

ISOTOPIC CONTENT OF BORON

ON THE MEASUREMENT OF NATURAL VARIATIONS
IN THE ISOTOPIC CONTENT OF BORON

By
CHARLES BRIAN CRAGG, B.A.

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University

October 1957

MASTER OF SCIENCE (1957)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: On the Measurement of Natural Variations in the Isotopic
Content of Boron.

AUTHOR: Charles Brian Cragg, B.A. (University of Toronto)

SUPERVISOR: Professor H. G. Thode

NUMBER OF PAGES: vi, 23

SCOPE AND CONTENTS: An investigation was undertaken to check the difference in isotopic content between two boron samples measured earlier in this laboratory by using different methods of sample preparation from those used in the previous investigation. Yields of preparation were measured throughout. Measurements using methyl borate and boron trifluoride indicated a difference of slightly over 2% in the isotopic content of the samples, whereas the difference found in the previous investigation was 3.5%.

ACKNOWLEDGMENTS

The author wishes to express his thanks to Dr. H. G. Thode, under whose directorship this work was carried out, and to Dr. W. H. Fleming for his instruction and assistance with the mass spectrometry.

TABLE OF CONTENTS

Descriptive Note	<u>Page</u> (ii)
Acknowledgments	(iii)
Table of Contents	(iv)
List of Tables and Illustrations	(vi)
<u>INTRODUCTION</u>	(1)
(A) General	
(B) Historical	
(1) Discovery of the Stable Isotopes	
(2) The Separation of Isotopes	
(3) Natural Abundance of the Isotopes	(2)
(4) The Isotopes of Boron	(3)
(C) Problems of Measuring Isotopic Abundance Ratios	
(D) Scope of the Present Investigation	(6)
<u>EXPERIMENTAL</u>	(8)
(A) Preparation of Samples	
(1) Preparation of Methyl Borate	
(2) Preparation of Boron Trifluoride	(9)
(3) Preparation of Diborane	(12)
(B) Mass Spectrometry	
(1) Mass Spectrum of Methyl Borate	
(2) Measurement of the B^{11}/B^{10} Ratio Using Methyl Borate	(14)

TABLE OF CONTENTS (Cont.)

(3) Measurement of the B^{11}/B^{10} Ratio Using Boron Trifluoride	<u>Page</u> (15)
<u>RESULTS</u>	(16)
(1) Measurements on Methyl Borate	
(2) Measurements on Boron Trifluoride	
<u>DISCUSSION</u>	(17)
<u>CONCLUSION</u>	(21)
<u>REFERENCES</u>	(22)

LIST OF TABLES AND ILLUSTRATIONS

Fig. 1	Apparatus for preparing BF_3 .	<u>Page</u> (11)
Table 1	Methyl Borate Spectrum Used.	(14)
Table 2	Comparison of Boron Samples.	(18)

INTRODUCTION

(A) General

In 1948, Thode and others (1) found variations of as much as 3.5% in the isotopic content of boron in nature. Since then various workers (2, 3, 4) have carried out similar investigations but with conflicting results, some finding no variations to within the precision of their measurements. The present work is an attempt to resolve these discrepancies and investigate the errors in this type of measurement.

(B) Historical

(1) Discovery of the Stable Isotopes - The name "isotope" was invented by Frederick Soddy in 1913 to designate elementary substances identical in chemical behavior and atomic spectrum but differing in radio active properties. The first indication of the existence of isotopes of non-radioactive elements was the positive ray experiments on neon by J. J. Thomson (5) in which particles of mass 22 were observed along with the expected particles of mass 20. Unsuccessful attempts to isolate this unknown constituent by chemical methods followed, which, together with Aston's investigation of neon with the mass spectrograph (6), suggested that the constituents of mass 22 and 20 were isotopes of neon. Examination of other elements with the mass spectrograph revealed that many of them were composed of isotopic mixtures.

(2) The Separation of Isotopes - Although the isotopes of an element

were believed to be chemically identical, it was shown by Lord Rayleigh (7) that gases differing only in the masses of the molecules could be separated by diffusion. This was experimentally realized by Hertz (8), who achieved considerable separation of the isotopes of neon. Fractionation of the isotopes of mercury by distillation was demonstrated by Bronsted and Hevesy (9) using sensitive density measurements.

The application of quantum statistical mechanics to chemical thermodynamics and kinetics predicted that equilibrium and rate constants of reactions involving isotopes of an element should be slightly different for the different isotopes. Such differences were calculated for several reactions of light elements by Urey and Greiff (10). Chemical fractionation of the hydrogen isotopes was achieved by Washburn and Urey (11) using the electrolysis of water.

(3) Natural Abundance of the Isotopes - Aston measured isotopic compositions by photometric methods on his mass spectrograms, but the precision was only sufficient to show consistency with atomic weight values. Dempster (12) measured the ratio of potassium 39 to potassium 41 using an electrometer to detect the ion beams.

Atomic weights had been found to be constant within experimental error until Briscoe and Robinson (13) found variations in the atomic weight of boron coming from different sources. The calculations of Urey and Greiff suggested that the isotopic content of the light elements might vary in nature. A mass spectrometric investigation by Nier (14) on the C^{12}/C^{13} ratio in various samples of carbon showed variations

depending on the source, e.g. between marine carbonates and petroleum. Since then, variations in the abundance of the boron, nitrogen, oxygen, and sulphur isotopes have been reported.

(4) The Isotopes of Boron - The isotopes of boron, B^{10} and B^{11} , were discovered, their masses measured, and their abundance ratio estimated photometrically by Aston (15). The first mass spectrometric investigation of the isotopic abundance ratio was performed by Inghram (16) on boron trifluoride supplied by the Harshaw Chemical Company. Thode and others (1) measured the isotopic abundance ratios of boron from a variety of sources and found differences in the ratios of up to 3.5%. A similar project was undertaken by Osberghaus (2), who examined boron from various sources but found the ratios constant to within his experimental error of 0.5%. V. Shiuttse (3) demonstrated large isotopic fractionations in the thermal decomposition of potassium fluoborate and the evaporation of boric oxide and found a difference of over 3% in the isotopic abundance ratio between boron from a Central Asian source and boron from an Italian source. Wickman and others (4) examined boron of geologically different origins ranging from igneous silicates to sea water but found no variations in isotopic content outside of their experimental error of 0.2% except for sea water boron which was 0.2% enriched in B^{11} over their other samples. It was in an effort to resolve these apparent discrepancies that the present work was undertaken.

(C) Problems of Measuring Isotopic Abundance Ratios

The investigations described above have been concerned with two

problems:

- (1) the measurement of the isotopic content of a sample of an element,
- (2) the measurement of differences in isotopic content among several samples of an element.

As might be expected, the second problem is the more difficult.

In the mass spectrometric measurement of an isotopic abundance ratio, the sample must be processed to a form suitable for ionizing in the ion source, i.e. a gas or a solid depending on the instrument used. A portion of the sample is ionized by an electron beam, the ions accelerated by an electric field, collimated into a beam by slits, deflected by a magnetic field and those of a particular mass-to-charge ratio collected by a Faraday cup. The ion current passes through a very large resistor (about 10^{10} ohms) in going from the cup to ground potential: the voltage across this resistor is amplified and the resulting signal read on some indicating device, usually a servo-operated chart recorder. Systematic errors in the isotopic abundance ratio can be classified as:

- (1) fractionation of isotopes in the processing of the sample,
- (2) mass discrimination in the spectrometer,
- (3) non-linearity in the measurement of the ion current.

Fractionation of the isotopes in physical and chemical processes has been demonstrated (see section B (2) above) and can be expected to occur if the sample used in the instrument has been prepared from the original sample by methods giving less than 100% yield. Mass discrimination can be described as resulting from the dependence upon mass

of the efficiency of the instrument in ionizing the sample in the source and collecting the ion beam at the Faraday cup. This effect is serious if the masses being measured are selected by varying the electric accelerating field (electrostatic scanning), since this field strongly affects the efficiency of the source. Non-linearity can occur in the collector cup resistor (since it is difficult to make a very high resistance that obeys Ohm's law exactly), the amplifier and the recorder.

Non-linearity can be detected by straight forward electrical measurements on the various components. If the yield of preparation of the sample is known, an upper limit to the isotopic fractionation occurring in this step can often be estimated. Mass discrimination, however, is both theoretically intractable and experimentally inaccessible by mass spectrometric measurements. The most that can be said is that consistent results can be obtained from different instruments under certain conditions, but there seems to be no way to detect any systematic error common to all. True isotopic abundance ratios will probably require the use of standards determined by other methods, possibly synthetic preparations of separated isotopes.

The problem of comparing samples with respect to isotopic abundance ratio presents fewer difficulties. Since the quantity sought is the ratio of the isotopic abundance ratios for two samples, the mass discrimination factor cancels out entirely and the non-linearity factor becomes a second order effect provided both samples are measured at about the same signal level. Isotopic fractionation in the sample preparation can present serious difficulties, however, since workers in

this field are often interested in samples of different chemical origins and, unless yields are close to 100%, isotopic fractionation differing in extent between samples can be expected to occur.

Random errors are produced by fluctuations in the operating conditions of the instrument, upon which the mass discrimination factor depends. Hence, the greatest possible stability is required of the control devices, and, to keep the effect of drifting of the operating conditions to a minimum, the samples should be compared in the shortest possible time. Satisfying this later requirement leads to difficulties with certain compounds which exhibit "memory effects."

"Memory effects" are produced by compounds which have a strong tendency to be adsorbed on the walls of the spectrometer, the most notable example being boron trifluoride. Aston (17) remarked on "the extraordinary power (of boron trifluoride) of resurrecting the spectra of gases which had been previously used in the discharge bulb." Hence, if two samples are being compared, a sample may be contaminated with the one previously measured, even though its ion current has completely disappeared. The only remedy is long flushing with the sample to be measured before measurements are taken, but precision is then reduced because of instrument drift.

(D) Scope of the Present Investigation

The experiments described below were undertaken to check the differences in isotopic abundance ratio found previously in this

laboratory (1) in view of the recent reports indicating little or no variation in isotopic content of natural boron samples, and to study the preparation of different boron compounds to improve the precision of comparing isotopic abundance ratios.

A desirable compound for use in a gas-type spectrometer must:

- (1) be preparable in high yield from the required starting material,
- (2) be sufficiently volatile at room temperature to be easily handled in a vacuum system,
- (3) show no "memory effect", which will be satisfied if it does not readily form co-ordinate bonds.

A class of compounds showing very little tendency to form co-ordinate bonds is the alkyl esters of boric acid. The most volatile member, methyl borate, was chosen for investigation. Boron trifluoride was also studied, partly because it is a step in the preparation of deuterated diborane, for which a study is planned.

The samples studied are the two boric acid samples which showed the greatest difference in isotopic abundance ratio in the previous investigation, from Stassfurt, Germany, and Tres Morros, Argentina prepared by Borax Consolidated, London, England.

EXPERIMENTAL

(A) Preparation of Samples

(1) Preparation of Methyl Borate - Methyl borate was prepared following the method of Schlesinger and others (18). 0.1 moles of boric acid was converted to boric oxide by heating at 200°C in a vacuum for two hours or more. The boric oxide was added to about 0.6 moles of methanol (synthetic grade dried by refluxing with magnesium) in boiling flask and the mixture distilled through a fractionating column. The methyl borate-methanol azeotrope was taken off at about 54°C: at the end of the reaction, the overhead temperature rose fairly sharply to 64°C. The azeotrope (about 75% methyl borate) was treated with about 2 gms. vacuum-dried lithium chloride, which dissolved in the methanol, causing two layers to form, with the methyl borate on top and lithium chloride-saturated methanol below. The methyl borate was then separated by pipetting. Care had to be taken to keep contact of the ester with moist air to a minimum, since it hydrolyses extremely rapidly.

During the trial preparations using U.S.P. boric acid crystals, two fractionating columns were used, an electrically-heated Fodbelniak column 50 cm. high and 8 mm. in diameter rated at 20 plates at total reflux and a glass helix-packed column 60 cm. high and 10 mm. in diameter estimated at around 10 plates. Yields obtained

with either column were around 65 - 70%. Varying the methanol-boric acid mole ratio between 6:1 and 12:1 did not appreciably affect the yield.

The samples of boric acid from Stassfurt and Argentina were made into methyl borate using the helix-packed column and a methanol-boric acid mole ratio of 7:1. The yields obtained were 34% and 31% respectively.

The desirable size of sample to use with the mass spectrometer is 10^{-4} moles. Separating this amount and transferring it to a sample tube presents some problems, since the losses by hydrolysis due to exposure to moist air of such a small amount of methyl borate might produce severe isotopic fractionation. The method finally adopted was to draw the methyl borate into an ampoule of a suitable size made of 1 mm. bore glass capillary tubing. The ampoule was sealed at both ends and put into a vacuum system provided with break-seal sample tubes. With the system evacuated, the ampoule was broken with an iron breaker and the methyl borate frozen into a sample tube.

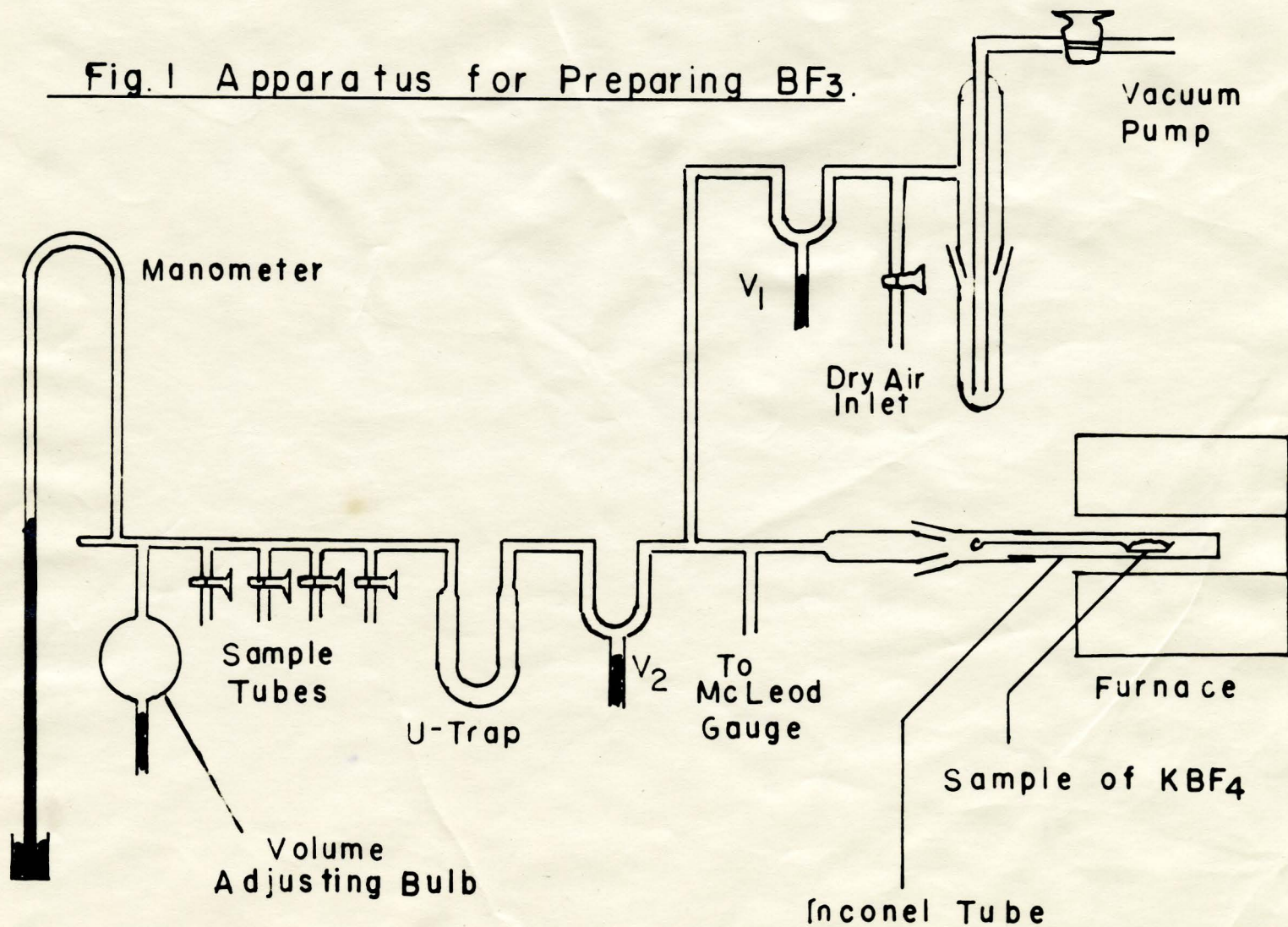
(2) Preparation of Boron Trifluoride - Boron trifluoride was prepared by the thermal decomposition of potassium fluoborate, which was prepared following the method in Inorganic Syntheses (19). 0.02 moles of boric acid was added slowly to 3.5 gms. of chilled 48% hydrofluoric acid in a Teflon dish, and the resulting solution left for 6 hours at room temperature. The solution was then chilled again in an ice bath and 5M. potassium hydroxide added until the mixture was neutral to

methyl orange. At this point the mixture was a thin paste. After a half hour, it was filtered in a fritted glass crucible and the solid on the filter washed with cold water, alcohol and ether. The potassium fluoborate was a white chalk-like powder. The yields were around 93 - 95%.

To make boron trifluoride, 0.01 moles of potassium fluoborate was placed in a nichrome boat provided with a long nichrome wire handle. This was inserted into an inconel tube with one end sealed and the other end connected to a ground glass joint by means of a Kovar seal. The tube was connected to the vacuum system as shown (Fig. 1) and evacuated to below 10^{-5} mm. of mercury pressure. The mercury float valve V_1 was closed, the U-trap immersed in liquid air, and an electric furnace at about 600°C was placed around the inconel tube. After 2 hours, the furnace was removed, valve V_2 closed, and the U-trap allowed to warm to room temperature. The mercury level in the volume adjusting bulb was fixed at the bottom of the bulb and the pressure read on the manometer. From the pressure and the volume of the system, the yield of boron trifluoride was calculated. The pressure was then adjusted by means of the volume adjusting bulb to 30 cm. mercury, and a sample taken by closing the stopcock between the sample tube and the system, freezing the boron trifluoride in the sample tube, and sealing it off with a glass-blowing torch.

Before this reaction was carried out, the vacuum system was pumped out for at least 6 hours with the furnace around the inconel tube and the glass parts repeatedly flamed in order to remove any

Fig.1 Apparatus for Preparing BF₃.



throughout this investigation was a 180° direction-focussing instrument of the Nier type. Ion current measurements were made with an Applied Physics Corporation Vibrating-reed electrometer coupled to a Leeds and Northrup Speedomax recorder.

The methyl borate spectrum was scanned using an accelerating potential of 1500 volts and a beam of ionizing electrons of 80 e.v. energy. The principal peaks were observed at masses 10 to 18, masses 28 to 31, masses 40 to 42, masses 71 to 73, and masses 102 to 104. The first group of peaks was attributed to B, CH₃, and H₂O and their fragments, the second to OCH₃, the third to B (OCH₃), the fourth to B (OCH₃)₂, and the last group to B (OCH₃)₃. The distribution of fragments containing boron was 22%, 63%, 11%, and 0.5% for the B (OCH₃)₃, B (OCH₃)₂, B (OCH₃) and B fragments respectively.

The B^{11}/B^{10} ratio measured from the B peaks was around 3.8: this value is so far from other experimental values that severe mass discrimination in the source appears to have taken place. Hence it was decided to measure the B^{11}/B^{10} ratio using the B (OCH₃)₂ peaks.

The spectrum in this region was complicated by the presence of the B (OCH₃)₂ fragment with one or two hydrogen atoms removed by electron impact, as is shown in Table (1).

Table 1

Methyl Borate Spectrum Used

Mass No.	Fragments
70	$B^{10} (OCH_3)_2 - 2H$
71	$B^{10} (OCH_3)_2 - H, B^{11} (OCH_3)_2 - 2H$
72	$B^{10} (OCH_3)_2, B^{11} (OCH_3)_2 - H$
73	$B^{11} (OCH_3)_2$

The rarer isotopes of carbon and oxygen were not taken into account, since their effect on measuring the difference in isotopic abundance ratios of two samples would be small. From the measurements of the peaks at the mass numbers shown, simultaneous equations can be set up in the B^{11}/B^{10} ratio and the ratio of the amounts of fragments with one and two hydrogen atoms removed to the amount of the original fragment.

It was found that the $B (OCH_3)_2 - H / B (OCH_3)_2$ ratio was about 0.15 and the $B (OCH_3)_2 - 2H / B (OCH_3)_2$ ratio about 2×10^{-3} for the operating conditions used. The resulting correction reduced the precision of the B^{10}/B^{11} ratio values to 1/2 that of the ratio of the 72 and 73 peaks.

(2) Measurement of the B^{11}/B^{10} Ratio Using Methyl Borate - The spectrum was scanned (by varying the magnetic deflecting field) from mass 73 to 70, the direction of scanning reversed, and the same peaks scanned in the reverse direction. This procedure was repeated six times,

then the sample was changed and a set of peaks taken in the same manner with the new sample. The two samples being compared were measured alternately in this way until three or four sets of peaks were obtained with each sample. The rapidity with which the ion currents disappeared upon removing the sample suggested that the methyl borate showed little tendency to be adsorbed on the wall of the spectrometer tube.

The difference in isotopic content for the two samples was expressed as the ratio of their B^{11}/B^{10} ratios. This was calculated by dividing the B^{11}/B^{10} ratio obtained from a set of readings on the one sample, by the average B^{11}/B^{10} ratio obtained from the two "bracketing" sets of readings on the other sample.

(3) Measurement of the B^{11}/B^{10} Ratio Using Boron Trifluoride - The mass spectrum of boron trifluoride has been described by Inghram (16), who found that over 90% of the boron detected occurs at the BF_2^+ fragment. This fragment was used for the measurements and, to allow correction for interference from the SiF^+ ion, mass 47 was included in the scanning along with masses 48 and 49. The measurements were carried out in the same manner as with methyl borate except that, after the sample was introduced into the spectrometer, it was allowed to flush the spectrometer for 10 minutes before measurements were started in order to reduce the "memory effect" of the previous sample. The total time required to make a set of measurements, including the sample change, was about 30 minutes.

RESULTS

(1) Measurements on Methyl Borate - The average ratio of B^{11}/B^{10} for the Stassfurt sample to B^{11}/B^{10} for the Argentine sample was 1.023 with a standard deviation of 0.007 for six measurements. The average B^{11}/B^{10} ratio for the Stassfurt sample was 4.17 ± 0.03 , for the Argentine sample, 4.08 ± 0.02 . The standard deviations for the B^{11}/B^{10} ratios obtained from each set of six readings ranged from 0.6% to 1.2%.

(2) Measurements on Boron Trifluoride - The average ratio of B^{11}/B^{10} for the Stassfurt sample to B^{11}/B^{10} for the Argentine sample, calculated in the same manner as with the methyl borate results, was 1.021 with a standard deviation of 0.003 for five measurements. The average B^{11}/B^{10} ratio for the Stassfurt sample was 4.156 ± 0.006 , for the Argentine sample, 4.067 ± 0.015 . The standard deviations for the B^{11}/B^{10} ratios obtained from each set were about 0.2%. Corrections for the effect of SiF^+ were about 1%.

DISCUSSION

The results obtained from measurements on the boric acid samples from Stassfurt and Argentina by Thode and others (1) and by the author are shown in Table (2).

The variations in the ratio of (B^{11}/B^{10}) Stassfurt to (B^{11}/B^{10}) Argentina, with which this work is mainly concerned, are difficult to account for, since, as explained previously, one would not expect a systematic error in this ratio arising from the mass spectrometry.

The exception is the "memory effect", which would produce low results for the difference in isotopic content because of contamination of one sample by the other. This effect would be expected to be greater in the boron trifluoride measurement than in the methyl borate measurement, since the ester is known to be inert with respect to the formation of co-ordinate bonds. The methyl borate results, however, agree with the lower boron trifluoride results: therefore, the memory effect appears to have been small in these measurements.

Table 2

Comparison of Boron Samples

Ion Used	B^{11}/B^{10}	B^{11}/B^{10}	B^{11}/B^{10}	Method of Measurement
	Stassfurt	Argentina	$\frac{\text{Stassfurt}}{\text{Argentina}}$	
(a) BF_2	4.483 ± 0.010	4.320 ± 0.009	1.037	90° sector mass spectrometer magnetic scanning
(a) BF_2	4.371 ± 0.004	4.278 ± 0.003	1.022	180° mass spectrometer elect- rostatic scanning
(a) B	4.422 ± 0.004	4.270 ± 0.001	1.035	180° mass spectrometer magnetic scanning
(b) B (OCH ₃) ₂	4.17 ± 0.03	4.08 ± 0.02	1.023 ± 0.007	180° mass spectrometer magnetic scanning
(b) BF_2	4.156 ± 0.006	4.067 ± 0.015	1.021 ± 0.003	180° mass spectrometer magnetic scanning

(a) Thode and others (1).

(b) Present work.

A low yield in the preparation of a sample could produce a systematic error due to isotopic fractionation, but it is claimed that the first two measurements listed in table 2, which show a large discrepancy, were made on the same preparation of boron trifluoride.

However, the results are sufficiently consistent to indicate a difference of 2% or more in the isotopic content of the two boric acid samples. The possibility of isotopic fractionation in the preparation of boric acid from the original minerals must be considered. In the case of the Stassfurt sample, the boron occurred originally as boracite, $Mg_3 B_7 O_{13} Cl$. Boric acid is obtained by adding hydrochloric acid to the mineral in aqueous solution, at which the boric acid is precipitated. The Argentine sample was obtained from ulexite, $Na Ca B_5 O_9 \cdot 10H_2O$, from which boric acid is precipitated in a similar manner, using sulphuric acid. Unless yields are very different, the similarity of the processes makes it unlikely that an appreciable difference in isotopic content would be produced. The differences in isotopic content observed, therefore, probably represent variations in the original minerals.

In considering the results of those workers who found no variation in the isotopic content of boron from various sources, it must be remembered that without more information on isotopic fractionation mechanisms for boron, it is a matter of chance whether samples are selected that differ measurably in isotopic content. However, the wide extent of the investigation of Wickman and others should have ensured

the inclusion of samples showing these differences, if they exist. The memory effect of boron trifluoride (used throughout their investigation) would give errors tending to suppress differences in isotopic content. Although this effect appears to have been small in the present work, it would be increased by the following factors:

- (1) large adsorptive tendencies of the surfaces in contact with boron trifluoride,
- (2) quick and frequent sample changes as is presently the practice in comparing the carbon and sulphur isotopic content of different samples.

As can be seen from the foregoing, the measurement of variations in the isotopic content of boron lags considerably in precision behind such measurements of some other elements. In the case of the methods used in this investigation, the memory effect of boron trifluoride makes necessary long intervals between sample changes causing errors due to instrument drift, while the complexity of the methyl borate molecule produces errors due to the indirect method required to calculate the results. Moreover, the yields of preparation of these compounds are too low to give confidence that differences in isotopic content have not been produced in the preparations. These difficulties will have to be overcome before the measurement of differences in isotopic content of boron can be applied to other problems.

CONCLUSION

The variation in isotopic content between two boron samples measured by Thode and others has been confirmed but the values obtained differ by an amount greater than would be expected from the precision claimed.

REFERENCES

- (1) H. G. Thode, J. Macnamara, F. P. Lossing, and C. B. Collins,
J.A.C.S. 70, 3008, (1948).
- (2) O. Osberghaus Zeit. f. Physik 128, 366, (1950)
- (3) V. Shiuttse J. Exper. Theoret. Phys. USSR 29,
486, (1955).
Soviet Physics 2, 402, (1956).
- (4) A. Parwell, H. vonUbisch, and F. E. Wickman
Geochimica & Cosmochimica Acta 10, 185, (1956).
- (5) J. J. Thomson Rays of Positive Electricity and Their
Applications to Chemical Analysis.
(Longmans, Green & Co. 1913).
- (6) F. W. Aston Phil. Mag. 38, 709, (1919).
- (7) Lord Rayleigh Phil. Mag. 42, 493, (1896).
- (8) H. Hertz Naturwiss. 26, 494
Zeit f. Physik 79, 108, (1932).
- (9) J. N. Bronsted and G. Hevesy
Nature, Sept. 30, 1920.
- (10) H. C. Urey and Lotti J. Greiff
J.A.C.S. 57, 321, (1935).
- (11) E. W. Washburn and H. C. Urey
Proc. Nat. Acad. Sci. 18, 496, (1932).

