify the solution prior to measurement. Note that due to the moisture in the soil, the value obtained needs to be adjusted as it was for the initial permanganate dose. To correct for the soil moisture Eqn 3 is used.

$$\text{Eqn 3} \quad [\text{KMnO}_4]_{t48} = [\text{Measured } [\text{KMnO}_4]_{t48}] / (1 - \% \text{Moisture})$$

13.7.1 In the above example if the measured concentration of KMnO_4 was 1.5 g/Kg at 48 hours for Test 2, the $[\text{KMnO}_4]_{t48}$ would be calculated as:

$$[\text{KMnO}_4]_{t48} = 1.5 \text{ g/Kg} / (1 - 0.10)$$

$$[\text{KMnO}_4]_{t48} = 1.67 \text{ g/Kg}$$

14 Calculation or Interpretation of Results

14.1 Calculate the PSOD-T1 (Eq. 4) value on a wet (as is) and dry weight basis as g KMnO_4 per kg of soil.

The PSOD-T1 is calculated by subtracting the residual concentration obtained at 48 hours ($[\text{KMnO}_4]_{t48}$) from the initial permanganate concentration (dose, = $[\text{KMnO}_4]_{t0}$). Both these values have been corrected for soil moisture.

$$\text{Eqn. 4} \quad \text{PSOD-T1} = [\text{KMnO}_4]_{t_0} - [\text{KMnO}_4]_{t_{48}}$$

For the example above the PSOD-T1 for Test 2 would be:

$$\text{PSOD-T1} = 3.3 \text{ g/Kg} - 1.67 \text{ g/Kg}$$

$$\text{PSOD-T1} = 1.63 \text{ g/Kg}$$

In most cases, the permanganate dosages given above will meet most soil types. However, there may be cases where the dosage is either too high or too low. In the case where the lowest permanganate dose (e.g. 3g/Kg) is too high, lower dosages such as 0.5 or 1.0 g/Kg can be substituted. In the event that the permanganate is consumed at the high dose (30g/Kg) dosages of 60g/Kg and 100g/Kg are suggested. However at those levels, the consumption may be so significant that the use of permanganate may not be viable. Site by site evaluation of these results would be needed.

15 Report The following information will be reported

15.1 PSOD-1 The permanganate oxidant demand determined at 48 hours for each soil sample

15.2 Wet and Dry Mass of soil specimen.

15.3 The moisture of each soil specimen.

15.4 Volume and the type of make-up water used (e.g. site or DI).

15.5 Background information and technology suitability.

16 Precision and Bias

16.1 Precision—Test data on precision is not presented due to the nature of the soil and ground water materials tested 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.

16.1.1 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.

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

17 Keywords

17.1 Potassium permanganate, sodium permanganate, soil oxidant demand