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# NBS SPECIAL PUBLICATION 260-24

## *Standard Reference Materials:*

## COMPARISON OF REDOX STANDARDS

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NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, *Director*

# *Standard Reference Materials:*

# Comparison of Redox Standards

K. M. Sappenfield, G. Marinenko, J. L. Hague

Institute for Basic Standards
National Bureau of Standards
Washington, D.C. 20234

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Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

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# COMPARISON OF REDOX STANDARDS

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The methods described in this publication are those that have been used at the National Bureau of Standards for the comparison of the current oxidimetric standard reference materials with each other and for the determination of the effective purity of these standard reference materials. The methods, which are modifications of well-established and previously published methods, were selected or designed for their accuracy and dependability. An accurate method was devised for the determination of the effective purity of the arsenic trioxide standard SRM 83c by adding solid iodine and determining the excess iodine photometrically.

Key words: Analytical procedures, arsenic-iodine method, comparison, effective purity, oxidimetric standards.

## I. INTRODUCTION

The National Bureau of Standards issued its first oxidimetric Standard Reference Material, SRM 40, Sodium Oxalate, in 1912. Before the issuance of this standard, analytical chemists had raised objections that the commercially obtainable material was variable and untrustworthy. In 1927 arsenic trioxide standard SRM 83 was added to the list of standard reference materials available from NBS and in 1944 potassium dichromate standard SRM 136 was issued.

The materials for standard reference materials are purchased under special specifications to insure uniformity in size and composition of the crystals so that an entire lot of each standard reference material can be issued under one certificate of analysis. Such materials are specially prepared by the manufacturers for NBS.

This publication gives in detail the methods that have been used at NBS for the certification of the current oxidimetric standard reference materials. Also the methods for the intercomparison of the oxidimetric standard reference materials and for assay by coulometry are described.

The methods described are essentialy the classical ones with modifications to improve the accuracy and precision of the assay of standard reference materials. Weight burets were used instead of volumetric burets, all weighings were corrected to vacuum, and oxygen and carbon dioxide were removed from solutions when they would interfere with the reactants. The detection of the end points was studied and improved and excess reagent, needed for end point detection, was more accurately determined. Also included are the coulometric procedures for assay of arsenic trioxide and potassium dichromate.

All of these standard reference materials have been issued with a provisional certificate but in the near future SRM 40h, Sodium Oxalate; SRM 83c, Arsenic Trioxide; and SRM 136c, Potassium Dichromate, will be assigned a final certificate value. The current certificates are shown in Appendix I.

The final section gives a complete summary of the intercomparisons of the oxidimetric standard reference materials now being issued by the National Bureau of Standards. SRM 136b, Potassium Dichromate, was included in this discussion since its effective purity had been determined by an independent method, coulometry.

# II. SRM 83c, ARSENIC TRIOXIDE

## A. Introduction

Arsenic trioxide solution was first applied in titrimetric analysis by Gay Lussac in 1815 [1]. He used it in chlorimetry with an indigo indicator. In improving the method Penot [2] dissolved the arsenic trioxide in a sodium hydroxide solution instead of hydrochloric acid and used strips of starch iodide paper as the indicator. Mohr [3] made further improvements and it is essentially his procedure which is used at the present time. This procedure entails the use of a standard iodine solution instead of chlorine water as the titrant and the starch solution indicator is added directly to the analate.

In 1918, Chapin [4] proposed the use of arsenic trioxide as a primary standard in iodimetry. In a series of experiments, he showed that arsenic trioxide meets the criteria for a primary standard. The National Bureau of Standards first issued arsenic trioxide as a standard reference material for iodimetry in 1927. Since then three renewals have been issued, SRM 83c, Arsenic Trioxide, being the current standard reference material.

The arsenic trioxide, issued as SRM 83c, was produced commercially to meet special specifications of high homogeneity and purity so that the entire lot could be issued under one certificate of analysis.

## B. Sampling

The material was received from the supplier in thirty glass jars containing 25 pounds each of arsenic trioxide. After the jars were thoroughly mixed by rolling, a representative sample of 30 g was removed from each. Five gram portions from each of the above representative samples were combined into two composite samples. One composite was made from samples obtained from the odd numbered jars and one from the even numbered jars.

### C. Homogeneity

The individual representative samples were compared, using SRM 136b, Potassium Dichromate, to determine whether the material was homogeneous and could be issued under one certificate of analysis.

All 30 individual representative samples were assayed once and eight were repeated. Three of the values were outside 2 σ and were not included in the average. (In this paper any number omitted from the average in any Table is greater than 2 σ and is not used to calculate the σ given in the Table.) After discarding these values, the standard deviation was 0.007 percent which indicates the arsenic trioxide was homogeneous within the limits specified. The results are given in Table 1 and Figure 1.

### D. Impurities

Although arsenic trioxide is not hydroscopic, samples of the material were dried at 105 to 110 °C to eliminate surface moisture. After 1 hour of heating the loss was 0.001 percent and after 24 hours 0.002 percent. All samples used in homogeneity testing and in the determination of effective purity of SRM 83c were dried at 105 to 110 °C for 2 hours.

The arsenic trioxide was analyzed and found to meet the ACS Specifications [5] (Table 2). Spark source mass spectrometric analysis also showed that sodium was present at the 50 ppm level but no other element was detected at a level greater than 1 ppm.

### E. Effective Purity of SRM 83c, Arsenic Trioxide

The effective purity of SRM 83c was determined by comparison with SRM 83b, Arsenic Trioxide; by comparison with SRM 136b and SRM 136c, Potassium Dichromate; by coulometry; and by comparison with purified iodine. The effective purity of SRM 83c for the provisional certification was determined by the comparison with SRM 136b, Potassium Dichromate.

Table 1. Homogeneity and effective purity of SRM 83c, Arsenic Trioxide, compared with SRM 136b, Potassium Dichromate.

| SRM 83b | | SRM 83c | | |
|---|---|---|---|---|
| g $As_2O_3$ per g $K_2Cr_2O_7$[a] | Effective purity(%) | Jar No. | g $As_2O_3$ per g $K_2Cr_2O_7$[a] | Effective purity(%) |
| 1.00856 | 99.997 | 1 | 1.00867 | 99.986 |
| 1.00855 | 99.998 | 2 | 1.00860 | 99.993 |
| 1.00849 | 100.003 | 1[b] | 1.00865 | 99.988 |
| 1.00854 | 99.999 | 3 | 1.00857 | 99.996 |
| 1.00848 | 100.004 | 6 | 1.00863 | 99.990 |
| 1.00847 | 100.005 | 9 | 1.00858 | 99.995 |
| 1.00857 | 99.996 | 12 | 1.00847 | 100.005 |
| 1.00857 | 99.996 | 15 | 1.00859 | 99.994 |
| 1.00857 | 99.996 | 18 | 1.00857 | 99.996 |
| 1.00735[c] | 100.117[c] | 21 | 1.00864 | 99.989 |
| 1.00855 | 99.998 | 24 | 1.00866 | 99.987 |
| 1.00852 | 100.000 | 27 | 1.00857 | 99.996 |
| 1.00856 | 99.997 | 30 | 1.00837 | 100.015 |
| 1.00850 | 100.002 | 2[b] | 1.00511[c] | 100.340[c] |
| 1.00862 | 99.991 | 5 | 1.00840 | 100.012 |
| 1.00846 | 100.006 | 11 | 1.00864 | 99.989 |
| 1.00898[c] | 99.955[c] | 14 | 1.00851 | 100.001 |
| 1.00852 | 100.000 | 17 | 1.00852 | 100.000 |
| | | 20 | 1.01048[c] | 99.807[c] |
| | | 23 | 1.00857 | 99.996 |
| | | 26 | 1.00853 | 100.000 |
| | | 29 | 1.00867 | 99.986 |
| | | 4 | 1.00866 | 99.987 |
| | | 7 | 1.00863 | 99.990 |
| | | 10 | 1.00848 | 100.004 |
| | | 13 | 1.00857 | 99.996 |
| | | 16 | 1.00859 | 99.994 |
| | | 19 | 1.00861 | 99.992 |
| | | 22 | 1.00857 | 99.996 |
| | | 25 | 1.00860 | 99.993 |
| | | 28 | 1.00858 | 99.995 |
| | | 8 | 1.00883[c] | 99.970[c] |
| | | 5[b] | 1.00852 | 100.000 |
| | | 8[b] | 1.00850 | 100.002 |
| | | 10[b] | 1.00861 | 99.992 |
| | | 12[b] | 1.00854 | 99.999 |
| | | 20[b] | 1.00862 | 99.991 |
| | | 30[b] | 1.00852 | 100.000 |
| Ave. 1.00853 | 99.999 | | 1.00857 | 99.995 |
| σ 0.00004 | 0.0044 | | 0.000071 | 0.0070 |

---

[a] Effective purity of SRM 136b, Potassium Dichromate = 99.979%.

[b] Repeat analysis. [c] Omitted from average.

Note: SRM 83c would have an effective purity of 99.992% when compared to SRM 83b (99.996%).

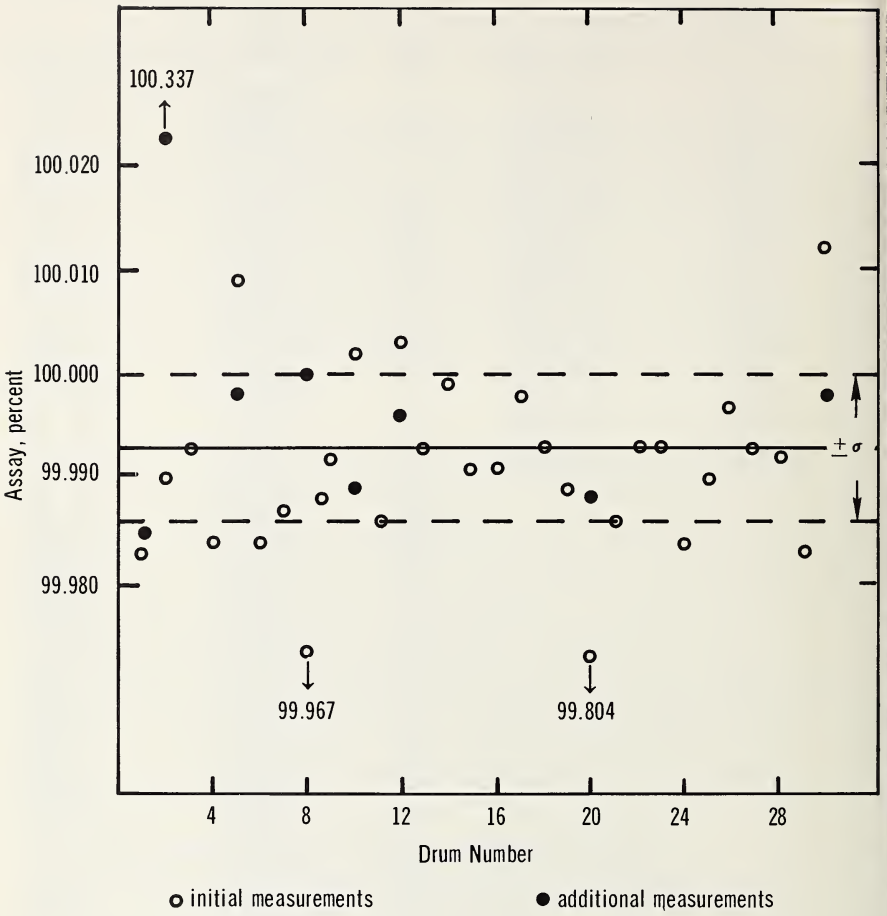

Figure 1. Homogeneity of SRM 83c, Arsenic Trioxide, compared with SRM 136b, Potassium Dichromate.

Table 2. SRM 83c, Arsenic Trioxide, ACS Specifications.

| Test | Requirements not more than (%) | Found (%) |
|---|---|---|
| Residue after ignition | 0.020 | 0.006 |
| Insoluble in HCl | 0.010 | 0.001 |
| Chloride (Cl) | 0.005 | <0.005 |
| Sulfide (S) | To pass test (.001%) | Pass test |
| Antimony (Sb) | 0.001 | 0.0005 |
| Iron (Fe) | 0.0005 | 0.0001 |

### 1. Comparison with SRM 83b, Arsenic Trioxide

a. Comparison through SRM 136b, Potassium Dichromate - SRM 83c was compared to SRM 83b at the same time the effective purity for certification and the homogeneity of the material were determined through SRM 136b, Potassium Dichromate.

In the published methods for the determination of dichromate ion with an arsenite solution, an excess of arsenite solution is added and this excess is determined iodiometrically [6] or with a standard potassium bromate solution [7]. A direct potentiometric titration of the dichromate ion with arsenic trioxide has been described in which manganous sulfate and a catalyst (1 drop 0.025 M KI or $KIO_3$ solutions) are added to the solution at the start of the titration [8].

From the intercomparison of the potassium dichromate standards with ferrous ammonium sulfate it was known that the approach of the endpoint was rapid and easily detected. Using this information a method involving addition of excess potassium dichromate to the arsenic trioxide solution and back-titrating with a ferrous ammonium sulfate solution was developed.

Method:

The arsenic trioxide was dissolved in a sodium carbonate solution and acidified with sulfuric acid. The potassium dichromate, dissolved in a little water, was added and the excess potassium dichromate was titrated potentiometrically with a dilute ferrous ammounium sulfate solution.

Reagents:

(a) Water - All the water used was freshly boiled and cooled distilled water.

(b) Standard ferrous ammonium sulfate solution (8 g/l) - Eight grams of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ were transferred to a liter volumetric flask and 200 ml of $H_2SO_4$ (1+19) were added. When the salts were dissolved, the solution was diluted to the mark with $H_2SO_4$ (1+19) and thoroughly mixed. Standardization-- 0.050 g of potassium dichromate was transferred to a 600 ml beaker and 300 ml of $H_2SO_4$ (1+19), freshly boiled and cooled, were added. After the salt was dissolved, the solution was titrated potentiometrically with the ferrous ammonium sulfate solution. Grams of potassium dichromate equivalent to 1 ml of ferrous ammonium sulfate solution is calculated.

Procedure:

One gram of arsenic trioxide accurately weighed to the nearest 0.00001 g was transferred to a 150 ml beaker and 10 g of solid sodium carbonate were added. Twenty ml of water were added in 5 ml portions and the solution was warmed to dissolve the sample. The solution was transferred to a 750 ml Erlenmeyer flask and 30 ml of sulfuric acid (1+1) were cautiously added in small portions through a short stem funnel inserted in the flask. When the reaction ceased, 1.000 g of potassium dichromate, accurately weighed to the nearest 0.00001 g, was dissolved in 10 ml of water, and was added. The solution was allowed to stand for 10 minutes, then transferred to a 600 ml beaker and diluted to 300 ml with water.

The solution was cooled in ice water and the excess potassium dichromate was titrated potentiometrically with the standard solution of ferrous ammonium sulfate. All weights were corrected to vacuum.

Effective purity of $As_2O_3$, in percent $= \frac{A-BC}{C} \times \frac{EF}{G}$

where

A = g of potassium dichromate added,

B = ml of standard ferrous ammonium sulfate solution,

C = g of potassium dichromate equivalent to 1 ml ferrous ammonium sulfate solution,

D = g of arsenic trioxide taken,

E = effective purity of potassium dichromate in percent,

F = equivalent weight $As_2O_3$, and

G = equivalent weight $K_2Cr_2O_7$.

The effective purity of SRM 83c is 0.004 percent lower than the effective purity of SRM 83b when compared through SRM 136b (Table 1). Since SRM 83b was certified for 100.00 percent (99.996) the effective purity of SRM 83c would be 99.99 percent (99.992).

b. Comparison through Purified Iodine - The arsenic trioxide standards were also compared during the determination of the effective purity of SRM 83c by comparison with purified iodine. A procedure involved the addition of solid iodine and the excess iodine beyond the end point of the titration was determined photometrically.

The method for titration of arsenic trioxide with iodine was developed by Mohr [3] in 1859 and today it is used essentially in its original form. The arsenic trioxide is dissolved in a sodium hydroxide solution and the starch indicator solution is added directly to the arsenic trioxide solution followed by the iodine titrant. In order to improve the precision and accuracy of the method by reducing possible errors such as impurities in iodine, end point detection, loss of material, use of solid iodine, etc., the method was investigated.

(1) Impurities in iodine: The impurities in the iodine were removed by purifying the iodine according to Treadwell and Hall [9]. Commercial resublimed iodine was again resublimed from a potassium iodide-ignited calcium oxide mixture.

The iodine was then resublimed two more times without the use of potassium iodide and the calcium oxide. The iodine was crushed in an agate mortar, transferred to a glass stoppered bottle and stored over magnesium perchlorate in an ungreased desiccator.

(2) Detection of end point: A slight excess of iodine is needed to detect the end point of the titration regardless of whether the solution is titrated potentiometrically or an indicator is used. The excess iodine is usually determined by adding the iodine solution to a solution containing all reagents with the exception of arsenic trioxide either to an indicator or the potentiometric end point. All titrations are corrected for the amount of iodine used to titrate the blank solutions. Anhorn and Hunt [10] have shown that the iodine color is sensitive enough to detect the end point in titrations with 0.02 N or stronger iodine solutions if the solution being titrated is clear. Using this information the iodine solution itself is the indicator and the excess iodine is determined by photometry. In this procedure, an accurate correction can be applied to each determination because the excess iodine is determined for each titration.

(3) Use of solid iodine: In the preparation of the standard iodine solution for the assay of arsenic trioxide, the iodine was added to a potassium iodide solution in a storage flask and after the iodine dissolved, the solution was diluted to the desired volume [11,12,13,14,15]. Weight burets are used to increase the precision and accuracy of the delivery of the standard iodine solution by weight instead of volume. During this investigation it was observed that iodine, after standing in a glass stoppered bottle, did not lose weight. Using this information a weighed amount of solid iodine, less than the calculated equivalent of the arsenic trioxide, was added to the reaction flask containing the arsenic trioxide solution and the titration completed with a few ml of 0.05 N iodine solution. The use of solid iodine

allows one to determine the iodine equivalent of arsenic trioxide more accurately.

(4) Loss of material: The above procedure gave good results but when the sodium carbonate solution of arsenic trioxide was neutralized, the escaping carbon dioxide caused a fine mist above the solution and a small amount of arsenic trioxide could be carried along with the carbon dioxide and might be lost. The iodine-arsenic trioxide reaction proceeds quantitatively up to a pH of 9.2 [16, p. 218], and when the neutralization step was omitted the pH of the solution, even after the titration, was below 9.2, therefore the neutralization of the sodium carbonate was deleted.

### Method:

After the arsenic trioxide was dissolved in a sodium carbonate solution, a sodium bicarbonate solution and potassium iodide salt were added. After the potassium iodide was dissolved, a weighed amount of iodine, less than the calculated equivalent of the arsenic trioxide, in a glass stoppered weighing bottle was added. When the iodine had dissolved and reacted with the arsenic trioxide the remaining arsenic trioxide was titrated with a 0.05 N iodine solution previously standardized against arsenic trioxide. The titration was stopped when the yellow color of iodine appeared and the excess iodine determined by photometry. For the preparation of the calibration curve see Appendix II. The weight of arsenic trioxide was corrected for the arsenic trioxide equivalent of the iodine solution used in the titration and the weight of iodine was corrected for the photometrically determined excess iodine.

### Reagents:

(a) Iodine - Resublimed iodine (ACS grade) was additionally resublimed thrice [9].

(b) Water - All the water used was freshly boiled and cooled distilled water.

(c) Sodium bicarbonate solution (60 g/l) - Sixty grams of $NaHCO_3$ were dissolved in 900 ml of water and diluted to one liter.

(d) Standard iodine solution (0.05 N) - To a liter volumetric flask 200 ml of water and 100 g of potassium iodide were added. When the potassium iodide was dissolved 6.3 g of iodine were added and after the iodine dissolved the solution was diluted to the mark with water. Standardization of iodine solution--10 g of sodium carbonate were transferred to a 600 ml beaker and 25 ml of water were added. When the salt was dissolved, 100 ml of sodium bicarbonate solution were added and the solution diluted to 200 ml with water. The solution was cooled in ice water and 25 ml of the standard arsenic trioxide solution (e) and 10 g of potassium iodide were added. When the potassium iodide was dissolved the solution was titrated with the iodine solution to the yellow color of iodine. The solution was diluted to 300 ml with water and the excess iodine determined photometrically.

$$\text{Grams of } As_2O_3 \text{ equivalent to 1 ml of } I_2 \text{ solution} = \frac{AB}{C-D}$$

where

A = ml of arsenic trioxide solution,
B = g of arsenic trioxide per ml arsenic trioxide solution,
C = ml iodine solution used, and
D = excess ml iodine solution determined photometrically.

(e) Standard arsenic trioxide solution (1 mg/ml) - One gram of the arsenic trioxide SRM weighed to the nearest 0.00001 g was transferred to a 500 ml Erlenmeyer flask and 10 g of sodium carbonate were added and the salts mixed. Twenty-five ml of water were added in 5 ml portions and the solution was warmed to dissolve the salts. The solution was made just acid by adding sulfuric acid (1+1) through a short stem funnel inserted in the flask. The solution was transferred to a liter volumetric flask and diluted to the mark with water.

Procedure:

A 1 g sample of arsenic trioxide accurately weighed to the nearest 0.00001 g was transferred to a 500 ml glass stoppered Erlenmeyer flask, 10 g of sodium carbonate were added and the contents of the flask was thoroughly mixed. A short stem funnel was inserted into the flask and 25 ml of water were added in 5 ml portions. The flask was warmed to dissolve the arsenic trioxide and sodium carbonate. When the salts were dissolved the solution was cooled in ice water, 100 ml of the sodium bicarbonate solution were added and the solution was thoroughly mixed. Ten grams of potassium iodide were added and the flask was swirled to dissolve the salt. The funnel was rinsed and removed from the ice bath.

A small weighing bottle containing 2.5 g solid iodine weighed to the nearest 0.00001 g was added to the solution and the flask stoppered. When the iodine was dissolved, the excess arsenic trioxide was titrated with the standard iodine solution to the yellow color of iodine.

The solution was diluted to 300 ml with water and the excess iodine was determined photometrically at 375 nm using water as reference for zero absorbance.

Effective purity of $As_2O_3$, in percent $= \frac{A-B}{C-D} \times 100 \frac{E}{F}$

where

A = g of solid iodine added,

B = g of excess iodine used to detect the end point and determined photometrically,

C = g of arsenic trioxide,

D = g of excess arsenic trioxide found by the iodine titration,

E = equivalent weight $As_2O_3$, and

F = equivalent weight of $I_2$.

Table 3. Effective purity of SRM's 83b and 83c, Arsenic Trioxide, compared with purified iodine.

| | SRM 83b | | | SRM 83c | |
|---|---|---|---|---|---|
| Date | g $I_2$ per g $As_2O_3$ | Effective purity (%) | Composite No. | g $I_2$ per g $As_2O_3$ | Effective purity (%) |
| 7/12/62 | 2.56565 | 99.9950 | I | 2.56527 | 99.9802 |
| | | | II | 2.56537 | 99.9841 |
| 7/17/62 | 2.56578 | 100.0000 | I | 2.56529 | 99.9809 |
| | 2.56548 | 99.9883 | II | 2.56525 | 99.9794 |
| 7/19/62 | 2.56551 | 99.9895 | I | 2.56506 | 99.9720 |
| | | | II | 2.56538 | 99.9845 |
| 7/23/62 | 2.56569 | 99.9965 | I | 2.56582 | 100.0016 |
| | 2.56569 | 99.9965 | II | 2.56546 | 99.9876 |
| 7/25/62 | 2.56567 | 99.9957 | I | 2.56581 | 100.0012 |
| | 2.56567 | 99.9957 | II | 2.56559 | 99.9926 |
| 7/27/62 | 2.56557 | 99.9918 | I | 2.56418[a] | 99.9377[a] |
| | 2.56552 | 99.9899 | II | 2.56529 | 99.9810 |
| 7/31/62 | 2.56567 | 99.9957 | I | 2.56575 | 99.9989 |
| | 2.56562 | 99.9938 | II | 2.56545 | 99.9872 |
| | | | I | 2.56553 | 99.9903 |
| 8/2/62 | 2.56556 | 99.9914 | I | 2.56538 | 99.9845 |
| | 2.56540 | 99.9852 | II | 2.56553 | 99.9903 |
| | | | I | 2.56573 | 99.9981 |
| Average | 2.56561 | 99.9932 | | 2.56547 | 99.9879 |
| σ | 0.00011 | 0.0040 | | 0.00022 | 0.0085 |

---

[a] Omitted from average.

Note: SRM 83c would have an effective purity of 99.991% when compared to SRM 83b (99.996%).

The effective purity of SRM 83c is 0.005 percent lower than the effective purity of SRM 83b when compared through purified iodine (Table 3). Since SRM 83b was certified as 100.00 percent (99.996), the effective purity of SRM 83c would be 99.99 percent (99.991).

### 2. Comparison with SRM's 136b and 136c, Potassium Dichromate

The provisional certification of the effective purity of SRM 83c, Arsenic Trioxide, was based on a direct comparison of the composite samples with SRM 136b, Potassium Dichromate. Since the homogeneity of the arsenic trioxide was determined by comparison with SRM 136b, a supplementary determination was available for consideration in the certification of the effective purity.

The arsenic trioxide was dissolved in a sodium carbonate solution, acidified with sulfuric acid, and an excess of potassium dichromate added. After the oxidation of the arsenic trioxide, the excess potassium dichromate was titrated potentiometrically with a standard ferrous ammonium sulfate solution. The details of the method followed are given in Section II.E.1.a.

The effective purity of SRM 83c was 99.995 percent with a standard deviation of 0.007 percent when compared to SRM 136b (99.979%). This value is the combined results of Table 1, page 5 and the comparison to the composite sample of SRM 83c, Arsenic Trioxide, Table 4.

Table 4. Effective purity of SRM 83c, Arsenic Trioxide, based on composites compared with SRM 136b, Potassium Dichromate.

| Composite No. | g $As_2O_3$ per g $K_2Cr_2O_7$[a] | Effective purity (%) |
|---|---|---|
| I | 1.00853 | 100.000 |
| II | 1.00863 | 99.990 |
| II | 1.00802[b] | 100.050[b] |
| I | 1.00874 | 99.979 |
| I | 1.00848 | 100.004 |
| II | 1.00860 | 99.993 |
| II | 1.00847 | 100.005 |
| I | 1.00849 | 100.003 |
| Average | 1.00856 | 99.996 |
| σ | 0.00010 | 0.010 |

---

[a] Effective purity of SRM 136b, Potassium Dichromate = 99.979%.

[b] Omitted from average.

SRM 83c was also compared to the composites of SRM 136c for the certification of SRM 136c. Using the effective purity value of 99.983 percent for SRM 136c (obtained by coulometry) SRM 83c would have an effective purity of 99.986 percent with a standard deviation of 0.006 percent. The results are given in Table 5.

Table 5. Effective purity of SRM 83c, Arsenic Trioxide, compared to SRM 136c, Potassium Dichromate.

| SRM 136c Composite No. | g $K_2Cr_2O_7$[a] per g $As_2O_3$ | Effective purity (%) |
|---|---|---|
| I | 0.991294 | 99.979 |
| II | 0.991358 | 99.985 |
| III | 0.991259 | 99.975 |
| IV | 0.991278 | 99.977 |
| IV | 0.991427 | 99.992 |
| III | 0.991412 | 99.990 |
| II | 0.991375 | 99.987 |
| I | 0.991447 | 99.994 |
| I | 0.991384 | 99.988 |
| II | 0.991397 | 99.989 |
| III | 0.991340 | 99.983 |
| IV | 0.991424 | 99.992 |
| Average | 0.991366 | 99.986 |
| $\sigma$ | 0.000062 | 0.006 |

---

[a] Effective purity of SRM 136c, Potassium Dichromate = 99.983%.

### 3. Coulometry

The basis for precise iodimetry was established by the work of Edward Washburn who treated the subject in detail [12] in 1908.

For coulometry it has been shown that for current densities between 1.25 and 3 mA/cm$^2$, iodine can be generated with 100 percent current efficiency to better than 1 part in 10$^6$ [17].

On the basis of these measurements the coulometric titration of SRM 83c with electrogenerated iodine was preformed utilizing 0.1 M KI solutions and a current of 100 mA with an anode area of 40 cm$^2$, corresponding to a current density of 2.5 mA/cm$^2$ - i.e., conditions under which the efficiency of the generation of iodine should be 99.9999+ percent.

The supporting electrolyte, selected for these titrations, was 0.05 M with respect to $KH_2PO_4$, 0.05 M with respect to $Na_2HPO_4$, and 0.1 M in KI.

The end point indicator system was similar to the one used by Ramsey, Farrington and Swift [18]. It consisted of two 1 $cm^2$ platinum electrodes, arranged in horizontal planes, facing each other and approximately 0.5 cm apart, with 150 mV impressed between them. A recording polarograph was used as the source for applying the potential across the two indicator electrodes as well as for recording the indicator current.

Although at the end point, the generating current was passed increment-wise, recording of the indicator current helped in deciding when equilibrium was reached.

The high accuracy timing and coulometric current measuring circuit is shown in Figure 2. After an initial warm up period of approximately 1 hour, its output seldom changed by more than 0.001 percent in the course of any one day. The accurate value of the current was determined by comparison of the IR drop

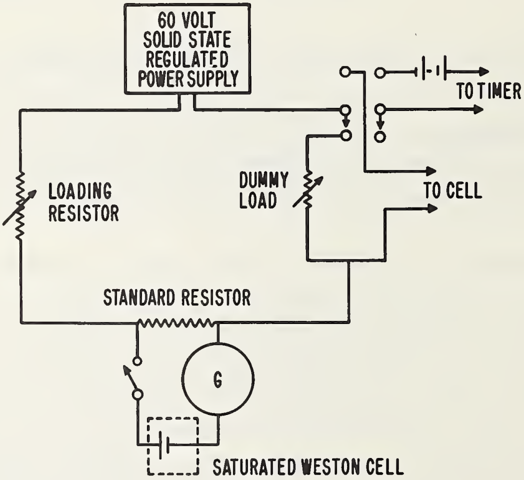

Figure 2. High accuracy constant-current and timing circuit.

across a standard resistor with the voltage of a saturated Weston cell. The error signal was displayed as the deflection of a galvanometer. The comparison of these quantities was made continually throughout the whole titration and the output of the power supply was adjusted whenever the difference between the voltage of the Weston cell and the IR drop across the standard resistor differed by more than 0.0003 percent.

It was thought desirable to investigate experimentally the changes which one might anticipate in arsenite-iodine reaction stoichiometry as a function of pH. This point was treated by Washburn in detail [12]. In contrast to his work, we felt that, for the purpose of titration, 5 minutes time for equilibration of the system after addition of each increment of reagent was ample and any longer period of waiting would be impractical.

The dependence of the assay of arsenic trioxide on pH is shown in Figure 3. For the purpose of this comparison, the

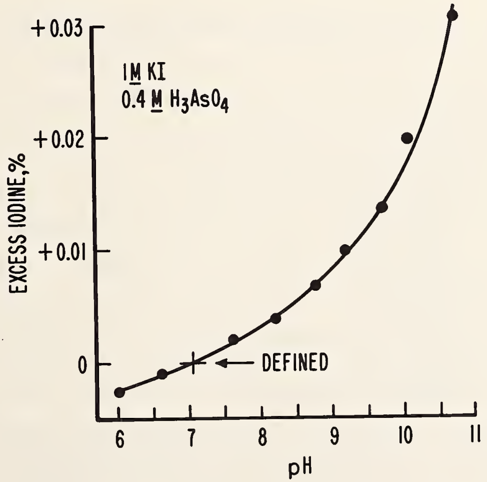

Figure 3. Effect of pH on the stoichiometry of arsenite-iodine reaction.

assay at pH 7 was defined as 100 percent. It can be seen that between pH 6 and 8 the difference in the amount of required iodine to bring the system to the end point is on the order of 0.004 percent. The error rapidly increases on the alkaline side, and at pH 9 it is of the order of 0.01 percent. On the acid side, on the other hand, below pH 6 the rate of the reaction becomes extremely slow and with the 5-minute waiting period no meaningful data could be obtained. Therefore it must be concluded that for titrations where accuracy higher than 0.01 percent is desired, pH must be maintained below a value of 9 and above a value of 6.

An assessment of all known sources of error accounts for approximately half of the experimental titration uncertainty or approximately 15 ppm. It must be assumed that the other half of the uncertainty results from indeterminate sources of error such as oxidation of trivalent arsenic by the residual oxygen, loss in transfer, sample inhomogeneity, etc.

Procedure:

The arsenic trioxide samples were weighed into 125 ml Erlenmeyer flasks, dissolved in 10 ml of 10% NaOH solution, deaerated by purging with $N_2$, delivered into the cell containing 100 ml of deaerated 0.1M $KH_2PO_4$-0.1M KI solution, and titrated with iodine, electrogenerated in situ at 101 mA. When the precalculated amount of iodine was generated (equal to 99.9 percent of the theoretically required amount), the passage of the coulometric current was stopped. The intermediate compartments of the coulometric cell were emptied and rinsed back and forth by applying vacuum or nitrogen pressure as required. Finally, only a minute amount of solution was left in the intermediate compartments to enable the passage of a small current. The pH of the solution was measured and adjusted to 7.00 by the addition of deaerated NaOH or $H_3PO_4$ as required. Then generation of iodine was resumed increment-wise, using a current of 6.43 mA and indicator current readings were taken after the passage of each increment of charge.

The indicator current remained constant and close to zero before the end point. After the end point, the indicator cathode was depolarized by the excess iodine and the indicator current was a linear function of the excess iodine with a slope of approximately 150 μA/μeq of iodine. The intersection of this function with the residual current, recorded prior to delivery of arsenious acid, was taken as the equivalence point.

A set of results for titration of 0.5 gram samples of SRM 83c, Arsenic Trioxide, is shown in Table 6. It can be seen that in these titrations, a precision of 32 ppm has been obtained. On the basis of these titrations and after making adjustments for changes in NBS volt and the value of the faraday [19], an assay value of 99.9873 percent is assigned to SRM 83c, Arsenic Trioxide, with a standard deviation of 0.0032 percent.

Table 6. Effective purity of SRM 83c, Arsenic Trioxide, by coulometry.

| Titration No. | Assay, % |
|---|---|
| 1 | 99.9859 |
| 2 | 99.9834 |
| 3 | 99.9844 |
| 4 | 99.9896 |
| 5 | 99.9830 |
| 6 | 99.9904 |
| Average | 99.9861[a] |
| σ | 0.0032 |

---

[a] After applying the corrections for the changes in the values of the ampere and the faraday [19], the average assay becomes 99.9873 percent.

### 4. Comparison with Purified Iodine

SRM 83c, Arsenic Trioxide, was assayed by a direct titration with purified iodine. After the arsenic trioxide was dissolved in a sodium carbonate solution, a sodium bicarbonate solution and potassium iodide were added. When the potassium iodide dissolved, a weighed amount of iodine, less than the calculated equivalent of the arsenic trioxide, in a glass stoppered weighing bottle was added. After the iodine had dissolved and reacted with the arsenic trioxide, the excess arsenic trioxide was titrated with a 0.05 N iodine solution previously standardized with arsenic trioxide to the appearance of the yellow color of iodine. The excess iodine was then determined by photometry. The weight of arsenic trioxide was corrected for the arsenic trioxide equivalent of the iodine solution used in the titration and the weight of iodine was corrected for the photometrically determined excess iodine. The details of the method are given in Section II.E.1.b.

The effective purity of SRM 83c based on titrations with purified iodine is 99.9879 percent with a standard deviation of 0.0085 percent. The results are given in Table 3 (page 14).

### 5. Summary

In chemical characterization of materials, as in any other area of metrology, one is compelled at some point to either make an absolute determination of the measured parameter or define a "standard state", to which all other measurements are compared.

To date two absolute methods are available for the determination of trivalent arsenic content in arsenic trioxide: titration with high purity iodine and coulometric titration of arsenic (+3) with electrogenerated iodine. These two methods can serve conveniently as the starting point for correlation of the measurements of a chemical property to the fundamental system of units. In the case of the former method the measurements involve only the mass of iodine required to react with a given mass of arsenic trioxide. The accurate knowledge of the molecular weight of arsenic trioxide and the atomic weight of iodine is mandatory in order to arrive at an accurate value of the assay (where the assay represents the molar ratio of moles of arsenic trioxide found to the moles of arsenic trioxide calculated and expressed in percent). Thus this method involves only accurate mass measurements and as such it is absolute.

Coulometry is also an absolute method. It entails the measurement of charge needed to convert the constituent in question from some initial state to a final state (i.e. $As^{+3} \rightarrow As^{+5} + 2e$). Three measurement parameters are involved here; mass, electrical current and time.

Both methods were employed independently for the determination of the assay of SRM 83c, Arsenic Trioxide, and these determinations consistitute the basis for the final certification of this material. The coulometric assay is 99.9873 percent ($\sigma$=0.0032%) and the assay by comparison with iodine is 99.9879 percent ($\sigma$=0.0085%). The best value for the effective purity of SRM 83c is 99.9876 percent. The results are given in Table 7.

The assay values obtained by other comparison which can not be considered absolute are given in the lower part of the table. Since SRM 83b was certified, the method for comparing arsenic trioxide to iodine has been improved to give more precise and accurate results. SRM 136b, Potassium Dichromate, was certified on the basis of comparisons to SRM 136 and SRM 136a. The comparison of SRM 136c, Potassium Dichromate, to SRM 83c was used for the certification of SRM 136c, therefore this comparison was not used for the certification of SRM 83c. A summary of the effective purity of SRM 83c, Arsenic Trioxide, is given in Table 7.

Table 7. Effective purity of SRM 83c, Arsenic Trioxide.

| | Effective purity (%) | Standard deviation (σ) |
|---|---|---|
| | For Certification | |
| Coulometry | 99.9873 | 0.0032 |
| Purified Iodine | 99.9879 | 0.0085 |
| Average | 99.9876 | |
| | Comparison with other SRM's | |
| SRM 83b (thru $K_2Cr_2O_7$) | 99.992 | 0.007 |
| SRM 83b (thru $I_2$) | 99.991 | 0.009 |
| SRM 136b | 99.995 | 0.007 |
| SRM 136c | 99.986 | 0.006 |

## III. SRM 136c, POTASSIUM DICHROMATE

### A. Introduction

The use of potassium dichromate as a titrant was first proposed by Penny in 1850 [20] for the determination of iron in ores. He standardized the potassium dichromate against harpsichord wire and used potassium ferricyanide as an external indicator. Sarver and Kolthoff [21] proposed the use of diphenylaminesulfonic acid as an internal indicator. Since the presence of tungstates does not interfere, this indicator is generally used today. An advantage is that the barium and sodium salt of the indicator are soluble in water.

The Bureau issued the first SRM 136, Potassium Dichromate, in 1944 and has had three renewals since then. The present potassium dichromate standard, SRM 136c, was issued in March 1970.

The material for the potassium dichromate standards was purchased under special specifications to insure high homogeneity and purity so that the entire lot could be issued under one certificate of analysis.

### B. Sampling

Five hundred pounds of potassium dichromate in 20 fiberboard drums, lined with polyethylene bags, of 25 lbs each were received as the renewal for SRM 136b. After thorough mixing by rolling, a 30 g sample was removed from each drum by taking equal portions of material from the top, middle and bottom while the drum was lying on its side. After the material was tested for homogeneity, four composite samples were prepared by combining 10 g of material from the five representative samples with the highest assay values, the five representative samples with the lowest assay values, the five representative samples with the high medium assay values and the five with the low medium assay values. Composite I was composed of drums 4, 5, 8, 9 and 18 (high); Composite II - drums 1, 2, 10, 11 and 17 (high medium); Composite III - drums 3, 6, 12, 14 and 15 (low medium); and Composite IV - drums 7, 13, 16, 19 and 20 (low).

## C. Homogeneity

The representative samples of each jar were compared through ferrous ammonium sulfate to determine if these lots were homogeneous and could be issued under one certificate of analysis.

In the testing of SRM 136c each of the representative samples was run. Since those run on the first day of testing were higher than on the other days, they were repeated along with two outliers. The standard deviation was 0.0046 percent which indicates the potassium dichromate was homogeneous within the limits specified. The results are given in Figure 4 and Table 8. In the determination of the effective purity by coulometry each of the representative samples was run and the homogeneity of the material was confirmed. The standard deviation of the coulometric results was 0.0028 percent. For the results see Figure 5 and Table 12 (page 47).

## D. Impurities

The material for SRM 136c conforms with the ACS specifications for analytical reagent grade material [5]. Emission spectrometry reported only traces of impurities. Spark source mass spectrometry reported vanadium present at 8 ppm in SRM 136c and detected no other impurity at a level greater than 1 ppm.

Potassium dichromate is not hygroscopic but water can be occluded in the crystals. SRM 136c was heated at 260 °C and the water occluded in the crystals was found to be 0.018 percent.

## E. Effective Purity of SRM 136c, Potassium Dichromate

The effective purity of SRM 136c was determined by comparing it with SRM 136b, Potassium Dichromate, by comparing it with SRM 83c, Arsenic Trioxide, and by coulometry.

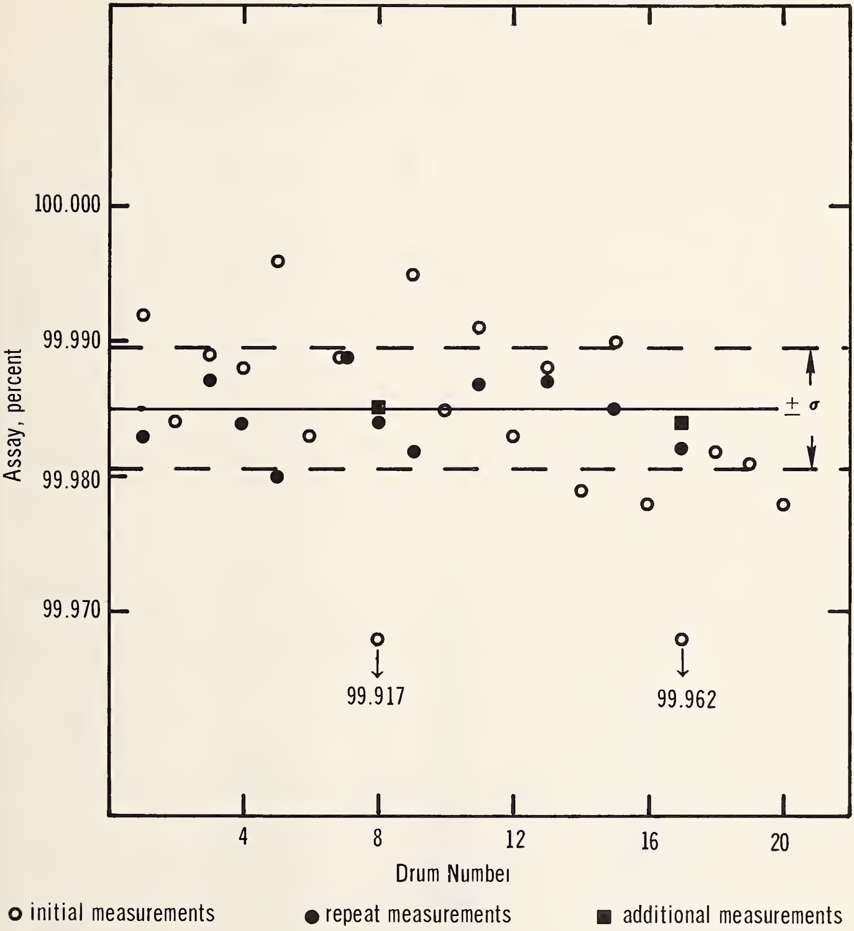

Figure 4. Homogeneity of SRM 136c, Potassium Dichromate, compared with SRM 136b, Potassium Dichromate.

Table 8. Homogeneity and effective purity of SRM 136c, Potassium Dichromate, compared with SRM 136b, Potassium Dichromate.

| SRM 136b[a] | | SRM 136c | | |
|---|---|---|---|---|
| Date | g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$ | Drum No. | g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$ | Effective purity(%) |
| 9/15/69 | 8.00960 | 1 | 8.01025 | 99.995 |
| | 8.00969 | 3 | 8.01003 | 99.992 |
| | 8.00928 | 5 | 8.01056 | 99.999 |
| | | 7 | 8.01002 | 99.992 |
| | | 9 | 8.01048 | 99.998 |
| | | 11 | 8.01013 | 99.994 |
| | | 13 | 8.00991 | 99.991 |
| | | 15 | 8.01004 | 99.992 |
| 9/17/69 | 8.00896 | 17 | 8.00784[b] | 99.965[b] |
| | 8.00906 | 19 | 8.00935 | 99.984 |
| | | 2 | 8.00962 | 99.987 |
| | | 4 | 8.00992 | 99.991 |
| | | 6 | 8.00951 | 99.986 |
| | | 8 | 8.00423[b] | 99.920[b] |
| | | 10 | 8.00964 | 99.987 |
| | | 12 | 8.00948 | 99.985 |
| 9/19/69 | 8.00844 | 14 | 8.00918 | 99.982 |
| | 8.00858 | 16 | 8.00909 | 99.981 |
| | | 18 | 8.00944 | 99.985 |
| | | 20 | 8.00910 | 99.981 |
| | | 4[c] | 8.00956 | 99.986 |
| | | 5[c] | 8.00924 | 99.982 |
| | | 8[c] | 8.00962 | 99.987 |
| | | 17[c] | 8.00941 | 99.985 |
| 10/13/69 | 8.00892 | 1[c] | 8.00951 | 99.986 |
| | 8.00877 | 8[c] | 8.00965 | 99.988 |
| | 8.00878 | 9[c] | 8.00947 | 99.985 |
| | | 17[c] | 8.00961 | 99.987 |
| 10/16/69 | 8.00883 | 3[c] | 8.00983 | 99.990 |
| | 8.00895 | 7[c] | 8.00998 | 99.992 |
| | 8.00868 | 11[c] | 8.00985 | 99.990 |
| | | 13[c] | 8.00983 | 99.990 |
| | | 15[c] | 8.00970 | 99.988 |
| Average | 8.00896 | | 8.00971 | 99.988 |
| σ | 0.00037(0.0046%) | | 0.00037 | 0.0046 |

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[a] Effective purity of SRM 136b, Potassium Dichromate = 99.979%.

[b] Omitted from average. [c] Repeat analysis.

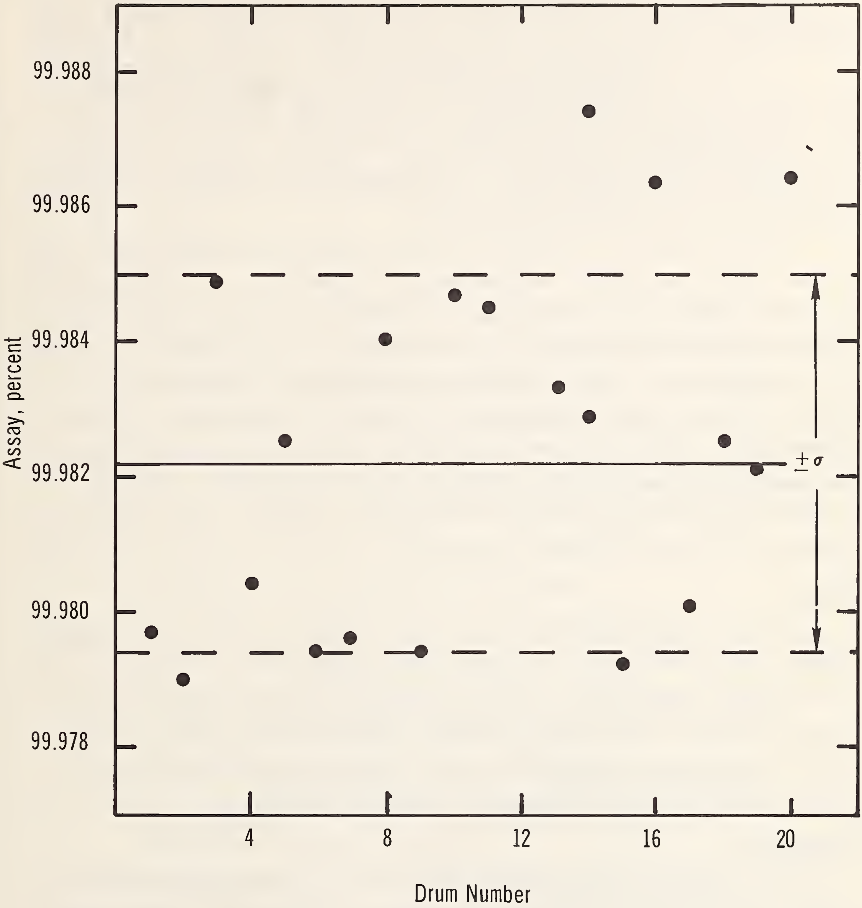

Figure 5. Coulometric determination of the homogeneity of SRM 136c, Potassium Dichromate.

### 1. Comparison with SRM 136b, Potassium Dichromate

SRM 136c was compared with SRM 136b through ferrous ammonium sulfate hexahydrate and through SRM 83c, Arsenic Trioxide.

a. Comparison through Ferrous Ammonium Sulfate - The end point in the titration of chromate ion with ferrous ion was determined potentiometrically with a direct current voltmeter of the Garman and Droz design [22] using a platinum electrode and a calomel electrode.

Several lots of ferrous ammonium sulfate hexahydrate had to be tested to obtain satisfactory material. In fact, with all lots tested the variation of the results was larger than the acceptable precision for the assay of the potassium dichromate standards. One lot of the material was crushed in an agate mortar to an approximate fineness of 100 mesh and, when tested, the variation was reduced so that the material met the desired homogeneity. Enough ferrous ammonium sulfate hexahydrate was crushed and thoroughly mixed at one time to complete all anticipated titrations.

Method:

In the intercomparison of the potassium dichromate standards, the potassium dichromate was dissolved in sulfuric acid (1+19) and solid ferrous ammonium sulfate hexahydrate (less than the calculated amount required) was added. The excess potassium dichromate was titrated potentiometrically with a dilute ferrous ammonium sulfate solution.

Reagents:

(a) Sulfuric acid solution (1+19) - One hundred twenty-five ml of sulfuric acid were added to 2375 ml of distilled water in a 3 liter Florence flask. The solution was boiled for 1/2 hour and cooled to room temperature. The flask was covered with a plastic cover.

(b) Ferrous ammonium sulfate solution (8 g/l) - Eight grams of ferrous ammonium sulfate hexahydrate were transferred to a 1 liter volumetric flask and 200 ml of sulfuric acid

(1+19) were added. When the salt was dissolved, the solution was diluted to the mark with sulfuric acid (1+19) and mixed thoroughly. Standardization--0.050 g of potassium dichromate was transferred to a 600 ml beaker and 300 ml of sulfuric acid (1+19) were added. After the salt was dissolved, the solution was titrated potentiometrically with the ferrous ammonium sulfate solution. Grams of potassium dichromate equivalent to 1 ml of the ferrous ammonium sulfate solution was calculated.

Procedure:

A 0.98 g sample of potassium dichromate weighed to the nearest 0.00001 g was transferred to a 600 ml beaker and 300 ml of sulfuric acid (1+19) were added. The solution was cooled in ice water and when the potassium dichromate was dissolved, 7.8 g of solid ferrous ammonium sulfate hexahydrate were added. After the salt was dissolved the excess potassium dichromate was titrated potentiometrically with the ferrous ammonium sulfate solution.

All weights were corrected to vacuum.

Grams $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ equivalent to 1 g $K_2Cr_2O_7 = \frac{A}{B-CD}$

where

A = g of ferrous ammonium sulfate hexahydrate added,
B = g of potassium dichromate taken,
C = ml ferrous ammonium sulfate solution used, and
D = g potassium dichromate equivalent to 1 ml of ferrous ammonium sulfate solution.

SRM 136c was found to have an effective purity of 99.990 percent with a standard deviation of 0.0034 percent when the composite samples were compared to SRM 136b through ferrous ammonium sulfate hexahydrate and 99.988 percent with a standard deviation of 0.0046 when the homogeneity testing was compared to SRM 136b. The results of the comparisons are given in Table 8 page 28 and Table 9.

Table 9. Effective purity of SRM 136c, Potassium Dichromate, compared with SRM 136b, Potassium Dichromate.

| | SRM 136b[a] | | SRM 136c | |
|---|---|---|---|---|
| | g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$ | Composite No. | g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$ | Effective purity (%) |
| | 8.00892 | I | 8.00994 | 99.993 |
| | 8.00877 | II | 8.01009 | 99.995 |
| | 8.00878 | III | 8.00965 | 99.989 |
| | 8.00883 | IV | 8.00962 | 99.989 |
| | 8.00895 | IV | 8.00950 | 99.987 |
| | 8.00867 | III | 8.00976 | 99.991 |
| | | II | 8.00952 | 99.988 |
| | | I | 8.00923 | 99.984 |
| Ave. | 8.00882 | | 8.00966 | 99.990 |
| $\sigma$ | 0.00012(0.0015%) | | 0.00027 | 0.0034 |

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[a] Effective purity of SRM 136b, Potassium Dichromate = 99.979%.

b. Comparison through SRM 83c, Arsenic Trioxide - SRM 136c was also compared to SRM 136b through SRM 83c, Arsenic Trioxide. The arsenic trioxide was dissolved in a sodium carbonate solution and acidified with sulfuric acid. An excess of the potassium dichromate was added and after the chromium equivalent to arsenic trioxide was reduced the excess potassium dichromate was titrated with a dilute ferrous ammonium sulfate solution. Details of the method are given in Section II.E.1.a.

$$\text{Effective purity of } K_2Cr_2O_7\text{, in percent} = \frac{A}{B-CD} \times \frac{EF}{G}$$

where

A = g of arsenic trioxide taken,
B = g of potassium dichromate added,
C = ml of standard ferrous ammonium sulfate solution used,
D = g of potassium dichromate equivalent to 1 ml of ferrous ammonium sulfate solution,
E = effective purity of arsenic trioxide in percent,
F = equivalent weight of potassium dichromate, and
G = equivalent weight of arsenic trioxide.

The effective purity of SRM 136c is 0.012 percent more than the effective purity of SRM 136b when compared through SRM 83c, Arsenic Trioxide, therefore SRM 136c has an effective purity of 99.991 percent when compared with SRM 136b. The results are given in Table 10.

2. Comparison with SRM 83c, Arsenic Trioxide

The effective purity of SRM 136c was determined by a comparison with SRM 83c, Arsenic Trioxide. The arsenic trioxide was dissolved in a sodium carbonate solution and acidified with sulfuric acid. Potassium dichromate (more than the calculated amount required) was added and after the reaction with the arsenic trioxide was complete the excess potassium dichromate was titrated with a dilute ferrous ammonium sulfate solution. Details of the method are given in Section II.E.1.a.

Table 10. Effective purity of SRM's 136c and 136b, Potassium Dichromate, compared with SRM 83c, Arsenic Trioxide.

| | SRM 136b | | | SRM 136c | |
|---|---|---|---|---|---|
| | g $As_2O_3$[a] per g $K_2Cr_2O_7$ | Effective purity(%) | Composite No. | g $As_2O_3$[a] per g $K_2Cr_2O_7$ | Effective purity(%) |
| | 1.00854 | 99.968 | I | 1.00878 | 99.992 |
| | 1.00866 | 99.980 | II | 1.00872 | 99.986 |
| | 1.00868 | 99.982 | III | 1.00882 | 99.996 |
| | 1.00846 | 99.960 | IV | 1.00880 | 99.994 |
| | 1.00855 | 99.969 | IV | 1.00865 | 99.979 |
| | 1.00859 | 99.973 | III | 1.00866 | 99.980 |
| | 1.00859 | 99.973 | II | 1.00870 | 99.984 |
| | 1.00859 | 99.973 | I | 1.00863 | 99.977 |
| | 1.00865 | 99.979 | I | 1.00869 | 99.983 |
| | | | II | 1.00868 | 99.982 |
| | | | III | 1.00874 | 99.979 |
| | | | IV | 1.00865 | 99.985 |
| Ave. | 1.00859 | 99.973 | | 1.00871 | 99.985 |
| σ | 0.00007 | 0.0069 | | 0.000064 | 0.0063 |

---

[a] Effective purity of SRM 83c, Arsenic Trioxide = 99.988%.

Note: SRM 136c would have an effective purity of 99.991% when compared to SRM 136b (99.979%).

Only the composite samples of SRM 136c were compared to SRM 83c. The effective purity of SRM 136c was found to be 99.985 percent with a standard deviation of 0.0063 percent. SRM 136b was also compared to SRM 83c at the same time as SRM 136c. The effective purity of SRM 136b was found to be 99.973 percent with a standard deviation of 0.0069 percent. These results are also given in Table 10.

### 3. Coulometry

The effective purities of SRM 136b and SRM 136c were determined coulometrically. SRM 136b was assayed in connection with the evaluation and development of a highly precise and accurate analytical method for a typical oxidation-reduction titration by coulometry [23]. SRM 136c was assayed coulometrically for certification of effective purity.

Coulometric methods are absolute methods in that the results depend directly upon the reliability of measured physical quantities. This is in contrast to many analytical methods which are comparative in principle, in that an unknown is compared with a material of known composition.

The application of constant-current coulometric titrations to the analysis of dichromate is not novel [24,25,26], but highly precise and accurate results have not been reported. The method developed consists of the reduction of dichromate with electrogenerated ferrous ion. The technique and procedure were refined to permit results reliable to a few parts in 100,000, which are about two orders of magnitude better than those reported by previous investigators.

The conditions for 100-percent efficient generation of ferrous ion at a platinum cathode are readily obtained from current density versus potential studies of the supporting electrolyte alone and with several additions of ferric ion. This technique has been employed by Lingane and co-workers for the evaluation of the current efficiency of generation of ceric ion [27,28].

From this study, solutions more concentrated than 0.01 M with respect to ferric ion in a supporting electrolyte of 2 M sulfuric acid can be reduced with a current efficiency of 100 percent, provided the current density is less than 1.2 $mA/cm^2$.

It is also indicated that the presence of phosphoric acid is not essential for theoretically efficient reduction of ferric ion to ferrous ion, as has been reported by previous investigation [24]. In fact, it is evident that the presence of phosphoric acid lowers the limiting current-density for efficient reduction of ferric ion.

In this work ferrous ion was pregenerated from a solution 0.4 M with respect to ferric ion in 2 M sulfuric acid supporting electrolyte at current densities never exceeding 0.6 $mA/cm^2$. The pregeneration technique, described later, reduced the ferric ion concentration to 0.3 M but this was well above the limit for efficient generation of ferrous ion.

The end points of these titrations were determined amperometrically using a polarized platinum indicator anode and a saturated calomel electrode as the nonpolarizable reference cathode. Using this electrode system the current-voltage curves shown in Figure 6 were obtained. An applied-potential of +0.85 v is midway on the diffusion-current plateau for the reaction $Fe^{++} \rightarrow Fe^{+++} + e^-$. In actuality, this plateau is not completely flat; however, this voltage corresponds to a region where the indicator current is the least dependent on the applied voltage.

From studies of Anson [29], it is evident that the oxide film which is formed on platinum affects the behavior of the ferrous-ferric couple at the electrode. According to him, the reduction of such a film is easily accomplished by ferrous ion in a sulfuric acid medium. If such a film were not removed prior to generation of ferrous ion, it would cause positive errors in the final analysis of oxidant, dichromate in the present case. To avoid such interference, precautions were

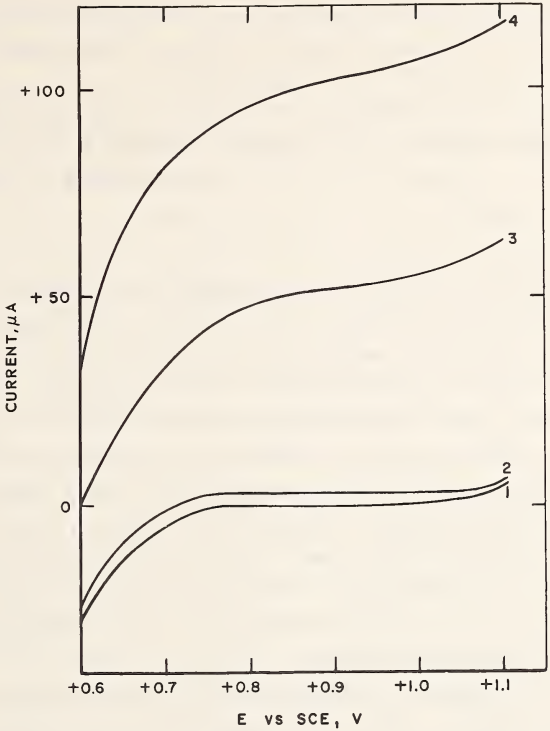

Figure 6. Current, potential curves for oxidation of ferrous ion at a polarized platinum electrode.

1. 2 M $H_2SO_4$; 0.5 M $Fe^{+++}$; 40 μeq $K_2Cr_2O_7$
2. 2 M $H_2SO_4$; 0.5 M $Fe^{+++}$; 40 μeq $Cr^{+++}$; 0.5 μeq $Fe^{++}$
3. 2 M $H_2SO_4$; 0.5 M $Fe^{+++}$; 40 μeq $Cr^{+++}$; 10 μeq $Fe^{++}$
4. 2 M $H_2SO_4$; 0.5 M $Fe^{+++}$; 40 μeq $Cr^{+++}$; 20 μeq $Fe^{++}$

taken. The electrodes (both the indicator anode and the generator cathode) were pretreated by immersion for 10 minutes in a chromic acid solution with subsequent rinsing, followed by a 10 minute immersion in 0.1 M ferrous ammonium sulfate solution in 2 M $H_2SO_4$. Thus the electrode surfaces were freshly "reactivated" prior to each titration.

All calculations were based on the 1967 $^{12}C$ atomic weight scale [30]. From it the molecular weight of potassium dichromate was calculated to be 294.1918.

The value of the faraday constant which was used in the calculations was 96,487.2 coul/g-equiv (based on the determination of D. N. Craig et al. [31] and corrected to the $^{12}C$ atomic weight scale).

Apparatus:

The titration cell used in this work was similar to the one described by Marinenko and Taylor [32]. The anode and cathode compartments are separated by a connecting tube containing a series of porous glass frits to provide two intermediate sections. Tubes sealed to the tops of these sections permit application of suction or pressure to fill or empty the compartments. A silicic acid gel plug, prepared by gelation of sodium silicate solution with sulfuric acid, was formed on the fine-porosity disk of the anode compartment to eliminate flow of electrolyte. The plug remained for long periods of time without deterioration provided it was kept wet with supporting electrolyte.

A piece of corrugated platinum foil (5×16 cm) served as the generator cathode. The anode was constructed from sheet lead (12×10×0.2 cm) which was contoured to fit the anode compartment of the cell.

The electric circuit was the same as the one used by Marinenko and Taylor [32]. The current was adjusted manually to maintain the IR drop across a standard resistor constant and equal to the voltage of a saturated standard cell. Because the dummy resistance only approximated that of the electrolytic cell, a momentary initial imbalance was invariably observed. Such imbalances were small and corrected quickly so that they could not affect the titrations by more than 0.00001 percent.

The saturated standard cell and the standard resistor used in this work were calibrated by the appropriate sections of the NBS. Although the resistor was placed in a thermostated oil-bath, there was always a slight temperature rise of the resistor due to heat dissipation. The correction for this temperature change was applied using the mean temperature value of the resistor for a given titration and the appropriate temperature coefficients.

The time was measured by means of a 100 kHz-quartz crystal controlled time interval meter (TIM) whose calibration was checked with respect to standard frequency signals of WWV: the calibration was found to be accurate to at least 1 ppm.

Near the equivalence point of the titration, it was more convenient to pass current increment-wise using a commercially-available constant-current coulometric source. The current and timing accuracy of this apparatus were calibrated and the current times time (I×t) product was found to be accurate to ±0.005 percent. Since the fraction of the total titration performed with this instrument was of the order of 0.0005, the errors encountered as a result of the use of this equipment were negligible.

The amperometric indicator system consisted of a platinum foil electrode (1 $cm^2$ in area) and a saturated calomel electrode with a 3-percent agar-agar gel in 0.1 N potassium chloride in a salt bridge. A recording polarograph was used as the source of applied emf (0.85 V) between these two electrodes and also as the microammeter for measuring or recording the indicator current.

All weighings were done on a 20 g capacity microbalance of the single-arm, constant-load type and were accurate to ±0.003 mg. All weights were corrected for air buoyancy.

## Procedure:

The potassium dichromate standards were dried at 110 °C for 6 hours and stored in a desiccator over $P_2O_5$.

One-half gram of SRM 136b (1 g of SRM 136c) contained in a platinum boat was weighed by the method of substitution using a calibrated tantalum weight. Sample weights agreed with the nominal value and with each other within 3 mg. The difference between the mass of the sample and the calibrated mass was determined on the optical scale of the balance. The weighed samples were transferred from the boat into 30-ml weighing bottles and stored in a desiccator until used.

The weighings were done in sets, each representing a number of samples weighed on the same day. Measurements were made of air temperature, barometric pressure, and relative humidity during the weighings and the appropriate corrections for air bouyancy were applied.

The supporting electrolyte was prepared in advance and was 0.4 M with respect to ferric ion and 2 M with respect to sulfuric acid. Ferric ammonium sulfate, reagent grade salt, or electrolytically oxidized ferrous ammonium sulfate served as the source of the ferric ion.

The anode and cathode compartments were filled with 100 ml of 2 M sulfuric acid and 120 ml of supporting electrolyte, respectively. At this point about 1 ml of 0.005 N potassium dichromate was delivered into the cathode compartment to remove traces of ferrous ion and to facilitate the pretitration step described later.

Dissolved air was removed from the catholyte by purging with nitrogen gas that was introduced through the coarse frit of the side compartment adjacent to the cathode compartment. The nitrogen used for this purpose was pretreated by passing it through a heated copper-filled tube to remove oxygen and through towers containing acidified potassium permanganate, ferrous ammonium sulfate and supporting electrolyte respectively.

After purging, the catholyte was permitted to flow into the intermediate compartments to the extent that it would just cover the bottom of each compartment, thus establishing electrolytic contact between the cathode and anode compartments. This was accomplished by application of suction to each intermediate compartment.

The catholyte was then pretitrated by passage of increments of current equivalent to 0.200 μeq, using the 0.643 ma current range of the coulometric power supply. At the conclusion of each increment, the indicator current was observed. This was small and essentially constant up to the equivalence point, exhibited a curvature in the vicinity of the equivalence point, and became a linear function of the ferrous ion concentration with slope of about 5.0 μa/μeq beyond the equivalence point. This linear portion was extrapolated graphically and its intersection with the zero-current line was taken as the end point.

After completion of the pretitration, the intermediate compartments were rinsed by repeated emptying and filling with catholyte by applying suction or nitrogen pressure as required. The walls of the cathode compartment and its cover were rinsed by withdrawing catholyte using a syringe in which a glass tip replaced the hypodermic needle. The tip was bent so that the expelled catholyte would wash down all parts of the cathode chamber. The final reading of the indicator current was then taken from which the amount of over-titration of the pretitration step was determined.

The intermediate compartments of the cell were then filled with catholyte and ferrous ion was electrogenerated at constant current using the high precision circuit and the TIM. The amount of ferrous ion generated was a predetermined quantity sufficient to reduce about 99.95 percent of the dichromate in a given sample.

After the generation of this major portion of ferrous ion, a dry funnel was inserted into the cover of the cathode compartment through an auxiliary opening which was stoppered with a piece of glass rod during the time of generation of ferrous ion. The stem of this funnel reached slightly below the level of the liquid in the cell. The weighing bottle containing the weighed sample was inverted into the funnel and lightly tapped, so that all visible crystals of the dichromate were delivered into the cell. A complete dissolution of sample took place in about 5 min after delivery into catholyte. Following dissolution of sample the intermediate compartments were successively emptied by applying nitrogen pressure until only the bottoms of these compartments were wetted enough to make the electrical contact between the anolyte and the catholyte. The compartment which is adjacent to the cathode compartment was rinsed several more times, by permitting the catholyte to flow into it, and by forcing the same out with nitrogen pressure. This was done because a perceptible amount of ferrous ion diffused into that compartment during the course of its generation. Thus, it required more than one rinse to remove all ferrous ion which was entrapped in the glass frits. The second compartment contained an imperceptible amount of ferrous ion.

At this point the titration was continued increment-wise, using the coulometric current source as in the case of pretitration. When the first rise of the indicator current was observed, the cell walls, the cell cover, and the intermediate compartments were rinsed as already described, and the weighing bottle which originally contained the sample and the delivery funnel were rinsed with catholyte withdrawn from the cell by the syringe. This procedure was repeated after each succeeding increment. The extrapolation of the indicator current line, where it becomes a straight line function of the ferrous ion concentration was again taken as the end point at the point where it intersects the zero current line. A typical end-point determination is shown in Figure 7.

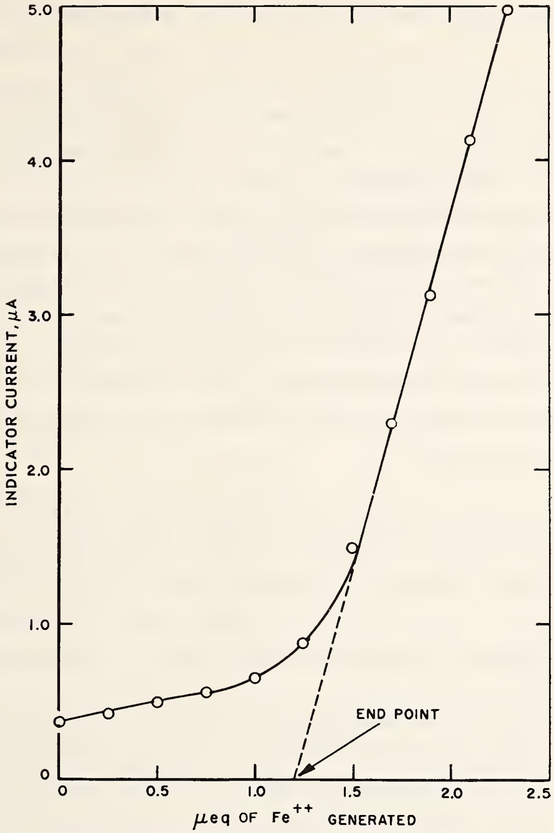

Figure 7. Typical end-point determination.

Discussion:

The factors affecting the precision and accuracy of coulometric titrations have been discussed in previous papers [32,33]. In the present work, much effort was expended to minimize all errors to produce results of high reliability. An attempt has been made to evaluate the precision of all measurements involved. These are summarized in the following:

Weighings were precise to about 3 μg, which amounts to 0.0006 percent in the case of 0.5 g samples and uncertainties in the buoyancy corrections did not exceed 0.0003 percent. Manual control of the current was maintained within a 0.5 cm galvanometer deflection which would amount to 0.00015 percent. Timing errors are not believed to exceed 0.0001 percent for the 10,000-second period of electrolysis. Uncertainties in the current due to temperature fluctuation of the standard resistor were no more than 0.00007 percent, while endpoint uncertainties may have amounted to about 0.02 μeq which represents 0.0002 percent in a 10-meq sample. On the basis of these estimates an overall precision of 0.0008 percent should have been attained, which is about one-third of the standard deviation of the results.

There are of course other sources of error, the magnitudes of which are difficult to estimate. Such indeterminate errors include mechanical losses due to transfer of sample, spray losses, and residual amounts of oxygen in the cell. Efforts were made to minimize some of the indeterminate errors by the washing procedure already described and by pretreatment of the electrolyte.

The stability of the generating current was greatly improved by the pregeneration technique, and this was the reason for its adoption. In preliminary work, it was found that the current became quite unsteady when about 30 percent of a 10 meq sample of dichromate which had been added directly to the supporting electrolyte was reduced. Potential measurements showed that the cathode potential shifted abruptly at this point from that of the dichromate-chromic couple to that of the ferric-ferrous couple. Undoubtedly, due to concentration polarization effects, the primary electrode reaction changed from the reduction of dichromate to reduction of ferric ion, well in advance of the stoichiometric end point. The transition was too rapid to compensate by manual means and consequently large uncertainties were introduced. The pregeneration of the ferrous ion as already described eliminates this uncertainty.

Another improvement in precision of the endpoint determination resulted from the pretitration technique. Some uncertainty was introduced by small but measurable variations in the current prior to the complete reduction of dichromate (residual current). However, by alternate reduction and oxidation in the region of the end point, it became evident that extrapolations of the linear residual-current curve to zero current gave reliable values for a sample added to one previously titrated, and the pretitration technique described earlier was adopted. Also, it was hoped that this procedure would eliminate blank corrections, but it was observed that a pretreatment of the supporting electrolyte was required as well.

It has also been shown conclusively that a pretreatment technique is required for the supporting electrolyte if the results of highest obtainable degree of accuracy and precision are desired.

The results for the determination of the effective purity of SRM 136b are given in Table 11 and for SRM 136c in Table 12. The average value for the effective purity of SRM 136b is 99.9772 percent with a standard deviation for all measurements of 0.0029 percent. After correction of the assay value for changes in the value of NBS ampere and the faraday [19] the assay of SRM 136b is 99.9786. The average value for SRM 136c is 99.9822 with a standard deviation of 0.0028 percent. No correction is needed for SRM 136c because the assay was determined after the value of NBS ampere and the faraday had been changed.

## 4. Summary

SRM 136c, Potassium Dichromate, will be issued with a final "Certificate of Analysis" with an effective purity of 99.983 percent. This value is based on the direct coulometric method and on the comparison with SRM 83c, Arsenic Trioxide.

Table 11. Effective purity of SRM 136b, Potassium Dichromate, by coulometry.

| Sample No. | Set I | Set II | Set III | Set IV | Set V |
|---|---|---|---|---|---|
| 1 | 99.9800 | 99.9755 | 99.9742 | 99.9835 | 99.9785 |
| 2 | 99.9788 | 99.9736 | 99.9734 | 99.9737 | 99.9777 |
| 3 | 99.9751 | | 99.9735 | | 99.9772 |
| 4 | 99.9757 | 99.9739 | 99.9747 | | 99.9771 |
| 5 | 99.9789 | 99.9787 | 99.9778 | | 99.9762 |
| 6 | 99.9812 | 99.9783 | | | |
| Average | 99.9783 | 99.9760 | 99.9747 | 99.9786 | 99.9773 |
| σ | 0.0024 | 0.0024 | 0.0018 | 0.0049 | 0.0009 |

| Sample No. | Set VI | Set VII | Set VIII | Set IX | Set X |
|---|---|---|---|---|---|
| 1 | 99.9769 | 99.9846 | 99.9789 | | |
| 2 | 99.9766 | 99.9820 | 99.9771 | 99.9783 | 99.9760 |
| 3 | 99.9775 | 99.9685 | 99.9764 | | 99.9769 |
| 4 | 99.9784 | 99.9752 | 99.9785 | 99.9787 | |
| 5 | 99.9787 | | 99.9796 | | |
| 6 | | | | 99.9769 | |
| Average | 99.9776 | 99.9776 | 99.9781 | 99.9780 | 99.9765 |
| σ | 0.0009 | 0.0060 | 0.0013 | 0.0010 | 0.0005 |

Average all values 99.9772[a] σ 0.0029

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[a] After applying the correction for the change in the values of NBS ampere and the faraday [19] the average assay value becomes 99.9786 percent.

Table 12. Effective purity of SRM 136c, Potassium Dichromate, by coulometry.

| Titration Sequence | Drum No. | | Assay (%) |
|---|---|---|---|
| 1 | 3 | | 99.9849 |
| 2 | 19 | | 99.9821 |
| 3 | 8 | | 99.9840 |
| 4 | 10 | | 99.9847 |
| 5 | 1 | | 99.9797 |
| 6 | 11 | | 99.9845 |
| 7 | 2 | | 99.9790 |
| 8 | 17 | | 99.9801 |
| 9 | 5 | | 99.9825 |
| 10 | 20 | | 99.9864 |
| 11 | 14 | | 99.9874 |
| 12 | 15 | | 99.9792 |
| 13 | 12 | | 99.9786 |
| 14 | 6 | | 99.9794 |
| 15 | 9 | | 99.9794 |
| 16 | 18 | | 99.9825 |
| 17 | 4 | | 99.9804 |
| 18 | 16 | | 99.9863 |
| 19 | 7 | | 99.9796 |
| 20 | 13 | | 99.9833 |
| | | Average | 99.9822 |
| | | $\sigma$ | 0.0028 |

The coulometric assay is an absolute method and depends only on the accuracy of the measurements of mass, electrical current and time. SRM 83c was assayed by the absolute methods, coulometry and comparison with iodine, therefore the effective purity is accuratey known. The certified value is also compatible with the previous potassium dichromate standard, SRM 136b. The summary is given in Table 13. The lower part of the table gives the assay of SRM 136c when compared to SRM 136b.

Table 13. Effective purity of SRM 136c, Potassium Dichromate.

| | Effective purity (%) | Standard deviation (σ) |
|---|---|---|
| For Certification | | |
| SRM 83c, $As_2O_3$ (composite) | 99.985 | 0.006 |
| By coulometry | 99.982 | 0.0028 |
| Average | 99.983 | |
| Other Comparisons | | |
| SRM 136b (thru $Fe^{++}$-composite) | 99.990 | 0.003 |
| SRM 136b (thru $Fe^{++}$-homogeneity) | 99.988 | 0.005 |
| SRM 136b (thru $As_2O_3$) | 99.991 | |

In studies of SRM 136 [34] and SRM 136b [35], it was shown that the removal of occluded water by appropriate heat treatment increases the assay of the standard to 100.000 ±0.005 percent. In one study [34], the occluded water was determined and in the other the standard was assayed after the removal of the occluded water. From our limited determination of water and the work of other investigators [34,35], SRM 136c would have an effective purity of 100.000 percent with a standard deviation of 0.006 percent if it were heated to remove occluded water.

## IV. SRM 40h. SODIUM OXALATE

### A. Introduction

The use of sodium oxalate as a primary standard was suggested by Sorensen [36] who described its preparation, testing and use in subsequent papers [37]. The National Bureau of Standards issued the first Standard Reference Material, Sodium Oxalate, as an oxidimetric standard in 1912. Since then, 8 renewals have been issued with the SRM 40h, Sodium Oxalate, as the present Standard Rreference Material.

The sodium oxalate was purchased under special specifications to insure high homogeneity and purity so that the entire lot could be issued under one certificate of analysis.

### B. Sampling

Twenty-eight fiberboard drums containing 25 lbs each of sodium oxalate were received to be used as the renewal for SRM 40g. Each drum was lined with a polyethylene bag. After thoroughly mixing by rolling each drum, a 30 g sample was removed by taking equal portions of material from the top, middle and bottom while the drum was lying on its side. Four composite samples were prepared from the above representative samples as follows:

Composite I - drums 1, 5, 9, 13, 17, 21 and 25;
Composite II - drums 2, 6, 10, 14, 18, 22 and 26;
Composite III - drums 3, 7, 11, 15, 19, 23 and 27;
Composite IV - drums 4, 8, 12, 16, 20, 24 and 28.

### C. Homogeneity

The individual samples were titrated with a 0.1 N potassium permanganate solution to determine whether the material was homogeneous and could be issued under one certificate of analysis.

The results of the titrations of the 28 representative samples of SRM 40h are given in Table 14 and Figures 8 and 9. With the exceptions of Nos. 9 and 23 of the 0.1 N potassium

Table 14. Homogeneity of SRM 40h, Sodium Oxalate, and comparison with SRM 40g, Sodium Oxalate.

| SRM 40g | SRM 40h | | | |
|---|---|---|---|---|
| | $KMnO_4$ Solution No. 3 | | $KMnO_4$ Solution No. 4 | |
| g $KMnO_4$ per g $Na_2C_2O_4$ | Drum No. | g $KMnO_4$ per g $Na_2C_2O_4$ | Drum No. | g $KMnO_4$ per g $Na_2C_2O_4$ |
| 128.5644 | 1 | 128.5846 | 1 | 153.9448 |
| 128.5339 | 2 | 128.6202 | 2 | 153.9608 |
| 127.9741[a] | 8 | 128.5773 | 3 | 153.9650 |
| 128.5897 | 9 | 128.7467[a] | 4 | 153.9485 |
| 128.5627 | 15 | 128.5806 | 5 | 153.9711 |
| 128.5339 | 16 | 128.5613 | 6 | 153.9425 |
| 128.4785 | 22 | 128.5435 | 7 | 153.9582 |
| 128.5703 | 23 | 127.9985[a] | 8 | 153.9568 |
| 128.5740 | 3 | 128.5619 | 9 | 153.9583 |
| 128.5660 | 4 | 128.5917 | 10 | 153.9718 |
| 128.5372 | 10 | 128.5567 | 11 | 153.9705 |
| | 11 | 128.5573 | 12 | 153.9748 |
| | 17 | 128.5349 | 13 | 154.0024 |
| | 18 | 128.5201 | 14 | 153.9513 |
| | 24 | 128.5475 | 15 | 153.9919 |
| | 25 | 128.5491 | 16 | 153.9498 |
| | 5 | 128.5128 | 17 | 154.0072 |
| | 6 | 128.4923 | 18 | 153.9909 |
| | 12 | 128.5236 | 19 | 154.0012 |
| | 13 | 128.6025 | 20 | 154.0056 |
| | 19 | 128.6024 | 21 | 154.0116 |
| | 20 | 128.6139 | 22 | 153.9811 |
| | 26 | 128.5183 | 23 | 153.9837 |
| | 7 | 128.6384 | 24 | 153.9893 |
| | 14 | 128.6145 | 25 | 153.9817 |
| | 21 | 128.6034 | 26 | 153.9745 |
| | 27 | 128.5948 | 27 | 153.9996 |
| | 28 | 128.6351 | 28 | 153.9672 |
| | 6[b] | 128.5834 | 15[b] | 153.9829 |
| | 23[b] | 128.6179 | 13[b] | 153.9788 |
| | 9[b] | 128.5947 | | |
| Ave. 128.5511 | | 128.5736 | | 153.9758 |
| σ 0.0316(0.026%) | | 0.0390(0.030%) | | 0.0199(0.013%) |

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[a] Omitted from average.

[b] Repeat runs.

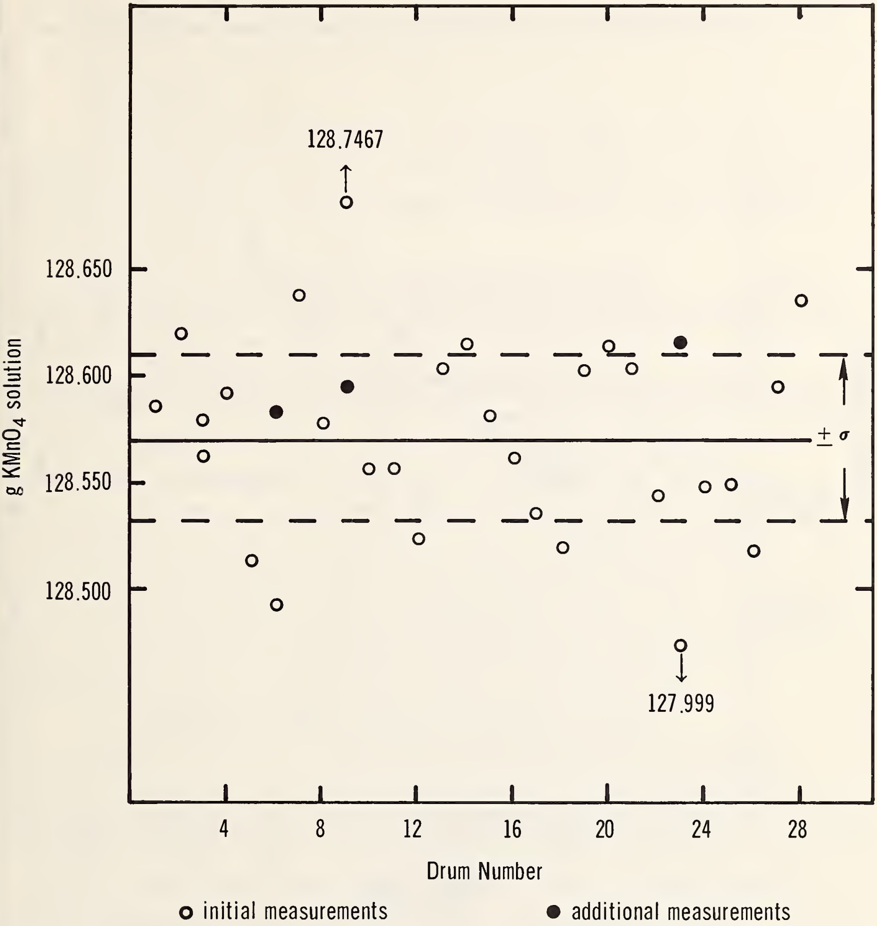

Figure 8. Homogeneity of SRM 40h, Sodium Oxalate, using KMnO$_4$ solution no. 3.

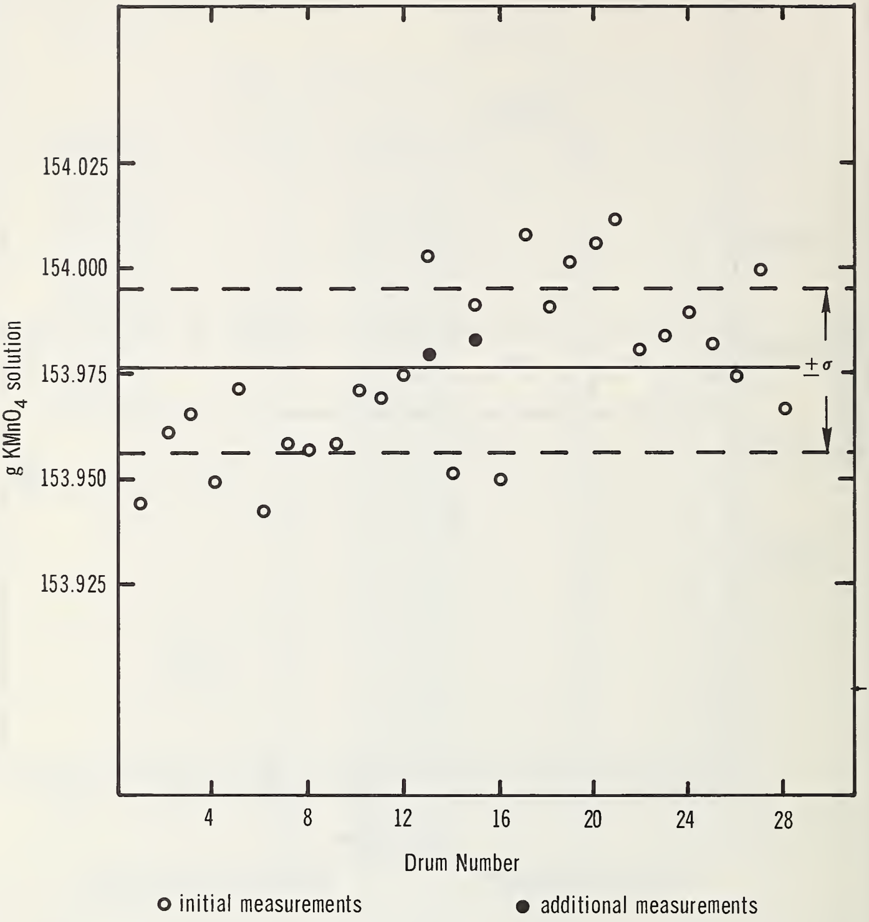

Figure 9. Homogeneity of SRM 40h, Sodium Oxalate, using $KMnO_4$ solution no. 4.

permanganate solution No. 3 all results fell within the limits of acceptance for this lot of material. On repeat runs these outliers fell within this limit.

## D. Impurities

SRM 40h, Sodium Oxalate, conforms to the American Chemical Society specifications for reagent-grade material [5] but small amounts of water, sodium hydrogen oxalate and sodium bicarbonate are present.

## E. Effective Purity of SRM 40h, Sodium Oxalate

The effective purity of SRM 40h for the provisional certification was determined by comparison with SRM 40g, Sodium Oxalate, and by determining the impurities most likely to effect the neutrality of the sodium oxalate. SRM 40h has also been compared to SRM 83c, Arsenic Trioxide, using a 0.1 N potassium permanganate solution to titrate both standards. SRM 40h was also compared to SRM's 136b and 136c, Potassium Dichromate. Since sodium oxalate and potassium dichromate do not react efficiently with one another, the sodium oxalate and ferrous ammonium sulfate hexahydrate were titrated with a 0.1 N potassium permanganate solution and then the ferrous ammonium sulfate compared with SRM's 136b and 136c.

### 1. Comparison with SRM 40g, Sodium Oxalate

The provisional Certificate of Analysis for SRM 40h, Sodium Oxalate, was issued on the basis of the determination of the impurities and also comparison with SRM 40g by titrating with 0.1 N potassium permanganate solutions. The procedure used in these titrations was generally that recommended by R. M. Fowler and H. A. Bright [38].

### Method

The sodium oxalate was dissolved in sulfuric acid (1+19) and most of the potassium permanganate solution was added. The solution was heated to 55 - 60 °C and the titration completed. The excess potassium permanganate solution was determined with a sodium thiosulfate solution.

Reagents:

(a) Potassium Permanganate Solution (0.1 N) - Twenty-five and six tenths grams of recrystallized potassium permanganate were transferred to a 10 liter glass bottle and 8 liters of water were added. When the salt was dissolved and the solution thoroughly mixed it was allowed to stand in the dark for 2 weeks. The solution was filtered through a fine porosity glass filter to remove the precipitated manganese dioxide and was stored in the dark.

(b) Starch Solution - Two and one half grams of soluble starch were triturated with 5 ml of water to a thin paste which was then poured into 250 ml of boiling water and boiled for 10 minutes. The solution was cooled, diluted to 500 ml with water and stored in the refrigerator in a polyethylene bottle.

(c) Sodium Thiosulfate Solution (0.02 N) - Five grams of sodium thiosulfate pentahydrate was dissolved in 1 liter of water, freshly boiled and cooled. Ratio of the sodium thiosulfate solution to the potassium permanganate solution--One gram of the 0.1 N potassium permanganate solution was transferred to a 600 ml beaker containing 300 ml of sulfuric acid (1+19) freshly boiled and cooled. A 0.5 g portion of potassium iodide was added and the liberated iodine was titrated with the sodium thiosulfate solution. Two ml of the starch solution were added just before the yellow iodine color disappeared and the titration was continued to the starch-iodide end point.

Procedure:

A 0.3 g sample of sodium oxalate, dried at 110 °C and weighed to the nearest 0.00001 g, was transferred to a 500 ml glass stoppered Erlenmeyer flask and 250 ml of sulfuric acid (1+19), freshly boiled and cooled, were added. When the salt was dissolved, approximately 40 ml of 0.1 N potassium permanganate were added. The solution was stirred slowly until the color disappeared. The solution was heated to 55-60 °C and the titration completed to the pink color of potassium permanganate.

To determine the excess potassium permanganate, the solution was cooled to room temperature and 0.5 g of potassium iodide was added. The liberated iodine was titrated with the 0.02 N sodium thiosulfate solution. Two ml of the starch solution were added just before the yellow iodine color disappeared and the titration was continued to the starch-iodide end point [39].

Weight burets were used for the potassium permanganate solution and all weights were corrected to vacuum.

Grams of $KMnO_4$ solution equivalent to 1 g $Na_2C_2O_4$ $= \frac{A}{B-CD}$

where

A = g of sodium oxalate taken,

B = g of potassium permanganate solution used,

C = ml sodium thiosulfate solution used to determine excess $KMnO_4$, and

D = g of potassium permanganate solution equivalent to 1 ml of sodium thiosulfate solution.

The effective purity of SRM 40h is 0.02 percent more than SRM 40g or 99.97 percent when the homogeneity values are used and 0.03 percent more than SRM 40g or 99.98 percent when the composite values are used. The comparison from the homogeneity is considered to be the better value because a larger number of samples were run, spread over several days. The comparison of the composites to SRM 40g was performed in a single day. The results are given in Table 14 page 50 and Table 15.

### 2. Determination of Impurities

The impurities most likely present to effect the neutrality of sodium oxalate are sodium carbonate, sodium bicarbonate, sodium hydrogen oxalate and gaseous carbon dioxide. A spectrographic analysis of the sodium oxalate showed that metal impurities were less than 0.001 percent.

Table 15. Comparison of SRM 40g, Sodium Oxalate, with composites of SRM 40h, Sodium Oxalate.

| | SRM 40g | SRM 40h | |
|---|---|---|---|
| | g $KMnO_4$ sol per g $Na_2C_2O_4$ | Composite No. | g $KMnO_4$ sol per g $Na_2C_2O_4$ |
| | 128.6043 | I | 128.6214 |
| | 128.5635 | II | 128.5700 |
| | 128.5106 | III | 128.6548 |
| | | IV | 128.5137 |
| | | IV | 128.4295[a] |
| | | III | 128.5963 |
| | | II | 128.6131 |
| | | I | 128.6662 |
| Average | 128.5595 | | 128.6051 |
| $\sigma$ | 0.0470(0.037%) | | 0.0520(0.040%) |

---

[a] Omitted from average.

Since sodium bicarbonate and sodium carbonate are inert materials in the redox system, their effect is proportional to the amount present [40]. Sodium hydrogen oxalate causes a positive error of 16 percent of its amount. Sodium bicarbonate rather than sodium carbonate was present in SRM 40h because a solution of this standard gave a pH of 7.3 which is on the acid side of the neutral point [41].

a. Determination of sodium hydrogen oxalate - The sodium hydrogen oxalate present in the sodium oxalate would be equivalent to the amount of sodium hydroxide needed to neutralize a sample of sodium oxalate [41].

A two g sample of sodium oxalate was transferred to a 250 ml beaker containing 130 ml of carbon dioxide-free water. When the salts were dissolved the solution was titrated with a 0.01 N sodium hydroxide solution to a pH of 8.1. A carbon dioxide-free atmosphere was maintained above the solution during the dissolution and titration. A glass electrode - saturated calomel electrode system was used for measuring the pH of the solution. The percent sodium hydrogen oxalate in the sample was calculated from the reaction:

$$NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O.$$

The sodium hydrogen oxalate found in SRM 40h was 0.031 percent (Table 16). The correction for the sodium hydrogen oxalate is positive since more potassium permanganate would be needed to react with sodium hydrogen oxalate than with an equal weight of sodium oxalate. The correction for the sodium hydrogen oxalate in SRM 40h was +0.006 percent.

Table 16. Sodium hydrogen oxalate and sodium bicarbonate in SRM 40h, Sodium Oxalate.

| | Percent $NaHC_2O_4$ | Percent $NaHCO_3$ |
|---|---|---|
| | 0.029 | 0.022 |
| | 0.032 | 0.032 |
| | 0.032 | 0.035 |
| | 0.032 | 0.026 |
| | 0.032 | 0.028 |
| | 0.030 | 0.022 |
| | 0.030 | 0.022 |
| | 0.030 | 0.028 |
| | 0.030 | 0.026 |
| Average | 0.031 | 0.027 |
| $\sigma$ | 0.0012 | 0.0046 |

b. Determination of sodium bicarbonate - Sodium bicarbonate in a sodium oxalate solution was determined by making the solution acid with oxalic acid and then removing the carbon dioxide that was formed from the solution:

$$2\ NaHCO_3 + H_2C_2O_4 \rightarrow Na_2C_2O_4 + 2\ H_2CO_3$$

$$H_2CO_3 \rightarrow H_2O + CO_2 \uparrow .$$

After the carbon dioxide has been removed the oxalic acid was titrated with a sodium hydroxide solution. The difference between the amount of sodium hydroxide solution used in the titration and the amount of sodium hydroxide solution needed for the neutralization of the added oxalic acid is equivalent to the sodium bicarbonate present in the sodium oxalate.

After each 2 g sample of sodium oxalate was titrated with sodium hydroxide to a pH of 8.1, 10 ml of 0.01 N oxalic acid solution was added. A stream of carbon dioxide-free air was bubbled through the solution for 30 minutes to remove the carbon dioxide. While maintaining the carbon dioxide-free air above the solution, it was titrated with 0.01 N sodium hydroxide solution to the neutral point of a pH of 8.1.

The sodium bicarbonate found in SRM 40h was 0.027 percent. The results are given in Table 16.

c. Determination of gaseous carbon dioxide - The gaseous carbon dioxide was determined with the apparatus and method given in Hillebrand, Lundell, Bright and Hoffman [42]. The carbon dioxide was evolved by heating a hydrochloric acid solution, cleansed of impurities, absorbed by ascarite and weighed. Erratic results were obtained when carbon dioxide was first determined in SRM 40g. In an attempt to discover the cause of the erratic results, carbon dioxide was collected for additional 30 minute periods. The weight of the carbon dioxide increased from 0.001 to 0.002 g for each 30 minute period indicating the sodium oxalate was slowly decomposing (Table 17).

Table 17

Evolution of Carbon Dioxide on Boiling in Sodium Oxalate Solution

| Sample No. (10 g) | $CO_2$ evolved<br>1st 30 min (g) | 2nd 30 min (g) | 3rd 30 min (g) | 4th 30 min (g) |
|---|---|---|---|---|
| 1 | 0.0024 | 0.0021 | 0.0020 | |
| 2 | 0.0013 | 0.0012 | 0.0011 | |
| 3 | 0.0023 | 0.0013 | 0.0012 | 0.0013 |

Evolution of Carbon Dioxide Without Heating in Sodium Oxalate Solution

| Sample No. | $CO_2$ evolved<br>1st 1 1/2 hours | 2nd 1 1/2 hours | 3rd 1 1/2 hours |
|---|---|---|---|
| 1 | 0.0007 | 0.0000 | 0.0000 |
| 2 | 0.0010 | 0.0002 | 0.0000 |

Carbon dioxide can be removed from a solution at room temperature by a stream of carbon dioxide-free air [41]. By keeping the solution of sodium oxalate at room temperature, the probable sources of error of thermal decomposition of the sodium oxalate, steam distillation of oxalic acid and attack of chemicals on the glass apparatus were eliminated. Any carbon dioxide evolved would come from the entrapped carbon dioxide in the sodium oxalate or from sodium bicarbonate.

When the heating of the solution was eliminated the carbon dioxide evolved did not increase after the initial time period (Table 17). The procedure was modified to eliminate the heating of the solution.

Using the absorption train given in Hillebrand, Lundell, Bright and Hoffman [42], 125 ml of water and 30 ml hydrochloric acid (1+2) was delivered to the flask. Carbon dioxide-free air was bubbled through the solution for 30 min, the air flow stopped, and the carbon dioxide absorption tube attached. A 10 g sample of sodium oxalate was added and the air flow was started and continued for 30 minutes after the salt was dissolved. The absorption tube was detached and weighed.

The carbon dioxide found includes the gaseous carbon dioxide in the voids of the crystals and the carbon dioxide from the sodium bicarbonate present in the sodium oxalate. In order to eliminate any gaseous carbon dioxide, crushed samples of sodium oxalate were run. The sodium bicarbonate equivalent to the evolved carbon dioxide agreed with that found by titration indicating no gaseous carbon dioxide in SRM 40h.

d. Determination of water in sodium oxalate - Sodium oxalate is not hygroscopic and the small amount of surface water is removed by heating for 2 hours at 105 °C.

Three samples of SRM 40h, Sodium Oxalate, showed a loss of 0.0004, 0.0005 and 0.0001 percent in 2 hours and after 94 hours an additional loss of 0.0004, 0.0003 and 0.0004 percent (Table 18). Two hours of heating at 105 °C was considered to be sufficient for the removal of all surface water.

As with most materials crystallized from aqueous solutions, water could be entrapped in the sodium oxalate crystals. The removal of this water was accomplished by heating the sodium oxalate at 240 °C, which is below the 250-270 °C decomposition temperature. After the standards had been dried at 105 °C, SRM 40h showed a loss of 0.0088 and 0.0090 percent on heating at 240 °C (Table 18).

Table 18. Loss on heating of SRM 40h, Sodium Oxalate.

| | Percent loss | | |
|---|---|---|---|
| 10 g heated for | (1) | (2) | (3) |
| 2 hours at 105 °C | 0.0001 | 0.0004 | 0.0005 |
| +20 hours at 105 °C | 0.0000 | 0.0003 | 0.0000 |
| +74 hours at 105 °C | 0.0004 | 0.0001 | 0.0003 |
| Total at 105 °C | 0.0005 | 0.0008 | 0.0008 |
| 20 hours at 240 °C | ---- | 0.0088 | 0.0090 |

e. Calculation of effective purity of SRM 40h, Sodium Oxalate - The effective purity of the sodium oxalate was calculated by deducting (or adding) the effective percentage of impurities determined from 100. The total effect of the impurities in SRM 40h was minus 0.030 percent, therefore the effective purity of SRM 40h, Sodium Oxalate, is 99.97 percent (Table 19).

Table 19. Impurities in SRM 40h, Sodium Oxalate.

| Impurity | SRM 40h (%) |
|---|---|
| Water | -0.009 |
| $NaHC_2O_4$ | +0.006 |
| $NaHCO_3$ | -0.027 |
| $CO_3$ | ---- |
| Total | -0.030 |

3. Comparison with SRM 83c, Arsenic Trioxide

The sodium oxalate standard SRM 40h was compared to SRM 83c by using potassium permanganate as an intermediate standard. The sodium oxalate was titrated with a potassium permanganate solution as in Section IV.E.1. The direct titration of arsenic trioxide with potassium permanganate is unsatisfactory because the reaction is not stoichiometric, but the addition of a small amount (0.0025 M) of potassium iodide or potassium iodate acts as a catalyst for the complete reduction of potassium permanganate with arsenic trioxide in a slightly acidic solution [39].

a. Dissolution using sodium hydroxide and hydrochloric acid - In the methods given in the literature, the sodium carbonate solution containing the arsenic trioxide is acidified using hydrochloric acid. Also potassium iodide is generally used as the catalyst.

Method:

The arsenic trioxide was dissolved in sodium carbonate, acidified with hydrochloric acid and titrated either visually or potentiometrically [43]. When the visual end point was used the excess potassium permanganate was determined iodiometrically [39].

Reagents:

(a) Potassium iodide solution (0.0025 M) - 0.0415 g of potassium iodide was transferred to a 100 ml volumetric flask, diluted to the mark with water, and mixed.

(b) Potassium permanganate solution (0.1 N) - see Section IV.E.1.

(c) Starch solution - see Section IV.E.1.

(d) Sodium thiosulfate solution (0.02 N) - see Section IV.E.1.

Procedure:

A 0.25 g sample of arsenic trioxide was transferred to a 400 ml beaker and 10 ml of sodium hydroxide (20%) were added. When the arsenic trioxide was dissolved 100 ml of water, 10 ml of hydrochloric acid and one drop of the potassium iodide solution were added. The solution was titrated with the 0.1 N potassium permanganate solution to the visual pink color of potassium permanganate.

To determine the excess potassium permanganate, 0.5 g of potassium iodide was added and the liberated iodine was titrated with the 0.02 N sodium thiosulfate solution. Two ml of starch solution were added just before the yellow iodine color disappeared and the titration was continued to the starch-iodide end point [39].

Weight burets were used for the potassium permanganate solution and all weights were corrected to vacuum.

Grams of $KMnO_4$ solution equivalent to 1 g $As_2O_3$ $= \frac{A}{B-CD}$

where

A = g of arsenic trioxide taken,
B = g of potassium permanganate solution used,
C = ml sodium thiosulfate solution used to determine excess $KMnO_4$, and
D = g potassium permanganate solution equivalent to 1 ml of sodium thiosulfate solution.

Effective purity of $Na_2C_2O_4$, in percent $= \frac{AB}{C} \times \frac{D}{E}$

where

A = g of potassium permanganate solution equivalent to 1 g sodium oxalate,
B = effective purity of arsenic trioxide in percent,
C = g of potassium permanganate solution equivalent to 1 g arsenic trioxide,
D = equivalent weight of sodium oxalate, and
F = equivalent weight of arsenic trioxide.

Results:

In the first set of titrations a platinum electrode - saturated calomel electrode system was in the solution so that the titration could be followed potentiometrically as well as visually. In the second set, the titrations were performed visually with no electrodes present. The platinum electrode - saturated calomel electrode system appeared to have a system bias on the arsenic trioxide - potassium permanganate titration. For each set the potassium permanganate solution was standardized with SRM 83c and the effective purity of SRM 40h, Sodium Oxalate was calculated.

The effective purity of SRM 40h, Sodium Oxalate, when compared to SRM 83c, Arsenic Trioxide, is 99.862 with a standard deviation of 0.018 percent when the platinum electrode and saturated calomel electrode were present and 99.892 with a standard deviation of 0.018 percent when no electrodes were present. The results are given in Table 20.

b. <u>Investigation of the Conditions of the Arsenic Trioxide - Potassium Permanganate Reaction</u> - When hydrochloric acid was used to acidify the arsenic trioxide solutions the effective purity of SRM 40h appeared to be somewhat low. In order to determine the accuracy of this value the following conditions of the titration were studied: use of sulfuric acid and acidity, catalysts, heating, and end point detection.

(1) Use of sulfuric acid and acidity: Lowenthal and Lenssen [44] as early as 1862 showed that hydrochloric acid reacted to a small extent with potassium permanganate during the titration of sodium oxalate. Although later investigators [43,45,46] state that in the titration of arsenic trioxide with potassium permanganate the side reaction

$$2\ KMnO_4 + 16\ HCl \rightarrow 2\ MnCl_2 + 2\ KCl + 5\ Cl_2 + 8\ H_2O$$

does not occur, sulfuric acid was substituted for hydrochloric acid to eliminate the possibility of this side reaction.

Since a 1.8 N sulfuric acid solution is used in most titrations using sulfuric acid, this concentration was tried. The spread of the results was too large (0.4%) so 3.6 N, 0.7 N and 0.35 N sulfuric acid were tested. The 3.6 N sulfuric acid gave results similar to the 1.8 N sulfuric acid. In 0.35 N sulfuric acid the violet color of the potassium permanganate solution was slow to disappear and the end point was reached slowly and was too indistinct to be used. In 0.7 N sulfuric

Table 20. Effective purity of SRM 40h, Sodium Oxalate, compared with SRM 83c, Arsenic Trioxide (NaOH-HCl).

| | g $KMnO_4$ sol per g $As_2O_3$ | Composite No. | g $KMnO_4$ sol per g $Na_2C_2O_4$ | g $Na_2C_2O_4$ per g $As_2O_3$ [a] | Effective purity (%) |
|---|---|---|---|---|---|
| Platinum electrode and saturated calomel electrode in the solution | | | | | |
| | 197.5620 | I | 145.6637 | 0.737308 | 99.865 |
| | 197.5656 | II | 145.6523 | 0.737250 | 99.857 |
| | 197.5562 | III | 145.6498 | 0.737237 | 99.856 |
| | | IV | 145.6184 | 0.737078 | 99.834 |
| | | I | 145.6642 | 0.737310 | 99.865 |
| | | II | 145.6563 | 0.737270 | 99.860 |
| | | III | 145.7070 | 0.737527 | 99.895 |
| Average | 197.5613 | | 145.6588 | 0.737283 | 99.862 |
| σ | | | 0.0263 | 0.000133 | 0.018(0.018%) |
| No electrodes in the solution | | | | | |
| | 197.5199 | I | 145.6637 | 0.737524 | 99.894 |
| | 197.4868 | II | 145.6523 | 0.737466 | 99.887 |
| | 197.5049 | III | 145.6498 | 0.737453 | 99.885 |
| | | IV | 145.6184 | 0.737294 | 99.862 |
| | | I | 145.6642 | 0.737526 | 99.895 |
| | | II | 145.6563 | 0.737486 | 99.889 |
| | | III | 145.7070 | 0.737743 | 99.924 |
| Average | 197.5039 | | 145.6588 | 0.737499 | 99.892 |
| σ | | | 0.0263 | 0.000133 | 0.018(0.018%) |

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[a] Effective purity of SRM 83c, Arsenic Trioxide = 99.988%.

acid the spread of results was within the desirable limits (0.05%), therefore, in the procedure for the titration of arsenic trioxide with a potassium permanganate solution, a 0.7 N sulfuric acid solution was used.

(2) Catalysts: A catalyst is needed to accelerate the reaction between arsenic trioxide and potassium permanganate solution. One drop of potassium iodide solution (0.0025 M) has been used as the catalyst [45] but after the addition of 45 ml of the potassium permanganate solution, the decolorization of the solution was slow and the solution went through a greenish yellow color.

Since an osmium tetroxide solution (0.01 M) has been used as the catalyst in the standardizations with ceric ammonium sulfate solutions [47], the use of this catalyst was tried to determine whether the speed of the initial reaction could be increased. An improvement was noted in the reaction because the greenish-yellow color did not persist but, from 3 to 5 minutes was needed for the reaction with arsenic trioxide to go to completion and decolorize the solution. Also it was determined that 1 ml of osmium tetroxide solution (0.25 mg/ml) was sufficient to catalyze the reaction.

In order to reduce the time to decolorize the solution after the addition of the first 45 ml of potassium permanganate solution a manganous sulfate solution was added. It had been noted that in titration of sodium oxalate with potassium permanganate the potassium permanganate reduction was rapid after a little manganous ion was formed. Accordingly a manganous sulfate solution (0.3 mg/ml) was added to the arsenic trioxide solution and the potassium permanganate color disappeared in 30 seconds. The addition of a manganous sulfate solution and a osmium tetroxide solution was incorporated into the procedure.

(3) Heating: A series of experiments was performed to determine the effects of heating the solution during the titration. Arsenic trioxide solutions were titrated without heating, then arsenic trioxide solutions were heated to 55 -

60 °C after the addition of 45 ml of the potassium permanganate solution. No apparent change was observed on heating, therefore the heating of solutions was discontinued.

(4) End point detection: An attempt was made to determine the excess potassium permanganate needed for the detection of the end point iodimetrically but with the osmium tetroxide present no end point was reached in the sodium thiosulfate titration. When using the pink color of potassium permanganate as the end point of this titration the spread of the results was more than was desired. Although the values obtained for the potentiometric titration in hydrochloric acid appeared to be low, this end point detection was tried in a sulfuric acid solution and the results were more precise and appeared to be more accurate. Therefore, the arsenic trioxide in the sulfuric acid solution was titrated potentiometrically.

### c. Dissolution using Sodium Carbonate and Sulfuric Acid -

Method:

In this method, the arsenic trioxide was dissolved in a sodium carbonate solution and then was acidified with sulfuric acid. The solution was diluted to a 300 ml volume and osmium tetroxide solution and the manganous sulfate solution were added. Approximately 45 ml of the potassium permanganate were added and the solution stirred until it was decolorized. The titration was completed potentiometrically by adding the potassium permanganate solution dropwise.

Reagents:

(a) Water - All water used was freshly boiled and cooled distilled water.

(b) Manganese sulfate solution (0.3 mg/ml) - Forty-six mg of manganous sulfate monohydrate was transferred to a 50 ml volumetric flask, diluted to the mark with sulfuric acid (1+19) and mixed.

(c) Osmium tetroxide solution (0.25 mg/ml) - Two-hundred-fifty mg of osmium tetroxide was transferred to a 1 liter volumetric flask and 200 ml of 0.1 N sulfuric acid were added. When the oxide dissolved the solution was diluted to the mark with 0.1 N sulfuric acid and mixed.

(d) Potassium permanganate solution (0.1 N) - see Section IV.E.1.

Procedure:

A 0.25 g sample of arsenic trioxide was transferred to a 150 ml beaker, 5.00 g of sodium carbonate were added and thoroughly blended. Twenty ml of water were added in 5 ml portions and the solution was warmed to dissolve the sample. The solution was transferred to a 750 ml Erlenmeyer flask and 17.5 ml of sulfuric acid (1+1) were added cautiously through a short stem funnel. When the reaction ceased, the solution was transferred to a 600 ml beaker, 1 ml of the manganese sulfate solution and 1 ml of the osmium tetroxide solution were added, and the solution was diluted to 300 ml with water.

Approximately 45 ml of the 0.1 N potassium permanganate solution were added and the solution was stirred slowly until it was decolorized. The titration with the potassium permanganate solution was followed potentiometrically to the end point. The last ml was added dropwise and the last few drops were split.

Weight burets were used for the potassium permanganate solution and all weights were corrected to vacuum.

$$\text{Effective purity of } Na_2C_2O_2 = \frac{AB}{C} \times \frac{D}{E}$$

where

A = g of potassium permanganate solution equivalent to 1 g sodium oxalate,

B = effective purity of arsenic trioxide in percent,

C = g of potassium permanganate solution equivalent to 1 g arsenic trioxide,

D = equivalent weight of sodium oxalate, and

E = equivalent weight of arsenic trioxide.

Results:

In calculating the effective purity of SRM 40h, the average of the ratios of grams of potassium permanganate solution equivalent to 1 g of SRM 83c was used. The effective purity of SRM 40h is 99.941 percent with a standard deviation of 0.007 percent when compared to SRM 83c, Arsenic Trioxide. The results are given in Table 21.

### 4. Comparison with SRM's 136b and 136c, Potassium Dichromate

Sodium oxalate is not a strong enough reducing agent to reduce potassium dichromate therefore SRM 40h cannot be compared directly with SRM's 136b and 136c.

Since ferrous ion can also be titrated with a potassium dichromate solution, sodium oxalate was compared indirectly to potassium dichromate by titrating the sodium oxalate and ferrous ammonium sulfate hexahydrate with a potassium permanganate solution. The ferrous ammonium sulfate hexahydrate was then compared to potassium dichromate.

The method for the titration of sodium oxalate with a potassium permanganate solution is given in Section IV.E.1 above, and the method for the comparison of potassium dichromate to ferrous ammonium sulfate hexahydrate is given in Section IV.E.1.a. The method for the titration of ferrous ammonium sulfate hexahydrate with a potassium permanganate solution is given below.

Method:

The ferrous ammonium sulfate hexahydrate was dissolved in sulfuric acid and titrated potentiometrically with a potassium permanganate solution.

Reagents:

Potassium permanganate solution (0.1 N) - see Section IV.E.1.

Table 21. Effective purity of SRM 40h, Sodium Oxalate, compared with SRM 83c, Arsenic Trioxide ($Na_2CO_3$-$H_2SO_4$).

| | g $KMnO_4$ sol per g $As_2O_3$[a] | Composite No. | g $KMnO_4$ sol per g $Na_2C_2O_4$ | g $Na_2C_2O_4$ per g $As_2O_3$[a] | Effective purity (%) |
|---|---|---|---|---|---|
| | 196.7141 | I | 145.1841 | 0.737968 | 99.954 |
| | 196.6968 | II | 145.1777 | 0.737936 | 99.950 |
| | 196.7409 | III | 145.1539 | 0.737815 | 99.933 |
| | 196.7510 | IV | 145.1628 | 0.737860 | 99.939 |
| | 196.7263 | IV | 145.1459 | 0.737774 | 99.927 |
| | 196.7587 | III | 145.1624 | 0.737858 | 99.939 |
| | 196.6822 | II | 145.1695 | 0.737894 | 99.944 |
| | 196.7472 | I | 145.1598 | 0.737845 | 99.936 |
| | 196.7636 | I | 145.1730 | 0.737912 | 99.946 |
| | 196.7401 | II | 145.1718 | 0.737906 | 99.945 |
| | 196.7631 | III | 145.1715 | 0.737904 | 99.945 |
| | 196.8987[b] | IV | 145.1694 | 0.737893 | 99.943 |
| Average | 196.7349 | | 145.1668 | 0.737880 | 99.942 |
| σ | 0.0272(0.014%) | | 0.0104 | 0.000053 | 0.007 |

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[a] Effective purity of SRM 83c, Arsenic Trioxide = 99.988%.

[b] Omitted from average.

Procedure:

An accurately weighed 2.00 g sample of ferrous ammonium sulfate hexahydrate was transferred to a 600 ml beaker and 250 ml of sulfuric acid (1+19), freshly boiled and cooled, were added. When the salt was dissolved, 45 ml of the 0.1 N potassium permanganate solution were added and the solution was stirred until all the potassium permanganate had reacted. The titration with the potassium permanganate solution was continued potentiometrically to the end point. The last ml of the titration was added dropwise, splitting the last few drops.

Weight burets were used for the potassium permanganate solution and all weights were corrected to vacuum.

The effective purity of sodium oxalate $= \frac{AD}{BC} \times \frac{E}{F}$

where

A = g of potassium permanganate solution equivalent to 1 g sodium oxalate,
B = g of potassium permanganate solution equivalent to 1 g ferrous ammonium sulfate hexahydrate,
C = g of ferrous ammonium sulfate hexahydrate equivalent to 1 g potassium dichromate,
D = effective purity of potassium dichromate in percent,
E = equivalent weight of sodium oxalate, and
F = equivalent weight of potassium dichromate.

SRM 40h, Sodium Oxalate, has an effective purity of 99.973 percent when compared with SRM 136b, Potassium Dichromate. In the comparison of SRM 136b with ferrous ammonium sulfate hexahydrate, only four runs were made. One of these runs was discarded since the titration did not follow the expected pattern and the end point of the titration was doubtful. The average equivalent of SRM 136b to ferrous ammonium sulfate hexahydrate was used for the calculations of the grams of the potassium permanganate solution equivalent to 1 g potassium dichromate.

The average of these values was used to compute the effective purity. The results are given in Table 22.

SRM 40h has an effective purity of 99.967 percent when compared with SRM 136c, Potassium Dichromate. In the comparison of SRM 136c with ferrous ammonium sulfate hexahydrate, twelve runs were made because this standard is the present potassium dichromate Standard Reference Material. The effective purity of SRM 40h was calculated in the same manner as with SRM 136b. The results are given in Table 23.

### 5. Summary

SRM 40h, Sodium Oxalate, will be certified with an effective purity of 99.97 percent. This value is based on the comparisons of SRM 40h to SRM 40g and to SRMs 136b and 136c, Potassium Dichromate. The effective purity of SRM 40h is 99.97 percent when compared to SRM 40g through a potassium permanganate solution; 99.973 percent when compared to SRM 136b through a potassium permanganate solution and ferrous ammonium sulfate hexahydrate; 99.967 percent when compared to SRM 136c in the same manner as SRM 136b. The results are given in Table 24.

The lower part of the table gives the other determinations of the effective purity of SRM 40h. When the effective percentage of impurities were determined and subtracted from 100 percent the effective purity of SRM 40h is 99.97.

The effective purity of SRM 40h is 99.941 percent when compared with SRM 83c, Arsenic Trioxide. This value could be 0.03 percent low since the platinum electrode - saturated calomel electrode system was used for the detection of the end point. In the study for the detection of the end point (acidification with hydrochloric acid), an 0.03 percent lower value was found when electrodes were present in the solution than when the titration was performed visually.

Table 22. Effective purity of SRM 40h, Sodium Oxalate, compared with SRM 136b, Potassium Dichromate.

| | g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$ | g $KMnO_4$ sol per g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | g $KMnO_4$ sol per g $K_2Cr_2O_7$ | SRM 40h Composite No. | g $KMnO_4$ sol per g $Na_2C_2O_4$ | g $Na_2C_2O_4$ per g $K_2Cr_2O_7$ [a] | Effective purity(%) |
|---|---|---|---|---|---|---|---|
| | 8.00903 | 26.2957[b] | 210.5996[b] | I | 153.8730[b] | 0.730862[b] | 99.848[b] |
| | 8.00904 | 26.2904 | 210.5572 | II | 154.0710 | 0.731803 | 99.976 |
| | 8.00504[c] | 26.2885 | 210.5420 | III | 154.0741 | 0.731818 | 99.978 |
| | 8.00863 | 26.2898 | 210.5524 | IV | 154.0513 | 0.731709 | 99.963 |
| | | 26.2842 | 210.5075 | IV | 154.0492 | 0.731695 | 99.961 |
| | | 26.2869 | 210.5292 | III | 154.0679 | 0.731788 | 99.974 |
| | | 26.2856 | 210.5187 | II | 154.0646 | 0.731772 | 99.972 |
| | | 26.2862 | 210.5235 | I | 154.0953 | 0.731918 | 99.992 |
| | | 26.2879 | 210.5372 | I | 154.0486 | 0.731696 | 99.962 |
| | | 26.2887 | 210.5436 | II | 154.0395 | 0.731653 | 99.956 |
| | | 26.2889 | 210.5452 | III | 154.0902 | 0.731894 | 99.989 |
| | | 26.2885 | 210.5420 | III | 154.0470 | 0.731689 | 99.961 |
| | | | | IV | 154.0623 | 0.731762 | 99.971 |
| | | | | III | 154.0787 | 0.731839 | 99.981 |
| | | | | II | 154.0896 | 0.731891 | 99.988 |
| | | | | I | 154.0743 | 0.731819 | 99.978 |
| Ave. | 8.00890 | 26.2878 | 210.5362 | | 154.0669 | 0.731783 | 99.973 |
| σ | 0.00023(0.003%) | 0.0019(0.007%) | 0.0150(0.007%) | | 0.0177 | 0.000083 | 0.011 |

---

[a] Effective purity of SRM 136b, Potassium Dichromate = 99.979%.

[b] Omitted from average.

[c] End point was doubtful, not included in average.

Table 23. Effective purity of SRM 40h, Sodium Oxalate, compared with SRM 136c, Potassium Dichromate.

| | g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ per g $K_2Cr_2O_7$ | g $KMnO_4$ sol per g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | g $KMnO_4$ sol per g $K_2Cr_2O_7$ | SRM 40h Composite No. | g $KMnO_4$ sol per g $Na_2C_2O_4$ | g $Na_2C_2O_4$ per g $K_2Cr_2O_4$ [a] | Effective purity(%) |
|---|---|---|---|---|---|---|---|
| | 8.01026 | 26.2957[b] | 210.6220[b] | I | 153.8730[b] | 0.730785[b] | 99.841[b] |
| | 8.01025 | 26.2904 | 210.5795 | II | 154.0710 | 0.731725 | 99.970 |
| | 8.00965 | 26.2885 | 210.5643 | III | 154.0741 | 0.731740 | 99.972 |
| | 8.00948 | 26.2898 | 210.5747 | IV | 154.0513 | 0.731631 | 99.957 |
| | 8.00965 | 26.2842 | 210.5299 | IV | 154.0492 | 0.731622 | 99.955 |
| | 8.00994 | 26.2869 | 210.5519 | III | 154.0679 | 0.731710 | 99.968 |
| | 8.00961 | 26.2856 | 210.5411 | II | 154.0646 | 0.731695 | 99.965 |
| | 8.00911 | 26.2862 | 210.5459 | I | 154.0953 | 0.731840 | 99.985 |
| | 8.00965 | 26.2879 | 210.5595 | I | 154.0486 | 0.731619 | 99.955 |
| | 8.00971 | 26.2887 | 210.5659 | II | 154.0395 | 0.731575 | 99.949 |
| | 8.00996 | 26.2889 | 210.5675 | III | 154.0902 | 0.731816 | 99.982 |
| | 8.00995 | 26.2885 | 210.5643 | IV | 154.0470 | 0.731611 | 99.954 |
| | | | | IV | 154.0623 | 0.731684 | 99.964 |
| | | | | III | 154.0787 | 0.731762 | 99.975 |
| | | | | II | 154.0896 | 0.731813 | 99.982 |
| | | | | I | 154.0743 | 0.731741 | 99.972 |
| Ave. | 8.00975 | 26.2878 | 210.5586 | | 154.0669 | 0.731706 | 99.967 |
| σ | 0.00032(0.004%) | 0.0019(0.007%) | 0.0149(0.007%) | | 0.0177 | 0.000082 | 0.011 |

---

[a] Effective purity of SRM 136c, Potassium Dichromate = 99.983%.

[b] Omitted from average.

Table 24. Effective purity of SRM 40h, Sodium Oxalate.

| | Effective purity (%) |
|---|---|
| For certification | |
| SRM 136c ($K_2Cr_2O_7$) | 99.967 |
| SRM 136b ($K_2Cr_2O_7$) | 99.973 |
| SRM 40g ($Na_2C_2O_4$) | 99.97 |
| Average | 99.97 |
| Other comparisons | |
| Determination of Impurities | 99.97 |
| SRM 83c ($As_2O_3$) | 99.941 |

# V. SUMMARY OF RESULTS

The oxidimetric standard reference materials have been intercompared and a final certificate of analysis will be issued for each standard. The interrelationship of the SRM's is given in Figure 10 and the effective purity in Table 25.

Table 25. Effective purity of oxidimetric standard reference materials.

| SRM | Effective purity[a] (%) |
|---|---|
| 83c, Arsenic Trioxide | 99.988 |
| 136c, Potassium Dichromate | 99.983 |
| 40h, Sodium Oxalate | 99.97 |

---

[a] Error terms discussed in text.

In Figure 10 the basis of the intercomparison is the International System of Units (SI) with measurements through the coulomb and the mass of the iodine used in the titrations. The differences are recorded in the direction of the arrows. With the coulomb and mass of iodine taken as basic standards and following the arrows in any manner the value obtained for any SRM will agree within 0.007 percent except when the relationship of SRM 83c to SRM 40h is involved. However, in Section IV.E.5 it has been shown that the value for this relationship probably is in error and should be disregarded.

The coulomb and the mass of high purity iodine are taken as standards because their measurement is based on SI ampere, seconds and grams. Iodine is monomulcidic thus its atomic weight is known accurately to 1 part in 1,000,000. Using a microbalance the mass of iodine can be determined within one part in 100,000. The coulometoric measurement involves the measurement of time, current and mass. The current was measured by the use of a NBS calibrated secondary standard. A micro-

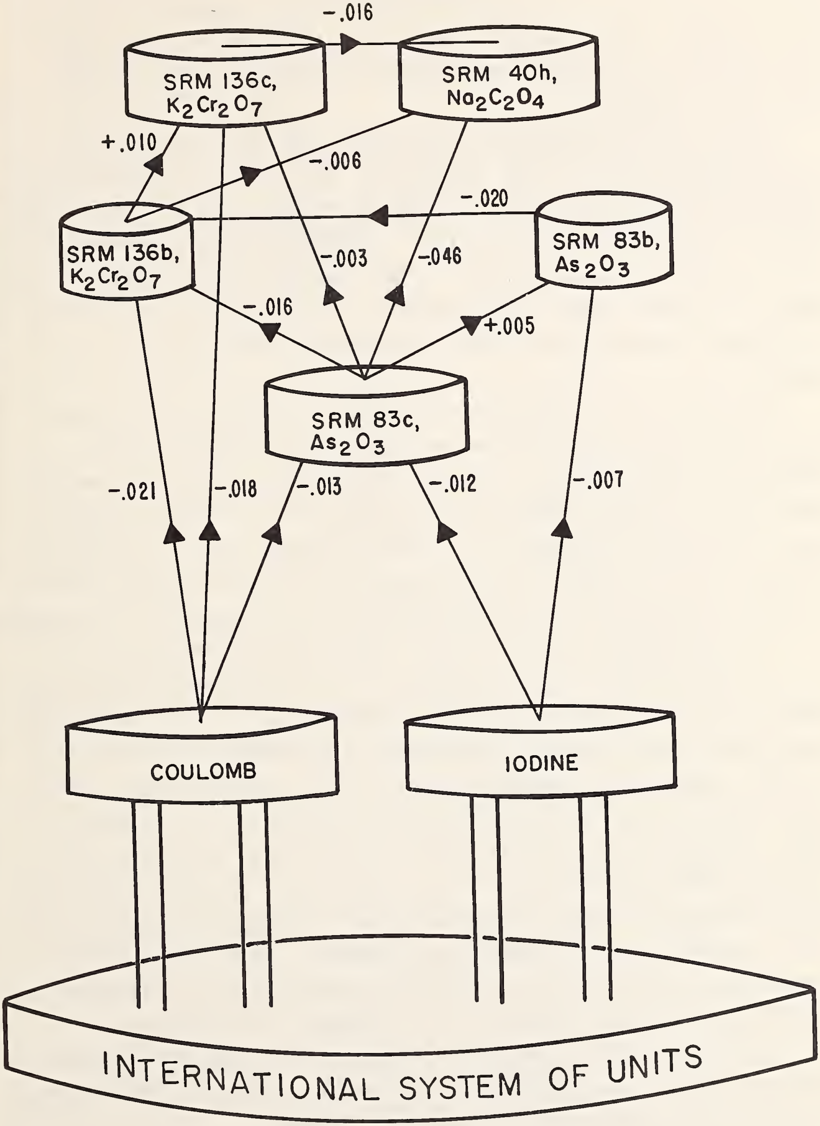

Figure 10. Intercomparison of redox Standard Reference Materials.

balance was used to obtain all weights and time was based on the standard 100 k Hz WWV frequency. Therefore, the charge involved in coulometric measurement is known within a few parts in 1,000,000.

The effective purity of SRM 83c, Arsenic Trioxide, is 99.988 percent and is the average of the values determined by comparison with purified iodine and by coulometry. The value for the comparison with purified iodine is 99.9878 percent with a standard deviation of 0.0085 percent for 16 degrees of freedom and the value for coulometry is 99.9873 percent with a standard deviation of 0.0032 percent for five degrees of freedom.

The effective purity of SRM 136c, Potassium Dichromate, is 99.983 percent and is the average value determined by comparison with SRM 83c, Arsenic Trioxide, and by coulometry. The value for the comparison with SRM 83c is 99.985 percent with a standard deviation of 0.0063 percent for 11 degrees of freedom and the value for coulometry is 99.982 percent with a standard deviation of 0.0028 percent for 19 degrees of freedom.

The effective purity of SRM 40h, Sodium Oxalate, is 99.97 percent and is the average of the values determined by comparisons with SRM 40g, Sodium Oxalate; SRM 136b, Potassium Dichromate; and SRM 136c, Potassium Dichromate. The value for the comparison with SRM 40g is 99.97 percent with a standard deviation of 0.030 percent for 29 degrees of freedom ($KMnO_4$ Solution No. 3) and 0.013 percent for 30 degrees of freedom ($KMnO_4$ Solution No. 4). The value for the comparison with SRM 136b is 99.973 percent with a standard deviation of 0.011 percent for 15 degrees of freedom. The value for the comparison with SRM 136c is 99.967 percent with a standard deviation of 0.011 percent for 15 degrees of freedom.

The final Certificates of Analysis for SRM 83c, Arsenic Trioxide; SRM 136c, Potassium Dichromate; and SRM 40g, Sodium Oxalate; will be issued in the near future.

# ACKNOWLEDGMENTS

The authors are indebted to Mrs. Virginia C. Stewart for the spectrographic analyses, to Paul J. Paulsen and Charles W. Mueller for the spark source mass spectrographic analyses, and to Rolf A. Paulson and William P. Schmidt for ACS Specification testing of these standards. Special appreciation is expressed for the assistance of Mrs. Joy J. Shoemaker in the preparation of this report.

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U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

# Certificate of Analysis

# STANDARD REFERENCE MATERIAL 136c

## Potassium Dichromate

## (Oxidimetric Standard)

Purity on basis of effective oxidizing power . . . . . . . . . . . . 99.98 ± 0.02 percent

This lot of material was prepared to ensure material of high purity and uniformity. It conforms to the American Chemical Society specification for analytical reagent grade material, but is not to be considered as entirely free from traces of impurities. It is certified only for its effective oxidizing power.

Standardizations have been made by the coulometric method by G. Marinenko (see NBS J. Res. 67A, 453 (1963)), by direct comparison with arsenic trioxide SRM 83c, and by comparison with the previous SRM 136b through ferrous ammonium sulfate by K. Sappenfield. Impurity tests to the ACS specifications were made by W. P. Schmidt, emission spectrography by V. Stewart, and spark-source mass spectrography by C. W. Mueller.

Drying tests indicate that losses of the order of 0.005 percent are obtained on a few hours drying at 105 °C; long time drying indicates that losses approach 0.01 percent. The problem of occluded and surface moisture will be studied before a final certificate is issued. The effective assay is based on the sample as issued. The tolerance indicated is at least as large as the 95 percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error.

The overall direction and technical measurements leading to certification were performed under the chairmanship of R. A. Durst.

The technical and support aspects in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
March 24, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

# Certificate

# STANDARD REFERENCE MATERIAL 83c

## Arsenic Trioxide

Purity on Basis of Effective Reducing Power . . 99.99 percent

This lot of arsenic trioxide was prepared to ensure material of high purity and uniformity. It conforms to the American Chemical Society specification for reagent grade material.

The assay, for the present, is based on a direct comparison with the potassium dichromate standard 136b. The value is compatible with the previous arsenic trioxide standard 83b, with the potassium dichromate standard 136b, and with high-purity normal uranium metal, using the 1961 table of Atomic Weights based on Carbon-12. The estimated experimental error is about 0.02 percent, and work is in progress on additional standardization procedures.

The sample as issued does not lose over 0.002 percent in weight on drying up to 24 hours at 105 °C. The assay value, for the present, is based on the material as issued.

Washington, D. C. 20234
February 6, 1962
(Reprinted April 16, 1970)

Harry C. Allen, Jr., Chief
Analytical and Inorganic
Chemistry Division

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

# Certificate of Analysis

## Standard Reference Material 40h
## Sodium Oxalate

$Na_2C_2O_4$, effective purity ............................99.95 ± 0.05 percent

This lot of sodium oxalate was prepared to ensure material of purity and uniformity compatible with its 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 (0.03%), and sodium hydrogen carbonate (0.03%). The material is not appreciably hygroscopic.

The effective purity of the sodium oxalate can be realized in the standardization of $KMnO_4$ solutions by use of the directions on this certificate. Homogeneity testing, effective purity, sodium hydrogen oxalate and sodium hydrogen carbonate determinations were made by K. M. Sappenfield; American Chemical Society specification tests were made by W. P. Schmidt of the Analytical Chemistry Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 24, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

*Standardization of 0.1N permanganate.* Transfer 0.3 g of sodium oxalate (dried at 105 °C) to a 600-ml beaker. Add 250 ml of diluted sulfuric acid (5+95) previously boiled for 10 to 15 minutes and then cooled to 27 ± 3 °C. Stir until the oxalate has dissolved. Add 39 to 40 ml (0.3 g of sodium oxalate requires approximately 44.8 ml of $0.1N$ $KMnO_4$) of $0.1N$ potassium permanganate at a rate of 25 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 permanganate is too strong, discard, and begin again, adding less of the $KMnO_4$ solution). Heat to 55 to 60 °C and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise, with particular care to allow the solution to become decolorized before the next drop is introduced.

Determine the excess of permanganate required to impart the permanent pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the specially treated dilute sulfuric acid at 55 to 60 °C. This correction usually amounts to 0.03 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 [*cf.* W. C. Bray, J. Am. Chem. Soc. 32, 1205 (1910)] 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 $0.02N$ thiosulfate. To obtain the ratio of the thiosulfate to the permanganate solution, add 1 ml of the $0.1N$ permanganate to 350 ml of the diluted sulfuric acid (5+95), stir, add 0.5 g KI, and titrate with the thiosulfate solution, adding starch just before the end point is reached.

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# APPENDIX II

## Preparation of Calibration Curve for the Determination of Excess Iodine

In the preparation of the calibration curve, the concentration of iodine in a 300 ml volume of solution was used since in all titrations the solution could be diluted to this volume. The calibration solutions were prepared by adding the iodine to 60 ml of a 300 ml solution which was prepared in the same manner as a titration solution except arsenic trioxide was omitted. After reading the absorbance of the calibration solutions the calibration curve was prepared by plotting iodine concentration in 300 ml volume against absorbance.

An absorption curve of iodine was prepared so that the appropriate wave length could be selected. A spectrophotometer was used and the absorption measured at intervals between 325 nm and 500 nm. A wave length of 375 nm was selected, for convenience, even though 365 nm gave the maximum absorbance.

### Reagents:

(a) Water - All the water used was freshly boiled and cooled distilled water.

(b) Sodium bicarbonate solution (60 g/l) - Sixty grams of $NaHCO_3$ were dissolved in 900 ml water and diluted to one liter.

(c) Standard iodine solution (0.00025 g I/ml) - Ten ml of 0.1 N iodine solution were transferred to a 500 ml volumetric flask and diluted to the mark with water.

### Procedure:

A 10 g sample of sodium carbonate was transferred to a 500 ml glass-stoppered Erlenmeyer flask and 25 ml of water were added. The solution was warmed to dissolve the salt and then was cooled in ice water. One hundred ml of the sodium bicarbonate solution and ten grams of potassium iodide were added. When the potassium iodide was dissolved, the solution was diluted to 300.0 ml with water.

To 60.0 ml portions of the solution, 0.0, 0.5, 1.0, 1.5 and 2.0 ml of the standard iodine solution were added respectively, and mixed. A suitable portion of each solution was transferred to a 2 cm photometric cell and the absorbance of the solution was measured using a 375 nm filter and using the absorbance of water as zero. The curve was drawn by plotting mg of iodine in a 300 ml of solution against absorbance. The data for the curve is given in Table 26 and the plot in Figure 11.

Table 26. Calibration curve.

| ml $I_2$ | mg $I_2$ in 60 ml | Equivalent $I_2$ in 300 ml | Absorbance (%) |
|---|---|---|---|
| 0.00 | 0.000 | 0.0000 | 0.000 |
| 0.50 | 0.1254 | 0.6267 | 0.181 |
| 1.00 | 0.2507 | 1.2535 | 0.357 |
| 1.50 | 0.3761 | 1.8802 | 0.516 |
| 2.00 | 0.5014 | 2.5070 | 0.638 |

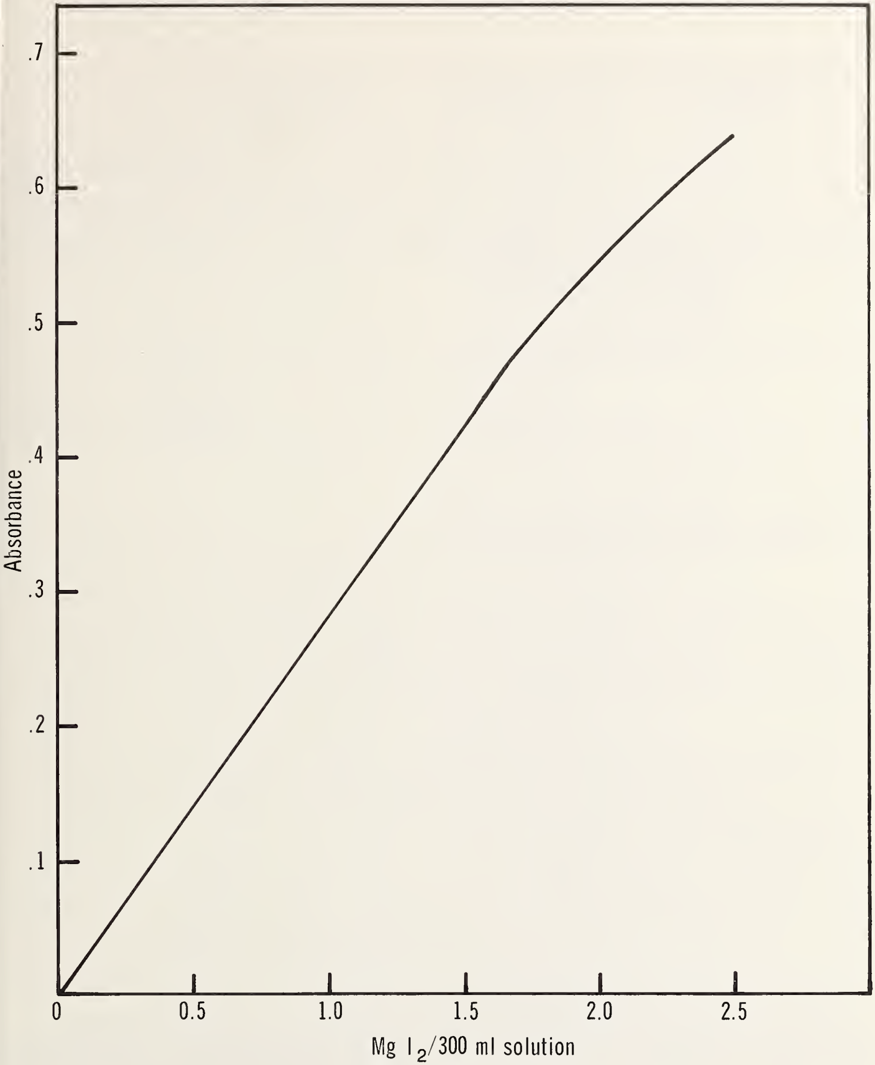

Figure 11. Photometric calibration curve for excess iodine.

FORM NBS-114A (1-71)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

The methods described in this publication are those that have been used at the National Bureau of Standards for the comparison of the current oxidimetric standard reference materials with each other and for the determination of the effective purity of these standard reference materials. The methods, which are modifications of well-established and previously published methods, were selected or designed for their accuracy and dependability. An accurate method was devised for the determination of the effective purity of the arsenic trioxide standard SRM 83c by adding solid iodine and determining the excess iodine photometrically.

17. KEY WORDS (Alphabetical order, separated by semicolons)

Analytical procedures; arsenic-iodine method; comparison; effective purity; oxidimetric standards.

18. AVAILABILITY STATEMENT

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