

**Standard Methods for the Examination of Water and Wastewater****4500-KMnO<sub>4</sub> POTASSIUM PERMANGANATE\*#(1)****4500-KMnO<sub>4</sub> A. Introduction****1. Occurrence and Significance**

Potassium permanganate, KMnO<sub>4</sub>, has been widely used in both potable and nonpotable water sources. It has been applied to water supplies to remove taste, odor, color, iron, manganese, and sulfides and to control trihalomethanes (THMs) and zebra mussels. Municipal and industrial waste treatment facilities use potassium permanganate for odor control, toxic pollutant destruction, bio-augmentation, and grease removal.

Potassium permanganate is produced as a dark black-purple crystalline material. It has a solubility in water of 60 g/L at 20°C. The color of potassium permanganate solutions ranges from faint pink (dilute) to deep purple (concentrated). Under normal conditions the solid material is stable. However, as with all oxidizing agents, avoid contact with acids, peroxides, and all combustible organic or readily oxidizable materials.

**2. Sampling and Storage**

If kept dry, solid potassium permanganate may be stored indefinitely. Potassium permanganate solutions, made in oxidant-demand-free water, are stable for long periods of time if kept in an amber bottle out of direct sunlight.<sup>1</sup> For samples obtained from other water sources (those having an oxidant demand), analyze potassium permanganate on site, as soon as possible after sample collection.

**3. Reference**

1. DAY, R.A. & A.L. UNDERWOOD. 1986. Quantitative Analysis, 5th ed. Prentice-Hall, Englewood Cliffs, N.J.

**4500-KMnO<sub>4</sub> B. Spectrophotometric Method****1. General Discussion**

*a. Principle:* This method is a direct determination of aqueous potassium permanganate solutions. The concentration (pink to violet color) is directly proportional to the absorbance as measured at 525 nm. The concentrations are best determined from the light-absorbing characteristics of a filtered sample by means of a spectrophotometer.

*b. Application:* This method is applicable to ground and surface waters.

*c. Interference:* Turbidity and manganese dioxide interfere. Remove by the filtration methods described below. Other color-producing compounds also interfere. Compensate for color by using an untreated sample to zero the spectrophotometer.

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*d. Minimum detectable concentration:* As a guide, use the following light paths for the indicated  $\text{KMnO}_4$  concentrations measured at 525nm. Sample dilution may be required, depending on the initial concentration.

Cell Path Length cm	Range mg $\text{KMnO}_4$ /L	Expected Absorbance for 1-mg/L $\text{KMnO}_4$
		Solution
1	0.5–100	0.016
2.5	0.2–25	0.039
5	0.1–20	0.078

### 2. Apparatus

*a. Photometric equipment:* Use one of the following:

1) *Spectrophotometer*, for use at a wavelength of 525 nm and providing a light path of 1 cm or longer.

2) *Filter photometer*, equipped with a filter having a maximum transmittance at or near 525 nm and providing a light path of 1 cm or longer.

*b. Filtration apparatus.* \*#(2)

*c. Filters:* Use 0.22- $\mu\text{m}$  filters that do not react with  $\text{KMnO}_4$  (or smallest glass fiber filters available).

### 3. Reagents

Use potassium-permanganate-demand-free water (¶ e below) for all reagent preparation and dilutions.

*a. Calcium chloride solution,  $\text{CaCl}_2$ , 1M:* Dissolve 111 g  $\text{CaCl}_2$  in water and dilute to 1 L.

*b. Sulfuric acid,  $\text{H}_2\text{SO}_4$ , 20%:* Add 20 g conc  $\text{H}_2\text{SO}_4$  slowly, with stirring, to 80 mL water. After cooling, adjust final volume to 100 mL.

*c. Sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , primary standard.*

*d. Sodium thiosulfate solution,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , 0.019M:* Dissolve 0.471 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water and dilute to 100 mL.

*e. Potassium-permanganate-demand-free water:* Add one small crystal  $\text{KMnO}_4$  to 1 L distilled or deionized water; let stand. After 1 to 2 d, a residual pink color should be present; if not, discard and obtain better-quality water or increase permanganate added. Redistill in an all-borosilicate-glass apparatus and discard initial 50 mL distillate. Collect distillate fraction that is free of permanganate: a red color with DPD reagent (see Section 4500-Cl.F.2b) indicates presence of permanganate.

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*f. Potassium permanganate standard,  $\text{KMnO}_4$ , 0.006M:* Dissolve 1.000 g  $\text{KMnO}_4$  in water and dilute to 1000 mL. Standardize as follows: Accurately weigh about 0.1 g primary standard grade sodium oxalate and dissolve it in 150 mL water in a 250-mL erlenmeyer flask. Add 20 mL 20%  $\text{H}_2\text{SO}_4$  and heat to 70 to 80°C. Titrate the warm oxalate solution with the potassium permanganate standard until a pink coloration persists (60 s). Calculate the potassium permanganate concentration:

$$\text{mg KMnO}_4/\text{L} = \frac{W \times 1000}{2.1197 \times V}$$

where:

$W$  = weight of sodium oxalate, mg, and  
 $V$  = mL  $\text{KMnO}_4$  titrant.

### 4. Procedure

*a. Calibration of photometric equipment:* Prepare calibration curve by diluting standardized potassium permanganate solution. Make dilutions appropriate for the cell path length and range desired. Plot absorbance ( $y$  axis) versus  $\text{KMnO}_4$  concentration ( $x$  axis). Calculate a best-fit line through the points. Preferably perform a calibration check with a known  $\text{KMnO}_4$  standard before any analysis to ensure that equipment is in proper working order.

*b. Potassium permanganate analysis:* Check zero on spectrophotometer at 525 nm with deionized water. If the water is soft (i.e., <40 mg/L hardness as  $\text{CaCO}_3$ ), add 1 mL  $\text{CaCl}_2$  solution/L sample (111 mg/L as  $\text{CaCl}_2$ ) to aid in removal of any colloidal manganese dioxide and suspended solids. Pass 50 mL sample through a 0.22- $\mu\text{m}$  filter. Rinse spectrophotometer cell with two or three portions of filtrate. Fill cell and check that no air bubbles are present in the solution or on the sides of the cell. Measure absorbance at 525 nm (Reading A). For best results, minimize time between filtration and reading absorbance. To 100 mL sample, add 0.1 mL  $\text{CaCl}_2$  solution. Add 0.1 mL sodium thiosulfate solution per 1 mg/L  $\text{KMnO}_4$  (based on Reading A). Pass through a 0.22- $\mu\text{m}$  filter and measure absorbance (Reading B).

### 5. Calculation

$$\text{Correct absorbance} = A - B$$

where:

$A$  = absorbance of sample, and  
 $B$  = absorbance of blank.

Compare corrected absorbance value obtained with the calibration curve and report the corresponding value as milligrams potassium permanganate per liter.

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### 6. Precision and Bias

Based on the results obtained by eight analysts in a single laboratory, the overall precision (pooled standard deviation) was determined to be 0.035 mg/L for a 1-cm cell. The mean recovery for 12 measurements at 4 initial concentrations was 98%. The method detection level (MDL), as determined using Method 1030, was 0.083 mg  $\text{KMnO}_4$ /L.

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### Endnotes

**1 (Popup - Footnote)**

\* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

**2 (Popup - Footnote)**

\* Millipore or equivalent.