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Standard Reference Materials:

Boric Acid; Isotopic and Assay Standard Reference Materials

U.S. DEPARTMENT
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Standard Reference Materials:

Boric Acid; Isotopic, and Assay Standard Reference Materials

**E. J. Catanzaro, C. E. Champion, E. L. Garner,
G. Marinenko, K. M. Sappenfield, and W. R. Shields**

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PREFACE

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Special Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

W. Wayne Meinke, Chief
Office of Standard Reference Materials

OTHER NBS PUBLICATIONS IN THIS SERIES

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ABSTRACT

A precise coulometric titration method has been developed for the assay of boric acid. The method is capable of providing boric acid assays precise to within 0.0025 percent (1 sigma) which is an order of magnitude better than existing techniques. Using this method, a lot of high purity boric acid has been assayed and found to be virtually stoichiometric H_3BO_3. Its acidimetric assay value of 100.00 ± 0.01 percent characterizes this material as a primary chemical standard for boron determinations.

Multiple samples of boric acid were studied and characterized with respect to homogeneity and the effect of relative humidity on stoichiometry. Procedures for precise preparation, aliquoting and storage of boric acid solutions were devised.

A mass spectrometric technique for the precise measurement of boron isotope ratios was developed. Single-filament tantalum-ribbon sources are used, and $^{11}B/^{10}B$ ratios are determined by measuring the relative abundances of $Na_2{}^{11}BO_2{}^+$ and $Na_2{}^{10}BO_2{}^+$ ions, at masses 89 and 88, respectively. The effects of various parameters such as sample mounting procedure, filament material, sample size, total sample composition and sodium concentration were studied and alternative procedures were evaluated.

Absolute values were obtained for the isotopic abundance ratios of two boron isotopic standards, using surface emission mass spectrometry. Samples of known isotopic composition, prepared from nearly pure separated boron isotopes, were used to calibrate the mass spectrometers. The resulting absolute values are: SRM 951, Boric Acid, $^{11}B/^{10}B = 4.04362 \pm 0.00137$; and SRM 952, Boric Acid, $^{11}B/^{10}B = 0.053199 \pm 0.000032$. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the means and allowances for effects of known sources of possible systematic error.

Key words: Absolute ratios; assay standards; boron; coulometry; isotopic standards; mass spectrometry.

INTRODUCTION

This publication describes in its entirety work by the Microchemical Analysis Section and the Analytical Mass Spectrometry Section of the National Bureau of Standards on the development and characterization of reference materials for the chemical assay and isotopic composition for boron.

The work culminated in the certification of two Standard Reference Materials. SRM 951, Boric Acid is a highly purified boric acid of normal boron isotopic abundances, for which both the acidimetric assay and the $^{10}B/^{11}B$ absolute abundance ratio are certified. SRM 952, Boric Acid is an enriched boron-10 boric acid which is certified in the same manner. Final certificates distributed with the samples are shown as Appendixes 1 and 2.

The abundance ratio determination depends upon the now well established method of mass spectrometric comparison of the material with standards prepared from high-purity separated isotopic solutions. This procedure required the development of a highly precise and accurate coulometric method which was also used for acidimetric assay of SRM 951, Boric Acid.

A. Development of a Coulometric Method for Assay of Boric Acid

1. Introduction

In aqueous solutions, boric acid is a very weak acid ($pK_a = 9.2$). The hydrolysis of borate ions, in the course of titration with a standard solution of base (or with electrogenerated base, in the case of coulometry), precludes accurate evaluation of the inflection point $[(\Delta pH/\Delta equiv.)_{max}]$ on the potentiometric curve. Fortunately, borate ions can be complexed and effectively removed from solution; and, with the decrease in borate concentration, the apparent dissociation constant of boric acid increases.

The most widely used methods for the determination of milligram quantities of boron involve titration of boric acid complexed with some polyhydric alcohol (polyol). These methods are somewhat empirical, particularly with respect to the amount of polyol required, and are generally precise to only a few tenths of one percent.

For the determination of the absolute isotopic composition of standard boron samples, it was necessary to prepare synthetic isotopic mixtures with an uncertainty less than 0.02%. A coulometric analytical method, developed by LeDuigou and Lauer [1], approached this requirement in that a standard deviation of 0.02% was obtained. However, a discrepancy of 0.1% between this method and conventional acidimetric titrimetry was noted which they were unable to resolve.

Extensive experience in the NBS Microchemical Analysis Section has established coulometry as perhaps the most accurate and precise chemical assay technique providing analyses of a variety of materials with an accuracy within a few parts in a hundred thousand. This provided the incentive to investigate pertinent parameters to develop a coulometric method suitable for the present analytical problem. This was successful and the research and method that was developed are described below and in a forthcoming publication [2].

2. Investigation of Analytical Parameters

a. Effect of Mannitol on the Apparent Ionization Constant of Boric Acid - For many years mannitol has been widely used as a complexing agent for boron, and various proposals have been made for the optimum mannitol/boron ratio. In this work, the question of optimum ratio was studied in a precise methodical manner by the measurement of the pK_a of boric acid as a function of mannitol concentration. The measurements were conducted in 1M KCl because it was anticipated that further coulometric work would be conducted in that electrolyte.

The results of the measurements are shown in Figure 1. The limiting value of the slope is:

$$\frac{dpK_a}{dpC_{mannitol}} = 2.$$

The highest concentration of mannitol investigated was 1.0M, which corresponds to a saturated solution at 25 °C.

The results show that varying the concentration of mannitol can produce a whole spectrum of "mannitoboric acids" with K_a varying smoothly over five orders of magnitude (pK_a from 4 to 9). This fact was successfully utilized to determine the relationship between the concentration of weak acid, K_a, and the difference between the inflection point and equivalence point in a titrimetric determination. The results show that Roller's equation [3,4] is equally applicable to the complex mannitol-KCl-boric acid system as it is to the monoprotic and polyprotic organic acids titrated in aqueous media.

Using Roller's equation, the error due to the difference between the inflection point and the equivalence point is given as:

$$\text{Error (\%)} = \frac{-300\ K_w}{cK_a}$$

where K_w is the dissociation constant of water, c is the concentration of borate at the end of the titration, and K_a is the dissociation constant of boric acid in the given medium. From a practical standpoint, above $cK_a = 3\times10^{-8}$, the error due to ΔpH between the inflection and equivalence points is less than 0.0001% and therefore negligible. All titrations reported here were carried out under conditions exceeding this minimum value.

b. Effect of Mannitol on the Electrochemical Reduction of Hydrogen-ion - Previous work in this laboratory has verified the accuracy of coulometric acidimetry conducted in 1M KCl medium. For example, measurements of the faraday in this laboratory by reduction of hydrogen-ion in benzoic

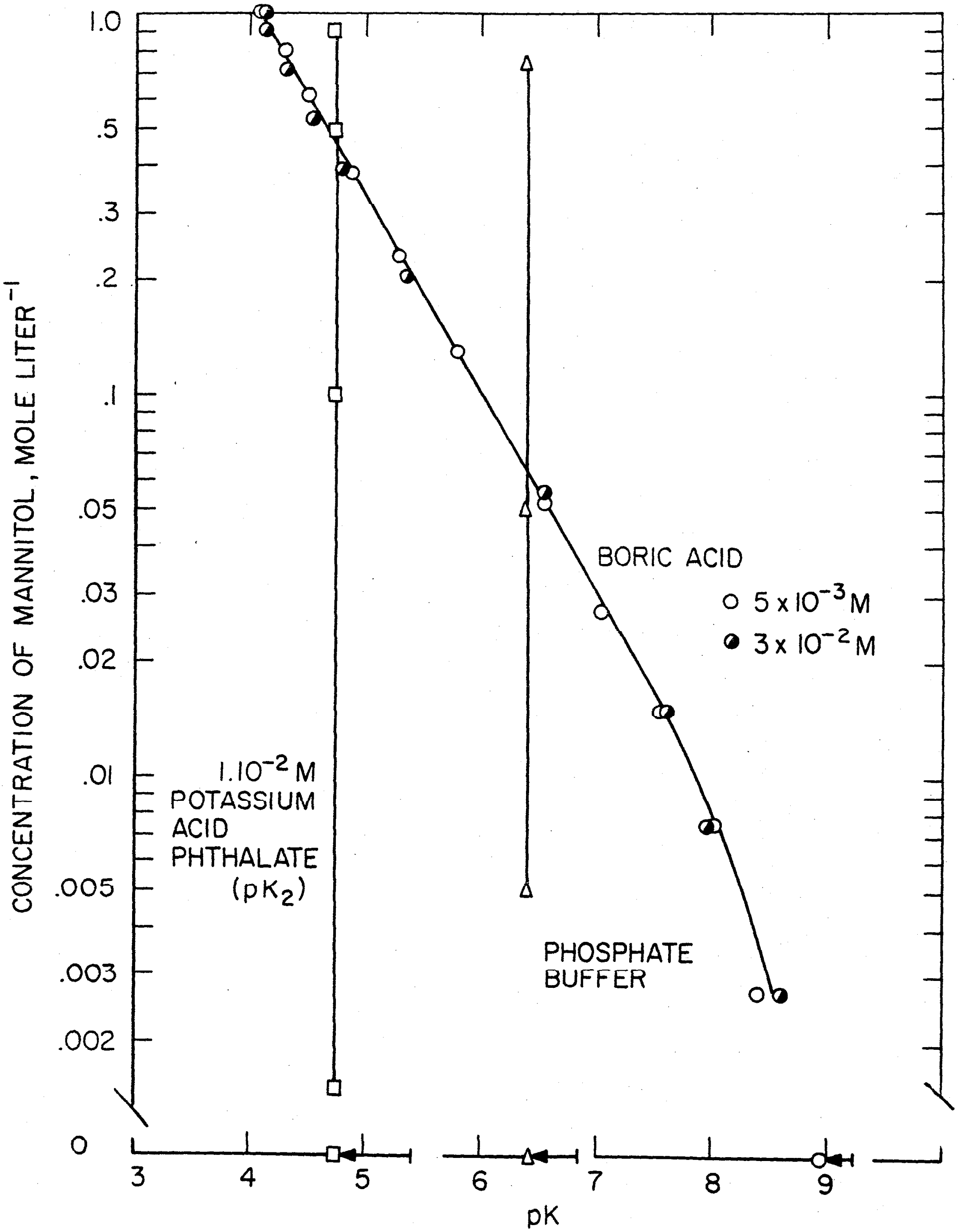

Figure 1. pK$_a$ of Mannitoboric Acid as a Function of the Concentration of Mannitol.

acid and in oxalic acid dihydrate coulometers [5], under conditions similar to those of the present boric acid experiments, yielded values of 96487.9 ± 2.5 and 96486.6 ± 3.4 abs $C(g\text{-equiv})^{-1}$, respectively. These results are in excellent agreement with the value for the faraday of 96487.0 ± 1.6 abs $C(g\text{-equiv})^{-1}$, recommended by NAS-NRC [6].

In titrations of boric acid, however, the supporting electrolyte is 1M KCl plus mannitol, and it is necessary to determine if the addition of the mannitol has any effect on the electrochemical reaction at the platinum cathode. Specifically, is the current efficiency 100% with respect to the reaction $H^+ + e = 1/2\ H_2$, or any equivalent reaction?

To answer this question, HCl solution, single crystal oxalic acid dihydrate, and acid potassium phthalate were each analyzed coulometrically in 1M KCl, both with and without mannitol. This choice of test materials was made to cover a large range of pK_a values including the pK_a value for mannitoboric acid (in 0.75M mannitol, the apparent K_a of boric acid is 4.17×10^{-5}).

The results (Table 1) for each pair of analyses, with and without mannitol, were identical to within 0.003%. It was therefore concluded that the accuracy of coulometric acidimetry is unaffected by the addition of mannitol to the 1M KCl solution. Moreover, it was noted that the pH of the inflection points on the potentiometric titration curves, obtained by use of the glass electrode - saturated calomel electrode system, is virtually unaffected by the presence of mannitol.

c. Effect of Variation of Mannitol Concentration - A number of samples of boric acid were assayed in the following electrolytes: 1M KCl - 0.25M mannitol, 1M KCl - 0.75M mannitol, and 1M KCl - 1.05M mannitol (saturated). The results showed no significant difference (<0.005%) between the three media for sample sizes of boric acid

Table 1. Effect of mannitol on electrochemical reduction of H^+ at platinum cathode.

Acid		**Electrolyte**			**Ratio**
		1M KCl		**1M KCl + 0.75M mannitol**	
Hydrochloric acid		2.18055 meq/g		2.18105 meq/g	
		2.18070		2.17992	
		2.18032		2.18060	
	Average	2.18052 meq/g	Average	2.18052 meq/g	1.00000
Oxalic acid[a] dihydrate[a]		99.985 percent			
		99.985			
		99.983			
		99.987		99.972 percent	
		99.987		99.987	
		99.983		99.988	
	Average	99.985 percent	Average	99.982 percent	1.00003
Potassium acid phthalate, SRM 84h				99.995	
				99.996	
	Average	99.992 percent[b]	Average	99.995 percent	0.99997

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[a] Single crystal chips

[b] The assay is the mean value obtained coulometrically during analysis of the material for NBS certification

ranging from 1 to 12 meq (Figure 2). However, in the case of the 0.25M mannitol solution, the slope of the potentiometric curve near the equivalence point was too small to permit precise evaluation of the end-point.

On the basis of the magnitude of the inflection point alone, an electrolyte containing 1.05M mannitol would be preferable. However, this solution has a rather high viscosity which is troublesome when it is forced through the fritted glass disks of the coulometric cell and also presents some difficulty of mixing during the course of the analyses.

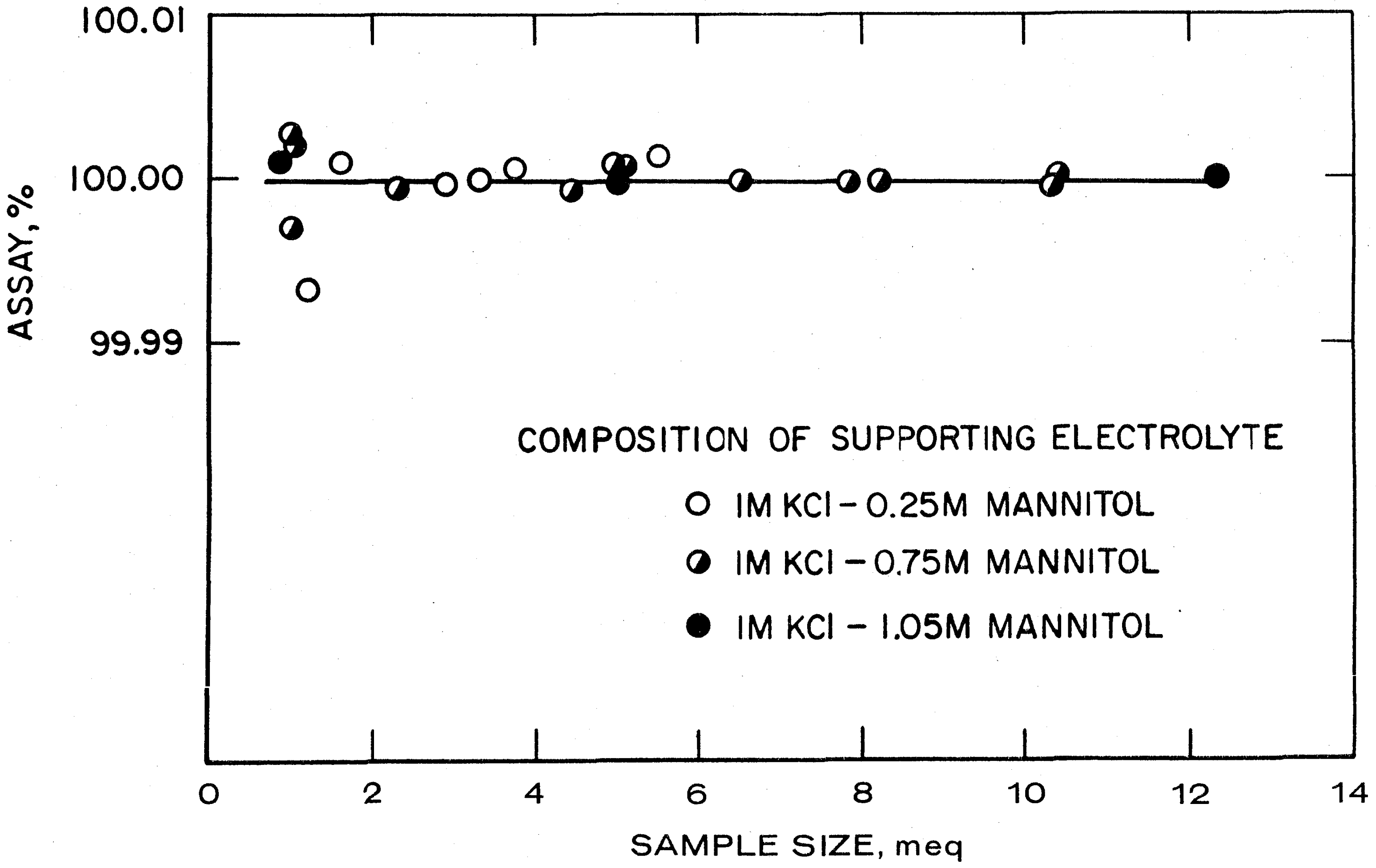

Figure 2. Effect of Mannitol Concentration and Sample Size on the Coulometric Titrations of Boric Acid.

Hence, as a matter of convenience, with no significant loss in the sensitivity of the end-point determination, a concentration of 0.75M mannitol was used in the subsequent work.

During the above-described tests, the boric acid sample size was varied from 0.02 to 1.0 g. Over this range of sample sizes, assay values were identical.

d. Evaluation of Analytical Bias - Boric acid of known purity was not available for evaluating the accuracy of the method described in this work. However, the absence of analytical bias due to composition of electrolyte or sample size supports the conclusion that the method is free of bias, with an accuracy limited only by the random measurement errors.

The various measurements related to this work were made with a high degree of reliability (see Section A.3.c., Constants and Standards), and numerous determinations of boric acid have shown that a relative standard deviation of at most 0.003 percent may be expected. This precision is consistent with that obtained for a wide variety of coulometric procedures developed in this laboratory.

3. Coulometric Procedure for Assay of Boric Acid

a. Introduction - The coulometric acidimetric titration method has been described previously [5]. It consists of the reduction (at the platinum cathode) of hydrogen-ions derived from the weighed acid in a suitable supporting electrolyte according to the reaction:

$$H^+ + e^- = 1/2\ H_2.$$

A glass electrode - saturated calomel electrode system is used for measuring the change in hydrogen-ion concentration as a function of the passed charge, to identify a differential potentiometric inflection point. The supporting electrolyte is initially acidified to facilitate the removal of CO_2, swept with scrubbed nitrogen, and then pretitrated to a pH of 6.98 by passing small increments of charge. The charge consumed in going from the end point of pretitration to the differential pH inflection point is then taken to be equivalent to the amount of hydrogen-ion introduced with the weighed acid.

b. Coulometric Cell - The coulometric cell used in this work is shown in Figure 3. The anode and cathode compartments are 180-ml electrolytic beakers connected horizontally by a 25-mm o.d. glass tube approximately 6 cm in length. Three sintered glass disks, one each of coarse, medium and fine porosity, are sealed in the connecting tube. Each of the two intermediate compartments between the disks has a tube with a stopcock which enables it to be filled or emptied by the application of a vacuum or nitrogen pressure. The volume of the compartment between the coarse and the medium porosity disks is about 10 ml while that between the medium and fine porosity disks is about 20 ml.

There are two advantages in using a cell of relatively small volume. Conventional end-point detectors, including the glass electrode system, are sensitive to concentration changes. With a decreased volume, a desired change in concentration can be achieved with a smaller amount of reagent. That is, for the same amount of reagent, the sensitivity of the detector system varies inversely with the volume. The second advantage of a smaller volume arises from the fact that, concentrations being the same, the total amount of impurities in the supporting electrolyte varies inversely with the volume.

The molded polyethylene cathode compartment cover can be snugly locked onto the beaker by means of a polyethylene lock ring. Both the covers and the lock rings are commercially available.

The following accessories are mounted in the cover of the cathode compartment: a combination glass electrode - saturated calomel electrode, an inlet tube to allow nitrogen to be passed over the solution, an outlet tube for the

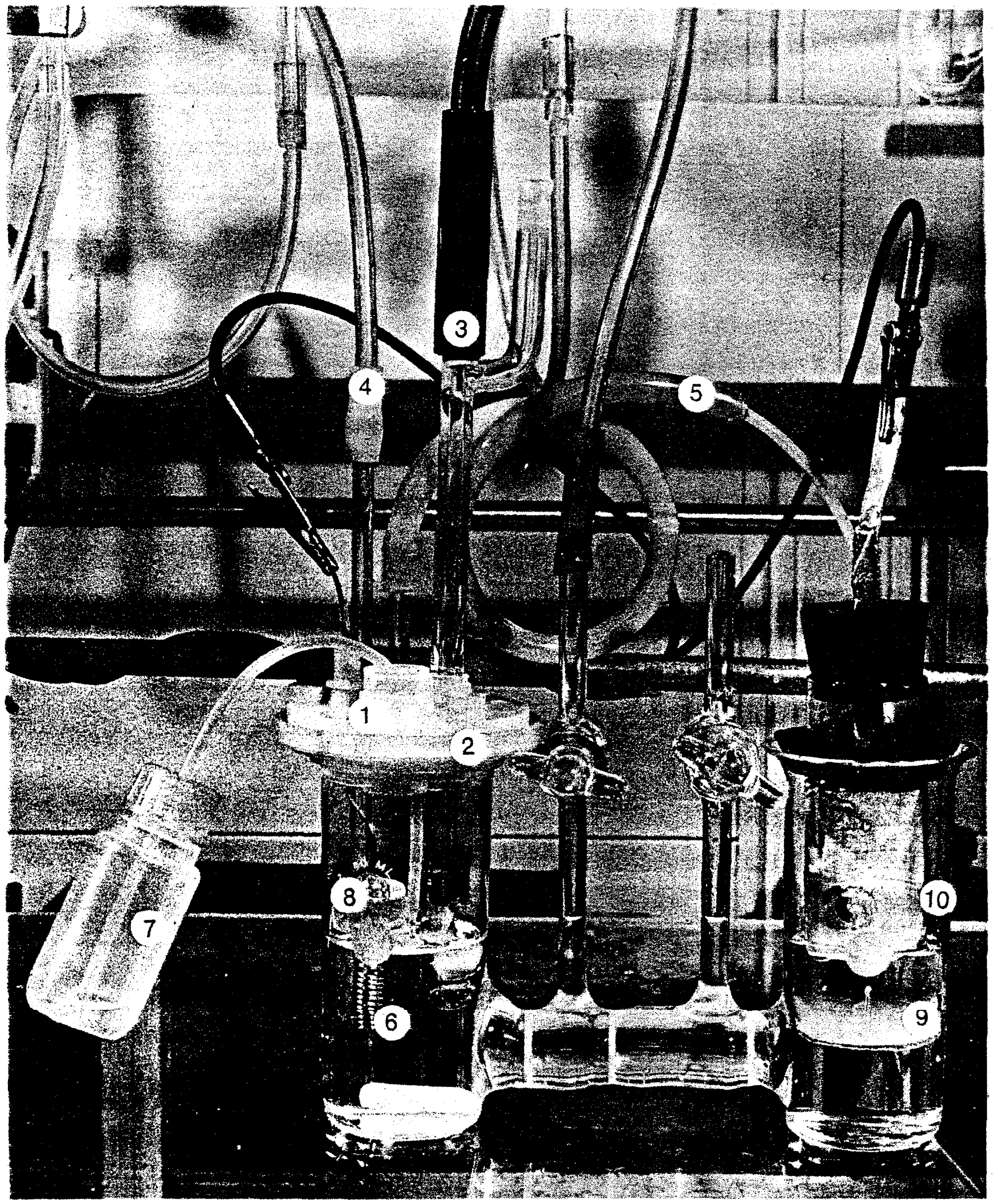

Figure 3. Coulometric Titration Cell for Precise Acidimetry.

1. polyethylene top; 2. polyethylene lock ring; 3. combination glass-calomel electrode; 4. nitrogen inlet tube; 5. nitrogen outlet tube; 6. platinum cathode; 7. liquid sample delivery and cell rinse assembly; 8. polyethylene spray shield; 9. 3% agar gel in 0.1M KCl; 10. silver anode.

nitrogen, a platinum coil cathode and a polyethylene tube with polyethylene bottle. The polyethylene tube-bottle system can be moved up and down to permit withdrawal of the solution from the cell. The withdrawn liquid may then be squirted back into the cell to rinse any material deposited on the cell walls and top as a result of the liberation of gas during the electrolyses. The system is also used for introduction of samples in the form of solutions.

A polyethylene cap is mounted about 1 cm above the top edge of the cathode. The purpose of this cap is to catch the spray resulting from the liberation of gaseous hydrogen at the platinum cathode.

The constant-current and timing circuits have been described elsewhere [5]. The charge passed through the coulometric cell (in excess of 100 coulombs, corresponding to about 1 meq of sample) can be measured accurately to a few tenths of a millicoulomb.

c. <u>Constants and Standards</u> - A number of constants and standards were used in this study. These are described or defined below.

1) Resistance: A ten-ohm resistor calibrated by the NBS Resistance and Reactance Section, was used. The value at 25 °C was certified to the nearest 10 μΩ and the equation

$$T_T = R_{25} [1 + \alpha (t-25) + \beta (t-25)^2]$$

was used to correct for the small temperature deviations encountered in the work.

2) Voltage: A set of saturated Weston cells, which were calibrated by the NBS Electrochemistry Section and kept in an air thermostat, was used as the emf reference source. The value of the most reproducible cell in the set is known to within ±0.8 μV and this cell was used as the primary emf reference.

3) Current: The ampere used in this work was based on the volt and ohm as maintained by the NBS.

4) Time: The time measurements were made by means of a 100-kHz quartz crystal oscillator time-interval meter which was calibrated against the WWV frequency and found to be accurate to better than within 0.001%.

5) Mass: The weights used in this work were calibrated by the NBS Mass and Volume Section. The mass of each individual weight was known to the nearest microgram.

6) Air Density: The density of air was computed on the basis of measurements of atmospheric pressure, temperature, and relative humidity.

7) pH: The NBS phosphate buffer, SRM 186b, (pH = 6.865 at 25 °C) was used in the standardization of the glass electrode - saturated calomel electrode system.

d. Procedure - The samples of acid were weighed by substitution on a 20-gram capacity, unequal-arm, constant-load microbalance. The standard deviation of the weighing process was 0.003 mg. The weighings were free of systematic error except, possibly for the uncertainties in the standard weights, which were less than 0.003 mg. The weight of each sample was corrected for air buoyancy, based on the density of the air at the time of the weighing.

In general, the titration procedure is the same as that described by Marinenko and Taylor [5]. The stirrer was operated only during the dissolution of the samples. It was not used during the titration for the following reasons: (1) to eliminate swirling of gas bubbles liberated at the cathode into the bulk of the solution, thereby minimizing spray-loss of the sample; (2) to minimize the transfer of impurities in the supporting electrolyte to the electrode surface; and (3) to minimize transfer of the sample into the intermediate compartments.

After electrolysis at about 102 mA, for a predetermined period of time sufficient to allow reaction with all of the sample if it were 100.00% stoichiometric H_3BO_3, the coulometric current was interrupted. The intermediate compartments were flushed and the cell wall and cover were rinsed in the manner previously described. The pH of the solution was measured to the nearest 0.001 pH unit and recorded. Then a small amount of HCl was added to the cell to return the system to a state well in advance of the equivalence point and, by successive passage of charge increments and measurements of pH, the equivalence point, identified by $(\Delta pH/\Delta C)_{max}$, is established. This procedure may be repeated as often as desired to increase the precision of locating this point. A correction is then applied for the difference between the pH of the system at the end of the titration and that of $(\Delta pH/\Delta C)_{max}$.

A step-by-step description of a complete typical analysis is given in Appendix 3.

B. Chemical Characterization of SRM 951, Boric Acid

1. Acidimetric Assay

This lot of boric acid was prepared to ensure material of high purity and homogeneity. It consisted of 550 pounds of acid prepared at one time and was received in 22 containers of approximately 25 pounds each. A preliminary spectrochemical survey analysis indicated a high degree of freedom from contaminants in that no metallic impurities were present at a greater concentration than a few parts-per-million.

The coulometric assay of this material was done using samples which had been equilibrated at 50% RH as described in Section B.2. Initially, 600-mg samples were used but this was later reduced to 200 mg to conserve analytical time, since earlier experiments had shown no significant differences in assay due to sample size.

Representative samples of approximately 50 g were taken from each of the containers and these were screened by a preliminary coulometric analysis. The results of these determinations are given in Figure 4 and Table 2. The initial

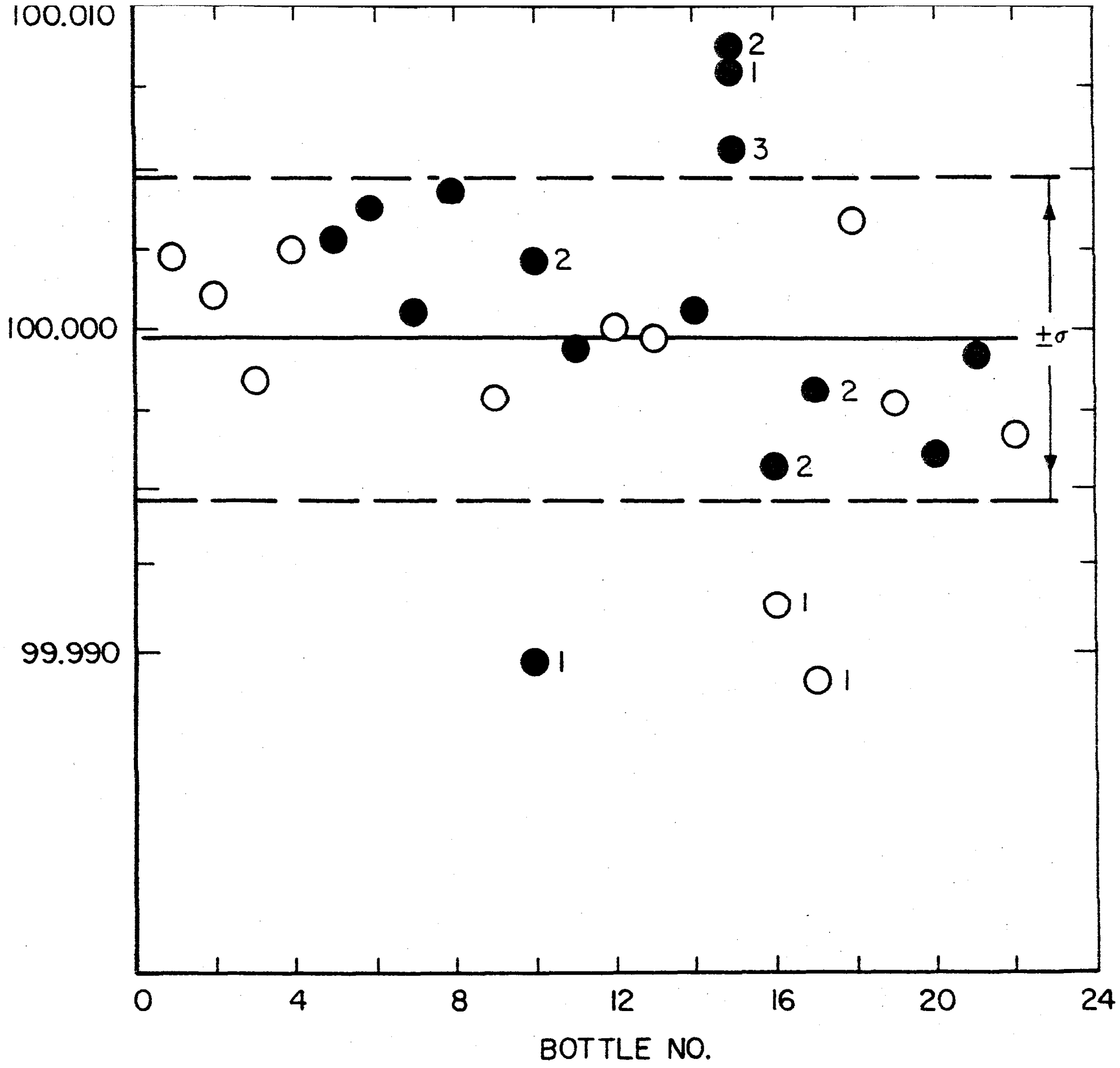

Figure 4. Homogeneity of SRM 951, Boric Acid.

NOTE: ● **200 mg Samples** ○ **600 mg Samples**

Numbers adjacent to the points in the figure represent the sequence of repeat measurements.

Table 2. Homogeneity of SRM 951, Boric Acid.

Date of analysis	Sample No.	Assay %
10-31-67	17	99.9889
11- 2-67	12	99.9999
11- 3-67	1	100.0022
	4	100.0024
	9	99.9978
11- 6-67	13	99.9997
	2	100.0010
11- 7-67	3	99.9983
11- 8-67	22	99.9964
	18	100.0032
11- 9-67	16	99.9910
	19	99.9975
11-13-67	7	100.0004
	10	99.9896
11-14-67	20	99.9960
	11	99.9993
11-15-67	21	99.9990
	5	100.0028
	15	100.0078
	14	100.0005
11-16-67	8	100.0042
	6	100.0037
11-20-67	10[a]	100.0020
	15[a]	100.0089
	16[a]	99.9955
11-21-67	17[a]	99.9975
	15[a]	100.0055
	Average	99.9989[b]
	σ =	0.0044[b]

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[a] Repeat runs.

[b] Based on initial runs, excluding Sample No. 15.

results for all containers, except numbers 10, 15, 16 and 17, fell within 0.005% of the mean which was considered to be a limit of acceptability. These four samples were reanalyzed. The duplicate analysis for the three samples which produced low assay values on the first runs (nos. 10, 16 and 17) fell within 0.005% of the mean. However, triplicate analysis of samples from container No. 15 remained outside the 0.005% limit. The material in this container appears to have slightly different composition from the others, perhaps due to the conversion of a minute amount of boric acid to boric oxide. Accordingly, this container has been set aside, and the material will not be used as SRM 951.

The overall acidimetric assay value may be obtained from a consideration of the analyses described above. From the initial analyses of the 22 containers (excluding container number 15), an average assay value of 99.9988 ± 0.0020% is obtained where the uncertainty represents the half width of the 95% confidence interval. The standard deviation of these measurements about their mean was 0.0044 which includes components of variation due to both measurement and compositional variations.

In a further evaluation of the assay of SRM 951, Boric Acid, the samples from the 22 original containers were combined into five composites, containing equal amounts of material from each bottle. The make-up was as follows: Composite I - 5, 6, 8, 15, 18 (the five containers that gave the highest results); Composite II - 10, 16, 17, 20, 22 (the five containers that gave the lowest results); Composite III - 1, 2, 4, 7, 12, 14; Composite IV - 3, 9, 11, 13, 19, 21; Composite V - equal amounts of I, II, III and IV. Figure 5 and Table 3 show the results of replicate analyses of the composites. Each symbol represents an individual titration plotted with respect to the sequence in which titrations were performed.

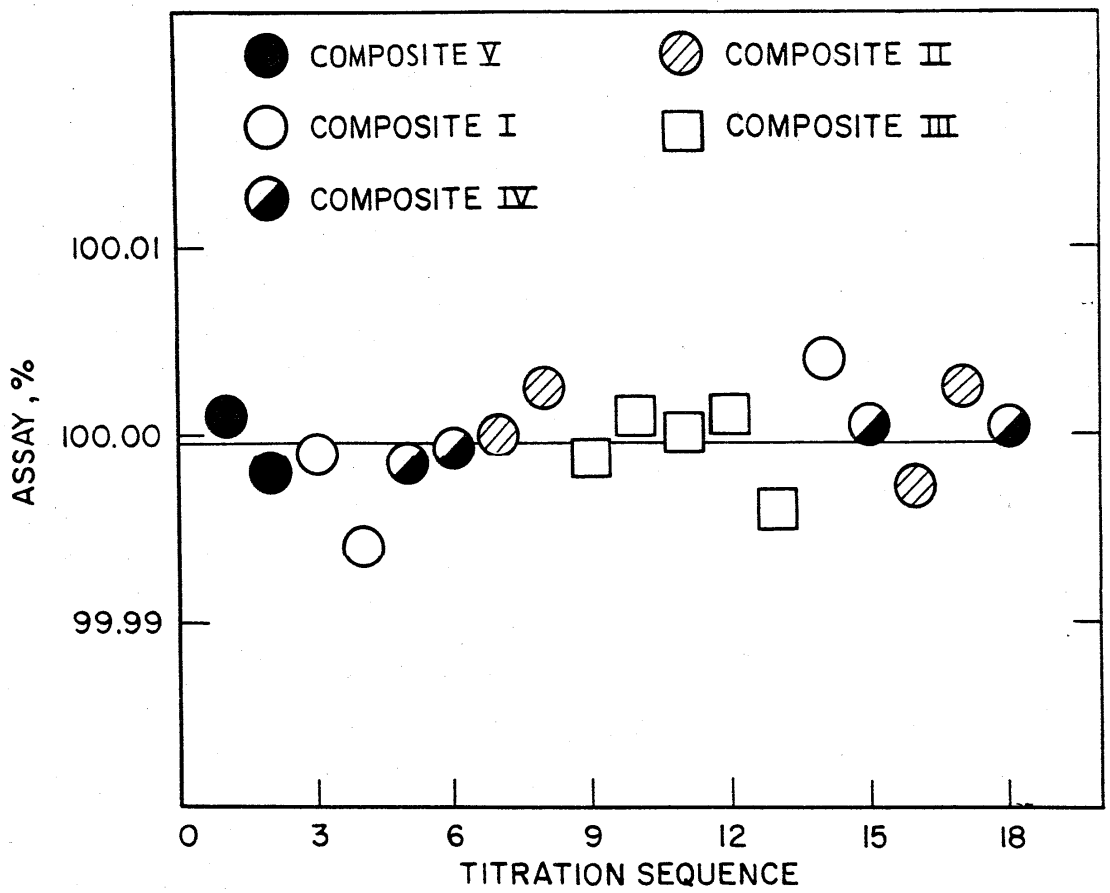

Figure 5. Effect of Titration Sequence and Composite Number on the Assay of SRM 951, Boric Acid.

Table 3. Assay of SRM 951, Boric Acid (equilibrated at 34% RH for at least 30 min).

Run No.	Composite No.	Assay, %	Run No.	Composite No.	Assay, %
1	V	100.0008	10	IV	100.0009
2	V	99.9978	11	IV	100.0002
3	I	99.9990	12	IV	100.0012
4	I	99.9941	13	IV	99.9961
5	II	99.9983	14	I	100.0042
6	II	99.9992	15	II	100.0007
7	III	99.9998	16	III	99.9973
8	III	100.0024	17	III	100.0025
9	IV	99.9987	18	II	100.0006

Average 99.9997 $\sigma = 0.0025$ $\frac{t_{95}\sigma}{\sqrt{n}}$ 0.0013

The average assay of each composite and the grand average of all measurements of the composites is shown in Table 4. The standard deviation of the individual measurements of the composites is from their respective average values and is based upon a total of 18 measurements providing a total of 13 degrees of freedom for the estimation of σ. This represents precision estimate for a single coulometric assay of boric acid.

Table 4. Assay of SRM 951, Boric Acid composites.

	Composite I	Composite II	Composite III	Composite IV	Composite V
	99.9990	99.9983	99.9998	99.9987	100.0008
	99.9941	99.9992	100.0024	100.0009	99.9978
	100.0042	100.0007	99.9973	100.0002	
		100.0006	100.0025	100.0012	
				99.9961	
Average	99.9991	99.9997	100.0005	99.9994	99.9993

Average of all determinations: 99.9997

Within-composite σ (pooled): 0.0027

Half-width 95%-confidence interval for mean, based on within-composite variations only: 0.0013

The excellent agreement between the average assays of the composites and the excellent agreement of this value with that obtained from the determinations of the original containers leads to considerable confidence in both the overall assay and the high degree of homogeneity of this standard reference material. The two series of assays allow a semiquantitative estimate to be made of the latter. In the first series, $\sigma_1 = \sqrt{\sigma_m^2 + \sigma_c^2}$ where σ_1 is the overall standard deviation, σ_m is the standard deviation of measurement, and σ_c is the standard deviation of the component of between-container varaibility. Taking $\sigma_m = 0.0025$ from measurements of the composites, and $\sigma_1 = 0.0044$, a value of $\sigma_c = 0.0036$ may be calculated.

For final certification purposes, an acidimetric assay value of 100.00 ± 0.01 has been established. The limit of uncertainty is believed to be a conservative estimate of any deviations in composition that might be encountered due to errors of assay, inhomogeneity of material, or departures from stoichiometry due to absorbtion of moisture under adverse conditions.

2. Effect of Relative Humidity on the Stoichiometry of SRM 951, Boric Acid

The study of the behavior of this lot of boric acid indicates that the material is somewhat deficient in water. Apparently it was prepared under conditions which resulted in the formation of small amounts of boric oxide. This conclusion is based on the fact that samples weighed directly from the original containers and then left standing in a room at 28% relative humidity for 30 minutes showed significant increases in weight (Table 5).

Table 5. Absorption of water by boric acid.

Sample number	Initial wt of H_3BO_3	Wt of H_3BO_3 after 30-min exposure to 28% RH	$\Delta w \times 10^6 g$	Change in weight, percent
1	1.351348g	1.351484g	+ 136	+ 0.010
2	1.340345	1.340394	+ 49	+ 0.004
3	0.934555	0.934655	+ 100	+ 0.011
4	1.685807	1.685968	+ 161	+ 0.010
5	2.249267	2.249379	+ 112	+ 0.005
6	1.343683	1.343823	+ 140	+ 0.010
			Average	+ 0.008%

The data in Figure 6 show that at 28% RH the time required to weigh out a sample (∿15 min) was not long enough for the material to absorb sufficient water to attain stoichiometric composition. At 34% RH this same weigh-out time allowed sufficient water adsorption so that assays of the material corresponded exactly to H_3BO_3 Once the stoichiometric amount of water had been absorbed, exposure of the material to even a very dry atmosphere did not result in a loss of water.

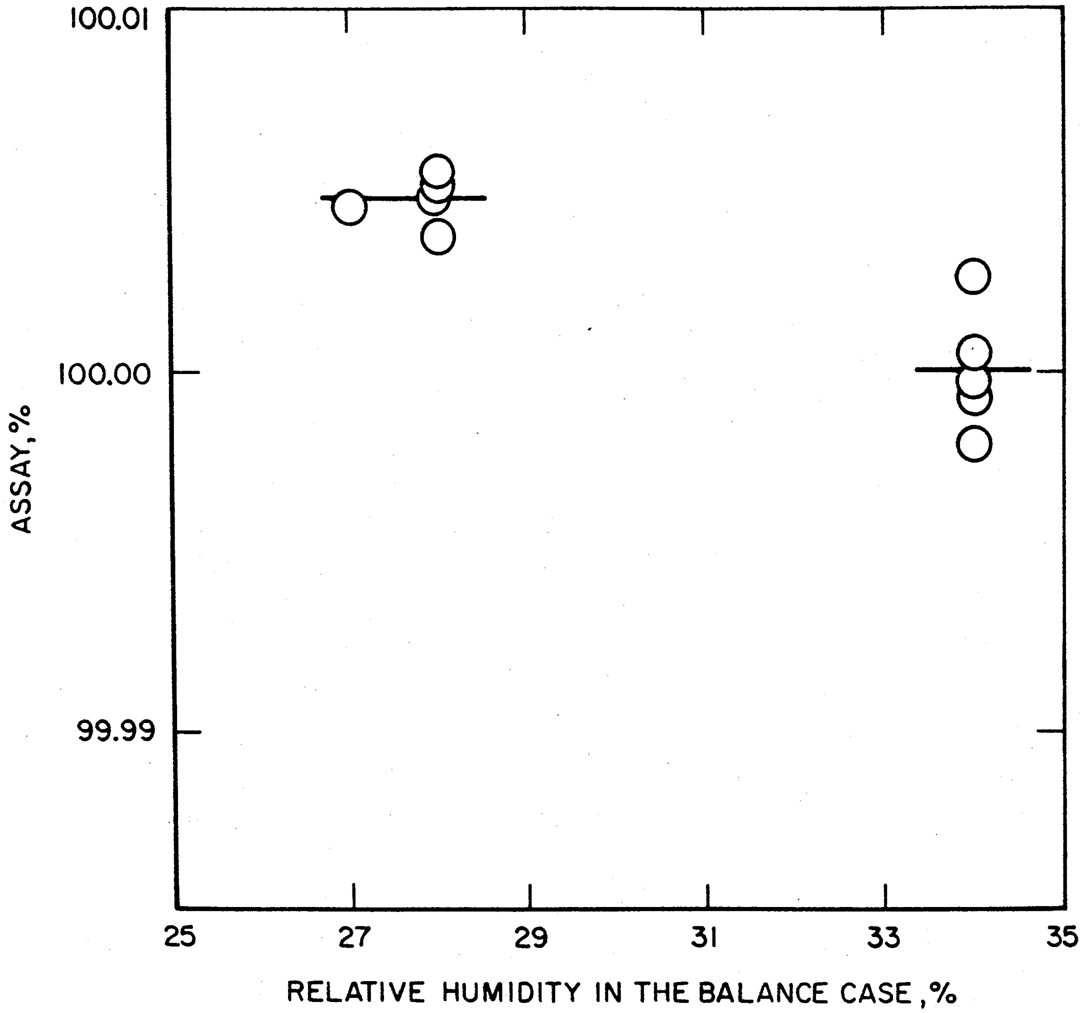

Figure 6. Effect of Relative Humidity in the Balance Case on the Approach of Boric Acid to H_3BO_3 Stoichiometry (15 min exposure time).

The effect of humidity was further tested by placing boric acid samples in various controlled humidity environments for periods of at least four days with occassional stirring of the crystals. The results of these tests are given in Figure 7. Within the 0 to 52% RH range, the assay of boric acid remained constant and close to stoichiometric H_3BO_3. At relative humidity greater than 52%, assay values decreased, reaching 99.98% at 90% RH. The assay decrease is undoubtedly due to the adsorption of water on the surface of the polycrystalline boric acid.

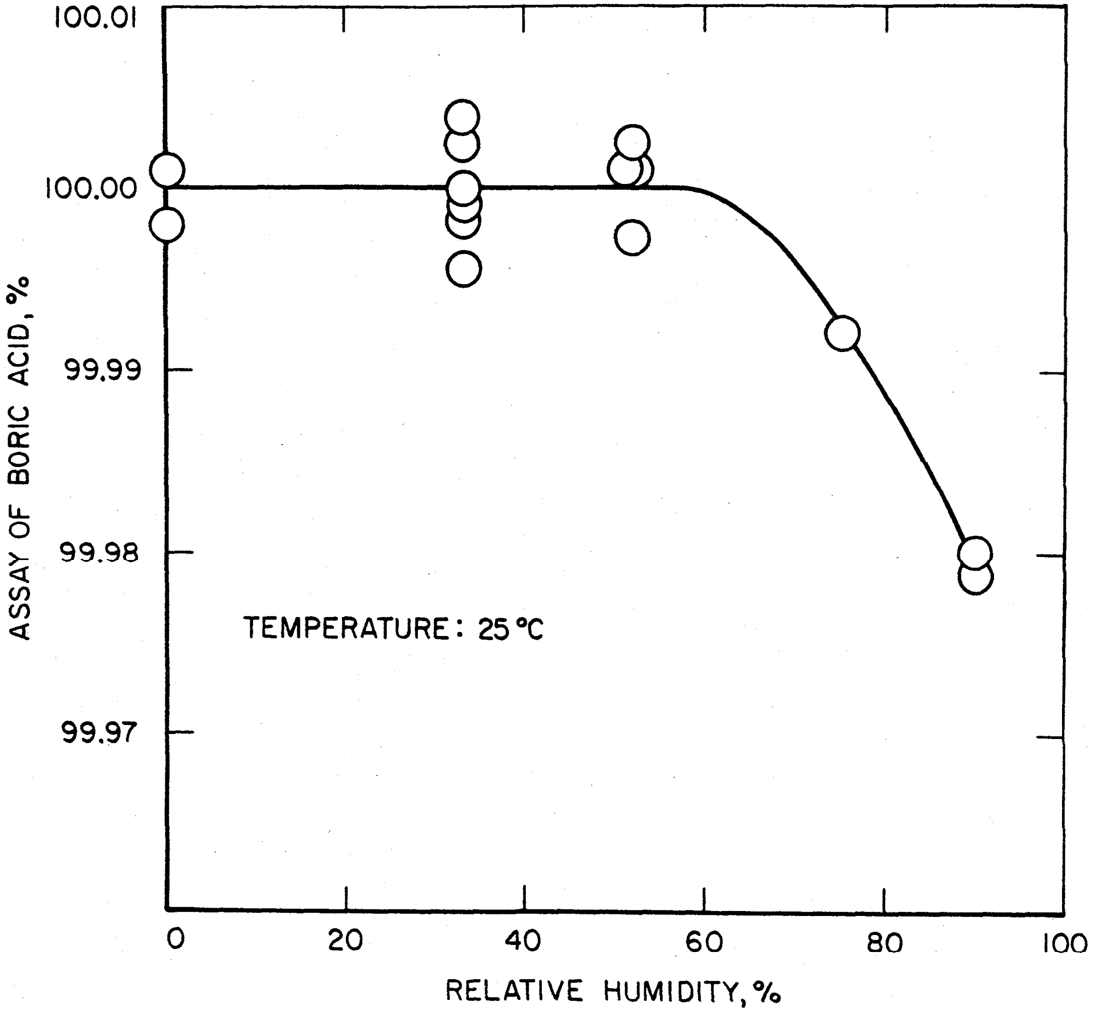

Figure 7. Effect of the Humidity of the Environment on the Assay of Boric Acid.

3. Determination of Strong Acid in Crystalline Boric Acid

For accurate coulometric analysis of boric acid solutions it is necessary to either prove that the titrated hydrogen ion is contributed totally by the boric acid or to correct for any hydrogen ion contributed by a contaminating acid. In other words, it is necessary to test the unknown solution for the presence of acids other than boric acid; and, pragmatically, this reduces to a test for strong acid. A simple procedure such as direct titration of strong acid in the presence of boric acid in 1M KCl solution is not sufficiently sensitive because of the buffering effect of the boric acid. Tests showed that under those conditions, it was impossible to resolve less than a few hundredths of a percent of strong acid in the boric acid. Preconcentration of the strong acid by extraction of boric acid into an organic solvent was unsatisfactory; tests showed that some of the HCl is also lost in the process.

The procedure finally developed is based on the 20-fold decrease in solubility of boric acid in water between 100 and 0 °C. A special sealed tube was devised to recrystallize the boric acid from which the supernatant liquid could be removed for determination of its strong acid content by direct titration. The results of analyses of SRM 951, Boric Acid, show that it contains 5.5 ppm of strong acid. Thus, after the correction for the strong acid, the B/H^+ ratio of this material is 0.999982 on a molar basis.

The above procedure requires large amounts of material (1 to 2 g) and, because of cost considerations and the availability of only small amounts of material, could not be directly used in the evaluation of the stoichiometry of $H_3{}^{10}BO_3$ and $H_3{}^{11}BO_3$ isotopically "pure" samples. Consequently a micro method had to be developed. The key to this problem was to establish the amount of strong acid in the SRM 951, Boric Acid, as described above. The solutions containing known widely varying concentrations of boric acid were prepared and their pH's measured. A three-dimensional calibration graph was constructed relating pH, concentration of boric acid, and concentration of strong acid (HCl). Then, knowing accurately the total acid concentration, from coulometric analyses, and the pH of the boric acid solution, one can calculate the concentration of strong acid by the method of successive approximations. The sensitivity of the three-dimenstional calibration graph is such that 0.01% to 0.001% of strong acid in the original sample of boric acid can be determined with an accuracy of a few relative percent.

C. Assay of SRM 952, Enriched Boric Acid

This standard reference material is an enriched boron-10 boric acid which was furnished by the Oak Ridge National Laboratory. The material as received was not deemed to be of sufficient purity for use as a standard reference material. Accordingly, it was recrystallized twice from a water solution to assure homogeneity and freedom from metallic impurities, and then dried at room temperature.

The purified acid was assayed by coulometric titration as described above. The results are shown in Table 6 in

Table 6. Assay of SRM 952, Boric Acid.

Sample No.	Assay, %
1	99.968
2	99.971
3	99.982
4	99.968
5	99.968
6	99.969
7	99.973
8	99.958

Average 99.970 $\sigma = 0.0066$ $\frac{t_{95}\sigma}{\sqrt{n}} = 0.0056$

which an average assay of 99.971% is indicated. An assay of 99.97% ± 0.02 is certified where the uncertainty limit is believed to be a conservative estimate of variation of composition of the material due to all causes. The deviation from stoichiometry results from the fact that the standard reference material is slightly contaminated by occluded mother liquor. Accordingly, the assay value should be used in the case of direct weighing for a "spiking" material for boron assays in mass spectrometry.

D. Preparation and Aliquoting of Separated Boron Isotope Boric Acid Solutions

One of the basic aims of this study was to develop a boron isotopic standard to be used in the absolute calibration of mass spectrometers. Toward this aim, the following subjects had to be investigated: the precision of aliquoting relatively small amounts of boric acid solutions; suitable conditions for accurate preparation and storage of boric acid solutions without significant changes in the composition of the solutions (storage for approximately one week); a reliable procedure for delivery of boric acid solution aliquots into the coulometric cell; evaluation of any possible bias which might be associated with the size of the aliquots; and, as previously described, development of a method for the determination of small amounts of strong acids in small samples of boric acid solutions. Composite II of the SRM 951, Boric Acid, was used throughout the exploratory part of this work.

The procedure developed for the aliuqoting of solutions [7] involves the use of 10-ml polyethylene syringes as weight burets. After the syringe is filled, the needle is removed and the syringe is closed with a special cap. The solutions were prepared of such concentrations that aliquots from 1 to 10 ml in size would bracket the sample sizes of separated isotope solutions required for the accurate preparation of the boron isotopic ratio standard solutions (approximately 0.3 meq/g of solution).

From such a syringe, solutions were weighed by difference into 4 oz polyethylene bottles. A closed syphon arrangement, shown in the cell assembly (Figure 3) was constructed which fitted tightly over the bottles and connected to the coulometric titration cell. With this arrangement, solution samples could be quantitatively transferred into the cell without the need for disassembling it. Such an arrangement is highly desirable since, in this closed system, nitrogen flowing over the electrolyte keeps atmospheric carbon dioxide out of the cell.

Initially two sets of experiments were conducted to establish the precision of aliquoting, transfer and titration. Equal-size samples of boric acid solutions were aliquoted on the same day and titrated soon thereafter (1 to 2 days later). The results of these analyses are summarized in Table 7. From these data the standard deviation of a single determination is 0.000052 meq/g of solution. On a percentile basis, this amounts to approximately 0.017%.

Table 7. Precision of aliquoting and analysis of boric acid solutions.

Solution	Aliquot No.	Wt of aliquot, g	meq found	meq/g
I	1	10.95358	2.988735	0.272855
	2	10.05553	2.742278	0.272713
	3	10.45754	2.852758	0.272794
	4	10.27975	2.804252	0.272794
			Average	0.272789
II	1	10.73511	2.964446	0.276145
	2	10.59936	2.926541	0.276105
			Average	0.276125

Estimated within–solution precision, based on 4 degrees of freedom: $\sigma = 0.000052$

Subsequently the procedure was refined and a study was done on the effect of the aliquot size on the analytical determination of boric acid. The samples were weighed on the same day and the results are given in Table 8. It can be seen from these data that there is no systematic difference between analytical results for the larger and smaller aliquots (within 0.01%).

Table 8. Effect of the size of boric acid solution aliquot on the coulometric determination of boric acid concentration.

Solution	Aliquot No.	Wt of aliquot, g	meq found	meq/g
b	3	10.20413	2.834423	0.277772
	4	2.02505	0.562549	0.277795
	5	2.20348	0.612081	0.277779
	6[a]	1.14274[a]	0.324266[a]	0.283762[a]
	7	1.17222	0.325603	0.277766
				0.277778
I	1	6.828209	1.193722	0.174822
	2	8.370246	1.463594	0.174857
	3	8.755848	1.531033	0.174858
				0.174846
II	1	8.493900	1.281755	0.150903
	2	8.303518	1.253004	0.150900
	3	21.30825	3.215547	0.150906
	4	9.040497	1.364261	0.150906
				0.150904

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[a] This sample is excluded from consideration. A gross error (2%) was apparently involved in handling it.

E. Containers and Conditions for Stable Storage of Boric Acid Solutions

The storing of boric acid solutions in polyethylene bottles stoppered with rubber septa and left at room atmosphere conditions was found to be unsuitable. This conclusion is based on the analytical data given in Table 9. Solution A was prepared and aliquoted on December 7, 1967, then aliquoted again on December 12 and on December 15. The data in Table 9 show the average concentration of the solution on the various days of aliquoting. The increase is obviously due to evaporation. The nonlinearity of the increase is understandable from the fact that the volume of the solution was constantly being depleted by the removal of aliquots, so that a constant rate of evaporation would yield an ever-increasing percentage loss per unit time.

Table 9. Concentration changes of solution (A) stored in polyethylene bottle in room atmosphere.

Date of aliquoting	Concentration, meq/g
December 7	0.277666
December 12	0.277778
December 15	0.279337

Storage of boric acid solutions in glass or Teflon at 90 to 100% RH appears to be totally satisfactory as illustrated by the data in Table 10, there was no significant change in concentration over the testing period of 20 days.

The last column in Table 10 shows percent recovery. These values are based on the ratio of meq H_3BO_3/g of solution calculated from the weight of boric acid originally used in the preparation of the solution to the meq H_3BO_3/g of solution found by coulometric analysis of each aliquot. The average is 100.0025, with a 95% confidence interval (df = 7) of 0.0021%.

Since the assay of the solid boric acid is 99.9997, with a 95% confidence interval (df = 17) of 0.0013%, the difference is not significant.

Table 10. Stability of H_3BO_3 solution stored in glass bottles in 90–100% RH atmosphere.

Date of aliquoting	Solution No.	meq/g calc.	meq/g found	Recovery, %
1- 3–68	1	0.277604	0.277609	100.0018
1- 3–68	1	0.277604	0.277622	100.0067
1–23–68	1	0.277604	0.277617	100.0047
1–23–68	1	0.277604	0.277603	99.9996
1- 4–68	2	0.150901	0.150903	100.0013
1- 5–68	2	0.150901	0.150900	99.9996
1- 5–68	2	0.150901	0.150906	100.0034
1- 8–68	2	0.150901	0.150906	100.0029
			Average	100.0025

$$\frac{t_{95}\sigma}{\sqrt{n}} = 0.0021\%$$

F. Development and Evaluation of a Mass Spectrometric Technique for Boron-Isotope Ratio Measurements and Evaluation of Possible Alternative Techniques

1. Introduction

Since the large percentage mass difference between $^{10}B^+$ and $^{11}B^+$ might cause prohibitive fractionation problems, the boron isotope ratios were measured using the molecular ion $Na_2BO_2^+$. The efficiency of production of this ion by surface ionization techniques was readily affected by variations in the chemical preparation, sample mounting procedure, filament material, sample size, total sample composition, sodium content, and filament temperature; and the development of a precise mass spectrometric technique necessitated a careful study of numerous variations and permutations of these parameters.

Argonne - II (ANL-II) boric acid was used as a reference standard in the testing and evaluating of all of the chemical and mass spectrometric parameters. Unless otherwise stated, all samples contained 1 mg of boron per ml of aqueous solution, with sufficient Na_2CO_3 added to give an atomic B:Na ratio of 1:1. In preliminary tests NaOH was tried as a Na source, but this proved inferior to Na_2CO_3 in the mass spectrometric analyses.

Preliminary work showed very quickly that mass spectrometric results varied quite drastically when different chemical preparation techniques were used. Studies showed that there was no isotopic fractionation during the chemical preparation but that differences in chemical preparation caused differences in the ionization efficiency of the mass spectrometric technique and these, in turn, caused variations in the biases involved in the surface ionization phenomenon. Consequently it became obvious that it would be necessary to use a meticulously consistent preparation procedure for all samples.

2. Sample Mounting Procedure

A sample was mounted on a tantalum-ribbon (1×30 mils) filament in the following manner: one small drop of solution ($\sim$5 μg B) was placed on the filament and dried with a heat lamp and a 1.2 A current for 5 minutes; the lamp was turned off and the current was increased until the sample color changed to gray-white (1.5 - 1.8 A); the current was maintained for 2 minutes after the color change. This procedure was selected over other variations because it led to good mass spectrometric performances and because the easily recognizable fiduciary point (the color change) allowed for consistency in the procedure.

Solutions which were dried only with a heat lamp, or with a heat lamp plus an electrical current of less than 1 A, usually lead to either intense ion currents that decayed too rapidly for precise measurements or ion currents that were not stable enough for precise measurements.

Solutions that were acid or neutral gave very low intensity ion currents (10^{-13} A). It appeared that the boron was lost through sublimation when these solutions were dried on the filaments. Basic solutions gave 10^{-12} A ion currents even when the filament was heated to a dull red color during the sample mounting. Limited experimentation with solutions with pH greater than 8 did not reveal any significant prospect for improving the analytical technique.

Sample mounting was performed in a hood and the variable draft made it impossible to impose rigid temperature controls on the drying procedure. Best results were obtained when the hood door was adjusted so that the color change in the sample occurred between 1.5 and 1.8 A. It was found that gross changes in the volume of air flowing across the filament could cause the color change to occur outside of the normal 1.5 - 1.8 A range.

3. Filament Material

Of the four materials tested (Ta, Re, W, Pt), tantalum was selected as the filament material because its ionization efficiency was most consistent over a wide range of sample mounting conditions and it was least sensitive to variations in total sample composition. In addition, tantalum filaments showed no strontium background ($<10^{-15}$ A) even at a temperature of 950 °C. No pre-baking was necessary. Both rhenium and tungsten had lower ionization efficiencies than tantalum and both required pre-baking in order to reduce the strontium background to $<10^{-15}$ A. Platinum filaments showed no strontium background at temperatures below 1000 °C.

Efforts to develop a triple-filament technique using any of the four filament materials were unsuccessful; the ion currents were usually unsuitable both in magnitude and stability.

Preliminary investigations with platinum filaments indicated that it is more efficient than tantalum for surface ionization of boron but is extremely sensitive to sample mounting conditions, total sample composition, and "age" of the solution. Efforts to demonstrate that the apparent gross changes in ionization efficiency are due to impurities which produced a poisoning or suppressive effect on the ionization process were unsuccessful. Investigations subsequent to the completion of the measurements of the absolute isotopic compositions of the two boron standards (Section G) have revealed that the use of platinum filaments gives excellent results when the B/Na ratio of the samples is >1. Although boric acid dissolved in water without any addition of sodium and solutions with B/Na = 1 did not yield ion currents of sufficient intensity or duration for good analyses, solutions with B/Na ratios from 2 to 80 yielded excellent analyses. It appears that the use of platinum filaments for the surface ionization of boron may eventually produce the best results but more work is needed to define the optimum conditions.

4. Sample Size

Sample sizes ranging from 5 to 100 μg were tested to determine the optimum amount of boron necessary for a good analysis. The experiments indicated that sample sizes >20 μg had a greater frequency of erratic emission and signal instability. The larger samples did not have long periods of signal growth, as might have been expected, but yielded decaying signals, as with smaller samples. In general it was more difficult to maintain standard intensities with larger samples than with smaller samples.

The final prepared sample size was 5 μg. This amount of boron yielded the same magnitude of ion currents as the larger samples without any detectable increase in fractionation. Ion signals were generally very stable and rejection of an analysis because of erratic emission was very rare.

5. Total Sample Composition

The presence of extraneous material in the boron samples was detrimental to the analytical precision of the mass spectrometry and was the most probable cause for some of the observed variations in ionization efficiency. In a series of tests, barium, calcium, and lead were added to ANL-II solutions in sufficient concentrations to give 20 to 40 μg sample sizes of known impurity per sample loading. The general effect of these impurities was to require higher filament temperatures to produce the standard (3 × 10^{-12} A) $Na_2BO_2^+$ ion currents. This in turn resulted in observed $^{11}B/^{10}B$ ratios significantly higher than those observed in analyses of high purity ANL-II solution, reflecting significant depletion of ^{10}B under the higher-temperature conditions.

In another series of tests approximately 2 μg aliquots of strontium were added to several tantalum filaments along with the normal 5 to 20 μg boron samples. There were no detectable ($<10^{-15}$ A) strontium signals at temperatures <950 °C.

6. Sodium Concentration

The effect of sodium concentration on the production of $Na_2BO_2^+$ was evaluated by preparing samples of ANL-II boric acid with known B/Na ratios. This experiment was conducted twice, over an 18 month interval, with two completely different sets of solutions. The purpose of the second set of experiments was to provide critical evaluation of previous conclusions formulated during the fluid stages of development when data was acquired under conditions where the criticalness and control of all parameters were not firmly established.

In the first experiment sufficient sodium, as NaOH, was added to solutions of ANL-II to yield solutions with B:Na ratios of 2:1, 1:1, 1:2 and 1:4. All of these solutions were analyzed under the conditions of standard ion current (1 - 2 × 10^{-12} A) and restricted filament current (1.15 - 1.30 A); results from analyses which could not meet these requirements were rejected. Under these conditions the observed $^{11}B/^{10}B$ ratios of the solutions with B:Na ratios of 1:1 and 2:1 were nearly identical and did not change grossly even after the filaments had been heated for several hours. The observed $^{11}B/^{10}B$ ratio of the solution with a B:Na ratio of 1:2 was 1 percent higher than that of the B:Na ratio of 1:1 and 2:1 solutions and was observed to change with time. However, under the standard conditions the rate of change was sufficiently slow so that precise ratio measurements could be made. For the solution with a B:Na ratio of 1:4 the $Na_2BO_2^+$ ion current was completely suppressed at normal filament temperatures. Even at a filament current of 1.5 A, the ion signal was only 1×10^{-13} A and decayed too rapidly to make precise ratio measurements.

On the basis of these observations, it was postulated that sodium ions, which are formed with a high degree of efficiency on most filament materials, were so voluminous for solutions with excess sodium that suppression of the $Na_2BO_2^+$ ion occurred. In order to obtain the standard signal intensity ($1 - 2 \times 10^{-12}$ A) it was therefore necessary to have a higher filament temperature. The higher filament temperature caused an increase in the rate of isotopic fractionation and the observed $^{11}B/^{10}B$ ratios reflected the consequent depletion in ^{10}B abundance. It was therefore concluded that excess sodium was to be avoided and that the absolute isotopic abundance measurements would have to be made with solutions that all had only one B:Na ratio - either 1:1 or 2:1.

The second experiment to evaluate the effects of sodium on the production of $Na_2BO_2^+$ was performed after completion of the measurements of the absolute isotopic compositions of the two boron standards (Section G), when the total analytical experience with this element was more than 1 year. Two groups of ANL-II solutions were prepared under identical chemical conditions. NaOH was added to one group and Na_2CO_3 was added to the other group. Within each group there were solutions with B:Na ratios of 2:1, 1:1, 1:2 and 1:4. In the mass spectrometric measurements the filament currents were adjusted to give specific temperatures as measured with an optical pyrometer. The filament current was not restricted to a particular range as in the first experiment nor was the ion current set to a specific magnitude as in the first experiment, although at the temperatures chosen the ion current was generally in the standard range (1 - 2 × 10^{-12} A). Duplicate analyses were made on each sample and within each analysis ratio measurements were made first at 750 °C and then at 780 °C. The results are summarized in Tables 11 and 12. The ratios given are not absolute; they have been corrected for the ^{17}O effect but not for filament bias.

Table 11. $^{11}B/^{10}B$ ratios (relative) of ANL-II boric acid solutions with known amounts of Na_2CO_3.

B/Na Ratio	$^{11}B/^{10}B$ at 750 °C	Ion current (A) at 750 °C	$^{11}B/^{10}B$ at 780 °C	Ion current (A) at 780 °C
2:1	4.0362	2.0–1.0 x 10^{-12}	4.0372	2.5–1.5 x 10^{-12}
	4.0339	1.2–0.8 x 10^{-12}	4.0367	3.0–2.2 x 10^{-12}
	4.0350		4.0370	
1:1	4.0368	2.5–1.5 x 10^{-12}	4.0416	4.0–3.0 x 10^{-12}
	4.0379	2.0–1.6 x 10^{-12}	4.0417	5.0–3.0 x 10^{-12}
	4.0374		4.0416	
1:2	4.0375	5.0–4.0 x 10^{-12}	4.0635	1.7–1.4 x 10^{-11}
	4.0379	3.2–2.0 x 10^{-12}	4.0574	1.3–1.1 x 10^{-11}
	4.0377		4.0604	
1:4	4.0477	7.0–5.0 x 10^{-12}	4.0686	1.7–1.4 x 10^{-11}
	4.0448	2.0–1.2 x 10^{-12}	4.0715	7.4–6.1 x 10^{-12}
	4.0462		4.0700	

Table 12. $^{11}B/^{10}B$ ratios (relative) of ANL–II boric acid solutions with known amounts of NaOH.

B/Na Ratio	$^{11}B/^{10}B$ at 750 °C	Ion Current (A) at 750 °C	$^{11}B/^{10}B$ at 780 °C	Ion Current (A) at 780 °C
2:1	4.0301	$1.2-0.8 \times 10^{-12}$	4.0336	$2.0-1.6 \times 10^{-12}$
	4.0318	$1.2-0.6 \times 10^{-12}$	4.0308	$2.5-1.5 \times 10^{-12}$
	4.0310		4.0322	
1:1	4.0391	$2.5-1.9 \times 10^{-12}$	4.0443	$6.4-4.5 \times 10^{-12}$
	4.0377	$2.0-1.6 \times 10^{-12}$	4.0407	$5.0-2.5 \times 10^{-12}$
	4.0384		4.0425	
1:2	4.0408	$2.0-1.5 \times 10^{-12}$	4.0594	$7.0-4.0 \times 10^{-12}$
	4.0483	$3.2-2.0 \times 10^{-12}$	4.0696	$1.3-0.9 \times 10^{-11}$
	4.0446		4.0645	
1:4	4.0645	$1.2-1.0 \times 10^{-12}$	4.0831	$2.6-1.0 \times 10^{-12}$
	4.0559	$1.3-1.0 \times 10^{-12}$	4.0806	$4.0-2.1 \times 10^{-12}$
	4.0602		4.0818	

From the results of the first experiment it had been expected that, in the second experiment, the observed $^{11}B/^{10}B$ ratios of samples with B/Na <1/2 would show significant depletion in ^{10}B when compared to observed $^{11}B/^{10}B$ ratios of samples with B/Na >1. The results (Tables 11 and 12) bear out this expectation, with the average effect (B/Na = 2 vs B/Na = 1/4) being significantly greater at 780 °C (1.0%) than at 750 °C (0.5%).

The complete suppression of the $Na_2BO_2^+$ ion signals from the sodium hydroxide solution with B/Na = 1/4, observed in the first experiment, was not observed in the second experiment. The first two analyses of this solution gave ion currents of $<5 \times 10^{-14}$ A at 750 °C, but at 800 °C currents of

1 to 2 × 10^{-12} A were obtained which were sufficiently stable for ratio measurements. The two analyses were made within one week after the completion of the chemical preparation of the sample. The solution was allowed to remain on the shelf for another two weeks without any additional processing. Then another mass spectrometric analysis was performed and ion currents of 2 × 10^{-12} A were obtained at 750 °C. This phenomenon was observed to occur in a small percentage of the many boron solutions that were prepared and is referred to as "aging". These boron solutions apparently changed in some manner while enclosed in sample vials and sitting on a shelf. For some samples this change improved the analytical performance of the sample on the mass spectrometer; for other samples the change caused a deterioration in the analytical performance of the sample with time. Most of the samples used in this study, and particularly those used for the absolute ratio determinations, did not show any aging effect, but this phenomenon presents the only plausible explanation for the discrepency between the results of the two experiments on the NaOH solution with B/Na = 1/4.

The data for the samples with B/Na >1 confirmed the general observations of the first experiment. The $^{11}B/^{10}B$ ratios did not change significantly during an analysis and were relatively insensitive to small temperature increases.

Within the sodium carbonate group of samples (Table 11) there is a strong indication that, at a given temperature, the ionization efficiency increases as the sodium concentration increases. The results from the sodium hydroxide group of samples (Table 12) are neutral in this respect but still contradict the conclusion, based on the first experiment, that excess sodium inhibits the production of $Na_2BO_2^+$ ions. However, in the final analysis, the samples with excess sodium do give observed ratios which are depleted in ^{10}B and changing with time, indicating that excessive fractionation is occurring.

Although there are some discrepancies in the observations of the two experiments, the conclusion that sodium concentration is a critical parameter which must be kept constant for all solutions is strengthened by both experiments. Failure to use a constant B/Na ratio for all samples will seriously affect both the precision and accuracy of the $^{11}B/^{10}B$ ratio measurements.

7. Filament Temperature

For precise isotopic ratio determination using surface ionization techniques it is important to be able to reproduce the same filament temperature for all analyses. Variations in the filament temperature of analyses will cause variations in the rate of isotopic fractionation and, consequently, variations in the observed ratios.

In the determination of the absolute isotopic compositions of two boron standards (Section G) a consistent temperature level was maintained through a combination of filament current and signal intensity settings. Preliminary work had established an average optimum temperature to be equivalent to a filament current of from 1.20 to 1.30 A. In general this filament temperature resulted in $Na_2BO_2^+$ ion signals of from 1 to 3×10^{-12} A. Any analysis in which the parameters were inconsistent with these ranges was discarded.

Admittedly, the use of filament currents and signal intensities as temperature indicators is imperfect. Even minor variations in the thickness of the filament materia and in the chemical compositions of the samples will affect these parameters. However, it was proven empirically that these temperature guides gave results with an analytical limit of error on the order of 0.1%, which was quite acceptable.

Subsequent to the determination of the absolute isotopic compositions of two boron standards (Section G), it was found that optical pyrometers available in the laboratory could be used for filament temperature measurements even though their minimum temperature measurement was 700 °C. At this low temperature it first appeared to be impossible to match the reference line of the pyrometer and the faint glow of the filament with any reasonable precision. However it was subsequently discovered that by turning off ceiling lights and/or shielding the pyrometer and source housing with a black cloth a precision of ±10 °C could be achieved in the range between 750 °C and 800 °C.

Use of the pyrometer quickly revealed that filament cur currents of 1.2 and 1.3 A corresponded approximately to temperatures of 710 °C and 830 °C, respectively. Taking data indiscriminately over this filament current range could produce $^{11}B/^{10}B$ results which differed by as much as 1%. By also restricting the ion current intensity, the variations in the ratio can be reduced to an acceptable level (0.10 - 0.15%), but use of the pyrometer to restrict filament temperatures to within ±10 °C of the optimum temperature gives the best precision.

8. Mass Spectrometric Procedure

The mass spectrometric procedure used in the determination of the absolute isotopic compositions of two boron standards (Section G) is as follows.

The filament current is rapidly increased (1.2 - 1.25 A) until the $Na_2BO_2^+$ ion current is barely detectable (1×10^{-13} A) on the transmission grid, then slowly increased until the grid ion current is $60 - 80 \times 10^{-13}$ A. The signal will decay slowly. At 18 minutes the filament current is increased to give a grid ion current of $60 \pm 2 \times 10^{-13}$ A. The signal will continue to decay slowly. At 24 minutes the filament current is increased to give a $50 \pm 2 \times 10^{-13}$ A grid ion current. The signal is given a final focussing; it will decay very slowly. At 30 minutes the signal should be $40 \pm 5 \times 10^{-13}$ A; if necessary it is adjusted to this level. The signal will continue to decay slowly for the remainder of the analyses. Data-taking begins at 40 to 42 minutes into the run. Ten peak sets (10 ratios) are taken and base line readings are taken immediately before and immediately after the data. The peak-top data are taken by step-wise changes in the magnet current and each peak-top is monitored for 30 seconds.

The filament heating procedure subsequently devised for use with an optical pyrometer is as follows.

The filament current is increased until the $Na_2BO_2^+$ ion current is barely detectable (1×10^{-13} A) on the transmission grid. At 6 minutes the filament temperature is adjusted to 720 °C. The ion current will usually grow to a maximum of $20 - 40 \times 10^{-13}$ A and then decay to $\sim 10 \times 10^{-13}$ A. At 18 minutes the filament temperature is increased to 750 °C; the ion current is normally $30 - 50 \times 10^{-13}$ A and will decay slowly for the remainder of the analyses. If the ion current is much less than 20×10^{-13} A at 30 minutes, the filament temperature may be increased slightly (750 - 760 °C). Data-taking begins at 40 - 42 minutes into the run and is accomplished as previously described.

G. Absolute Isotopic Abundance Ratios of Two Boron-Isotope Standards, SRM 951 and SRM 952

1. Introduction

The NBS is conducting a long-term program of absolute isotopic abundance ratio and physical atomic weight determinations using solid-sample surface or thermal ionization mass spectrometry. Previous elements studied include silver [8], chlorine [9], copper [10], bromine [11], chromium [12], magnesium [13] and lead [14]. The present work extends the study to boron.

The isotopic composition of natural boron appears to vary significantly [15], [16], [17], so there is little value in attempting to establish an atomic weight. So, the purpose of the present study was to establish the absolute isotopic compositions of a normal ($^{11}B/^{10}B \sim 4$) boron sample and an enriched ($^{10}B \sim 95\%$) boron sample. The former would be of great use as an absolute standard for people studying natural boron isotopic variations and the latter would be useful to people concerned with enriched ^{10}B samples used in nuclear reactors.

The mass spectrometers used in this study were calibrated for bias by the use of samples of known $^{11}B/^{10}B$ ratio, prepared from nearly pure separated ^{10}B and ^{11}B isotope solutions. The collector and recorder systems used in this laboratory have been designed so that any biases they might contribute are constant. The only "random" bias associated with the isotopic ratio measurements is due to the mass-dependent fractionation of the isotopes during ionization, and this bias is independent of the isotopic composition of the sample. Thus, for each instrumental system used in this study, a single experimentally determined correction factor is valid over the entire range of isotopic compositions measured. The validity of this single-correction factor assumption based on multiple previous studies was re-tested in this study by comparison of correction factors obtained with calibration mixes with $^{11}B/^{10}B$ ratios of approximately 4/1, 1/4, 1/12 and 1/18.

2. Experimental Procedure

a. Mass Spectrometry - Isotopic measurements of the calibration mixes and SRM samples were made with three different single-stage solid-sample mass spectrometers which are identical except for minor differences in the vacuum systems. Each instrument has a 6-inch radius of curvature 60° analyzer tube, 48° sector magnet and a Z lens in the source assembly [18]. Single filament tantalum-ribbon (1 × 30 mils) sources were used.

The samples were prepared to a concentration of 1 mg of boron per milliliter of boric acid solution containing enough sodium to yield B/Na of 1/1. One drop of solution was deposited on the filament and dried with a heat lamp and a 1.2 A current for 5 minutes; then the heat lamp was turned off and the current was slowly increased until the sample turned whitish-grey (1.6 - 1.8 A) and held there for two minutes.

An accelerating voltage of 6 kV was used. The $^{11}B/^{10}B$ ratios were determined by measuring the relative abundances of the $Na_2{}^{11}BO_2{}^+$ and $Na_2{}^{10}BO_2{}^+$ ions, at masses 89 and 88 respectively. Corrections for $Na_2{}^{10}B^{16}O^{17}O^+$ were made by measuring the $Na_2{}^{11}B^{16}O_2{}^+/Na_2{}^{11}B^{16}O^{17}O^+$ ratio of the ^{11}B separated isotope solution (masses:89/90).

Preliminary studies showed that isotopic fractionation was significant and varied with time and filament temperature. To minimize the effect of this fractionation, all analyses were made in an identical manner; data were always taken during the same time interval, and the total ion signal was always kept within strict limits.

b. <u>Purification of the Separated Isotopes</u> - Approximately 0.65 g each of electromagnetically separated ^{10}B and ^{11}B isotopes, in the form of boric acid (H_3BO_3), were obtained from the Isotopes Division, Oak Ridge National Laboratory, Union Carbide Nuclear Company. The $H_3{}^{10}BO_3$ was designated sample No. 98726, and the $H_3{}^{11}BO_3$ was designated sample No. 98802.

The chemical purity of the samples (Table 13) was not sufficient for their use as received and they were dissolved and eluted through hydrogen-form cation exchange columns to

Table 13. Estimation of impurities (%) in separated isotopes.

	$H_3{}^{10}BO_3$	$H_3{}^{11}BO_3$
Lithium	0.01	< 0.01
Magnesium	0.02	< 0.05
Silicon	0.05	< 0.05
Calcium	< 0.01	0.02
Copper	< 0.01	< 0.05
Sodium	0.05	< 0.01

Semi-quantitative determination at Oak Ridge National Laboratory by emission spectroscopy.

remove the cationic impurities. Unfortunately, the abundances of sodium and magnesium were sufficiently high so that, in the exchange, enough strong acid was produced so that a strong-acid correction to the assay could not be made with sufficient accuracy (refer to page 22). It was therefore decided to recrystallize the isotopic boric acids from water as a preliminary purification. This procedure was shown to be effective in removing NaCl (at the 0.1% level) from natural boric acid.

Each sample of isotopic boric acid was treated as follows: About 2.5 g of material was dissolved in 20 ml of water and the solution was filtered through a polyethylene filter. The filtrate was concentrated to about 10 ml at 80 °C and then cooled to about 5 °C. The recrystallized boric acid was caught on a polyethylene filter, washed with cold distilled water, and dried by passing clean dry air through the filter. In both cases the weight of the recrystallized separated isotope boric acid was about 1.6 g, or about 64% of the starting material. A second sample of $H_3{}^{10}BO_3$ was recrystallized in the same manner.

Two solutions of the "B10" separated isotope and one solution of the "B11" separated isotope were then prepare from the recrystallized materials and further purified in the following manner. About 1.2 g (B-10-2) and 1.08 (B-10-3) of $H_3{}^{10}BO_3$ and 1.6 g (B-11-2) of $H_3{}^{11}BO_3$ were transferred to platinum boats, weighed on a microanalytical balance and transferred to 125 ml teflon bottles. Each sample was then dissolved in 30 ml of water and eluted through a cation exchange column to remove any remaining cationic impurities. The elute was caught in a weighed 125 ml teflon bottle and the column was washed with 15 ml of water which was added to the original elute.

The cation exchange column consisted of a 0.5×8.8 cm polyethylene dropping pipet filled to a height of 3 cm with 100-200 mesh AG 50×8 cation exchange resin. The resin which was supplied in the hydrogen form, was pretreated by passing 10 ml of HCl (1+3) through the column and then washing it with 30 ml of water.

c. <u>Preparation and Boron Concentration of the Separated Isotope Solutions</u> - The three purified separated isotope solutions were diluted with water so that the concentration of boron was approximatel 3 mg per g of solution. A diluted solution of $H_3{}^{11}BO_3$ (B-11-4), with a concentration of approximately 0.45 mg of boron per g of solution, was then prepared by transferring 16 g of the first $H_3{}^{11}BO_3$ (B-11-2) solution to a weighed 125 ml teflon bottle and diluting it to 100 g with water. This diluted $H_3{}^{11}BO_3$ (B-11-4) solution was used to prepare calibration mixes with $^{11}B/^{10}B$ ratios <1/4.

Four samples containing from 1.2 to 1.5 meq of boron were withdrawn from each of the two $H_3{}^{10}BO_3$ (B-10-2 and B-12-3) and the $H_3{}^{11}BO_3$ (B-11-2) solutions, and seven samples, containing 0.45 meq of boron, were withdrawn from the diluted $H_3{}^{11}BO_3$ (B-11-4) solution, in the following manner.

The cap of the Teflon bottle containing the solution was replaced with a rubber serum stopper. A platinum hypodermic needle and another smaller hollow needle to serve as a vent were inserted through the stopper. The appropriate syringe was attached to the platinum needle and the aliquot was withdrawn. The tip of the needle was raised above the solution and a small amount of air was drawn into the syringe. The syringe was detached from the needle, the tip was wiped with a piece of tissue paper and capped with a Kel-F cap. The two needles which were still in the stopper were capped to prevent evaporation of the solution from the bottle.

The syringe was wiped with a damp towel to dissipate any static charge and it was weighed. The cap was removed from the syringe and the aliquot was discharged into a bottle (Polyethylene bottles were generally used, but Teflon bottles were used in the preparation of the synthetic mixtures). A little air was drawn into the syringe which was then recapped with the Kel-F cap. The syringe was wiped with a damp towel and weighed. The difference between the filled and empty syringe was taken as the weight of the aliquot.

The solutions were transferred to 4 oz polyethylene bottles and the boric acid concentrations were determined as described in Section C. Results are given in Table 14. Two samples, each containing 0.3 meq H_3BO_3, were withdrawn from each of the boric acid solutions for the determinations of strong acid concentrations. (see Section B.3) Results are given in Table 15.

d. Isotopic Analysis of the Separated Isotope Solutions - The separated isotope solutions were analyzed twelve times each; four times each on the standard 6-inch instrument described in Section G (MS-4), and 8 times each (four times each by two operators) on a 12-inch instrument [19] which was equipped with an electron multiplier.

Results are given in Table 16. All results were corrected for fractionation during ionization, as determined by analyses of the synthetic mixtures (see below), and the results from MS-1 were also corrected for the theoretical square-root-of-the-mass-ratio fractionation of the electron multiplier. Tests made with and without the multiplier showed that this correction was valid and necessary.

The isotopic compositions reported by ORNL are: "B10", 99.77 ± 0.03 atom percent ^{10}B and 0.23 ± 0.03 atom percent ^{11}B; "B11", 0.23 ± 0.05 atom percent ^{10}B and 99.77 ± 0.05 atom percent ^{11}B. The ORNL limits quoted express the precision of the measurements. From known sources of systematic error, the absolute error is estimated by ORNL to be less than one percent.

e. Preparation of the Calibration Mixes - Twelve calibration mixes were prepared by mixing weighed portions of the "B10" and "B11" solutions to produce ratios from $^{11}B/^{10}B \sim 0.05$ to $^{11}B/^{10}B \sim 4$ (Table 17). The B-11-4 solution (see Section G.2.c) was used to prepare calibration mixes whose $^{11}B/^{10}B$ ratios were 0.05, 0.08 and 0.25. In addition another calibration mix with $^{11}B/^{10}B \sim 0.25$ was prepared from the B-11-2 solution, thus providing a crosscheck of the two "B11" solutions.

Table 14. Concentration of boron isotope solutions.

Solution	Sample number	Weight of solution (grams)	Boron (meq)	Concentration meq boron/gram solution
B-10-2	1	5.18162	1.551955	0.299512
	2	5.08398	1.523070	0.299582
	3	5.00825	1.500280	0.299562
	4	5.07867	1.521378	0.299562
			Average	0.299554
			Correction for strong acid	– 0.000022
				0.299532
B-10-3	1	4.12724	1.243347	0.301254
	2	4.07599	1.227977	0.301271
	3	4.09591	1.233790	0.301225
	4	4.14870	1.249785	0.301247
			Average	0.301249
			Correction for strong acid	– 0.000027
				0.301222
B-11-2	1	5.22914	1.421235	0.271791
	2	4.98995	1.356285	0.271803
	3	5.12473	1.392860	0.271792
	4	5.14304	1.397974	0.271818
			Average	0.271801
			Correction for strong acid	– 0.000013
				0.221788
B-11-4	1	10.11226	0.447349	0.0442383
	2	10.36477	0.458675	0.0442532
	3	10.17779	0.450218	0.0442353
	4	10.13191	0.448150	0.0442315
	5	10.04164	0.444233	0.0442391
	6	10.26498	0.454081	0.0442359
	7	10.18005	0.450381	0.0442415
			Average	0.0442393
			Correction for strong acid	– 0.0000020
				0.0442373

Table 15. Determination of strong acid in boron isotope solutions.

Solution number	Strong acid in boric acid (percent)
B-10-2	0.0074
B-10-3	0.0090
B-11-2	0.0047
B-11-4	0.0046

Table 16. Isotopic composition of separated boron isotopes used in calibration samples.

Separated isotope		Isotopic composition (atom percent)
"B10"	^{10}B	99.8387 ± 0.0020[a]
	^{11}B	0.1613 ± 0.0020
"B11	^{10}B	0.1874 ± 0.0020
	^{11}B	99.8126 ± 0.0020

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[a] The uncertainties are based on a minimum error of 0.00002 for the ratio determinations. The calculated 95 percent confidence limits are below this level.

Table 17. Composition of boron calibration samples.

Sample number	Isotope		Weight of solution (grams)	Concentration meq boron/gram solution	Boron (meq)
9	11		4.41671	0.271788	1.200409
		10	1.01056	0.299532	0.302695
10	11		4.68554	0.271788	1.273474
		10	1.01110	0.299532	0.302857
11	11		1.94136	0.271788	0.527638
		10	1.88704	0.299532	0.565229
12	11		2.19255	0.271788	0.595909
		10	1.96047	0.299532	0.587224
13	11		1.11925	0.271788	0.304199
		10	4.09183	0.299532	1.225634
14	11		1.07284	0.271788	0.291585
		10	4.09134	0.299532	1.225487
17	11		3.73430	0.0442373	0.165195
		10	2.02290	0.301222	0.609342
18	11		3.37683	0.0442373	0.149382
		10	2.03744	0.301222	0.613722
19	11		2.27225	0.0442373	0.100518
		10	4.07287	0.301222	1.226838
20	11		2.28611	0.0442373	0.101131
		10	4.15804	0.301222	1.252493
21	11		1.89970	0.0442373	0.0840376
		10	5.12416	0.301222	1.543510
22	11		1.95068	0.0442373	0.0862928
		10	5.23751	0.301222	1.577653

All aliquots were withdrawn from the primary solutions and weighed in the manner previously described (Section G.2.c). To eliminate the effect of any possible changes in the concentrations of the separated isotope solutions with time, the aliquots for the calibration mixes were taken interspersed with those used for the determinations of the boron concentrations of the separated isotope solutions. All aliquots were taken within a single 5-hour time period.

f. Isotopic Analysis of the Calibration Mixes and SRM Samples - One complete and one partial set of analyses of the calibration mixes and SRM samples were made, by different operators on different mass spectrometers. The complete set of analyses consisted of 32 analyses of SRM 951 made alternately with 32 analyses (4 each) of calibration samples 9, 10, 11, 12, 13, 14, 17 and 18, plus 8 analyses of SRM 952 made alternately with 8 analyses (4 each) of calibration mixes 21 and 22. The partial set of analyses consisted of 12 analyses of SRM 951 made alternately with 4 analyses each of calibration mixes 9 and 10 and 2 analyses each of calibration mixes 11 and 12; plus 8 analyses of SRM 952 made alternately with 8 analyses (4 each) of calibration mixes 21 and 22. In addition, calibration mixes 19 and 20 were analyzed 4 times each by operator I and 2 times each by operator II.

Ten peak sets (10 ratios) were taken in each analysis and baseline readings were taken immediately before and after the data. The peak-top data were taken by step-wise changes in the magnet current and each peak-top was monitored for 30 seconds.

3. Results and Discussion

Table 18 summarizes the results for the calibration mixes. Although there appears to be a real difference between operators, due to slight differences in their procedures, there is no systematic variation of correction factor with isotopic composition. This reaffirms the conclusion, stated in Section G.1, that the biases of the mass spectrometers used in this laboratory are independent of isotopic composition for a particular element.

Table 18. Determination of mass spectrometric bias.

	Isotopic ration $^{11}B/^{10}B$			Correction factor	
Calibration mix no.	Calculated	Operator I	Operator II	Operator I	Operator II
9	3.93700	3.93417	3.93258	1.00072	1.00112
10	4.17247	4.17100	4.16652	1.00035	1.00143
11	0.93323	0.93268	0.93254[a]	1.00059	1.00074
12	1.01421	1.01306	1.01283[a]	1.00114	1.00136
13	0.24963	0.24943		1.00080	
14	0.23938	0.23920		1.00075	
17	0.27251	0.27226		1.00092	
18	0.24484	0.24454		1.00123	
19	0.083514	0.083491	0.083414[a]	1.00028	1.00120
20	0.082325	0.082268	0.082231[a]	1.00069	1.00114
21	0.056042	0.055992	0.055973	1.00089	1.00123
22	0.056292	0.056219	0.056229	1.00130	1.00112
Mean values of correction factors				1.00080	1.00119[b]

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[a] Average of 2 determinations, all others are average of 4 determinations.

[b] Weighted for average number of determinations.

Table 19 gives the observed and corrected ratios for the four sets of data. Table 20 gives the final absolute values for the ratios along with the overall limits of error and uncertainty components. Although more data was obtained by operator I, the data of operator II show a better internal precision. As a result, the standard errors for both sets of data are almost identical, and the final values are a straight

Table 19. Observed and corrected $^{11}B/^{10}B$ ratios of the SRM samples.

Sample	Operator	Observed $^{11}B/^{10}B$	Corrected $^{11}B/^{10}B$
SRM 951	I	4.04074	4.04397
	II	4.03847	4.04328
SRM 952	I	0.053138	0.053180
	II	0.053155	0.053218

Table 20. Absolute isotopic ratios for the SRM samples.

	$^{11}B/^{10}B$
SRM 951 Boric Acid	4.04362
Overall limit of error[a]	± 0.00137
Uncertainty components:	
95% confidence limits on ratio determination	± 0.00054
Bounds due to possible systematic error in correction factor (including errors in separated isotopes)	± 0.00060
Bounds due to possible systematic error in chemical analyses	± 0.00023
SRM 952 Boric Acid	0.053199
Overall limit of error[a]	± 0.000032
Uncertainty components:	
95% confidence limits on ratio determination (minimum = 0.00002)	± 0.000020
Bounds due to possible systematic error in correction factor (including errors in separated isotopes)	± 0.000009
Bounds due to possible systematic error in chemical analyses	± 0.000003

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[a] The overall limit of error is the sum of the 95% confidence limits for the ratio determinations and the terms covering effects of known sources of possible systematic error.

average of both sets of data. Because of instrumental uncertainties, such as dead zone and recorder nonlinearity, it is assumed that no ratio can be measured to better than 0.00002, so this figure is used as an error value whenever the statistically determined 95 percent confidence limit is smaller than 0.00002.

Table 21 gives the atom percents for each isotope in each standard, and the atomic weights ($^{12}C = 12$) of each standard. Nuclidic masses were taken from Mattauch et al. [20].

Table 21. Atom percents and atomic weights for the SRM samples.

			Uncertainty components		
		Overall[a] limit of error	Mass spectrometric analytical error	Possible systematic errors in correction factors and separated isotopes	Possible systematic error in chemical analysis
SRM 951 Boric Acid					
Atomic weight	10.811756	± 0.000053	± 0.00002	± 0.000023	± 0.000009
Atom percent:					
^{10}B	19.8270	± 0.0054	± 0.0021	± 0.0024	± 0.0009
^{11}B	80.1370	± 0.0054	± 0.0021	± 0.0024	± 0.0009
SRM 952 Boric Acid					
Atomic weight	10.063267	± 0.000029	± 0.000018	± 0.000008	± 0.000003
Atom percent:					
^{10}B	94.9488	± 0.0029	± 0.0018	± 0.0008	± 0.0003
^{11}B	5.0512	± 0.0029	± 0.0018	± 0.0008	± 0.0003

Nuclidic Masses: 10.012939, 11.009305

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[a] The overall limit of error is the sum of the 95% confidence limits for the ratio determinations and the terms covering effects of known sources of possible systematic error.

REFERENCES

[1] LeDuigou, Y.,and Lauer, K. F., Proc. Conf. High-Precision Analysis of Substances of Interest to Nuclear Energy, Bureau Central de Measures Nuclaires, Ic (1962) pp. 89-102.

[2] Marinenko, G. and Champion, C. E., Manuscript in preparation.

[3] Roller, P. S., J. Am. Chem. Soc., 50, 1 (1928).

[4] Marinenko, G. and Champion, C. E., Anal. Chem., 41, 1208 (1969).

[5] Marinenko, G. and Taylor, J. K., Anal. Chem., 40, 1645 (1968).

[6] NBS Technical News Bulletin, 47, No. 10 (1963).

[7] NBS Technical Note 425 (1967).

[8] Shields, W. R., Garner, E. L., and Dibeler, V. H., J. Res. NBS 66A (Phys. and Chem.), No. 1, 1 (1962).

[9] Shields, W. R., Murphy, T. J., Garner, E. L., and Dibeler, V. H., J. Am. Chem. Soc., 84, 1519 (1962).

[10] Shields, W. R., Murphy, T. J., and Garner, E. L., J. Res. NBS 68A (Phys. and Chem.), No. 6, 589 (1964).

[11] Catanzaro, E. J., Murphy, T. J., Garner, E. L., and Shields, W. R., J. Res. NBS 68A (Phys. and Chem.), No. 6, 593 (1964).

[12] Shields, W. R., Murphy, T. J., Catanzaro, E. J., and Garner, E. L., J. Res. NBS 70A (Phys. and Chem.), No. 2, 193 (1966).

[13] Catanzaro, E. J., Murphy, T. J., Garner, E. L., and Shields, W. R., J. Res. NBS 70A (Phys. and Chem.), No. 6, 453 (1966).

[14] Catanzaro, E. J., Murphy, T. J., Shields, W. R., and Garner, E. L., J. Res. NBS 72A (Phys. and Chem.), No. 3, 261 (1968).

[15] McMullen, C. C., Cragg, C. B., and Thode, H. G., Geochim. et Cosmochim. Acta 23, 147 (1961).

[16] Finley, H. O., Eberle, A. R., and Rodden, C. J., Geochim. et Cosmochim. Acta 26, 911 (1962).

[17] Shima, M., Geochim. et Cosmochim. Acta 27, 911 (1963).

[18] Shields, W. R., Editor, NBS Technical Note 426, (1967).

[19] Shields, W. R., Editor, NBS Technical Note 277, (1966).

[20] Mattauch, J. H. E., Thiele, W., and Wapstra, A. H., Nuclear Physics 67, 1 (1965).

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

National Bureau of Standards
A. V. Astin, Director

APPENDIX 1

Certificate of Analysis

Standard Reference Material 951

Boric Acid

H_3BO_3, acidimetric assay, weight percent	100.00	± 0.01
Absolute Abundance Ratio, $^{10}B/^{11}B$	0.2473	± 0.0002
Boron-10, atom percent	19.827	± 0.013
Boron-11, atom percent	80.173	± 0.013

The atomic weight of the boron, calculated from the absolute abundance ratio using the nuclidic masses 10.0129 and 11.0093, is 10.812.

This lot of boric acid was prepared to ensure material of high purity and homogeneity. As received, it was slightly deficient (approximately 0.01 percent) in moisture, but adjusts to a stoichiometric composition in about 30 minutes exposure to a normal room humidity (approximately 35 percent relative humidity). Once adjusted to composition, the material is relatively insensitive (<0.01 percent) to moisture changes between 0 and 60 percent relative humidity, and absorbs only about 0.02 percent excess moisture in room temperature humidities as high as 90 percent. The material cannot be heated as it decomposes with the loss of considerable water.

Assay was by coulometric titration of samples varying in size from 0.2 to 1.0 g of boric acid, dissolved in 100 ml of a preneutralized solution 1*M* in KCl and 0.75*M* in mannitol. The inflection point of the potentiometric curve obtained from measurements with a glass-calomel electrode system was taken as the end point. The pH of the maximum inflection point was taken as the end point. The pH of the maximum inflection point will vary from approximately 7.9 to 8.5 for the range of sample sizes given above, and the titration must, therefore, be conducted in the absence of carbon dioxide or carbonates. The indicated tolerance is at least as large as the 95 percent confidence level for a single determination of any sample in the lot of material, and the average essentially indicates a boron-hydrogen ion ratio of 1.0000, since separate examination shows the material contains less than 0.001 percent of free strong acid.

(continued on reverse)

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
February 28, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of August 9, 1968)

The abundance ratio was determined by single-filament solid-sample mass spectrometry using the ion $Na_2BO_2^+$. Mixtures of known $^{10}B/^{11}B$ ratio (at a 1:4, 1:1, and 4:1 ratio) were prepared from high-purity separated isotope solutions and used as comparison standards. Correction was determined for the $^{16}O/^{17}O$ ratio ($^{11}B/^{10}B$ ratio correction, -0.00079) by measuring mass 91 using the high-purity boron-11 separated isotope. The indicated tolerances are at least as large as the 95 percent confidence limits for a single determination which includes terms for inhomogeneities in the material as well as analytical error.

The material was prepared by the J. T. Baker Company of Phillipsburg, New Jersey, for the Argonne National Laboratory. Separated isotopes were purified and solutions prepared by K. M. Sappenfield and T. J. Murphy, coulometric titrations were made by G. Marinenko and C. E. Champion, mass-spectrometric measurements were made by E. J. Catanzaro and E. L. Garner, Analytical Chemistry Division. The various procedures developed have been published and are available in Special Publication 260-17.

S. Department of Commerce
Maurice H. Stans
Secretary
National Bureau of Standards
A. V. Astin, Director

APPENDIX 2

Certificate of Analysis

Standard Reference Material 952

Enriched Boric Acid

Absolute Abundance Ratio, $^{10}B/^{11}B$	18.80 ± 0.02
Boron-10, atom percent	94.949 ± 0.005
Boron-11, atom percent	5.051 ± 0.005
H_3BO_3, acidimetric assay, weight percent	99.97 ± 0.02

The preparation furnished is an enriched boron-10 boric acid. It is slightly contaminated by occluded mother-liquor but the assay value should make it useful by direct weighing for a "spiking" material for boron assays, as well as a useful material for the calibration of mass spectrometers. The atomic weight of the boron, calculated from the absolute abundance ratio and the nuclidic masses 10.0129 and 11.0093, is 10.063.

The abundance ratio was determined by single-filament solid-sample mass spectrometry, using the ion $Na_2BO_2^+$. Mixtures of known $^{10}B/^{11}B$ ratio were prepared from high-purity separated isotopes and used as comparison standards. Correction was determined for the $^{16}O/^{17}O$ ratio ($^{11}B/^{10}B$ ratio −0.00079) by measuring mass 91 using the high-purity boron-11 separated isotope. The indicated tolerance is at least as large as the 95 percent confidence limits for a single determination which includes terms for inhomogeneities in the material as well as analytical error.

Details of the preparations and measurements are available in Special Publication 260-17. The material was prepared by the Oak Ridge National Laboratory. The material and the separated isotopes were purified and solutions prepared by K. M. Sappenfield and T. J. Murphy, coulometric titrations were made by G. Marinenko and C. E. Champion, mass-spectrometric measurements were made by E. J. Catanzaro and E. L. Garner, 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
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APPENDIX 3

To clarify the titration procedure used in this work a specific example is considered. A sample of boric acid, contained in a polyethylene boat and weighing 0.599207 g (vacuum corrected weight), was delivered into the cathode compartment of the coulometric cell containing 100 ml of 1M KCl-0.75M mannitol supporting electrolyte which had been previously pretitrated to neutrality point (pH 6.98).

After passage of 935.204 C of charge at 101.784 mA, the current was interrupted, the intermediate cell compartments were rinsed, and a final pH reading of 8.234 was observed. A few drops of 0.1N HCl were added to the cathode compartment whereupon the pH of solution dropped to 7.567. Equal charge increments (0.100C) were passed through the cell at 10.178 mA and the pH was measured following passage of each increment. The data obtained is shown in Table 1 and plotted in Figure 1.

It can be seen that the inflection point occurred at pH = 8.095 (point A on the graph). The pH at the completion of passage of charge at high current was 8.234 (point B on the graph), corresponding to an overtitration of 0.178 C. Thus, 0.178 C must be subtracted, and the number of coulombs equivalent to the delivered sample of boric acid was 935.026 C. By Faraday's law this corresponds to 9.69069 meq of acid or the weight of boric acid of 0.599205 g. Since 0.599207 g of the acid was weighed out, the assay of the material is 99.9997 weight percent H_3BO_3.

Table 1. Determination of the end–point in coulometric titration of boric acid.

Charge, C	pH	ΔpH/ΔC
0.000	7.567	
		0.48
0.100	7.615	
		0.54
0.200	7.669	
		0.60
0.300	7.729	
		0.63
0.400	7.792	
		0.73
0.500	7.865	
		0.77
0.600	7.942	
		0.83
0.700	8.025	
		0.85
0.800	8.110	
		0.85
0.900	8.195	
		0.77
1.000	8.272	
		0.69
1.100	8.341	
		0.72
1.200	8.413	
		0.67
1.300	8.480	
		0.62
1.400	8.542	
		0.57
1.500	8.599	
		0.52
1.600	8.651	

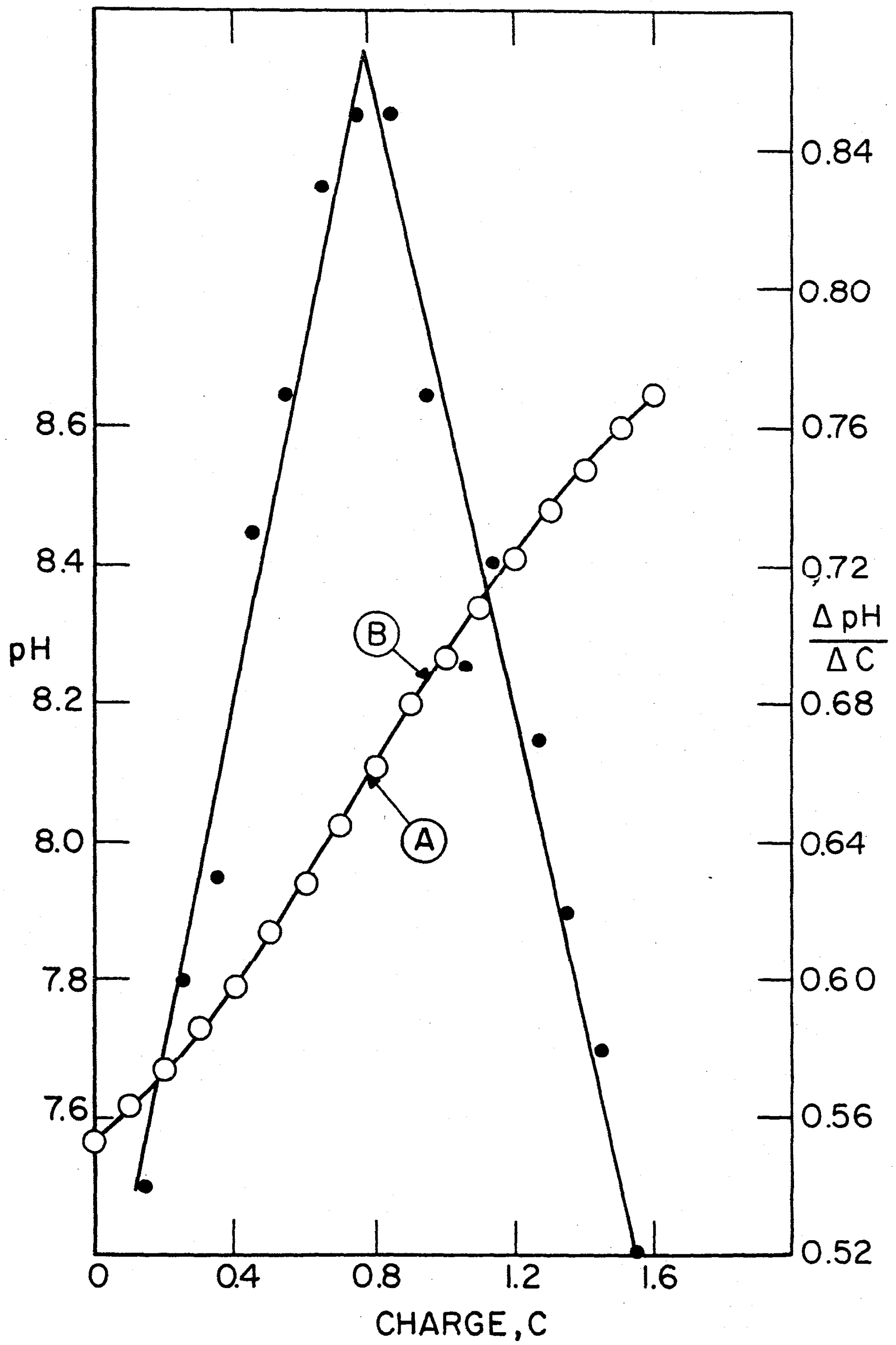

Figure 1. Determination of the End-Point in Coulometric Titration of Boric Acid.
○ – Points for pH = f(C); ● – points for $\Delta pH/\Delta C = f(C)$;
A – Inflection point $(\Delta pH/\Delta C)_{max}$; B – Final pH of titration