



Report of Investigation

Reference Material 8040

Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) Reductometric Standard

This Reference Material (RM) was prepared to provide material of uniform, high purity for use as a working standard for oxidation-reduction reactions. The material conforms to the American Chemical Society specification for reagent-grade material, but should not be considered as entirely free from impurities such as moisture, sodium hydrogen oxalate and sodium hydrogen carbonate. A unit of RM 8040 consists of one bottle containing 60 g of crystalline sodium oxalate.

Reference Mass Fraction Value and Uncertainty: The reference value below is based on the titration of sodium oxalate against ceric ammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, which had been standardized with SRM 40h, Sodium Oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, using a modification of the method described by Smith and Fly [1]. The reductometric assay is based on a molecular weight of 133.9985 g/mol [2]. Corrections for the effect of buoyancy of air were applied using the values of 2.34 g/cm³ and 2.61 g/cm³ for the densities of sodium oxalate [3] and ceric ammonium nitrate [1], respectively. The reductometric assay of the sodium oxalate can be used for standardizing potassium permanganate, KMnO_4 , solutions by following the procedure in this report. A NIST reference value is a noncertified value that is the best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty.

The expanded uncertainty of the reference value, U , is calculated as $U = ku_c(y)$, where $u_c(y)$ is the *combined standard uncertainty* calculated according to the ISO/JCGM Guide [4]. The value of $u_c(y)$ is intended to represent the combined effect of the uncertainty components associated with the measurement method and material homogeneity. The value of $u_c(y)$ has been multiplied by a coverage factor of $k = 2$, obtained from the Student's t -distribution with $\nu = \infty$ effective degrees of freedom, to obtain an expanded uncertainty, U , with an approximate 95 % confidence level. The measurand is the value based on the method indicated. The reference value is traceable to the SI derived unit of mass fraction (expresses as percent).

Reductometric Assay (mass fraction): 99.951 % \pm 0.038 %

Expiration of Value Assignment: **RM 8040** is valid, within the measurement uncertainty specified, until **29 October 2020**, provided the RM is handled and stored in accordance with the instructions given in this Report of Investigation (see "Instructions for Storage, Handling and Use"). This report is nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The experimental work in the production of this material was performed by T.W. Vetter of the NIST Chemical Sciences Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

NOTICE TO USERS

Source of Material: The sodium oxalate was obtained from a commercial company. This material conforms to the specifications of the American Chemical Society for sodium oxalate [5].

INSTRUCTIONS FOR STORAGE, HANDLING AND USE

Storage: This RM is stable when stored in its original container, with the cap tightly closed, in a dry environment, and under normal laboratory temperatures.

Drying Instructions: To remove the small amount of surface moisture (about 0.005 %), dry samples for two hours at 105 °C.

Directions for Use in Oxidimetry, Standardization of 0.02 mol/L [0.1 equivalents (eq)/L] Potassium Permanganate, KMnO_4 : Transfer 0.3 g of RM 8040, weighed to the nearest 0.1 mg, to a 600 mL beaker. Add 250 mL of dilute sulfuric acid (1 part concentrated to 20 parts final volume with deionized water) previously boiled for 10 minutes to 15 minutes and cooled to room temperature. Stir until the oxalate has dissolved. Add 39 mL to 40 mL, measured to the nearest 0.02 mL, of 0.02 mol/L KMnO_4 at a rate of 25 mL to 35 mL per minute while stirring slowly. Let stand until the pink color disappears [about 45 seconds; if the pink color should persist because the endpoint has been passed, discard, and begin again, adding less of the KMnO_4 solution (0.3 g of sodium oxalate requires approximately 44.8 mL of 0.02 mol/L KMnO_4)]. Heat to 55 °C to 60 °C and complete the titration by adding KMnO_4 solution until a faint pink color persists for 30 seconds. Add the last 0.5 mL to 1 mL dropwise, with particular care to allow the solution to become decolorized, before the next drop is introduced.

Determine the excess of KMnO_4 required to impart the permanent pink color to the solution. This can be done by matching the color by adding KMnO_4 solution to the same volume of the specially treated dilute sulfuric acid at 55 °C to 60 °C. This correction usually amounts to 0.03 mL to 0.05 mL.

In potentiometric titrations, the correction is negligible if the end point is reached slowly.

For the standardization of more dilute solutions, the same conditions are recommended, except that the initial volume and size of sample are proportionally reduced.

In very accurate work, the correction is best obtained iodometrically [6] as follows: Cool the titrated solution to 25 °C, add 0.5 g of KI, 2 mL of starch solution, and titrate the liberated iodine with 0.02 mol/L (0.02 eq/L) thiosulfate. To obtain the ratio of the thiosulfate to the KMnO_4 solution, add 1 mL of the 0.02 mol/L KMnO_4 to 350 mL of the diluted sulfuric acid (1 part concentrated to 20 parts final volume with deionized water), stir, add 0.5 g KI, and titrate with the thiosulfate solution, adding starch just before the end point is reached.

REFERENCES

- [1] Smith, G.F.; Fly, W.H.; *Anal. Chem.*; Vol. 21, p. 10 (1949).
- [2] IUPAC, *Inorganic Chemistry Division Commission on Atomic Weights and Isotopic Abundances*; *Pure Appl. Chem.*, Vol. 75, p. 6 (2003).
- [3] Lide, D.R.; *CRC Handbook of Chemistry and Physics*; 80th Ed., CRC Press: New York, pp. 4–86 (1999).
- [4] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Oct 2015); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <http://physics.nist.gov/Pubs/guidelines/TN1297/tn1297s.pdf> (accessed Oct 2015).
- [5] *Reagent Chemicals*; 9th Ed., American Chemical Society, Washington, DC (2000).
- [6] Bray, W.C.; *J. Am. Chem. Soc.*; Vol. 32 (1910).

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