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# ISOTOPIC ANALYSIS OF ENRICHED BORON- BY CHEMICAL IONIZATION MASS SPECTROSCOPY

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## ABSTRACT

A rapid and accurate CI-MS method has been developed for the isotopic analysis of enriched boron. This method involves the formation of volatile methyl borate from boric acid with direct introduction of the methyl borate into the source of a quadrupole mass spectrometer. Data acquisition and storage is computer-controlled. A subsequent BASIC computer program reads the data from the disc file, computes the average  $^{11}\text{B}/^{10}\text{B}$  ratio for up to 250 separate spectra per analysis and calculates the weight percent boron-10 from the corrected  $^{11}\text{B}/^{10}\text{B}$  ratio using a calibration factor based on a National Bureau of Standards boric acid standard. The relative standard deviation for the analysis of replicate samples of enriched boron with a boron-10 content in the 90-95% range does not exceed 0.005%. Analytical results on NBS certified enriched boron agreed to within 0.06% absolute.

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## INTRODUCTION

Boron is used extensively in the nuclear power industry as a neutron absorber in nuclear control rods, nuclear shielding, neutron detecting devices, and as a burnable poison in nuclear fuels. The boron-10 isotope with a natural abundance of 19.8 atom percent provides this property because of a relatively high thermal neutron capture cross section (3840 barns). The isotopic composition of boron can be a critical factor in the design of nuclear shielding and control systems and neutron detectors. Therefore, it is essential that the boron-10 content in boron used in nuclear facilities be known with a high degree of accuracy.

A number of analytical methods have been devised for the isotopic analysis of boron. Radioanalytical techniques based on the nuclear transformation of boron nuclei into activated or metastable nuclei and the subsequent measurement of the radioactive decay products have been used frequently for the determination of either boron-10 or boron-11. Although these techniques can be applied over a relatively broad boron concentration range, radioanalytical methods do not provide the analytical precision required for some analysis. Coincident measurement of complementary particles in a nuclear transformation have improved the analytical precision and enabled the simultaneous determination of boron-10 and boron-11.

Due to the large differences in the thermal neutron capture cross sections in the naturally occurring boron isotopes, neutron

## EXPERIMENTAL

### Reagents

Boron isotope standards used in this investigation were certified for total boron, boron-10, and boron-11 by the National Bureau of Standards. Reagent grade chemicals were used for sample preparation.

### Apparatus

The mass spectrometer-computer system used in this investigation consists of a Hewlett Packard Model 5982A interfaced to a HP Model 2100S computer with 32K of core memory. Ionization of the methane gas was accomplished by irradiation with a 70eV electron beam. The sample inlet assembly was constructed from  $\frac{1}{4}$ " stainless steel tubing and contained a precision needle valve to control the sample gas flow from the quartz reaction tube. A photograph of the sample inlet assembly is shown in Figure 1.

### General Procedure

Approximately 100 mg of boron powder was placed in a quartz test tube and allowed to react with  $\text{HNO}_3$  with heating. If the sample contained refractory materials, such as boron carbide, the boron was fused with  $\text{Na}_2\text{CO}_3$  according to a procedure described by Lerner ( ). The  $\text{Na}_2\text{CO}_3$  melt was dissolved in distilled water and acidified with  $\text{HNO}_3$ . The acidified sample solution was evaporated to dryness. Approximately 10-25 mg of the boric acid sample was transferred to a quartz reaction tube containing methanol. The methyl borate gas

absorption and transmission techniques have been applied successfully to the determination of boron-10 in boron. Other methods, such as atomic absorption and emission spectroscopy and nuclear magnetic resonance spectroscopy have been applied on a limited basis to the isotopic analysis of boron.

Mass spectroscopy is the most accurate method for the determination of boron-10 and boron-11 and is generally the method of choice when high precision is required. Most boron materials are analyzed isotopically by thermionic emission mass spectroscopy. The ion usually measured is generated from a charge material of sodium tetraborate on a heated filament. The major sources of error have been attributed primarily to variations in sample preparation. For example, a relatively high sodium concentration or the presence of extraneous material in the sample can lead to excessive isotope fractionation during ionization from a heated filament. However, these problems have been overcome by careful sample preparation and mounting. Other mass spectrometric techniques based on electron ionization of gaseous boron compounds, such as  $\text{BF}_3$ , have been seriously impaired by memory effects, resulting from sample sorption on the surfaces of the inlet system and ion source in the mass spectrometer. Previous efforts to control these problems have included purging the system to remove boron chemically or by extensive baking of the inlet system between samples. These procedures are very time-consuming and would be unacceptable for some analysis involving process control.

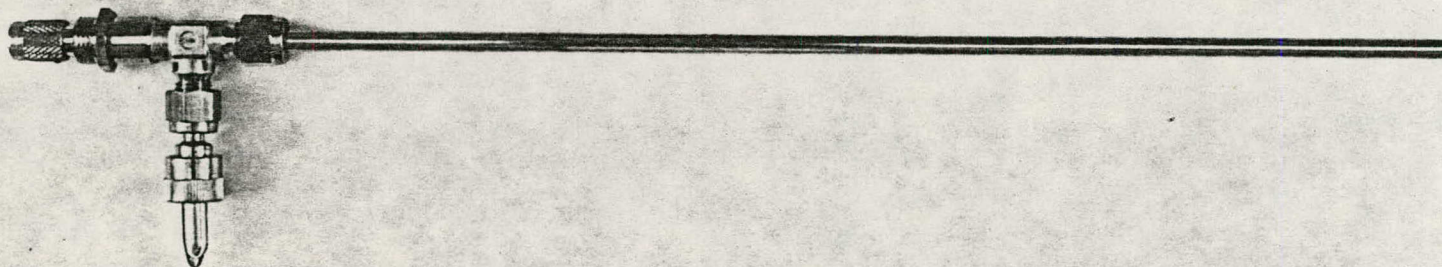
A new chemical ionization mass spectrometric technique has been developed and investigated for the isotopic analysis of enriched

boron. This method is based on the formation of volatile methyl borate from boric acid and methanol and the direct introduction of the trimethyl ester into a quadrupole mass spectrometer.

Ionization of methyl borate is achieved by reaction with ionized methane.



# **SAMPLE INLET ASSEMBLY**



formed in the reaction tube was directed into the ion source on the mass spectrometer through the sample inlet assembly. The sample gas flow was adjusted by means of the precision needle valve to achieve a maximum amplitude for the  $(\text{CH}_3\text{O})_3^{10}\text{BH}^+$  ( $m/e = 104$ ) and  $(\text{CH}_3\text{O})_3^{11}\text{BH}^+$  ( $m/e = 105$ ) mass peaks. The boron peaks at masses 104 and 105 and the spectral background at mass 100 were monitored using a dwell time 100 msec for 2 minutes. Under these conditions 230 individual measurements were made at each mass. The data was stored in a disc file for subsequent processing.

Data processing was accomplished with a computer program written in BASIC. The  $^{11}\text{B}/^{10}\text{B}$  ratio was calculated from the mass 105 and mass 104 peaks after correcting for background, and stored in the core memory of the computer.

For standardization of the mass spectrometer, a boron isotope standard such as NBS standard reference material 952 was used. The measured  $^{11}\text{B}/^{10}\text{B}$  ratio was compared with the certified  $^{11}\text{B}/^{10}\text{B}$  ratio and a calibration factor was calculated. The calibration factor was used to calculate a corrected  $^{11}\text{B}/^{10}\text{B}$  ratio from the measured ratio for each boron sample. The weight % boron-10 was calculated from the corrected  $^{11}\text{B}/^{10}\text{B}$  ratio. The values reported in subsequent tables in this paper correspond to 200 individual measurements for each sample and standard.

## RESULTS AND DISCUSSION

The formation of a molecular ion from methyl borate can be achieved either by direct electron bombardment (electron ionization) or by reaction of methyl borate with a reagent gas ion (chemical ionization), as shown in Figure 2. Electron bombardment of a sample molecule with a high energy electron beam can cause extensive fragmentation of the ionized molecule. However, the fragmentation pattern is often very characteristic for the parent ion and can be used advantageously for the classification of the sample molecule and for the elucidation of structural information. Conversely, chemical ionization results in the formation of a low-energy molecular ion. Therefore, fragmentation of the molecular ion is very minimal.

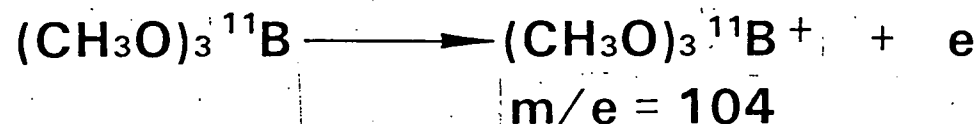
For the measurement of the boron isotope ratio in methyl borate, the experimental conditions are selected such that a single ionized species predominates in the ion source. This condition can be achieved readily by chemical ionization.

Ionization of methyl borate is dependent upon the relative concentrations of methyl borate and the reagent gas ions. In order to optimize the concentration of the methyl borate ion in the source unit, the reagent gas-to-sample ratio should be large in order to minimize electron ionization of the sample molecule.

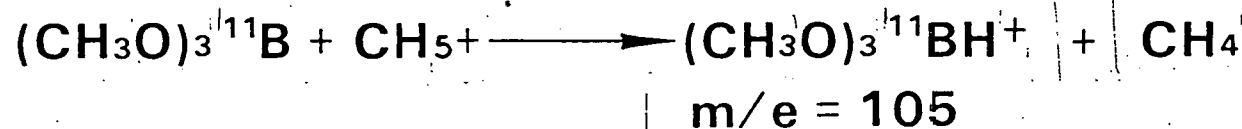
The optimum signal-to-background ratio for methyl borate was established by varying the reagent gas in the source unit and

# IONIZATION OF METHYL BORATE

## ELECTRON IONIZATION



## CHEMICAL IONIZATION



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monitoring the boron-10 and boron-11 mass peaks. The results shown in Figure 3 indicate that an optimum signal is achieved at a pressure of about  $2.4 \times 10^{-4}$  torr. However, the boron-11/boron-10 ratio was relatively constant over the source pressure range studied. These results indicate that electron ionization of the methyl borate molecule in the source unit is negligible. Electron ionization would lead to the formation of the methyl borate ions at  $m/e$  of 103 and 104 with a subsequent decrease in the 105/104 ratio.

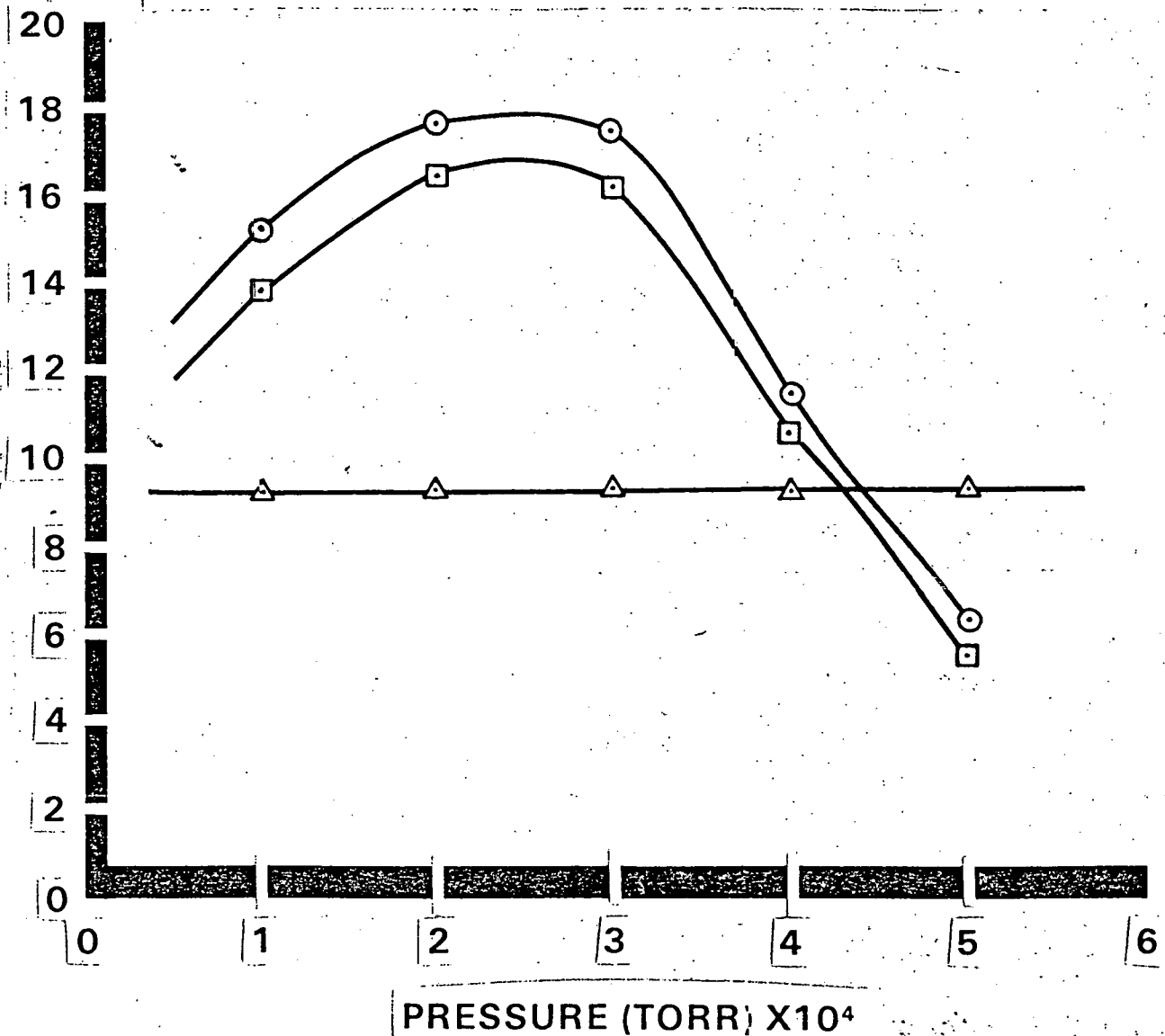
#### Examination of Memory Effects

One of the major problems which have confronted analysts attempting to utilize electron ionization for the isotopic analysis of boron has been memory effects resulting from sample sorption of the surfaces of the sample inlet and ion source. Efforts to control, reduce, or compensate for memory effects have met with very limited success. Even then, these analyses required very time consuming and laborious procedures.

With the chemical ionization technique described, memory effects in the ion source have been found to be negligible. This was established by alternately measuring a highly enriched and a natural boron sample. Table I lists the results which were obtained with the two boric acid samples. It is obvious from the experimental results that bias effects resulting from previous samples are totally absent since the measured ratios for each sample are nearly identical and are independent of the isotopic ratios of previous samples. Memory effects would be apparent from these results if the boron-10 content in samples 1 and 2 showed a systematic decrease and increase, respectively.

# EFFECT OF SOURCE PRESSURE

$^{10}\text{B}$  ( $\times 10^{-4}$ )  
 $^{11}\text{B}$  ( $\times 10^{-2}$ )  
 $^{11}\text{B}/^{10}\text{B}$  ( $\times 10^2$ )



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# ANALYTICAL RESULTS ON AN ENRICHED AND A NATURAL BORON SAMPLE

## WEIGHT % BORON-10

<u>RUN</u>	<u>SAMPLE #1</u>	<u>SAMPLE #2</u>
1	94.097	
2		19.997
3	94.123	
4		20.078
5	94.087	
6		20.071
AVERAGE	94.103	20.049



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Memory effects in the sample inlet system were found to be very severe. Extensive purging of the inlet tube and valve assembly with methanol and heating failed to completely remove residual boric acid and methyl borate from the sample inlet assembly. However, residual boron could be reduced to negligible levels by disassembly of the unit and cleaning.

#### Precision of the Mass Spectrometric Analysis

Mass spectroscopy is the most accurate method for the isotopic analysis of enriched boron. The National Bureau of Standards reported a relative 95% confidence limit of 0.038% on the  $^{11}\text{B}/^{10}\text{B}$  ratio in the SRM 952 boron isotope standard. These analyses were performed by thermionic emission of sodium tetraborate.

In order to establish the precision of the chemical ionization technique, SRM 952 was analyzed according to the described procedure with methane as the reagent gas. The reproducibility of the  $^{11}\text{B}/^{10}\text{B}$  ratio was established on a single sample and on replicate samples in order to establish the relative magnitude <sup>of</sup> the instrument instability and to determine the effects of repositioning the sample inlet system in the mass spectrometer. The comparative results shown in Table II show that the relative standard deviation for single and replicate analyses are nearly identical and that potential errors resulting from repositioning the sample inlet system are negligible.

The relative 95% confidence limit for the measurement of the  $^{11}\text{B}/^{10}\text{B}$  ratio was 0.043%. Therefore, the chemical ionization technique described in this paper is comparable to the thermionic emission technique utilized by the National Bureau of Standards.



# COMPARISON OF ANALYTICAL RESULTS ON SINGLE AND REPLICATE BORON SAMPLES

## SINGLE SAMPLE

WEIGHT %  $^{10}\text{B}$  = 94.471  $\pm$  0.004%

## REPLICATE SAMPLES

WEIGHT %  $^{10}\text{B}$  = 94.471  $\pm$  0.005%



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### Analysis of boron and boric acid samples

The accuracy of the chemical ionization method was investigated and established by analyzing a number of enriched boron and boric acid samples with a boron-10 content in the range from 90 to 95%. Boric acid samples of accurately known isotopic composition were prepared by mixing known quantities of NBS certified boron isotope standards. The experimental results shown in Table III are in excellent agreement with the calculated results and do not differ by more than 0.06%. These experiments were repeated with enriched boron which had been certified for  $^{10}\text{B}$  content by the New Brunswick Laboratory using a mass spectrometer procedure similar to that used by the NBS (Table IV). The agreement between the measured and certified values for five boron samples are excellent. In no case did the analytical results differ by more than 0.110%. These results show that chemical ionization mass spectroscopy can be applied to the rapid and accurate determination of the isotopic composition of enriched boron.

# COMPARATIVE ANALYTICAL RESULTS ON NBS BORON ISOTOPE STANDARDS

WEIGHT % BORON - 10

<u>STANDARD</u>	<u>CALCULATED</u>	<u>MEASURED</u>	<u>DIFFERENCE</u>
1	93.527	93.471	-0.056
2	92.607	92.633	+ 0.026
3	91.704	91.643	-0.061
4	90.828	90.812	-0.016
5	89.967	89.992	+0.025



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# COMPARATIVE ANALYTICAL RESULTS ON NBL CERTIFIED ENRICHED BORON

WEIGHT % BORON-10			
<u>SAMPLE</u>	<u>CERTIFIED</u>	<u>MEASURED</u>	<u>DIFFERENCE</u>
A	90.135	90.166	+0.031
B	90.881	90.839	-0.042
C	90.811	90.812	+0.001
D	91.081	90.971	-0.110
E	91.634	91.592	0.042



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## SUMMARY

Boron plays a critical role in the design of control systems and neutron detectors in nuclear facilities. This is due to the relatively large thermal neutron capture cross section of naturally occurring boron-10. Therefore, the boron-10 content in boron used in nuclear facilities must be known with a high degree of accuracy.

A number of techniques have been devised for the isotopic analysis of boron. Many analytical methods based on radioanalytical or neutron absorption techniques are inadequate for high precision isotopic analysis. Mass spectroscopy is the most accurate method for the isotopic analysis of boron. However, conventional mass spectrometric methods based on thermionic ionization or electron ionization of boron compounds are readily affected by variations in chemical preparation, sample composition, and instrument operating parameters.

A chemical ionization mass spectrometric method for the isotopic analysis of enriched boron has been developed and investigated in detail. This method is based on the formation of volatile methyl borate from methanol and boric acid and the direct introduction of the methyl borate into the ion source of a HP quadrupole mass spectrometer. Ionization of methyl borate is achieved by reaction with ionized methane. This technique is essentially free of interferences due to extraneous material in the boric acid sample

since potentially interfering constituents are not generated in the reaction tube and discharged into the ion source.

The precision of the CI-MS analysis is comparable to that of conventional thermionic emission methods. The relative standard deviation on replicate samples did not exceed 0.005% at the 95% boron-10 level. The analytical results on NBS certified boron isotope standards with a boron-10 content in the 90-95% range agreed to within 0.06% absolute. The analytical results on a number of NBL certified enriched boron samples did not differ by more than 0.11% absolute.

## **SUMMARY**

- I. DEVELOPED A RAPID AND ACCURATE CHEMICAL IONIZATION MASS SPECTROMETIC METHOD FOR THE ISOTOPIC ANALYSIS OF ENRICHED BORON.**
- II. ESTABLISHED THE OPTIMUM CONDITIONS FOR THE ANALYSIS OF ENRICHED BORON.**
- III. DEMONSTRATED THE COMPLETE ABSENCE OF SAMPLE MEMORY EFFECTS.**



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