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Sodium Perxenate Permits Rapid Oxidation of Manganese for Easy Spectrophotometric Determination

The spectrophotometric determination of manganese by the distinctive color of the permanganate ion has been used for many years. Two oxidizing agents, periodate and persulphate, have been previously used, but the oxidation time is fairly long, necessitating heating, maintaining at near-boiling temperature, and cooling to room temperatures before spectrophotometric measurement.

Sodium perxenate is a very powerful oxidizing agent and is capable of oxidizing Mn^{+2} to permanganate almost instantaneously in dilute acid solution and without a catalyst. A solution may be prepared by dissolving 200 mg of sodium perxenate in distilled water and diluting to 100 ml. This solution should be prepared daily.

The procedure is accomplished as follows:

Qualitative: Add a few milligrams of solid sodium perxenate to several milliliters of a dilute sulphuric, perchloric, or nitric acid solution of the sample in a test tube, and shake vigorously. The purple color of permanganate will appear immediately if manganese is present. The acidity must be at least 0.1 N to prevent formation of hydrated manganese dioxide.

Quantitative: Dissolve the sample, whose manganese content is to be determined, in nitric acid. Evaporate to remove excess acid, dilute to a convenient volume, and transfer a 10-ml aliquot to a 50-ml volumetric flask. The acidity should be in the range of 0.1 to 2 N. Slowly add 10 ml of the sodium perxenate solution from a pipette, shaking the flask as vigorously as possible during the addition. Dilute to volume, and measure the optical density at 525 mμ against a reference prepared by diluting a 10-ml aliquot of the sample solution to 50 ml. The amount of manganese is calculated from a c/a ratio or calibration curve.

Notes:

1. Ions that are more easily oxidized than Mn^{+2}, such as chloride, iodide, ferrous, or chromous ions, will interfere with the quantitative test, but the addition of a large excess of sodium perxenate will give a positive test provided these ions are not in unduly large amounts.
2. For the determination of manganese in dilute acid solutions containing no other metal ions or interfering anions, perxenate is superior to persulphate or periodate. However, suitability of sodium perxenate as an oxidizing agent should be tested for each application. Much remains to be done in investigating the effects of other metal ions, masking agents, and complexing agents, and in determining the optimum conditions for its use.
3. Sodium perxenate could well find wide use in other difficult oxidations. Other demonstrated oxidations include:
   - Chromous chromium ⟶ dichromate
   - iodate ⟶ periodate
   - $cobalt^{+2}$ ⟶ $cobalt^{+3}$
   - $neptunium^{+4}$ ⟶ $neptunium^{+6}$
   - $plutonium^{+4}$ ⟶ $plutonium^{+6}$
   - $americium^{+4}$ ⟶ $americium^{+6}$
4. Additional details are contained in *Jour. Soc. Anal. Chem. "Analyst"*, vol. 90, no. 1077, December 1965, p. 756–758.
5. Inquiries concerning this innovation may be directed to:

   Office of Industrial Cooperation
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(continued overleaf)

Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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