DEPARTMENT OF COMMERCE AND LABOR

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 40

SODIUM OXALATE AS A STANDARD IN VOLUMETRIC ANALYSIS

[1st Edition]
Issued October 1, 1912

WASHINGTON
GOVERNMENT PRINTING OFFICE
1912

DEPARTMENT OF COMMERCE AND LABOR

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 40

SODIUM OXALATE AS A STANDARD IN VOLUMETRIC ANALYSIS

[1st Edition]
Issued October 1, 1912

WASHINGTON
GOVERNMENT PRINTING OFFICE
1912

SODIUM OXALATE AS A STANDARD IN VOLUMETRIC ANALYSIS

CONTENTS

I. INTRODUCTION

1. PURPOSE AND SCOPE OF THE CIRCULAR

This circular is not issued for the purpose of publishing any new information or of entering into a critical discussion of volumetric standards, but rather to give a résumé of the work done at this Bureau and elsewhere, which has led to our selection of sodium oxalate as a primary standard.

2. REASONS FOR ISSUING A PRIMARY STANDARD

No argument is needed to show that the nature and purity of the primary standard employed is fundamental to the accuracy of any volumetric process. In adding to our standard analyzed samples a substance of high and known purity to serve as a primary volumetric standard, we hope to remove many of the discrepancies in analysis which arise from the use of unsuitable or impure standards. Examination of a number of samples of sodium oxalate, purchased both in the open market and upon specification, has shown that although some of the samples were of satisfactory purity, others, sometimes from the same makers, were far from pure and in some cases bore misleading lables. After considerable trouble and delay we have succeeded in obtaining a large amount of sodium oxalate of the requisite purity, manufactured especially for us by the Mallinckrodt Chemical Works, St. Louis, Mo., which is issued as standard sample No. 40, in bottles containing 120 and 200 grams, the fees for which are $2 and $3, respectively. With each sample is sent a certificate stating the composition of the material and brief directions for its use.

3. CONSIDERATIONS AFFECTING THE CHOICE OF A STANDARD

The criteria for the selection of a substance which may serve both as a primary and a working standard have been generally recognized, being summed up by McBride[1] as follows:

(a) There must be reasonable ease of preparation and accurate reproducibility.

(b) The purity must de determinable with sufficient accuracy, and the purified materials must be stable under ordinary conditions of the laboratory.

(c) The use of the material in regular work must demand neither complex apparatus nor difficult manipulations.

(d) Such precision must be obtainable when it is used with ordinary care that one, or at the most a very few determinations suffice for the fixing of the value of a standard solution.

(e) The accuracy obtained under ordinary conditions of its use in standardization must be at least as great as that required in the use of the solution to be standardized.

These various factors will be considered with special reference to their application to sodium oxalate, and the reasons which have led to its selection as a primary standard will be outlined.

II. PREPARATION OF SODIUM OXALATE

1. PURIFICATION

In his original paper upon the use of sodium oxalate as a volumetric standard, Sörensen[2] recommended two methods of purification, viz, crystallization from water and precipitation from the aqueous solution by alcohol. The latter process is recommended by him especially for the production of a voluminous finely divided precipitate, which shows less tendency toward decrepitation upon heating when used as an acidimetric standard. On the other hand, the alcohol precipitation has the disadvantage of yielding

---

[1] J. Am. Chem. Soc., **34**, p. 394; 1912. (See also Sörenson, Zs. anal. Chem., **44**, p. 142; 1905.)

[2] Zs. anal. Chem., **36**, p. 639, 1897.

a product which is slightly more hygroscopic than that crystallized from water (p. 7). Sörensen's observation that two crystallizations from water will usually be sufficient to effect the purification has been confirmed at this Bureau. The chief difficulties in the preparation of sodium oxalate on a large scale arise from (a) the sparing solubility of the salt (about 3 parts in 100 of water at 20° and 6 parts in 100 of water at 100°), and (b) the action upon the containing vessels, especially glass, by the sodium oxalate solution.[3] The latter is especially objectionable since it yields a product containing insoluble matter, e. g., calcium oxalate and silica, and excess alkali, usually in the form of sodium carbonate or bicarbonate. The question of suitable methods and apparatus for the purification upon a commercial scale was not investigated by this Bureau, though the poor quality and lack of uniformity of many of the commercial samples show the need of such a study on the part of the manufacturers. The fact that under proper conditions sodium oxalate of high purity can be produced on a large scale at reasonable expense justifies the selection of this material for the purpose under consideration.

2. REPRODUCIBILITY

The experience of this Bureau has shown that samples of pure sodium oxalate prepared from materials known to be impure and derived from various sources agreed within the limits of titration (about 1 part in 2000), both among themselves and with such purchased samples as satisfied the tests for purity described in the following section.

III. TESTING OF SODIUM OXALATE

1. GENERAL PRINCIPLES

Sörensen's conclusion in regard to the testing of standards is[4] as follows: "The purity of a primary volumetric standard should be investigated by means of qualitative tests, the performance and quantitative value of which must be accurately determined for each particular primary volumetric standard. Each newly prepared portion of a primary volumetric standard must, of course, be subjected to tests for purity." In accordance with this view he has devised a number of tests for impurities likely to be present in sodium oxalate.[5] These tests were used in practically the original form, except the test for neutrality, which was modified as the result of experiments conducted at this Bureau.[6] The following is a brief description of the tests employed and the results obtained with the lot of sodium oxalate now issued by the Bureau as a standard:

2. SPECIAL TESTS

(a) *Water.*—Hygroscopic water, determined by heating 10 g to constant weight at 105°, amounted to 0.005 per cent. Occluded water, deter-

---

[3] Blum, J. Am. Chem. Soc., 34, p. 130, 1912.

[4] Zs. anal. Chem., 36, p. 155, 1897.

[5] Zs. anal. Chem., 42, pp. 333–359, and 513–516, 1903. Merck, "Prüfung der Chemischen Reagenzien auf Reinheit," 1905. Krauch-Merck, "Chemical Reagents," 1907.

[6] Blum, J. Am. Chem. Soc., 34, p. 136, 1912.

mined by heating 10 g to constant weight at 240°, amounted to 0.027 per cent. An electric oven was used, since in a gas-heated oven absorption of sulphur compounds from the products of combustion may take place.

(b) *Neutrality.*—Water was freed from carbon dioxide by boiling for some time in a current of air free from carbon dioxide. Two grams of the salt was dissolved in 150 cc of this water in a flask of Durax glass, and 0.2 cc of phenolphthalein (1 per cent solution in alcohol) added. The solution was boiled for 10 minutes and cooled in a current of air free from carbon dioxide. The color of the resulting solution was compared with that of a solution representing 4 per cent transformation of phenolphthalein. This standard was prepared by adding 0.2 cc phenolphthalein to 150 cc of water containing 10 cc of 0.1 *N* sodium hydroxide, and diluting 6 cc of this solution to 100 cc. Each cc of 0.01 *N* acid or alkali required to titrate the test solution to the standard color indicates the presence of approximately 0.08 per cent $NaHCO_3$ or 0.06 per cent of $NaHC_2O_4$. (If 4.0 g of sodium oxalate be used, the standard color should be equivalent to 6 per cent transformation of phenolphthalein and each cc of 0.01 *N* acid or alkali would represent one-half the above percentages of $NaHCO_3$ or $NaHC_2O_4$.) By simple colorimetric comparison it was found possible to estimate the departure from neutrality within 0.01 per cent if the material was nearly pure and 2-g samples were employed. If any pink color is produced under these conditions, the material contains less than 0.02 per cent of $NaHC_2O_4$. Since several tests of this material produced a pink color only slightly lighter than the standard, the presence of less than 0.01 per cent of $NaHC_2O_4$ was indicated.

(c) *Insoluble Matter.*—This salt gave an almost perfectly clear solution, both before and after ignition to carbonate, and contained less than 0.01 per cent of material insoluble in water.

(d) *Sulphate.*—Ten grams of the salt was ignited to carbonate in a platinum crucible, using an alcohol burner to avoid contamination from a gas flame. The residue was dissolved in a small volume of water and made faintly acid with hydrochloric acid. The solution was heated to boiling, 5 cc of *N* barium chloride solution added, and the solution allowed to stand overnight, when a barely perceptible precipitate appeared.

(e) *Chloride.*—Ten grams of the salt was converted to carbonate by ignition in a platinum crucible, the residue was dissolved in water, acidified with nitric acid, and silver nitrate was added. No precipitate appeared on long standing.

(f) *Iron.*—Five grams of the salt converted to carbonate and dissolved in water produced a clear solution, which after acidification with hydrochloric acid gave no test for iron with sulphocyanate solution.

(g) *Potassium.*—Five grams of the salt converted to carbonate, dissolved in water, acidified with acetic acid, and treated with sodium cobaltinitrite solution, gave a very faint precipitate, which appeared only after standing for several hours.

(h) *Organic Impurity.*—One gram of the salt when heated in a recently ignited test tube with 10 cc of concentrated sulphuric acid until the appearance of fumes of sulphur trioxide produced no discoloration in the acid.

Of these tests the only one that is not conclusive is the last, since it is very evidently impossible to make a single test which will detect every foreign organic substance. This test was devised by Sörensen, who found that by means of it he could detect organic impurities present in oxalic acid, when the organic material nonvolatile at 130° amounted to 0.012 per cent, while with 0.042 per cent of such impurity present a decided brown coloration was produced. The purity of our standard sample was confirmed by the agreement of its reducing value, within the experimental limits, with samples prepared from different sources by successive crystallizations and alcohol precipitations.

IV. STABILITY OF SODIUM OXALATE

1. PRESERVATION IN THE DRY STATE

Observations at this Bureau extending over a period of two years have shown that dry sodium oxalate does not undergo any appreciable change in composition or properties when preserved in stoppered bottles, even when exposed to the light.

2. HYGROSCOPIC PROPERTIES

Sörensen[7] found that 10 g of his sodium oxalate absorbed only 0.0009 g (0.009 per cent) of water when exposed for three days to the influence of "air over water." Lunge,[8] however, found that two 5-g samples of sodium oxalate, when placed in a desiccator in a "moist atmosphere," absorbed respectively 0.0188 g and 0.0252 g of water. Neither of these experiments as described are conclusive; since in neither do we know the humidity to which the salt was exposed. Exposure to air saturated with moisture is not a satisfactory test, not alone because material to be used as a standard would seldom be exposed to atmosphere of such high humidity, but also because under such conditions a slight lowering in temperature, such as is likely to occur in a laboratory at night, will cause actual precipitation of moisture upon the walls of the vessel and of course upon the substance being tested. Numerous observations at this Bureau have shown that under such conditions substances which are not intrinsically hygroscopic may take up several per cent of moisture. The following method was therefore employed in some unpublished tests made here by Dr. William Blum. Ten-gram samples of sodium oxalate from various sources were dried at 240°, and were then exposed in a thin layer to air of known humidities, in dessiccators containing sulphuric acid of definite concentration and consequently having known aqueous vapor tension. The tests lasted over a period of two months, the samples being weighed at irregular intervals, in order to detect any erratic absorption. From these tests it was concluded that material crystallized from water (in very fine crystals) showed a maximum absorption of about 0.01 per cent of water in humidities up to 70 per cent; while samples precipitated by alcohol absorbed 0.04 per cent of water

---

[7] Zs. anal. Chem., **42**, p. 349, 1903.

[8] Zs. Angew. Chem., **18**, p. 1527, 1905.

under the same conditions, the greater absorption being due no doubt to its greater surface. No tests were conducted with humidities above 70 per cent, since the atmosphere in a balance room will seldom exceed that humidity. While the results are no doubt dependent upon the exact condition of the material, they indicate the order of magnitude of errors likely to arise from moisture absorbed on occasional exposure of this salt to the atmosphere. However, if the sample has been frequently opened and the presence of moisture is suspected, it may be readily redried by heating to 105°. No appreciable error is likely to arise through absorption of water while a sample for analysis is being weighed on an open watch glass. In general it may be stated that this salt possesses no intrinsic hygroscopic properties, but only such as are common to all substances in a similar state of division.

3. TEMPERATURE OF DECOMPOSITION

Sörensen[9] recommended the temperature of 240°–250° for drying sodium oxalate, after careful tests in which the loss in weight, residual moisture content, and degree of decomposition were determined. He found that after being heated to this temperature for several hours no more than 0.01 per cent H_2O remained in the salt and no decomposition had taken place. These experiments have been confirmed at this Bureau. Thus in one case a sample of sodium oxalate, previously heated to constant weight at 240°–250°, when heated to 300° for 72 hours lost only 0.03 per cent of its weight and contained a corresponding amount of sodium carbonate as determined by titration. A temperature of 240°–250° may therefore be recommended as a safe and necessary temperature for thorough initial drying of this salt.

4. STABILITY OF SOLUTIONS

It has been shown[10] that sodium oxalate solutions do not decompose appreciably upon boiling, but that they readily attack glass. This latter effect is noticeable to a lesser degree when the solutions are preserved in glass at the ordinary temperature, giving rise to a precipitate of calcium oxalate which renders difficult the accurate measurement of an aliquot. For this reason and also because of the possible decomposition of sodium oxalate solution by sunlight, the use of a stock solution for standardizing is not recommended.

V. USE OF SODIUM OXALATE

Sodium oxalate has been suggested as a primary standard both for oxidimetry and acidimetry, which uses will be considered separately, having regard to (a) the methods and apparatus employed, (b) the precision attainable, i. e., the reproducibility of results, and (c) the absolute accuracy of the results obtained.

---

[9] Zs. anal. Chem., 42, p. 349; 1903.

[10] Blum., J. Am. Chem. Soc., 34, p. 129; 1912.

1. OXIDIMETRY

(a) *Conditions for standardization.*—The principle of the standardization of permanganate solutions with sodium oxalate is the titration of the oxalic acid liberated by the action of sulphuric acid upon a weighed amount of the sodium oxalate. No special apparatus is required and the process is very simple. While various persons have used and recommended this salt as an oxidimetric standard since it was first proposed by Sörensen, few of them have investigated the exact conditions to be employed. Schillow [11] and Skrabal [12] have investigated the dynamics of the reaction between permanganate and oxalic acid. Schroeder [13] has studied the effect of conditions upon the titration of oxalic acid with permanganate, and recently McBride [14] has investigated at this Bureau the conditions for the standardization of permanganate with sodium oxalate. The latter author found that over a considerable range of conditions the variations were less than one part in a thousand, but recommended the following conditions as leading to satisfactory results:

"In a 400-cc beaker, dissolve 0.25–0.3 g of sodium oxalate in 200 to 250 cc of hot water (80 to 90°) and add 10 cc of (1:1) sulphuric acid. Titrate at once with 0.1 *N* $KMnO_4$ solution, *stirring the liquid vigorously and continuously.* The permanganate must not be added more rapidly than 10 to 15 cc per minute and the last 0.5 to 1 cc must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The solution should not be below 60° by the time the end point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as stirrring rod is most convenient in these titrations, as the variation of temperature is then easily observed."

(b) The *precision* obtained in the titration under these conditions was limited only by the apparatus employed. By the use of weight burettes agreement of duplicates to one part in two thousand could readily be obtained. The precision with volume burettes may be somewhat less than this, depending upon the accuracy of calibration and the care used in the reading of the volume and in maintaining the temperature of the solution constant. In view of the probable warming of the permanganate solution during the titration, the use of weight burettes is recommended whenever a precision greater than one part in one thousand is desired.

(*c*) The *absolute accuracy* of the results can not be assumed to be greater than one part in a thousand until an exhaustive investigation of the whole subject of volumetric standards is made. In such an investigation the effect of conditions upon the results obtained with various primary standards, e. g., iron, silver, and iodine, must be determined, and the conditions

---

[11] Ber., **36**, p. 2735; 1903.

[12] Zs. Anorg. Chem., **42**, p. 1; 1904.

[13] Zs. Oeffent. Chem., **16**, p. 270; 1910.

[14] J. Am. Chem. Soc., **34**, p. 393; 1912.

which lead to results of theoretical accuracy must be decided upon independently for each case, if possible. Then the results obtained by the various methods may be compared. In numerous such comparisons which have been made discrepancies of the order of one part in a thousand have been observed; but whether these are real or due to errors in the methods used can not be decided with our present knowledge. Thus, in the analysis of a Sibley iron ore (standard sample No. 27) at this Bureau, values found for iron gravimetrically agreed within one part in a thousand with those found volumetrically, using sodium oxalate as the primary standard. Aside from the difficulty in selecting the correct end points, as pointed out by McBride[15], the uncertainties of the atomic weights involved are often of the same magnitude as the discrepancies in question. Examination of the atomic weight tables for 1907 and 1912, respectively, shows that of fifteen of the elements commonly entering into the volumetric processes (viz, *As, Ca, C, Cl, Cu, I, Fe, Pb, Mn, N, P, K, Ag, Na, and S*), seven have had their atomic weights changed during the last five years to the extent of at least one part in a thousand, that of sodium being changed over one part in five hundred. Until the atomic weights of these common elements are more certainly and accurately known any claim to an absolute accuracy greater than one part in a thousand is manifestly unjustified. These same considerations apply with equal force to the use of sodium oxalate in acidimetry.

2. ACIDIMETRY

Since no investigation of the effect of conditions upon the use of sodium oxalate as an acidimetric standard has been made at this Bureau we are not in a position to certify it for that purpose, but will simply refer briefly to the literature upon this subject.[16]

The principle of its use in acidimetry depends upon the conversion to carbonate by ignition and subsequent titration of this carbonate (or rather of the total alkali) by means of the acid to be standardized. Sörensen recommends the following method of operation: The weighed sample of the salt is carefully heated in a covered platinum crucible, using an alcohol burner. Decomposition takes place in from 15 to 30 minutes, after which the crucible is partly uncovered and the heating continued until the carbon is burned off and the sodium carbonate begins to melt. The residue in the crucible after cooling is treated in a covered beaker with water and a slight excess of the acid to be standardized. The solution is heated on a water bath to expel the greater part of the carbonic acid and is then transferred to a flask in which, after addition of phenolphthalein, it is boiled during the passage of a current of air free from carbon dioxide. After cooling the excess of acid is titrated with sodium hydroxide of known ratio to the acid.

In a controversy over the relative merits of sodium oxalate and sodium carbonate as acidimetric standards Lunge has criticized the former on

---

[15] J. Am. Chem. Soc., **34**, p. 415; 1912.

[16] Consult Sörensen, Zs. anal. Chem., **36**, p. 639, 1897; **42**, pp. 333, 512, 1903; **44**, p. 141, 1905; Sörensen and Anderson, Zs. anal. Chem., **44**, p. 156, 1905; **45**, p. 217, 1906; Sebelien, Chem. Ztg., **29**, p. 195, 1904; Lunge, Zs. angew. Chem., **17**, p. 195, 1904; **18**, p. 1520, 1905.

account of the difficulties attending its use, especially the danger of mechanical losses when it is ignited and the complicated operations involved when phenolphthalein is used as the indicator. Sörensen, and Sörensen and Anderson, show that no appreciable errors arise even when the substance is decomposed rapidly, but that an alcohol flame must be used to avoid contamination by sulphur. Lunge, on the other hand, uses a gas flame and an asbestos shield to prevent contamination and mechanical losses. The net result of their controversy was to the effect that sodium oxalate and sodium carbonate yield results differing by no more than about 1 part in 1000, a difference which is negligible for practical purposes. In a recent investigation made here on the use of benzoic acid as an acidimetric standard, Morey[17] found that values obtained with sodium oxalate under approximately the conditions recommended by Sörensen, effecting the decomposition very slowly, however, agreed closely with those obtained with a number of other standards. The subject of acidimetric standards is one which will receive attention from this Bureau as soon as possible.

S. W. STRATTON,
Director.

Approved:
BENJ. S. CABLE,
Acting Secretary.

---

[17] J. Am. Chem. Soc., 34, p. 1027; 1912.

⁂