1. Introduction

Bromate is an inorganic by-product of disinfectants. It is one of the analytes of interest in wastewater analysis. Environmental laboratories have a regulatory need for their measurements to be traceable to NIST standards. Bromate is not currently certified as a NIST Standard Reference Material (SRM); thus, a traceable assay of potassium bromate (KBrO₃) is needed.

Bromate is a strong oxidizing agent, which oxidizes iron (II), arsenic (III) and oxalate (C₂O₄²⁻) [2] and titrates directly with antimony (III), thallium (I), and hydrazine in acid medium [3]. Bromate may be used for the titration of mercury (I) and hexacyanoferrate (II) [2]. Bromate has been used for the determination of certain organic compounds, which undergo bromination of the aromatic rings, e.g., phenol and 8-quinolinol [2].

Many of the bromate titration methods use a visual end point detection. Some irreversible indicators used for bromate titrations are methyl red (color changes from red to yellow), methyl orange (color changes from red to yellow), and indigo sulfonic acid (color changes from blue to colorless) [2]. Reversible redox indicators that may be used are p-ethoxychrysoiden (color changes from red to colorless), quinoline yellow (color changes from yellow-green to colorless), and α-naphthoflavone (color changes from pale yellow to orange brown) [2]. Bromate may be titrated against standardized thiosulfate in acid medium with iodine and a catalyst (ammonium molybdate) [3,4,5,6]. Bromate mass fraction has been determined by titration with arsenious oxide in acid solution using an amperometric end point [7]. The method chosen here to assay the potassium bromate is the redox titration of bromate with arsenious oxide in acid medium [8,9,10], because of the availability of the primary standard, SRM 83d, Arsenic Trioxide Reductometric Standard, and the simplicity of the reaction.

Potassium Bromate Assay by Redox Titrimetry Using Arsenic Trioxide

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2. Reagents

The following chemicals were used: Potassium bromate (KBrO₃), ACS reagent; SRM 83d, Arsenic Trioxide (As₂O₃); 5 mol/L sodium hydroxide (NaOH) prepared from analytical reagent grade; 10 mol/L high-purity hydrochloric acid (HCl); and 1 % (mass fraction) methyl red indicator in ethanol (200 proof). All water used was 18 MΩ·cm. The KBrO₃ was dried at 150 °C for 21 h, and the As₂O₃ was dried at 110 °C for 12 h. Both salts were stored over anhydrous magnesium perchlorate in a desiccator.

3. Procedure

Three solutions were prepared from the dried KBrO₃ to a nominal mass fraction of 0.012 g/g. Each solution was titrated on a separate day. The assay procedure [8,9,10] was a redox titration in which As₂O₃ was titrated with potassium bromate according to Eq. (1) and Eq. (2).

\[ 3 \text{As}_2\text{O}_3 + 2 \text{KBrO}_3 + 9 \text{H}_2\text{O} \rightarrow 6 \text{H}_3\text{AsO}_4 + 2 \text{KBr} \]  

\[ \text{BrO}_3^- + 5 \text{Br}^- + 6 \text{H}^+ \rightarrow 3 \text{Br}_2 + 3 \text{H}_2\text{O}. \]  

According to Eq. (2), after all the As₂O₃ has been consumed, the end point (first appearance of free bromine) is detected by irreversible decolorization of the indicator and/or change in potential.

A nominal 0.1 g sample of As₂O₃ was weighed (± 0.00001 g) in a platinum boat. After transferring the sample to a 150 mL beaker, 10 mL of 5 mol/L NaOH was added. The concentration of NaOH is important to insure complete dissolution. It takes about 5 min to 10 min for the As₂O₃ to dissolve, and difficulty in dissolution occurs with more dilute NaOH. A magnetic stir bar, 50 mL of water, and 10 mL of 10 mol/L HCl were added to the solution. The resulting acidic medium is required for the titration method. The indicator, two drops of methyl red indicator, was added just before the start of the titration. At the end point, the indicator turns from red to colorless.

The flow diagram (Fig. 1) illustrates the KBrO₃ titrant additions.

![](flow_diagram.png)

The remainder of the KBrO₃ (volumetric KBrO₃), about 0.4 mL of a more dilute solution with a nominal dilution factor of three, was titrated volumetrically to a potentiometric end point using an automated titrator. A visual end point from the indicator was also observed at this time. A combination platinum electrode (Schott Blue line 31 RX) was immersed in the solution on a sample changer and the titrant (dilute KBrO₃) was added from a 10 mL buret of an automated titrator. As the solution was mixed by the rotating stir bar, the automated titrator added equal-volume (0.006 mL) increments of dilute KBrO₃ titrant. Data stored included the volume of titrant added, V, with a corresponding measured potential, E, and numerical estimates of the first derivative (dE/dV). The end point was determined as the maximum of this first derivative. The amount of dilute KBrO₃ added to reach the end point was the volumetric KBrO₃. At least two blanks (reagents only, omitting As₂O₃) were titrated volumetrically with the dilute KBrO₃ titrant each day.

The amount of gravimetric KBrO₃ (g) and volumetric KBrO₃ (mL) were added to calculate the titrant (total KBrO₃) using Eq. (3) as follows:

\[ V \text{ol} \times \text{(mg/mL)} = \text{mg KBrO}_3 \]
\[ m_{\text{total titrant}} = \left( m_{\text{conc KBrO}_3} + \rho\left( V_{\text{dil KBrO}_3} - V_{\text{blank}} \right) \right) / DF \]  \hspace{1cm} (3)

where \( m_{\text{total titrant}} \) = mass of total \( \text{KBrO}_3 \) (g) at the end point

\( m_{\text{conc KBrO}_3} \) = mass of concentrated \( \text{KBrO}_3 \) solution (gravimetric \( \text{KBrO}_3 \)) (g)

\( \rho \) = density of dilute \( \text{KBrO}_3 \) solution (g/mL)

\( V_{\text{dil KBrO}_3} \) = volume of dilute \( \text{KBrO}_3 \) solution (mL)

\( V_{\text{blank}} \) = volume of dilute \( \text{KBrO}_3 \) solution titrated for the blank (mL)

\( DF \) = dilution factor.

According to Eq. (4) below, the mass fraction (\( w \)), in %, of \( \text{KBrO}_3 \) was calculated as the ratio of the \( \text{KBrO}_3 \) (g/g) from the titration with \( \text{As}_2\text{O}_3 \) (1st factor) to the \( \text{KBrO}_3 \) (g/g) from the preparation of the gravimetric solution (2nd factor) as follows:

\[ W_{\text{KBrO}_3} = \left( \frac{m_{\text{As}_2\text{O}_3} \cdot W_{\text{As}_2\text{O}_3} \cdot 2M_{\text{KBrO}_3}}{m_{\text{total titrant}} \cdot 3M_{\text{As}_2\text{O}_3}} \right) \times 100 \]  \hspace{1cm} (4)

where \( W_{\text{KBrO}_3} \) = mass fraction of \( \text{KBrO}_3 \) (%)

\( m_{\text{As}_2\text{O}_3} \) = mass of \( \text{As}_2\text{O}_3 \) (g)

\( W_{\text{As}_2\text{O}_3} \) = mass fraction of \( \text{As}_2\text{O}_3 \) (g/g)

\( M_{\text{KBrO}_3} \) = molecular weight of \( \text{KBrO}_3 \) (g/mol)

\( M_{\text{As}_2\text{O}_3} \) = molecular weight of \( \text{As}_2\text{O}_3 \) (g/mol)

\( m_{\text{total titrant}} \) = mass of total \( \text{KBrO}_3 \) (g)

\( m_{\text{grav KBrO}_3 \text{ soln}} \) = mass of \( \text{KBrO}_3 \) gravimetric solution prepared from \( \text{KBrO}_3 \) salt (g)

\( m_{\text{grav KBrO}_3 \text{ salt}} \) = mass of \( \text{KBrO}_3 \) (salt) for preparation of gravimetric solution (g).

The molecular weights (relative molecular masses) of \( \text{KBrO}_3 \) and \( \text{As}_2\text{O}_3 \) are 167.001 g/mol and 197.8412 g/mol, respectively [11]. The mass measurements were corrected for air buoyancy. The densities of the dilute and concentrated \( \text{KBrO}_3 \) solutions were determined. Corrections for air buoyancy were calculated based on densities [12] of 3.27 g/mL for \( \text{KBrO}_3 \), 3.738 g/mL for \( \text{As}_2\text{O}_3 \), 0.00117 g/mL for air, and 8.0 g/mL for the stainless steel calibration weights in the microbalance [13].

4. Purity Analysis of \( \text{KBrO}_3 \)

A potassium bromate sample was analyzed by glow discharge mass spectrometry (GDMS) [14]. Among the element impurities found were arsenic and chlorine, present at 1 \( \mu \)g/g and 10 \( \mu \)g/g, respectively. Assuming the worst situation that all arsenic is present as As (III), and all chlorine as Cl (V), the maximum relative effects on the \( \text{KBrO}_3 \) assay (mass fraction, %) of these two impurities are no greater than 0.001 % and 0.005 %, respectively, which is insignificant compared to the final expanded uncertainty (0.20 %) of the \( \text{KBrO}_3 \) assay (mass fraction, %). The arsenic impurity is probably present as As (V), since As(III), if present, would be oxidized to As (V) by the bromate matrix. However, to estimate the worst possible effect, arsenic (determined by GDMS) is assumed to be As (III). No correction or further consideration regarding the GDMS analysis is given.

5. Results and Discussion

The recommended mass fraction value for \( \text{KBrO}_3 \) and its uncertainty are summarized in Table 1. There is a difference among the titration results of the three solutions. The recommended value represents the combined mean mass fractions of the \( \text{KBrO}_3 \) in solutions 1, 2, and 3. The uncertainty assigned to the recommended value is calculated by combining the uncertainties of the measurements of \( \text{KBrO}_3 \) in the three solutions [15]. The resulting expanded uncertainty makes use of both within and between estimates of uncertainty. The within measurement uncertainty is calculated according to Eq. (5).

\[ u_{\text{within}} = \sqrt{u_1^2 + u_2^2 + u_3^2} \]  \hspace{1cm} (5)

where \( u_{\text{within}} \) = within measurement uncertainty

\( u_1 \) = combined uncertainty (\( u_c \)) of solution 1

\( u_2 \) = combined uncertainty (\( u_c \)) of solution 2

\( u_3 \) = combined uncertainty (\( u_c \)) of solution 3.

The between measurement uncertainty component is determined according to Eq. (6).

\[ u_{\text{between}} = \frac{\text{range}}{\sqrt{12}} \]  \hspace{1cm} (6)

where \( u_{\text{between}} \) = between measurement uncertainty

[range] = absolute value of the difference between the maximum mean value for a solution (2) and the minimum mean value for a solution (3).

The expanded uncertainty is found according to Eq. (7) using a coverage factor of 2 [15].

\[ U = 2 \sqrt{u_{\text{within}}^2 + u_{\text{between}}^2} \]  \hspace{1cm} (7)
Summaries of results for solutions 1, 2, and 3 are presented in Table 2. Uncertainties were determined using the ISO Guidelines [16]. The individual components of uncertainty (Type A and Type B) are listed in Table 3 for solution 1. The $u_i$ represent the standard uncertainties associated with each of the uncertainty components, and the $c_i$ represent the associated sensitivity coefficients [17]. Since the Type B uncertainty components for each solution are similar, only the uncertainty components of solution 1 are listed in Table 3. Comparisons of the individual uncertainty components are discussed later. Type A uncertainties are calculated from the standard deviations of the mean. Type A uncertainties represent the random variation in the following measurands: titration of KBrO$_3$, titration of blanks, density, and the assay of As$_2$O$_3$ [18]. The combined Type A uncertainty is calculated using the root-sum-of-square (RSS).

The combined Type B uncertainty is calculated in a manner similar to that used to calculate the Type A uncertainty. The components of Type B uncertainty include the following: mass of As$_2$O$_3$, molecular weight of both As$_2$O$_3$ and KBrO$_3$, mass of concentrated KBrO$_3$ solution (titrant), volume of dilute KBrO$_3$ solution, dilution factor of the dilute titrant (KBrO$_3$ solution), mass of concentrated KBrO$_3$ solution, mass of KBrO$_3$ salt used to prepare the concentrated KBrO$_3$ solution, and the mass of the concentrated KBrO$_3$ solution.

The uncertainty of the dilution factor is calculated by combining the uncertainties of the two mass measurements used to prepare the dilute KBrO$_3$ solution. A standard uncertainty of 30 $\mu$g for each mass measurement with a 10 $\mu$g resolution balance is estimated. The uncertainty of the mass of concentrated KBrO$_3$ solution (titrant) is 100 $\mu$g. This includes the uncertainties associated with the mass measurement of the filled syringe in a beaker, drift, and possible evaporation. It is calculated as the sum in quadrature of the uncertainty of the syringe before and after delivery of the titrant, and equals 141 $\mu$g. Because the actual mass value is most likely near the center of this range, the uncertainty distribution is best modeled as a triangular distribution. The standard uncertainty is then 58 $\mu$g (141 $\mu$g / $\sqrt{6}$). The mass measurement uncertainty of As$_2$O$_3$ is estimated to be 60 $\mu$g. Its uncertainty is calculated as the sum in quadrature of the uncertainty of each mass measurement (As$_2$O$_3$ was weighed by difference) and equals 85 $\mu$g. The corresponding standard uncertainty, using a triangular distribution, is 35 $\mu$g (85 $\mu$g / $\sqrt{6}$).

To calculate the uncertainty of the volume of dilute KBrO$_3$ solution, the uncertainty in the accuracy of the buret and the uncertainty associated with the volume

| Table 1. Summary of results for titrimetric assay of potassium bromate |
|---------------------------------------------------------------|
|                | Solution 1 | Solution 2 | Solution 3 | Combined |
| Determined value (mass fraction (%)) | 99.796 | 99.900 | 99.586 | 99.761 |
| Within component | $0.063^b$ | $0.041^b$ | $0.107^b$ | $0.044$ |
| Between component | | | | $0.091$ |
| Combined uncertainty ($u_c$) | | | | $0.101$ |
| Expanded uncertainty ($U$) | | | | $0.201$ |

Recommended value $^{a,c}$

| | 99.76 ± 0.20 |

$^{a}$ Buoyancy corrected.

$^{b}$ Table 2.

$^{c}$ [15]; $k = 2.$

| Table 2. Summary of results for titration assay of KBrO$_3$, solutions 1, 2, 3 |
|---------------------------------------------------------------|
| Potassium bromate | Mass fraction (%) |
|-------------------|-------------------|
| Measured value $^{a}$ | 99.796 | 99.900 | 99.586 |
| Uncertainties | | | |
| Type A ($c_i u_i$) | $0.045^b$ | $0.018^b$ | $0.098^b$ |
| Type B ($c_i u_i$) | $0.044$ | $0.037$ | $0.043$ |
| Combined uncertainty ($u_c$) | $0.063$ | $0.041$ | $0.107$ |

$^{a}$ Buoyancy corrected.

$^{b}$ $n = 12$ measurements.
additions from the titrator are combined in quadrature. The uncertainty in the accuracy of the 10 mL buret, according to manufacturer’s specification, is 0.15 % of the volume of dilute KBrO₃ solution added (about 0.4 mL). Assuming a uniformly probable distribution for buret error, this value is converted to a standard uncertainty by division by . The volume of dilute KBrO₃ solution additions from the titrator was 0.006 mL for solutions 2 and 3, and 0.01 mL for solution 1. Uncertainties for volume increments were computed as standard errors for assumed underlying triangular distributions (0.006 mL / for solutions 2 and 3, and 0.01 mL / for solution 1). The standard uncertainty of the volume of dilute KBrO₃ was larger for solution 1 than for solutions 2 and 3.

The uncertainties in the molecular weight of both As₂O₃ and KBrO₃ are calculated from the recommended uncertainties in the IUPAC assigned relative atomic masses [11] of the elements (As, O, K, Br) combined in quadrature. The corresponding standard uncertainty was calculated by dividing the IUPAC recommended uncertainty (99.7 % confidence interval) by 3. This estimation was based on interpretation by the NIST Statistical Engineering Division [19] of the language used in the IUPAC explanation [20].

The uncertainty of the mass of KBrO₃ salt used to prepare the concentrated KBrO₃ solution was calculated in a different way than the other mass measurements. The mass of KBrO₃ salt was measured at the end of a drying study (about 50 h drying time). In Fig. 2, the loss of mass of the KBrO₃ salt on drying is plotted versus drying time (h). The WB plot symbol identifies the weighing bottle for each sample and the ordinate identifies its corresponding mass loss. The four samples, taken from one bottle of KBrO₃, were dried, and then used in the solution preparation for the samples to be titrated. Between 80 % and 90 % of the total mass loss is observed after 21 h. We have recommended a drying time of 24 h at 150 °C for KBrO₃, unless this mass loss becomes a significant uncertainty component. Thus, the uncertainty of the mass of KBrO₃ salt for each solution (solution 1, 2, and 3) is calculated to account for the difference between the mass loss at about 21 h of drying and the average mass loss at about 50 h. The uncertainty applies to the specific mass loss differences of a specific weighing bottle and the solution (solution 1, 2, and 3) that was prepared.

The uncertainty of the mass of the concentrated KBrO₃ solution (preparation of solutions 1, 2, and 3) with a 1 mg resolution balance is 0.002 g. Assuming a rectangular distribution for the error in weighing (0.002 /√3 ) and considering that the mass of the concentrated KBrO₃ solution was determined from two mass measurements (multiplied by √2 ) the standard uncertainty is 0.00163 g.

### Table 3. Components of uncertainty for potassium bromate, solution 1

| Source                          | Type A | Type B |
|---------------------------------|--------|--------|
|                                 | uᵢ    | cᵢ    | uᵢ    | cᵢ    |
| Titration measurement replication | 4.48E-04 | 99.8 | 1 | 4.47E-02 |
| Mass fraction As₂O₃             | 3.36E-05 | 951 | 1/g | 3.29E-02 |
| Molecular weight As₂O₃          | 3.00E-04 | -0.504 | mol/g | 1.51E-04 |
| Molecular weight KBrO₃          | 4.50E-04 | 0.598 | mol/g | 2.69E-04 |
| Mass KBrO₃                      | 5.80E-05 | -19.0 | 1/g | 1.10E-03 |
| Volume dilute KBrO₃             | 4.10E-03 | -6.93 | g/mL | 2.84E-02 |
| Dilution factor                 | 3.15E-07 | 1.05 | 1 | 3.30E-07 |
| Mass KBrO₃ salt                 | 4.69E-04 | -19.1 | 1/g | 8.96E-03 |
| Mass KBrO₃ solution             | 1.63E-03 | 0.216 | 1/g | 3.52E-04 |
| Combined type A uncertainty     |        |        | 0.0453 |
| Combined type B uncertainty     |        |        | 0.0444 |

Effective degrees of freedom >30
The most significant sources of uncertainty are the following: measurement replication of the titration of KBrO₃, mass of As₂O₃, volume of dilute KBrO₃ solution and, to a lesser extent, mass of KBrO₃ salt. Generally, the Type A uncertainty varied the most. The uncertainty associated with measurement replication of solution 3 was greater than the measurement replication uncertainties of solution 1 (Table 3) and solution 2 because the uncertainties of the mass fractions of the titrant (KBrO₃) and dilute titrant were greater for solution 3. The combined Type A uncertainty for solution 3 was 2.3 times greater than its combined Type B uncertainty. The uncertainty associated with measurement replication of solution 2 was the lowest. The combined Type B uncertainty for solution 2 was 2.0 times greater than its combined Type B uncertainty. Better measurement agreement across replications might have been obtained with solution 1 if the automated titrator had added dilute titrant in smaller increments (0.006 mL instead of 0.01 mL). The Type B uncertainties for all 3 solutions were similar. The uncertainty of the mass of As₂O₃ is greater than the other mass measurements because of the small sample mass (0.1 g). The small mass is important to insure complete dissolution. However, the use of a microbalance with better than 10 µg resolution might improve this measurement. The uncertainty of the volume of dilute KBrO₃ might be decreased by smaller volume increments of the automated titrator, and/or a larger dilution factor of the dilute titrant.

Individual titration assay results for solutions 1, 2, and 3 are listed in Table 4.

| Solution | Potassium bromate mass fraction (%) |
|----------|-------------------------------------|
| 1        | 99.821 99.521 99.598 99.680 100.027 |
| 2        | 99.785 99.886 99.892 99.820 99.962 |
| 3        | 99.156 99.152 99.258 99.242 99.838 |

Table 4. Individual results for titration assay of KBrO₃.

Fig. 2. Relative mass loss of potassium bromate salt on drying vs drying time.

The relative mass loss of potassium bromate salt on drying vs drying time.
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6. References

[1] National Standards for Water Proficiency Testing Studies Criteria Document, U.S. Environmental Protection Agency, December 30, 1998, p. 1-113, A-1, and B-1.
[2] Gilbert H. Ayres, Quantitative Chemical Analysis, Harper and Brothers, New York (1958) p. 451, and p. 481-483.
[3] I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and Stanley Bruckenstein, Quantitative Chemical Analysis, 4th Ed., The Macmillan Company, New York (1969) p. 820.
[4] ACS Specifications, Reagent Chemicals, 8th Ed., April 1, 1993, p. 93.
[5] Harvey Diehl, Quantitative Analysis, 2nd Ed., Oakland Street Science Press, Ames, Iowa (1974) p. 244.
[6] I. M. Kolthoff and V.A. Stenger, Volumetric Analysis, Volume 1, 2nd Ed., Interscience Publishers, Inc., New York (1942) p. 179.
[7] Hobart W. Willard, Lynne Merritt, Jr., and John A. Dean, Instrumental Methods of Analysis, 5th Ed., D. Van Nostrand, Co., New York (1974) p. 737.
[8] L. F. Hamilton and S. G. Simpson, Quantitative Chemical Analysis, 11th Ed., The Macmillan Company, New York (1958) p. 283.
[9] G. E. Lundell, H. A. Bright, and J. L. Hoffman, Applied Inorganic Analysis, 2nd Ed., John Wiley and Sons, New York (1955) p. 188.
[10] Frank J. Welcher, Ed., Standard Methods of Chemical Analysis, 6th Ed., Volume 2, D. Van Nostrand Company, Inc., New Jersey (1963) p. 277.
[11] IUPAC Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. 71, 1593-1607 (1999).
[12] R. C. Weast, Ed., CRC Handbook of Chemistry and Physics, 47th Ed., The Chemical Rubber Co., Cleveland, OH (1966) p. B-213.
[13] R. S. Davis and W. F. Koch, in Physical Methods of Chemistry: Determination of Thermodynamic Properties, B.W. Rossiter and R.C. Baetzhold, Eds. 2nd Ed., Volume 1, Chapter 1, Eq. 1, John Wiley and Sons, New York (1992).
[14] Shiva Technologies, Inc., Job No. UJO551, Code 9510247, Shiva ID U00022831, March 6, 2000.
[15] M. S. Levenson, et. al., J Res Natl. Inst. Stand. Technol. 105, 571 (2000).
[16] International Organization for Standardization (ISO)"Guide to the Expression of Uncertainty in Measurement", ISBN 92-67-10188-9, 1st Ed., ISO, Switzerland, (1993).
[17] B. N. Taylor and C. E. Kuyatt, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, NIST Technical Note 1297, U. S. Government Printing Office, Washington, D. C. (1994) p. 17, (available at http://physics.nist.gov/Pubs).
[18] Certificate of Analysis, SRM 83d, Arsenic Trioxide Reductometric Standard.
[19] Personal communication from K. E. Eberhardt, NIST, Statistical Engineering Division to T. W. Vetter, June 11, 1998.
[20] IUPAC Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. 56, 6, 700 - 701 (1984).

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