

**INVESTIGATION OF THE REACTION OF BORON  
OXIDE WITH ALUMINIUM POWDER AND  
METHOD DEVELOPMENT FOR BORON  
DETERMINATION IN THE REACTION MIXTURE**

**A Thesis Submitted to  
the Graduate School of Engineering and Sciences of  
İzmir Institute of Technology  
in Partial Fulfillment of the Requirements for the Degree of**

**MASTER OF SCIENCE**

**in Chemistry**

**by  
Yelda DEMİRSAR**

**July 2007  
İZMİR**

We approve the thesis of **Yelda DEMİRSAR**

**Date of Signature**

.....  
**Prof. Dr. İ. Tamerkan ÖZGEN**  
Supervisor  
Department of Chemistry  
İzmir Institute of Technology

**19 July 2007**

.....  
**Assoc. Prof. Dr. Durmuş ÖZDEMİR**  
Department of Chemistry  
İzmir Institute of Technology

**19 July 2007**

.....  
**Assoc. Prof. Dr. Salih OKUR**  
Department of Physics  
İzmir Institute of Technology

**19 July 2007**

.....  
**Prof. Dr. Levent ARTOK**  
Head of Department  
İzmir Institute of Technology

**19 July 2007**

.....  
**Prof. Dr. M. Barış ÖZERDEM**  
Head of the Graduate School

## ACKNOWLEDGEMENTS

I would like to express my grateful thanks to my thesis supervisor Prof. Dr. Tamerkan ÖZGEN for his supervision, help, support, guidance and encouragement. He provided throughout my thesis.

I especially express my thanks to Assoc. Prof. Dr. Durmuş ÖZDEMİR for his valuable comments and help on DRIFTS and GILS studies of boron determination method.

I also would like to thank to other members of the thesis committee, Assoc. Prof. Dr. Durmuş ÖZDEMİR and Assoc. Prof. Dr. Salih OKUR.

I am grateful to my friends Betül ÖZTÜRK, Murat ERDOĞAN, Emel AKYOL and Nesrin HORZUM for their help, motivations, encouragement and support in every step of my study.

Special thanks go to all research assistants in the Department of Chemistry for their friendship and their help during this thesis study.

Finally, I am thankful to my family for their love, understanding and endless support.

## ABSTRACT

### INVESTIGATION OF THE REACTION OF BORON OXIDE WITH ALUMINIUM POWDER AND METHOD DEVELOPMENT FOR BORON DETERMINATION IN THE REACTION MIXTURE

In this study, a cheap method for the synthesis of elemental boron by the reduction of boron oxide with aluminum was investigated. However after various optimization studies, detectable boron amounts could not be found in the reaction mixtures by XRD and SEM-EDX analysis. Mainly aluminum borates were formed as products and these products were leached by 6 M HCl, however removal of borates could not be achieved. We think that the reason of this outcome is that we worked with simple experimental setup, therefore could not achieving the suitable experiment conditions and because of this we failed in the synthesis of boron.

In the second part of the study, a new method for the direct determination of boron was investigated. 96 %pure boron and KBr were mixed and analyzed with Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). No distinct differences for boron was observed in the DRIFT spectra. Then, different sample compositions were prepared with different amounts of boron and KBr. These samples were split as validation and calibration sets and their spectra were collected by DRIFTS. All collected spectral data were processed in a different computer where the data processing programs were installed. The genetic inverse least square (GILS) method was used in order to generate calibration model. Results obtained showed that boron amounts could be directly determined with maximum 3-4 % error. Afterwards, same procedure was also tried for boron and boron oxide binary mixtures and boron, boron oxide and aluminum ternary mixtures. In the binary mixture, determination of boron could be successfully achieved, however boron oxide determination could not be achieved as good as boron determination. In the ternary mixture, better results were obtained compared to binary mixture. Finally, the method was tried with the original samples, but not very satisfactory results were obtained. We think this result is due to the malfunction of FTIR instrument and personal error in the preparation of similar samples. More sample preparation and measurement could not be achieved because the FTIR instrument is not functioning at present.

## ÖZET

### BOR OKSİTİN ALÜMİNYUM TOZU İLE REAKSİYONUNUN İNCELENMESİ VE REAKSİYON KARIŞIMINDA BOR TAYİNİ İÇİN METOD GELİŞTİRİLMESİ

Bu çalışmada, bor oksiti alüminyum ile indirgerak elementel bor elde edilebilmesi için ucuz bir yöntem geliştirmeye çalışılmıştır. Ancak, üretim için yapılan çeşitli optimizasyon çalışmaları sonucunda, reaksiyon karışımları içinde XRD ve SEM-EDX ile gözlenebilir bor miktarı bulunamamıştır. Reaksiyon sonucu başlıca ürün olan alüminyum boratları uzaklaştırmak için örnekler 6 M HCl ile özütlenmiş, buna rağmen boratların uzaklaştırılması sağlanamamıştır. Yapılan çalışmanın bu şekilde sonuçlanmasına neden olarak, basit deney düzenekleriyle çalışılması, uygun deney şartlarının sağlanamaması ve buna bağlı olarak da bor sentezinin gerçekleştirilemediği düşünülmektedir.

Çalışmanın ikinci aşamasında, borun doğrudan tayini için yeni bir yöntem geliştirilmeye çalışılmıştır. % 96 saflıkta bor örnekleri KBr ile karıştırılarak Difüz Reflektans Infrared Fourier Dönüşümlü Spektrometresi (DRIFT) ile spektrumları alınmış ancak spektrumlarda ilk bakışta farklı bor miktarlarıyla ilgili belirli bir değişim gözlenememiştir. Bunun üzerine bor ve KBr, farklı oranlarda karıştırılarak bir dizi örnek hazırlanmış ve bu örnekler kalibrasyon ve validasyon örnekleri olarak ayrılıp DRIFT spektrumları alınmıştır ve bütün spektrum verileri bilgisayara aktararak genetik ters en küçük kareler (GILS) yöntemiyle Matlab 5.3 program dili kullanılıp analiz edilmiştir. Elde edilen sonuçlarda borun bu yöntemle direkt olarak en fazla % 3-4 hatayla tayin edilebileceği görülmüştür. Daha sonra aynı işlemler, bor ve bor oksit ikili karışımları ve bor, bor oksit ve alüminyum üçlü karışımları için de denenmiştir. Bor ve bor oksit karışımında borun tayini yapılabilmiş ancak, bor yanında bor oksit tayininin daha zor olduğu görülmüştür. Üçlü karışımlarda ikili karışımlara göre daha iyi sonuçlar elde edilmiştir. Yöntem sentezlenen örneklerle denendiğinde tatminkar sonuçlar alınamamıştır. Bu sorunun, FTIR cihazının düzgün çalışmamasından ve örneklerin tekrar edilebilir bir şekilde hazırlanamamasından kaynaklandığı düşünülmektedir. Ayrıca FTIR cihazının düzenli çalışmaması nedeniyle daha fazla örnek hazırlanamamış ve sonuçları alınamamıştır.

# TABLE OF CONTENTS

LIST OF FIGURES .....	ix
LIST OF TABLES .....	xi
CHAPTER 1. INTRODUCTION .....	1
1.1. Boron .....	1
1.1.1. Occurrences and Concentration .....	1
1.1.2. Structure and Polymorphism .....	4
1.1.3. Physical Properties.....	5
1.1.4. Chemical Properties.....	6
1.1.4.1. Reaction of Boron with Halogens .....	7
1.1.4.2. Reaction of Boron with Acids .....	7
1.1.5. Application Areas .....	7
1.1.6. Production.....	8
1.1.6.1. Reduction of Boric Oxide with Magnesium.....	9
1.1.6.2. Reduction of Boron Halides or Fluoroborates with Metals .....	10
1.1.6.3. Reduction of Boron Halides with Hydrogen .....	10
1.1.6.4. Thermal Decomposition of Boron Compounds.....	10
1.1.6.5. Electrolysis of Molten Borates or Fluoroborates.....	10
1.1.7. Determination .....	11
1.1.8. Storage .....	12
1.2. Components Used in Experimental Studies.....	12
1.2.1. Aluminum .....	12
1.2.1.1. Chemical and Physical Properties.....	13
1.2.2. Boronoxide.....	13
1.2.2.1. Chemical and Physical Properties.....	14
1.3. Equipment Used in Experimental Studies .....	15
1.3.1. Microwave Oven.....	15
1.3.2. Tube Furnace .....	15
1.4. Characterization of Solid Samples.....	15
1.4.1. X-Ray Powder Diffraction (XRD).....	16

1.4.2. Scanning Electron Microscopy (SEM).....	16
1.4.3. Fourier Transform Infrared Spectroscopy (FTIR).....	17
1.4.3.1. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).....	18
 CHAPTER 2. MULTIVARIATE CALIBRATION MEDHODS.....	 19
2.1. Multivariate Calibration Methods.....	19
2.1.1. Classical Least Squares Method (CLS).....	19
2.1.2. Inverse Least Squares Method (ILS).....	20
2.2. Genetic Algorithms.....	22
2.2.1. Genetic Inverse Least Squares Method (GILS).....	22
2.3. Aim of This Work.....	25
 CHAPTER 3. EXPERIMENTAL METHODS.....	 27
3.1. Instrumentation and Apparatus.....	27
3.2. XRD, SEM, EDX, DRIFTS Analysis.....	27
3.3. Boron Synthesis.....	27
3.3.1. Muffle Furnace.....	28
3.3.1.1. Effect of Temperature.....	28
3.3.1.2. Effect of Reaction Time.....	28
3.3.2. Microwave Oven.....	29
3.3.3. Experiments Carried in the Tube Furnace.....	30
3.3.3.1. Experimental Design for Boron Synthesis.....	30
3.4. Further Studies in Boron Determination.....	31
3.4.1. Determination of Boron With DRIFTS and GILS.....	32
3.4.1.1. Random Design.....	32
3.4.1.2. Mixture Design.....	32
3.4.1.3. Random Mixture Design.....	33
3.4.1.4. Ternary mixture Design.....	34
 CHAPTER 4. RESULTS AND DISCUSSIONS.....	 38
4.1. Boron Synthesis.....	38
4.1.1. Muffle Furnace.....	38
4.1.1.1. Effect of Temperature.....	38

4.1.1.2. Effect of Reaction Time .....	39
4.1.2. Microwave Oven.....	40
4.1.3. Experiments Carried in the Tube Furnace .....	41
4.1.3.1. Experimental Design for Boron Synthesis .....	41
4.2. Further Studies in Boron Determination.....	42
4.2.1. Determination of Boron with DRIFTS and GILS .....	42
4.2.1.1. Random Design .....	43
4.2.1.2. Mixture Design .....	45
4.2.1.3. Random Mixture Design .....	47
4.2.1.4. Ternary mixture Design.....	49
 CHAPTER 5. CONCLUSION.....	 58
 REFERENCES .....	 60



## LIST OF FIGURES

<b><u>Figure</u></b>	<b><u>Page</u></b>
Figure 1.1. (a) $\beta$ -rhombohedral, (b) $\alpha$ -rhombohedral, (c) tetragonal boron.....	4
Figure 2.1. Flow Chart of the GILS Algorithm.....	23
Figure 4.1. The XRD Spectra for Boron Synthesis at Different Temperatures .....	39
Figure 4.2. The XRD Spectra for Boron Synthesis at Different Time Interval .....	40
Figure 4.3. The XRD Spectra for Boron Synthesis at Mixture Ratio .....	41
Figure 4.4. The XRD Spectrum Before and After Acid Leaching.....	42
Figure 4.5. The DRIFT Spectrum for Pure Boron in KBr .....	43
Figure 4.6. Actual versus GILS Predicted Concetration of Boron for Random Design.....	45
Figure 4.7. Actual versus GILS Predicted Concetration of Boron for Mixture Design .....	46
Figure 4.8. Actual versus GILS Predicted Concetration of Boron Oxide for Mixture Design .....	47
Figure 4.9. Actual versus GILS Predicted Concetration of Boron for Random Mixture Design.....	48
Figure 4.10. Actual versus GILS Predicted Concetration of Boron Oxide for Random Mixture Design.....	49
Figure 4.11. Actual versus GILS Predicted Concetration of Boron for Fifty Samples.....	50
Figure 4.12. Actual versus GILS Predicted Concetration of Boron Oxide for Fifty Samples .....	51
Figure 4.13. Actual versus GILS Predicted Concetration of Aluminum for Fifty Samples .....	51
Figure 4.14. Actual versus GILS Predicted Concetration of Boron for Hundred Samples.....	52
Figure 4.15. Actual versus GILS Predicted Concetration of Boron Oxide for Hundred Samples .....	53
Figure 4.16. Actual versus GILS Predicted Concetration of Aluminum for Hundred Samples.....	53

Figure 4.17. Actual versus GILS Predicted Concentration of Boron for Twenty-five Samples .....	55
Figure 4.18. Actual versus GILS Predicted Concentration of Boron Oxide for Twenty-five Samples .....	55
Figure 4.19. Actual versus GILS Predicted Concentration of Aluminum for Twenty-five Samples .....	56
Figure 4.20. The DRIFT Spectrum of Calibration Sample .....	57
Figure 4.21. The DRIFT Spectrum of Produced Sample.....	57

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 1.1. Boron Minerals .....	2
Table 1.2. Distribution of Boron.....	2
Table 1.3. Boron Reserves in the World.....	3
Table 1.4. Boron Reserves in Turkey .....	3
Table 1.5. Physical Properties of Boron .....	5
Table 1.6. Chemical Properties of Boron.....	6
Table 1.7. Chemical and Physical Properties of Aluminium.....	13
Table 1.8. Chemical and Physical Properties of Boron Oxide .....	14
Table 3.1. Experimental Data Scheme for B Synthesis Experiment .....	30
Table 3.2. Experimental Design Scheme for B Synthesis Experiment.....	31
Table 3.3. Random Design Scheme for B.....	32
Table 3.4. Mixture Design Scheme for B and B <sub>2</sub> O <sub>3</sub> .....	33
Table 3.5. Random Mixture Design Scheme for B and B <sub>2</sub> O <sub>3</sub> .....	34
Table 3.6. Ternary Mixture Design Scheme for B, B <sub>2</sub> O <sub>3</sub> and Al for Fifty Samples.....	35
Table 3.7. Ternary Mixture Design Scheme for B, B <sub>2</sub> O <sub>3</sub> and Al for Hundred Samples.....	36
Table 3.8. Ternary Mixture Design Scheme for B, B <sub>2</sub> O <sub>3</sub> and Al for Twenty-five Samples .....	37
Table 4.1. Parameters for Random Design of B .....	44
Table 4.2. Parameters for Mixture Design of B and B <sub>2</sub> O <sub>3</sub> .....	46
Table 4.3. Parameters for Random Mixture Design of B and B <sub>2</sub> O <sub>3</sub> .....	47
Table 4.4. Parameters for Ternary Design of B, B <sub>2</sub> O <sub>3</sub> and Al for Fifty Samples .....	49
Table 4.5. Parameters for Ternary Design of B, B <sub>2</sub> O <sub>3</sub> and Al for Hundred Samples.....	51
Table 4.6. Parameters for Ternary Design of B, B <sub>2</sub> O <sub>3</sub> and Al for Twenty- five Samples.....	54

# CHAPTER 1

## INTRODUCTION

### 1.1. Boron

Boron compounds have been known for thousands of years. In early Egypt, mummification depended upon an ore known as natron, which contained borates as well as some other common salts. Borax glazes were used in China since 300 AD, and boron compounds were used in glassmaking in ancient Rome (WEB\_1 2006).

The element was isolated in 1808 by Sir Humphry Davy, Joseph Louis Gay-Lussac, and Lois Jacques Thenard, to about 50 percent purity. These scientists did not recognize the substance as an element. Jöns Jakob Berzelius identified boron as an element in 1824. The first pure boron was produced by the American chemist W. Weintraub in 1909 (WEB\_1 2006).

#### 1.1.1. Occurrences and Concentration

The elemental boron (B) is widely distributed in nature. Because of its high affinity for oxygen, boron always occurs in nature bound to oxygen, in the form of inorganic borates (Table 1.1). Apart from their occurrence in a few commercially exploitable deposits (mainly as sodium or calcium borate minerals), borates are present everywhere at low concentrations, in rocks (15-300 mgB/kg), soils (<10-20 mgB/kg), fresh waters (<1 mgB/kg) and sea water (5 mgB/kg). The content of boron in the lithosphere by mass is about  $1 \cdot 10^{-3}$ . Table 1.2 gives data on the distribution of boron in various compounds of the earth's crust.

Igneous rocks generally have low borate content. Sedimentary rocks have a higher borate content, which is related to the salinity of the water at the time of deposition. The borate content from such marine segments ranges between 15-300 mgB/kg. The weathering of rocks, rainfall and erosion from rivers, provides a continuous small source of borate into the soil and the aqueous environment. Soils of low borate content (<10 mgB/kg) are most common on earth (ECETOC 1995).

Table 1.1. Boron Minerals.

(Source: US Geological Survey Minerals 2004)

<b>Boron Minerals</b>	<b>Chemical Composition</b>
Boracite (stassfurite)	$Mg_3B_7O_{13}Cl$
Colemanite	$Ca_2B_6O_{11}.5H_2O$
Datolite	$CaBSiO_4OH$
Hydroboracite	$CaMgB_6O_{11}.6H_2O$
Kernite (rasortie)	$Na_2B_4O_7.4H_2O$
Priceite (pandermite)	$CaB_{10}O_{19}.7H_2O$
Probertite (kramerite)	$NaCaB_3O_9.5H_2O$
Sassolite (natural boric acid)	$H_3BO_3$
Szaibelyite (ascharite)	$MgBO_2OH$
Tincal (natural borax)	$Na_2B_4O_7.10H_2O$

Table 1.2. Distribution of Boron.

(Source: Walker 1975)

<b>Source</b>	<b>Weight%</b>	<b>Source</b>	<b>Weight%</b>
Earth's Crust	$1 \times 10^{-3}$	Iron ores (maritime)	$5 \times 10^{-2}$
Inside rocks	$1 \times 10^{-4}$	Iron ores (nonmaritime)	$5 \times 10^{-4}$
Acid rocks (granites, etc.)	$1.5 \times 10^{-3}$	Lime stones	$5 \times 10^{-4}$
Sedimentary rocks	$1.2 \times 10^{-2}$	Meteorites	$3 \times 10^{-4}$
Soils	$1 \times 10^{-3}$	Sea water (dry residue)	$1.5 \times 10^{-2}$
Granite pegmatites	$(1-10) \times 10^{-2}$	Salt Springs (dry residue)	$(3-20) \times 10^{-3}$
Marine clays	$5 \times 10^{-2}$	Salt lakes (dry residue)	$(1-60) \times 10^{-2}$

Large deposits of borate minerals are rare. The only known massive deposits are located in the Mojave Desert of California, USA, and in western Turkey.

The world reserve is 885 billion tons and Turkey has 64% of these boron reserves. The distribution of boron reserves in the world and in Turkey is given in Table 1.3 and Table 1.4, respectively.

Table 1.3. Boron Reserves in the World (million tons, as B<sub>2</sub>O<sub>3</sub>).

(Source: Kılıç 2004)

	<b>Proven Economic Reserve</b>	<b>Probable &amp; Possible Reserve</b>	<b>Total Reserve</b>	<b>% in Total Reserve</b>	<b>Reserve Life-span (year)</b>
Turkey	224,000	339,000	563,000	64	389
USA	40,000	40,000	80,000	9	55
Russia	40,000	60,000	100,000	11	69
China	27,000	9,000	36,000	4	25
Chile	8,000	33,000	41,000	5	28
Bolivia	4,000	15,000	19,000	2	13
Peru	4,000	18,000	22,000	2	15
Argentina	2,000	7,000	9,000	1	6
Kazakhstan	14,000	1,000	15,000	2	10
<b>TOTAL</b>	<b>363,000</b>	<b>522,000</b>	<b>885,000</b>	<b>100</b>	<b>610</b>

Table 1.4. Boron Reserves in Turkey.

(Source: Kılıç 2004)

<b>Production Area</b>	<b>Mineral</b>	<b>Reserve</b>			
		<b>Million Tons</b>	<b>Content of B<sub>2</sub>O<sub>3</sub>%</b>	<b>Capacity (Ton/Year)</b>	<b>Production (Ton/Year)</b>
Kırka Bor Plant	Tincal	605.5	25.8	200,000	558
Bigadiç Bor Plant	Ulexite	49.2	29.1	200,000	200
	Colemanite	576.4	29.4	200,000	90
Emet Bor Plant	Colemanite	835,6	27.5-28.5	500,000	300
Kestelek Bor Plant	Colemanite	7.7	25-33.2	100,000	60
<b>TOTAL</b>		<b>2074.4</b>		<b>1,200,000</b>	<b>1208</b>

### 1.1.2. Structure and Polymorphism

There are several allotropic forms of boron. Boron compounds can be classified into two groups. These are amorphous boron and crystalline boron. Well established crystalline boron is  $\alpha$ -rhombohedral boron, and  $\beta$ -rhombohedral boron. In addition, four tetragonal forms have been described. However, these are probably stabilized by small amounts of nitrogen or carbon (Ullmann 2002).

The  $\beta$ -rhombohedral form is the thermodynamically stable modification at all temperatures. Amorphous boron slowly converts to the  $\beta$ -rhombohedral form at  $\sim 1200$  °C and to  $\alpha$ -rhombohedral boron above 1500 °C. Any type of boron recrystallizes in  $\beta$ -rhombohedral structure when heated above the melting point and cooled. The unit cell of  $\beta$ -rhombohedral boron contains 105 boron atoms grouped  $84B + 2 \times 10B + 1B$  in complex arrangement. The structure of  $\alpha$ -rhombohedral boron can be described as a slightly deformed cubic close packing of  $B_{12}$  icosahedra. The unit cell contains 12 B atoms at the vertices of the icosahedron (Ullmann 2002).

Amorphous boron exhibits broad reflections in the X-ray diffraction pattern. It is believed to be a frozen-in intermediate between the  $\alpha$ - and  $\beta$ -modifications or a microcrystalline deposit of  $\beta$ -rhombohedral boron. Amorphization can be achieved by intensive milling of  $\beta$ -rhombohedral samples (Ullmann 2002).

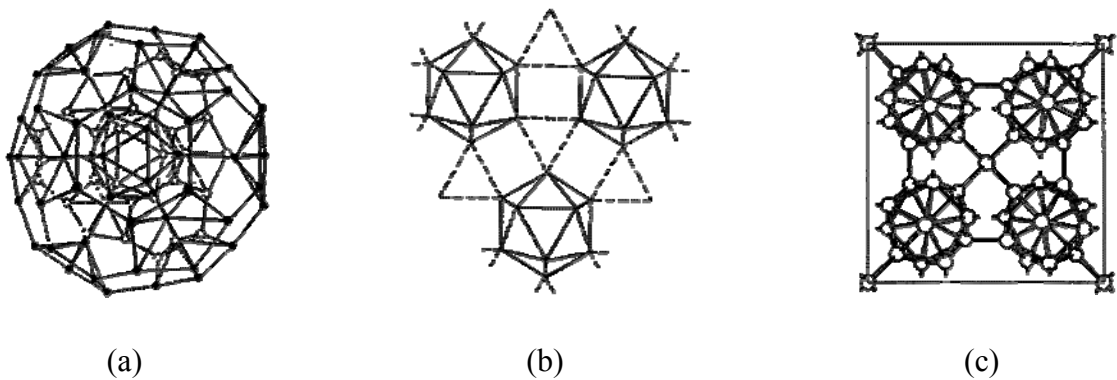


Figure 1.1. (a)  $\beta$ -rhombohedral boron, (b)  $\alpha$ -rhombohedral boron, (c) tetragonal boron.

### 1.1.3. Physical Properties

The physical properties of elemental boron are significantly affected by purity and crystal form (Kirk-Othmer 2001).

Boron is the second hardest element, the diamond allotrop of the carbon being the hardest.  $\alpha$ -Rhombohedral boron is the red to brown;  $\beta$ -rhombohedral boron lustrous gray black; and amorphous material is brown to gray. The electrical resistivity changes drastically with temperature, varying from  $10^{11} \Omega \text{ cm}$  at  $-160 \text{ }^\circ\text{C}$  to  $10^6 \Omega \text{ cm}$  at  $20 \text{ }^\circ\text{C}$  and to  $0.1 \Omega \text{ cm}$  at  $700 \text{ }^\circ\text{C}$  for polycrystallin  $\beta$ -rhombohedral boron, behavior characteristic of a semiconductor (N.N. Greenwood 1973).

Table 1.5. Physical Properties of Boron.

(Source: Ullman 2002)

Property	Value
Atomic weight	10.81±0.005
Melting point	2190±20 °C
Boiling point	3660 °C
Density of boron (Crystalline, 25-27 °C)	2.33±0.002 g/cm <sup>3</sup>
Density of boron (Amorphous, 25-27 °C)	2.3 g/cm <sup>3</sup>
Hardness, mineralogical scale	9.3
Heat capacity	1.54+0.0044·T cal/g-atom·deg
Heat of combustion	306±1 kcal/g-atom
Heat of transition, $B_{am} \rightarrow B_{cryst}$	0.4 kcal/g-atom
Heat of vaporization	128 kcal/g-atom
Heat of fusion	5.3 kcal/g-atom
Mohs hardness	11
Knoop hardness	2,100-2,580 HK
Vickers hardness	5000 HV
Oxidation number	3



### 1.1.4. Chemical Properties

The chemical behavior of elemental boron depends upon the morphology and particle size. Generally speaking, crystalline boron is rather unreactive, whereas amorphous boron does react more readily. At room temperature all modifications of boron are relatively resistant to chemical attack (Ullmann 2002).

Boron occurs as two isotopes;  $^{11}\text{B}$  and  $^{10}\text{B}$ . Their natural abundances are 81.17 % and 18.83 % respectively. The average atomic weight of boron is 10.81 (Budavari et al 1989).

The electron configuration of boron is  $1s^2 2s^2 2p^1$ . Compounds of boron often behave as Lewis acids, readily bonding with electron-rich substances. Therefore, most of its bonds are covalent, and forms planar, trivalent derivatives that are electron deficient (Kirk-Othmer 2001).

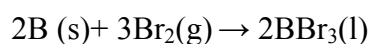
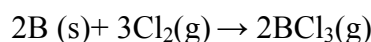
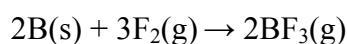
Reaction with oxygen starts at  $\approx 600^\circ\text{C}$  but is restrained by the formation of a glassy liquid  $\text{B}_2\text{O}_3$  film on the boron particles. Boron reacts with sulfur to form glassy  $\text{B}_2\text{S}_3$  and with Se to  $\text{B}_2\text{Se}_3$ , both at  $\approx 600^\circ\text{C}$ . There is no reaction with Te. With nitrogen, boron nitride,  $\text{BN}$ , is formed at  $1100^\circ\text{C}$ . Phosphorus reacts completely at  $1000^\circ\text{C}$  to give  $\text{BP}$  (Ullmann 2002).

Table 1.5. Chemical Properties of Boron.  
(Source: WEB\_2 2007)

Property	Value
First ionization energy	798 kJ/mol (8.27eV)
Second ionization energy	2426 kJ/mol (25.15eV)
Third ionization energy	3658 kJ/mol (37.92eV)
Standard electrode potential	-0.73 V
Electron affinity	32 kJ/mol (0.332 eV)
Electronegativity (Pauling)	2.04
Electronegativity (Mulliken)	2.01
Ionic radius	0.25 nm
Atomic radius	0.80-0.95 nm (depending on type of bonding)

### 1.1.4.1. Reaction of Boron with Halogens

Boron reacts vigorously with halogens fluorine, F<sub>2</sub>, chlorine, Cl<sub>2</sub>, bromine, Br<sub>2</sub>, to form trihalides boron(III) fluoride, BF<sub>3</sub>, boron(III) Chloride, BCl<sub>3</sub>, and boron(III) bromide, BBr<sub>3</sub> respectively (WEB\_2 2007) as show below.



### 1.1.4.2. Reaction of Boron with Acids

Crystalline boron does not react with boiling hydrochloric acid (HCl), or boiling hydrofluoric acid (HF). Powdered boron oxidizes slowly when threated with concentrated nitric acid (HNO<sub>3</sub>) (WEB\_2 2007).

### 1.1.5. Application Areas

Boron compounds may be classified under two groups with respect to their production technologies and usage areas:

1) Compounds which are produced in large quantites: Boron mineral concentrates which are produced in large quantities with classic chemical engineering unit operations and find widespread application areas, i.e. agriculture, glass production and detergents, etc.

2) Specialty boron chemicals that are produced in limited amounts and have special application areas. Elemental boron, boron fiber, boron carbide and similar specialty boron compounds require special production technologies and generally are used in high technology areas.

Elemental boron is used in very diverse industries from metallurgy to electronics. Other areas of application include ceramic, propulsion, pyrotechnics, and nuclear chemistry. Boron is nontoxic. Workplace hygienic practices, however, include avoiding the breathing of boron dust or fine powder (Kirk-Othmer 2001).

Boron is used in pyrotechnics and flares to produce a green color. It has use in some rockets as an ignition source. Boron is also used in air bags, placed in automobiles as safety devices, for initiating the sodium azide which fills the bag with nitrogen (Kirk-Othmer 2001). Boron-10, one of the naturally occurring isotopes of boron, is good absorber of neutron and is used in the control rods of nuclear reactors, as a radiation shield and as a neutron detector. Boron filaments are used in aerospace industry because of their high-strength and lightweight (WEB\_2 2007).

Dispersed mixture of boron and another metal as deoxidizing and degassing agents to harden steel, to increase the conductivity of copper in turbojet engines, and in making of brass and bronze. Two examples are alloys of ferroboron and magnese boron (Kirk-Othmer 2001) .

Cleaning and washing products use boron compounds. In North America, boron is mostly used as a washing aid and softener where ten percent of boron consumption is used in the cleaning industry. In Western Europe, sodium perborate is used as a bleaching agent in soap and detergent. Over 41% of their boron consumption is cleaning products (Butterwick et al. 1989).

Boron, an essential trace element for plant growth, is often added to crops as a fertilizer. In higher concentrations, it can also be used as a non-selective herbicide for weed control, insecticide, algacide in water treatment and as a timber preservative. The United States uses approximately 5% of its boron consumption in the agrochemical field (Butterwick et al. 1989).

Boron compounds are widely employed in many branches of the national economy, for example in medicine for the preparation of disinfectants and drugs, in the glass industry for the production of optic and chemical stable glass (glass products use 53.6% of the boron consumption in the United States, and 32.7% in Western Europe (Butterwick et al. 1989). Boron compounds are also used in cosmetic, leather, textile, rubber and paint industries. They also find application in the wood-processing industry as a protection againts molds (ECETOC 1995).

### **1.1.6. Production**

A variety of preparative methods have been described. The following are the most important methods (Ullmann 2002).

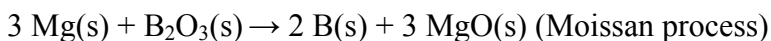
- 1) Reduction of boric oxide with magnesium
- 2) Reduction of boron halides or fluoroborates with sodium or another metal
- 3) Reduction of boric halides with hydrogen
- 4) Thermal decomposition of boron compounds, especially boron halides and hydrides
- 5) Electrolysis of molten borates or fluoroborates

The modification of boron formed, depends primarily on temperature and reaction time (Vandenbulcke 1979). As a rule of thumb, temperature below 900 °C and short reaction time produce amorphous boron; temperature above 1400 °C and long reaction time produce  $\beta$ -rhombohedral or the tetragonal modifications. The optimum conditions for formation of  $\alpha$ -rhombohedral boron are in between (Ullmann 2002).

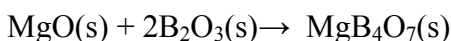
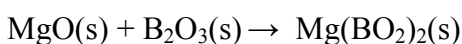
### 1.1.6.1. Reduction of Boric Oxide with Magnesium

The Moissan process, reduction of boric oxide with magnesium, is the most widely set commercial process for producing boron. Although boric oxide can be reduced by many other agents, including calcium and potassium, the most efficient is magnesium. This process yields material which is 90-92 % pure. The boron then leached with acid to separate it from the magnesium oxide formed in the process followed by multiple washing and finally drying. Chemical processing can increase this purity to 95-97 % purity (Kirk-Othmer 2001).

The principles of this method date back to the work of Henri Moissan.

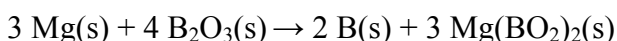
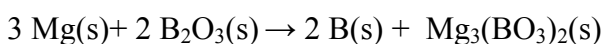


Simultaneously MgO reacts with excess  $\text{B}_2\text{O}_3$ :



The reduction is very quick and highly exothermic; finely divided material may react explosively.

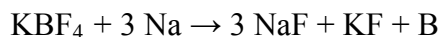
Reaction is smoother if there is an excess of  $\text{B}_2\text{O}_3$ :



The optimum ratio  $\text{B}_2\text{O}_3$ : Mg is about 1.8:3. Reaction is carried out in vertical steel retorts shielded from oxygen by a flow of argon. It is initiated by electric spark and igniter mixture or by external heating (Ullmann 2002).

### **1.1.6.2. Reduction of Boron Halides or Fluoroborates with Metals**

Reduction of  $\text{KBF}_4$  by sodium;



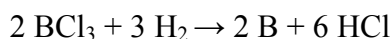
This method was used for the commercial production of boron in Germany until the end of the 1950 (Ullmann 2002).

A common problem of metallothermic reduction is incomplete reaction and formation of nonremovable metal borides (Ullmann 2002).

### **1.1.6.3. Reduction of Boron Halides with Hydrogen**

Samples of very pure boron, >99% B, can be obtained by reduction of boron halides with hydrogen, especially  $\text{BBr}_3$  and  $\text{BCl}_3$ . The halides can be purified by distillation prior to reduction (Naslain 1970). However, the efficiency of the hydrogen reduction process is rather low, yields of 5-25 % being the usual.

Unreacted boron halide must be recycled, washed out, or removed by other methods. This complicates the process and makes it expensive (Ullmann 2002).



### **1.1.6.4. Thermal Decomposition of Boron Compounds**

Very pure boron is also obtained by thermal decomposition of  $\text{BI}_3$ ,  $\text{BBr}_3$ , or boron hydrides on tungsten wires or another type of incandescent filament. Boron of 99.9999% purity was obtained by decomposition of diborane and subsequent zone melting (Ullmann 2002).

### **1.1.6.5. Electrolysis of Molten Borates or Fluoroborates**

When molten  $\text{KBF}_4\text{-KCl}$  or  $\text{KBF}_4\text{-KF-KCl}$  or  $\text{KBF}_4\text{-KCl-NaCl}$  mixture is electrolyzed, elemental boron is obtained.

### 1.1.7. Determination

The determination of boron has become a task of growing interest in different fields of analytical applications, such as environmental technology, industrial hygiene, and agriculture, because of the increasing use of boron compounds in metallurgy, microelectronics, glass products, fertilizers, and even cosmetics (Sarica and Ertaş 2001).

Boron concentrations has been determined utilising spectrophotometry, potentiometry, chromatography, flame atomic emission and absorption spectrometry, inductively coupled plasma (ICP), optical emission (OES) and mass spectrometry (MS), and neutron activation analysis using neutron radiography and prompt- $\gamma$  activation analysis (Sah and Brown 1997).

For boron determination, several techniques have previously been used, such as UV-Visible molecular absorption spectrometry, and DC plasma optical emission spectroscopy. However, these are more complex and slower methods than those based on atomic absorption spectrometry. The determination of boron by electrothermal atomic absorption spectrometry (ET-AAS) is one of the most difficult tasks in analytical practice. Boron forms oxides, nitrides and carbides of high thermal stability, both in the condensed phase and in the gas phase. For that reason, boron determination by AES may be carried out either using more energetic excitation sources (such as DCP or ICP plasmas) or employing boron oxide as the analytical species to be measured (Sarica and Ertaş 2001).

ICP-MS has outperformed all previous analytical methods for trace element determination for B<sup>10</sup>. Nevertheless, the conventional flame atomic emission and flame atomic absorption methods have limited applications in the determination of boron owing to their poor sensitivity and a large number of interferences (Sarica and Ertaş 2001).

Boron determination by AES, measuring boron oxide emission, has been performed using different types of flames. However, these methods in general have low sensitivity and, occasionally, suffer interference problems (Sarica and Ertaş 2001).

### **1.1.8. Storage**

Dry boron is not very sensitive to oxidation. It is packaged in airtight metal drum, cardboard or plywood containers, or glass bottles. Boron powder, like other combustible material, presents a dust explosion hazard. The lower explosive limit was determined to be 125g/m<sup>3</sup> in air. Boron ignites in air at 600-800 °C but does not burn violently because of the formation of glassy boric oxide film that prevents the material from oxidizing rapidly. Burning boron should be covered with sand, aluminium oxide, Sodium chloride, or the like. Water must not be used, because of the formation of inflammable hydrogen. Boron is an explosion hazard when mixed with strong oxidizing agents, such as nitrites, chlorates, lead dioxide, and silver fluoride. Such mixtures can react violently and even explode (Ullmann 2002).

## **1.2. Components Used in Experimental Studies**

### **1.2.1. Aluminum**

Aluminum is the chemical element in the periodic table that has the symbol Al and atomic number 13. It is a silver and ductile member of the poor metal group of chemical elements. Aluminum is found primarily as the ore bauxite and is remarkable for its resistance to corrosion and its light weight (WEB\_ 5 2007).

Aluminum is a soft and lightweight metal with a dull silver appearance, due to a thin layer of oxidation that forms quickly when it is exposed to air. Aluminum is nontoxic, non-magnetic, and non-sparking. Pure aluminum has a tensile strength of about 49 megapascals and 400 megapascals if it is formed into an alloy. Aluminum is about one-third as dense as steel or copper; is malleable, ductile, and easily machined and cast; and has excellent corrosion resistance and durability due to the protective oxide layer (WEB\_ 5 2007).

### 1.2.1.1. Chemical and Physical Properties

Physical and chemical properties of aluminum are given in Table 1.7.

Table. 1.7. Chemical and Physical Properties of Aluminum.  
(Source: WEB\_5 2007)

Property	Value
Atomic weight	26.9815386 g/mol
Melting point	660.32 °C
Boiling point	2519 °C
Density (near r.t.)	2.70 g/cm <sup>3</sup>
Heat of vaporization	294.0 kJ/mole
Heat of fusion	10.71 kJ/mole
Heat capacity	(25 °C) 24.2 J/(mol.K)
Electonegativity	1.61 (Pauling scale)
First Ionization Energy	577.5 kJ/mole
Second Ionization Energy	1816.7 kJ/mole
Third Ionization Energy	2744.8 kJ/mole
Atomic Radius	125 pm
Atomic Radius (calc)	118 pm
Covalent Radius	118 pm
Oxidation number	3

### 1.2.2. Boron Oxide

Boron oxide (B<sub>2</sub>O<sub>3</sub>) is the only commercially important oxide. It is also known as diboron trioxide, boric anhydride, or anhydrous boric acid. B<sub>2</sub>O<sub>3</sub> is normally encountered in vitreous state. It is usually prepared by dehydration of boric acid at elevated temperatures. It is mildly hygroscopic at room temperature. The reaction with water is exothermic (Kirk-Othmer 2001).





Boric oxide is an excellent Lewis acid. It coordinates weak Bases to form four-coordinate borate species. At high temperatures ( $>1000\text{ }^{\circ}\text{C}$ ) molten boric oxide dissolves most metal oxides and thus very corrosive to metals in the presence of oxygen (Kirk-Othmer 2001).

In the United States a high (99%  $\text{B}_2\text{O}_3$ ) purity grade is produced by fusing refined, granular boric acid in a glass furnace fired by oil or gas. The molten glass is solidified in a continuous ribbon as the melt flows over chill-rolls. The amorphous solid product is crushed, screened, and packed in sacks or drums with moisture-proof liners. Boric oxide is no longer commercially produced by mixing borax and sulfuric acid in a furnace. There is no commercial source of crystalline boric oxide (Kirk-Othmer 2001).

Boron oxide reacts with water to form boric acid, with halogens to form boron trihalides, with halogen salts to form glasses. It is also a powerful Lewis acid solvent for dissolving metal oxides, has a low surface tension, and readily wets metal surfaces.

The uses of boric oxide relate to its behavior as a flux, an acid catalyst, or a chemical intermediate. The fluxing action of  $\text{B}_2\text{O}_3$  is important in preparing many types of glass, glazes, frits, ceramic coatings, and porcelain enamels. Boric oxide is used as a catalyst for many organic reactions. It also serves as an intermediate in the production of boron halides, esters, carbide, nitride, and metallic borides (Kirk-Othmer 2001).

### 1.2.2.1. Chemical and Physical Properties

Chemical and physical properties of boron oxide are given in Table 1.8.

Table 1.8. Chemical and Physical Properties of Boron Oxide.  
(Source: Kirk-Othmer 2001)

Property	Value
Melting point	$450\text{ }^{\circ}\text{C}$
Density (near r.t.)	$1.844\text{ g/cm}^3$
Boiling point	$2316\text{ }^{\circ}\text{C}$
Heat capacity ( $25\text{ }^{\circ}\text{C}$ )	$62.969\text{ J/kg.K}$
Heat of vaporization ( $25\text{ }^{\circ}\text{C}$ )	$431.4\text{ kJ/mole}$

## **1.3. Equipment Used in Experimental Studies**

### **1.3.1. Microwave Oven**

Solid-state reactions are often carried out by extremely long reaction times caused by slow diffusion rates in solids. Consequently, the use of alternative synthesis techniques have been explored in order to achieve faster reaction rates. Several research groups have recently demonstrated the utility a number of solid-state materials, such as chalcopyrite semiconductors, and metal dichalcogenides, oxide superconductors, and metal halides. All these microwave techniques take advantage of rapid resistive heating of fine metal particles caused by electrical currents induced in them by microwave field. Using relatively low-power microwave generators, such as those found in standard home-use microwave ovens, many metal powders will heat rapidly and without noticeable electrical dis-charges (Houmes and Loye 1997).

### **1.3.2. Tube Furnace**

A tube furnace is designed to heat a part of the tube that is usually 50 to 100 cm in length and from 25 to 100 mm in diameter. Samples are placed inside the tube in ceramic or metal boats using a long push rod. The tube is surrounded by heating elements which may also incorporate a thermocouple. Tube furnaces have a significant advantage over other types of furnaces. The ends of the furnace tubes do not get very hot and so a variety of different adapters may be placed on the ends. This permits one to perform a reaction under a controlled atmosphere. In a typical setup, gas flows in one end of the tube and then the gas exits through a bubbler (WEB\_ 7 2007).

## **1.4. Characterization of Solid samples**

Characterization of the solid samples was carried out by using X-Ray Diffraction, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).

### **1.4.1. X-Ray Powder Diffraction (XRD)**

X-Ray powder diffraction finds frequent use in material science because sample preparation is relatively easy, and the test itself is often rapid and non-destructive. The vast majority of engineering materials is crystalline, and even those which do not yield some useful information in diffraction experiments.

The pattern of powder diffraction peaks can be used to quickly identify materials, and changes in peak width or position can be used to determine crystal size, and texture (WEB\_3 2006).

### **1.4.2. Scanning Electron Microscopy (SEM)**

Scanning electron microscopy is the best known and most widely-used surface analytical techniques. High resolution images of surface topography, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 - 30 keV, and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). High sensitivity to topographic features on the outermost surface (<5 nm) is achieved when using a primary electron beam with an energy of <1 keV (WEB\_4 2006).

In addition to low energy secondary electrons, backscattered electrons and X-rays are also generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron (WEB\_4 2006).

SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used

to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and specialized (WEB\_4 2006).

### 1.4.3. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared (IR) spectroscopy is an analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. Based upon the wavenumber, infrared light can be categorized as far infrared ( $4 \sim 400 \text{ cm}^{-1}$ ), mid infrared ( $400 \sim 4,000 \text{ cm}^{-1}$ ) and near infrared ( $4,000 \sim 14,000 \text{ cm}^{-1}$ ) (WEB\_6 2007).

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular fingerprint.

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb energy. For any given transition between two states the energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state ( $E_0$ ) and the first excited state ( $E_1$ )] (WEB\_8 2007).

Difference in energy states = Energy of light absorbed

$$E_1 - E_0 = hc / \lambda \quad (1.1)$$

Where  $h$  is Planck's constant,  $c$  is speed of light and  $\lambda$  is the wavelength of light.

### **1.4.3.1. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)**

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique that collects and analyzes scattered IR energy. It is used for measurement of fine particles and powders, as well as rough surface. Sampling is fast and easy because little or no sample preparation is required.

When the IR enters the sample, it can either be reflected off the surface of a particle or be transmitted through a particle. The IR energy reflecting off the surface is typically lost. The IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in the sample, which increases the pathlength. Finally, such scattered IR energy is collected by a spherical mirror that is focused onto the detector. The detected IR light is partially absorbed by particles of the sample, bringing the sample information (WEB\_7 2007).

There are some ways to prepare samples for DRIFTS measurements:

1) Fill the micro-cup with powder (or the mixture of the powder and KBr). The diffuse reflectance accessory uses a focusing mirror to focus the beam on the sample surface and collect the IR energy. The micro-cup needs to be filled consistently in order to keep the focus.

2) Scratch the sample surface with a piece of abrasive (SiC) paper and then measuring the particles adhering to the paper.

3) Place drops of solution on a substrate. If colloids or powders are dissolved or suspended in a volatile solvent, you can put a few drops of the solution on a substrate, and evaporate the solvent, subsequently analyze the remaining particles on the substrate.

It is well known that particle size is a key variable in a transmission measurement with the pellet method. Large particles will result in the scattering of the energy, leading to the shift of the spectrum baseline and the broadening of IR bands. The scenario becomes worse in a diffuse reflectance measurement, because the infrared light travels in the sample for a long period and the optics collects a large portion of the distorted energy. It is important to grind the sample particles to 5 microns or less (WEB\_7 2007).

## CHAPTER 2

### MULTIVARIATE CALIBRATION METHODS

#### 2.1. Multivariate Calibration Methods

Modern spectroscopic instruments are too fast. Therefore, they can produce hundreds of spectra in minutes for a sample. Samples contain multiple components. In spectroscopy, multivariate calibration deals with data that contains instrument responses measured on multiple wavelengths for a sample containing more than one component. Multivariate calibration methods can handle multiple pieces of data to predict concentration of a given analyte, for example, the instrumental noise effect in prediction is decreased by performing signal averaging. In addition to this, it is possible to estimate presence of interfering species in samples though this does not guaranty the elimination of bias due to those interfering species (Özdemir 1999).

In recent years, several multivariate calibration methods for the analysis of complex chemical mixtures have been developed with the help of advances in chemometrics and computers. Some of the most commonly used multivariate calibration methods in spectrochemical analysis are Classical Least Square (CLS), Inverse Least Square (ILS) which is sometimes referred as Multiple Linear Regression (MLR), Partial Least Square (PLS) and Principal Component Regression (PCR) (Özdemir 1999).

##### 2.1.1. Classical Least Squares Methods (CLS)

The CLS method assumes the Beer's Law model with the absorbance at each wavelength being proportional to the component concentrations (Haaland and Thomas 1988). Model errors are assumed to be due to error in spectral absorbances. In matrix notation, the CLS model for  $m$  calibration samples containing  $l$  chemical components whose spectra contains  $n$  wavelength is given by:

$$A = CK + E_A \quad (2.1)$$

where  $\mathbf{A}$  is the  $m \times n$  matrix of calibration spectra,  $\mathbf{C}$  is the  $m \times l$  matrix of component concentrations,  $\mathbf{K}$  is the  $l \times n$  matrix of absorptivity-pathlength products and  $\mathbf{E}_A$  is the  $m \times n$  matrix of spectral errors or residuals not fit by the model.  $\mathbf{K}$  shows the matrix of pure component spectra at unit concentration and unit pathlength.  $\mathbf{K}$  matrix can be predicted by using the method of least-squares (Özdemir 1999). The least-squares prediction of the  $\mathbf{K}$  is defined as:

$$\hat{\mathbf{K}} = (\mathbf{C}'\mathbf{C})^{-1}.\mathbf{C}'\mathbf{A} \quad (2.2)$$

first of all, the predicted  $\hat{\mathbf{K}}$  matrix is found, and an unknown sample concentrations can be estimated from its spectrum by:

$$\hat{\mathbf{c}} = (\hat{\mathbf{K}}.\hat{\mathbf{K}}')^{-1}.\hat{\mathbf{K}}.\mathbf{a} \quad (2.3)$$

where the spectrum of the unknown sample is  $\mathbf{a}$  and the vector of estimated component concentrations is  $\hat{\mathbf{c}}$  (Özdemir 1999).

All the species present in a given sample need to be known and included in the  $\mathbf{C}$  matrix, in the calibration step from equation 1 to set up a good model. This is a major disability of the CLS method. Because concentrations of all the species are usually not known exactly. Therefore, the instrument response can not be modelled owing to this interfering species and this causes a large error. On the other hand, CLS offers several advantages when the content of the sample is known. Since the full spectrum can be used by CLS in order to construct the model, the accuracy of the analysis is significantly improved compared to the methods that are restricted to single or a small number of wavelengths. Also in CLS, spectral base lines are fitted simultaneously and predicted pure component spectra made available along with the residuals for better examination of the model (Özdemir 1999).

### **2.1.2. Inverse Least Squares Methods (ILS)**

In the ILS method, a component concentration is modelled as a function of absorbance. Since modern spectroscopic instruments are stable and can produce excellent signal-to-noise (S/N) ratios, it is believed that majority of errors lie in the

reference values of the calibration sample, rather than the measurement of their spectra. Indeed, in many cases the concentration data of calibration set is produced from another analytical technique that already has its inherent errors which might be higher than those of the spectrometer (Özdemir and Öztürk 2007).

The ILS model for  $m$  calibration samples with  $n$  wavelegths for each spectrum is described by:

$$C = AP + E_C \quad (2.4)$$

where  $C$  is the  $m \times l$  matrix of the component concentrations,  $A$  is the  $m \times n$  matrix of the calibration spectra,  $P$  is the  $n \times l$  matrix of the unknown calibration coefficients relating  $l$  component concentrations to the spectral intensities and  $E_C$  is the  $m \times l$  matrix of errors in the concentrations not fit model. In the calibration step, ILS minimizes the squared sum of the residuals in the concentrations (Özdemir and Öztürk 2007). The equation 4 can be decreased for the analysis of single component at a time because the analysis is based on an ILS model invariant with respect to the number of chemical components in the analysis. This is a major advantage of ILS. The reduced model is given as:

$$c = Ap + e_c \quad (2.5)$$

where  $c$  is the  $m \times l$  vector of concentrations for the component that is being analyzed,  $p$  is  $n \times l$  vector of calibration coefficients and  $e_c$  is the  $m \times l$  vector of concentration residuals unfit for the model. During the calibration step, the least-squares estimate of  $p$  is

$$\hat{p} = (A'.A)^{-1}.A'.c \quad (2.6)$$

where the vector of predicted calibration coefficients is  $\hat{p}$ . Once  $\hat{p}$  is computed, the concentration of the analyte of intrest can be predicted with the equation below.

$$\hat{c} = a'.\hat{p} \quad (2.7)$$

Where the scalar estimated concentration is  $\hat{c}$  and the spectrum of unknown sample is  $a$ . The capability to estimate one component at a time without knowing the



concentrations of interfering species has made ILS one of the most frequently used calibration methods (Özdemir and Öztürk 2007).

The number of wavelength in the calibration spectra should not be more than the number of calibration samples. This is a major drawback of the ILS method because, most of the time the number of wavelengths in a spectrum is much more than the number of calibration samples. Besides, the selection of wavelength generating the best fit for the model is not a trivial process (Özdemir and Öztürk 2007).

## **2.2. Genetic Algorithms**

Genetic algorithms (GA) are search algorithms founded upon the principles of natural evolution and selection laid down by Darwin (Lucasius and Kateman 1993). GA is fairly simple and consists of five steps that included initialization of a gene population, evaluation of the population, selection of the parent genes for breeding and mating, crossover and mutation and replacing parents with their offspring. These steps have taken their names from the biological foundation of algorithm (Özdemir and Öztürk 2007).

### **2.2.1. Genetic Inverse Least Squares (GILS)**

GILS is an implementation of a GA in order to select wavelengths to multivariate calibration models with decreased data set. GILS follows the same basic initialize / breed / mutate / evaluate algorithm as other GA's to select a subset of wavelengths which is unique in the way it encodes genes (Özdemir and Öztürk 2007). Flow chart is shown in Figure 2.1. for the GILS algorithm.

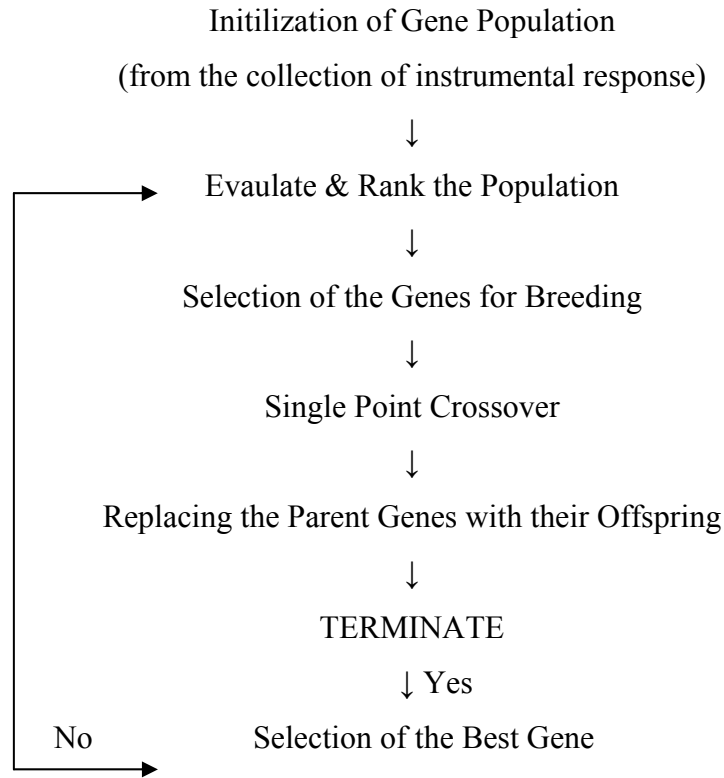


Figure 2.1. Flow Chart of the GILS Algorithm.

The collection of instrumental response at the wavelength range is described gene and the collection of individual genes give the population.

The first generation of genes is created randomly with a fixed population size. The gene pool size is a user defined even number to let breeding of each gene in the population. The number of instrumental responses in a gene is described randomly between a fixed low limit and high limit. First, the initial gene population is created. In the second step, genes are evaluated and ranked. These genes are used in a fitness function, which is the inverse of the standard error of calibration (SEC) (Özdemir and Öztürk 2007). The SEC is calculated as:

$$SEC = \sqrt{\frac{\sum_{i=1}^m (c_i - \hat{c}_i)^2}{m - 2}} \quad (2.8)$$

Where  $c_i$  is the actual concentration  $\hat{c}_i$  is the predicted concentration of  $i^{\text{th}}$  sample for  $m$  number of samples.

The next step is where the basic principle of natural evolution is put to work for GILS. This step involves the selection of parent genes from the population for breeding using a roulette wheel selection method according to their fitness values. After the selection procedure is completed, the selected genes are allowed to mate top-down in pairs whereby the first gene mates with the second gene and the third one with the fourth one (Özdemir and Öztürk 2007). These steps are illustrated below.

Parents

$$S_1 = (A_{347}, A_{251}, \# A_{349}, A_{218}) \quad (2.9)$$

$$S_2 = (A_{225}, A_{478}, \# A_{343}, A_{250}, A_{451}, A_{358}, A_{231}, A_{458}) \quad (2.10)$$

# show where the genes are cut for mating.

Offspring

$$S_3 = (A_{347}, A_{251}, A_{343}, A_{250}, A_{451}, A_{358}, A_{231}, A_{458}) \quad (2.11)$$

$$S_4 = (A_{349}, A_{218}, A_{225}, A_{478}) \quad (2.12)$$

where  $S_1$  and  $S_2$  show the first and second parent genes and  $S_3$  and  $S_4$  are the corresponding genes for the offspring.  $A_{347}$  is the instrument response at the wavelength given in subscript. Here  $S_3$  is composed of the first part of  $S_1$  and the second part of  $S_2$  likewise  $S_4$  is composed of the second part of  $S_1$  and the first part of  $S_2$ . After crossover, the parent genes are replaced by their offspring and the offspring are evaluated. The ranking process is based on their fitness values following the evaluation step. Then the selection for breeding/mating starts all over again. This is repeated until a predefined number of iterations is reached (Özdemir and Öztürk 2007).

The GILS method is an iterative algorithm and therefore the method can easily overfit the calibration data so that the predictions for independent sets could be poor. For this reason, cross validation is used in which one spectrum is left out of the calibration set and the model is constructed with  $m - l$  samples to eliminate possible overfitting problems. After the concentration of leftout sample is estimated by this

model. This process is continued until all samples are left out at least once in the iteration (Özdemir and Öztürk 2007).

Finally, the model is built by the selected genes with the lowest SEC (highest fitness). The concentration of components being analyzed in the validation (test) set is estimated by this model. The success of the model in the validation of the test set is evaluated using standard error of prediction (SEC), given as

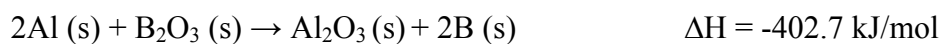
$$SEC = \sqrt{\frac{\sum_{i=1}^m (c_i - \hat{c}_i)^2}{m}} \quad (2.13)$$

Because random processes are heavily involved in GILS as in all the GA's, the program has been set to run several times for each component in a given multi-component mixture. The best run is selected for the evaluation and further analysis. The termination of the algorithm can be done in many ways. The easiest way is to set a predefined iteration number for the breeding / mating cycles (Özdemir and Öztürk 2007).

This method has some major advantages different from the classical univariate and multivariate calibration methods. The most important thing is that it is simple in terms of mathematics that involved in the model building and prediction steps. But, at the same time it has the advantages of multivariate calibration methods with a reduced data set because the full spectrum is used by GILS to extract genes. It is able to eliminate nonlinearities that can be present in the full spectral region by selecting a subset of instrument responses (Özdemir and Öztürk 2007).

### 2.3. Aim of This Work

The purpose of this work is to propose a new method that is more economical and suitable for industrial synthesis of elemental boron. Aim of the study is to reduce boron oxide (B<sub>2</sub>O<sub>3</sub>) with easily available and considerably cheap metal such as aluminum. The process can be shown in the following equation.



For this purpose, several experimental procedures, different furnaces, reaction mixture and different temperatures were tried. Characterization of the products was firstly done by X-Ray powder diffraction and SEM-EDX.

In addition to this, a new method for the determination of boron in the samples was tried with DRIFTS and GILS. For this purpose, several designs were planned and calibration and validation models were prepared.

## CHAPTER 3

### EXPERIMENTAL METHODS

#### 3.1. Instrumentation and Apparatus

In the first part of studies in our experiments, Protherm FLY 120/10 model muffle furnace was used. In the second part of the study, SINBO SMO-3607 model kitchen type microwave oven was used. Some modifications were made in the oven according to the literature (WEB\_10 2006). Turning tray of the oven was removed and air flow holes inside the oven were blocked. A tube furnace was used in the third part of our study. This tube furnace was designed and built.

#### 3.2. XRD, SEM-EDX, DRIFTS Analysis

X-Ray powder diffraction (XRD) data were collected on a Philips X'Pert Pro diffractometer using Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). Samples were prepared by compressing in the cassette sample holder without any adhesive substance.

SEM/EDX characterization was carried out using a Philips XL-30s FEG type instrument. Prior to analysis, the solid samples were sprinkled onto Al or C tapes which are adhesive and supported on metallic disks. Images of the sample surfaces were recorded at different magnifications.

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) data were collected by a Nicolet Magna- IR<sup>TM</sup> Spectrometer 550 and Perkin-Elmer Spectrum BXII FT-IR system.

#### 3.3. Boron Sythesis

Our study progressed in three stages;

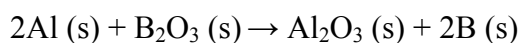
1) Studies on production of elemental boron in a muffle furnace using metallic aluminum as a reductant.

2) Studies on production of elemental boron in a microwave oven using metallic aluminum as a reductant.

3) Studies on production of elemental boron in a tube furnace using metallic aluminum as a reductant.

### **3.3.1. Muffle Furnace**

In order to obtain accurate and reproducible results, the first part of the study was focused on the optimization of parameters for boron synthesis. Synthesis of boron is influenced by several factors such as the reaction time and temperature.



a. Experiments were made by heating  $2\text{Al} + \text{B}_2\text{O}_3$  to various temperatures (650 °C, 700 °C, 750 °C, 800 °C, 850 °C) in a porcelain crucible. 750 °C was found as the optimum temperature.

b. Experiments were made by heating  $2\text{Al} + \text{B}_2\text{O}_3$  for various time intervals (5, 10, 15, 20, 25, 30 minutes)

#### **3.3.1.1. Effect of Temperature**

Samples composed of aluminum and boron oxide to the stoichiometric ratio were prepared and grinded by a ball-mill to get homogenous mixture and smaller particles for easier reaction. These were heated to different temperatures (650 °C, 700 °C, 750 °C, 800 °C, 850 °C ) and kept at these temperatures for 5 minutes in crucibles. Samples were analyzed by XRD and SEM-EDX. 750 °C was selected as optimum.

#### **3.3.1.2. Effect of Reaction Time**

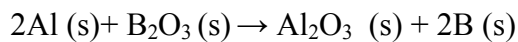
Samples composed of aluminum and boron oxide were prepared in the stoichiometric ratio and grinded by ball-mill and heated for different time intervals at 750 °C (5 min, 10 min, 15 min, 20 min, 25 min, 30 min). Samples were analyzed by XRD and SEM-EDX.

### 3.3.2. Microwave Oven

Microwave heating is used even in metal molting (WEB\_10 2006). This maintains fast and sufficient heating. Microwave heating was also tried in our experiments. For this purpose a kitchen type microwave oven was modified. Its turntable was removed for focussed heating and air vantilation inside the oven was prevented by blocking air holes. Following procedure were tried.

**a- For Finding Focal Point;** First of all, experiments to find the microwave focal point at various levels inside the microwave oven were done. For this purpose, ytong and alçıpan blocks with various thickness were put inside the oven. Over the blocks wet thermal paper was placed and the oven was operated for a few seconds. Focus points were seen as dark points on the thermal paper.

**b- For Investigating Mixture Ratio Effect;** Different amounts of aluminum and boric oxide were grinded by a ball mill and put in porcelain crucibles. They were placed on focus points of the microvawe oven to investigate the optimum mixture. Their compositions were investigated with SEM-EDX and XRD.



1. In the first experiment, reaction was carried with the stoichiometric ratio, so two moles aluminum and one mole boric oxide was mixed.

$$\text{Al} = 0.506\text{g} \qquad \qquad \text{B}_2\text{O}_3 = 0.651\text{g}$$

2. In the second experiment, while Boric oxide amount was stable, aluminum amount was taken twice the amount of the stoichiometric ratio.

$$\text{Al} = 1.005\text{g} \qquad \qquad \text{B}_2\text{O}_3 = 0.649\text{g}$$

3. In the third experiment, boric oxide amount was taken twice the amount of the stoichiometric ratio, while aluminum amount was fixed.

$$\text{Al} = 0.504\text{g} \qquad \qquad \text{B}_2\text{O}_3 = 1.308\text{g}$$

In all of these attempts sufficient heating was obtained. The samples were heated up to red-hot and even white-hot temperatures which are above their reaction



temperatures. However air isolation could not be accomplished. Therefore oxides and aluminum borates formed in these experiments instead of elemental boron.

### 3.3.3. Experiments Carried in the Tube Furnace

To obtain an inert (Ar) atmosphere a tube furnace was designed and manufactured. Both ends of the ceramic tube were capped with metal caps with a metal tube connected at center for Ar flow. The copper tubing of the outlet end was extended in to a fume cupboard. The center of the ceramic tube was heated from outside by Ni-Cr wires and temperature was measured by a thermocouple. Heating of the tube could be controlled upto 1200 °C with  $\pm 5$  °C accuracy.

#### 3.3.3.1. Experimental Design for Boron Synthesis

Three main parameters showed to be very effective during the experiments. These were temperature, reaction time, and mixture ratios. Argon atmosphere was kept constant throughout the experiments, so it was not included as a parameter. The limits for temperature, reaction time, and mixture ratios shown Table 3.1 were selected after some preliminary experiments. Various experiments were carried out to get optimum yield for boron production. After the experiments were completed, product samples were leached with 6M HCl. Experimental Design set up for the experiments are given in table 3.2 below. Samples were analyzed by XRD and SEM-EDX.

Table 3.1. Experimental Data Scheme for B Synthesis Experiment

Coded Value	Temperature (°C)	Reaction Time (Hour)	Mixture Ratio
-1	800	1	2 mole B <sub>2</sub> O <sub>3</sub> + 2 mole Al
0	1000	2	1 mole B <sub>2</sub> O <sub>3</sub> + 2 mole Al
1	1200	3	1 mole B <sub>2</sub> O <sub>3</sub> + 4 mole Al

For Response: % B Amount in the Reaction Mixture

Table 3.2. Experimental Design Scheme for B Synthesis Experiment

Experiment Number	Temperature	Reaction Time	Compounds Amount
1	1	1	1
2	1	1	0
3	1	1	-1
4	1	0	1
5	1	0	0
6	1	0	-1
7	1	-1	1
8	1	-1	0
9	1	-1	-1
10	0	1	1
11	0	1	0
12	0	1	-1
13	0	0	1
14	0	0	0
15	0	0	-1
16	0	-1	1
17	0	-1	0
18	0	-1	-1
19	-1	1	1
20	-1	1	0
21	-1	1	-1
22	-1	0	1
23	-1	0	0
24	-1	0	-1
25	-1	-1	1
26	-1	-1	0
27	-1	-1	-1

### 3.4. Further Studies in Boron Determination

#### 3.4.1. Determination of Boron with DRIFTS and GILS

A new method for the direct determination of boron with DRIFTS and GILS was tried to improve. For this purpose, different designs were tried.

##### 3.4.1.1. Random Design

In this design, 96 % pure boron was used which was obtained from Boronsan. KBr was used as background. For each sample 1000 mg KBr and different amounts of boron was mixed and 25 different samples were prepared. Samples were filled in a micro-sample container. Spectra were collected using a Nicolet Magna-IR™

spectrometer 550 between 4000 and 400  $\text{cm}^{-1}$ . Number of scan was selected as 256. Resolution of DRIFTS was selected as 16  $\text{cm}^{-1}$ .

The sample set was split into two subsets, calibration set and validation set as outlined in Table 3.3 All spectral data were then transferred to a computer where the data processing programs were installed. The GILS method was written in MATLAB programming language using Matlab 5.3 student version (MathWorks Inc., Natick, MA).

Table 3.3. Random Design Scheme for B.

Calibration Set		Validation Set	
Sample	B(mg)	Sample	B(mg)
1	6.00	1	2.50
2	1.90	2	1.70
3	6.40	3	0.80
4	9.10	4	9.90
5	8.50	5	10.2
6	0.30	6	13.1
7	14.2	7	18.3
8	16.5	8	17.3
9	12.8	9	18.5
10	12.1	10	2.50
11	11.3		
12	12.0		
13	13.4		
14	14.7		
15	20.1		

### 3.4.1.2. Mixture Design

KBr was used as background. For each sample 1000 mg KBr and different amounts of boron and boron oxide were mixed. Boron oxide was taken from Kırka Bor plant. 28 samples were prepared. Samples were filled into a micro-sample container. Spectra were collected using a Nicolet Magna-IR<sup>TM</sup> spectrometer 550 between 4000 and 400  $\text{cm}^{-1}$ . Number of scan was selected as 256. Resolution of DRIFTS was selected as 16  $\text{cm}^{-1}$ .

The sample set was split into two subsets, calibration set and validation set as outlined in Table 3.4 All spectral data were then transferred to a computer where the data processing programs were installed. The GILS method was written in MATLAB programming language using Matlab 5.3 (MathWorks Inc., Natick, MA).

Table 3.4. Mixture Design Scheme for B and B<sub>2</sub>O<sub>3</sub>.

Calibration Set			Validation Set		
Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)
1	4.00	0.00	1	12.2	0.00
2	8.10	0.00	2	24.2	0.00
3	16.2	0.00	3	15.9	7.90
4	20.1	0.00	4	16.2	19.9
5	28.3	0.00	5	0.00	4.20
6	16.0	4.10	6	0.00	16.3
7	16.0	12.2	7	0.00	28.1
8	15.9	16.1	8	12.1	16.3
9	16.0	24.1	9	24.4	16.3
10	16.0	28.0			
11	0.00	8.30			
12	0.00	12.2			
13	0.00	20.0			
14	0.00	24.3			
15	4.10	16.2			
16	8.20	16.3			
17	16.2	16.1			
18	20.0	16.1			
19	28.1	15.9			

### 3.4.1.3. Random Mixture Design

KBr was used as a background. For each sample 1000 mg KBr and different amounts of boron and boronoxide was mixed. 30 samples were prepared. Spectra were collected using a Nicolet Magna-IR<sup>TM</sup> spectrometer 550 between 4000 and 400 cm<sup>-1</sup>. Number of scan was selected as 256. Resolution of DRIFTS was selected as 16 cm<sup>-1</sup>.

The sample set was split into two subsets, calibration set and validation set as outlined in Table 3.5 All spectral data were then transferred to a computer where the data processing programs were installed.

Table 3.5. Random Mixture Design Scheme for B and B<sub>2</sub>O<sub>3</sub>.

Calibration Set			Validation Set		
Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)
1	28.85	22.85	1	21.90	21.90
2	11.80	21.15	2	30.00	4.900
3	13.00	19.00	3	24.00	30.10
4	26.10	22.90	4	24.90	8.000
5	21.10	6.800	5	18.90	16.90
6	5.000	5.000	6	10.00	15.90
7	8.100	9.000	7	17.30	10.00
8	5.900	16.10	8	6.900	12.20
9	7.000	30.10	9	15.40	5.300
10	12.20	12.00	10	18.90	21.90
11	7.900	22.00			
12	22.10	13.20			
13	6.000	15.90			
14	18.20	7.900			
15	14.90	16.10			
16	5.000	25.20			
17	12.90	26.80			
18	30.00	15.10			
19	15.00	24.00			
20	24.80	15.00			

#### 3.4.1.4. Ternary Mixture Design

**a. For Fifty Samples;** KBr was also used as background in this design. For each sample 1000 mg KBr and different amounts of boron, boronoxide and aluminium was mixed. 50 samples were prepared. Two different set designs were set. Samples and KBr were filled a micro-sample container.

The sample set was split into two subsets, calibration set and validation set as outlined in Table 3.6 and 3.7.

Table 3.6. Ternary Mixture Design Scheme for B, B<sub>2</sub>O<sub>3</sub> and Al.

Calibration Set				Validation Set			
Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Al(mg)	Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Al(mg)
1	28.1	13.8	44.9	1	47.8	32.2	28.8
2	48.1	38.9	10.0	2	21.3	16.1	7.90
3	28.9	18.0	45.9	3	32.1	32.1	20.0
4	19.7	37.0	17.9	4	43.9	22.1	18.1
5	9.30	28.9	10.9	5	40.9	34.0	43.8
6	13.0	14.9	13.0	6	41.9	7.20	5.00
7	5.90	25.1	20.1	7	20.8	5.10	41.8
8	16.3	9.00	29.8	8	17.9	45.9	8.20
9	45.0	35.9	46.8	9	44.1	46.1	13.2
10	28.1	38.0	39.7	10	27.9	14.3	45.0
11	13.2	40.1	13.0	11	21.2	48.1	7.80
12	48.1	49.0	21.2	12	5.80	29.0	18.0
13	26.1	20.0	26.9	13	24.0	11.0	46.9
14	30.9	32.9	20.1	14	23.9	34.1	15.9
15	9.90	20.0	20.0	15	20.1	19.8	23.9
16	34.1	38.1	16.9	16	30.3	45.8	41.9
17	11.7	4.90	30.9	17	8.00	49.3	49.1
18	17.0	21.8	46.1	18	29.1	30.2	35.9
19	11.9	26.0	32.0	19	33.9	44.1	19.2
20	4.80	15.0	25.0	20	32.0	40.1	7.00
21	47.2	6.10	28.0				
22	30.9	6.90	11.0				
23	15.0	48.0	39.9				
24	33.8	24.0	41.1				
25	29.0	50.0	42.1				
26	5.00	34.0	17.0				
27	8.80	5.00	20.3				
28	14.0	32.1	38.2				
29	36.1	14.0	15.2				
30	29.1	45.0	12.1				

Table 3.7. Ternary Mixture Design Scheme for B, B<sub>2</sub>O<sub>3</sub> and Al.

Calibration Set				Validation Set			
Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Al(mg)	Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Al(mg)
1	28.0	14.0	45.2	1	48.0	39.2	10.1
2	29.2	18.2	45.9	2	48.0	32.0	29.0
3	20.9	16.0	8.30	3	20.3	37.0	17.9
4	9.30	28.9	11.1	4	12.8	15.2	13.0
5	32.1	31.9	20.2	5	43.9	22.1	17.8
6	6.10	25.2	20.1	6	16.3	9.00	30.0
7	44.8	36.2	47.2	7	40.7	34.0	43.9
8	41.8	7.30	4.80	8	28.0	38.1	40.1
9	12.8	40.0	13.3	9	47.8	49.1	21.1
10	21.2	5.00	42.0	10	18.1	46.2	7.80
11	25.8	20.0	26.9	11	31.2	33.0	19.6
12	10.0	19.7	20.2	12	43.8	45.8	13.0
13	28.3	13.9	44.8	13	33.7	38.2	17.2
14	11.8	5.00	31.1	14	16.8	22.1	46.2
15	20.8	48.3	7.90	15	5.70	29.0	18.0
16	12.5	26.1	32.1	16	5.10	15.4	25.1
17	47.2	6.10	27.9	17	24.2	11.1	47.3
18	24.3	34.1	16.1	18	31.3	6.90	10.8
19	14.9	47.8	40.2	19	34.3	24.0	41.0
20	20.0	20.1	24.0	20	30.2	45.8	41.7
21	29.3	50.1	42.1	21	4.80	34.1	17.0
22	8.90	4.90	19.9	22	8.20	49.3	49.3
23	28.7	30.0	35.9	23	13.9	32.3	37.8
24	36.2	14.1	14.8	24	29.0	44.7	11.8
25	34.0	44.0	19.1	25	31.7	40.2	7.00

**b. For a Hundred Samples;** In this study, two sets in step a was combined and new calibration and validation set was composed.

**c. For Twenty Five samples;** KBr was used as background in this design. For each sample 3000 mg KBr and different amounts of boron, boronoxide and aluminum were mixed. 25 samples were prepared.

The sample set was split into two subsets, calibration set and validation set as outlined in Table 3.8.

Table 3.8. Ternary Mixture Design Scheme for B, B<sub>2</sub>O<sub>3</sub> and Al.

Calibration Set				Validation Set			
Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Al(mg)	Sample	B(mg)	B <sub>2</sub> O <sub>3</sub> (mg)	Al(mg)
1	20.1	37.1	17.9	1	13.2	15.2	12.8
2	9.10	28.9	10.9	2	44.9	36.1	46.7
3	44.1	22.0	17.9	3	48.0	48.9	21.2
4	16.1	8.90	30.1	4	28.1	14.0	45.3
5	41.2	33.9	43.7	5	12.3	26.1	32.0
6	12.7	40.0	13.3	6	23.8	11.0	47.2
7	17.9	45.7	8.00	7	8.80	4.90	19.9
8	25.8	20.2	26.8	8	36.2	13.9	15.1
9	16.8	22.0	45.9				
10	21.0	47.7	8.00				
11	5.30	14.9	25.3				
12	47.1	5.70	28.2				
13	30.7	6.90	11.1				
14	34.2	24.2	40.7				
15	8.00	49.2	48.9				
16	29.0	30.1	36.0				
17	33.8	43.9	19.1				

**d. For Produced Samples;** Samples prepared for experimental design were analyzed by Perkin-Elmer Spectrum BXII FT-IR system between 4000 and 400 cm<sup>-1</sup>. Number of scan was selected as 64. Resolution of DRIFTS was selected as 16 cm<sup>-1</sup>. For sample preparation, amount of samples range between 40.8 mg and 40.6 mg were taken and mixed with 3000 mg KBr. Results were compared with calibration model and predicted boron amounts were evaluated from these samples



## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1. Boron Synthesis

##### 4.1.1. Muffle Furnace

##### 4.1.1.1. Effect of Temperature

Aim of this study was to select an optimum temperature to boron synthesis. Therefore, different temperatures were tried. XRD results show that major changes were observed at 750 °C. Therefore, 750 °C was selected for further studies. This change is shown figure 4.1. Results show two compounds, mostly unreacted aluminum but not elemental boron. As seen in the Figure 4.1 while aluminum amount decreases with increasing temperature, aluminum borate amount increases with increasing temperature.

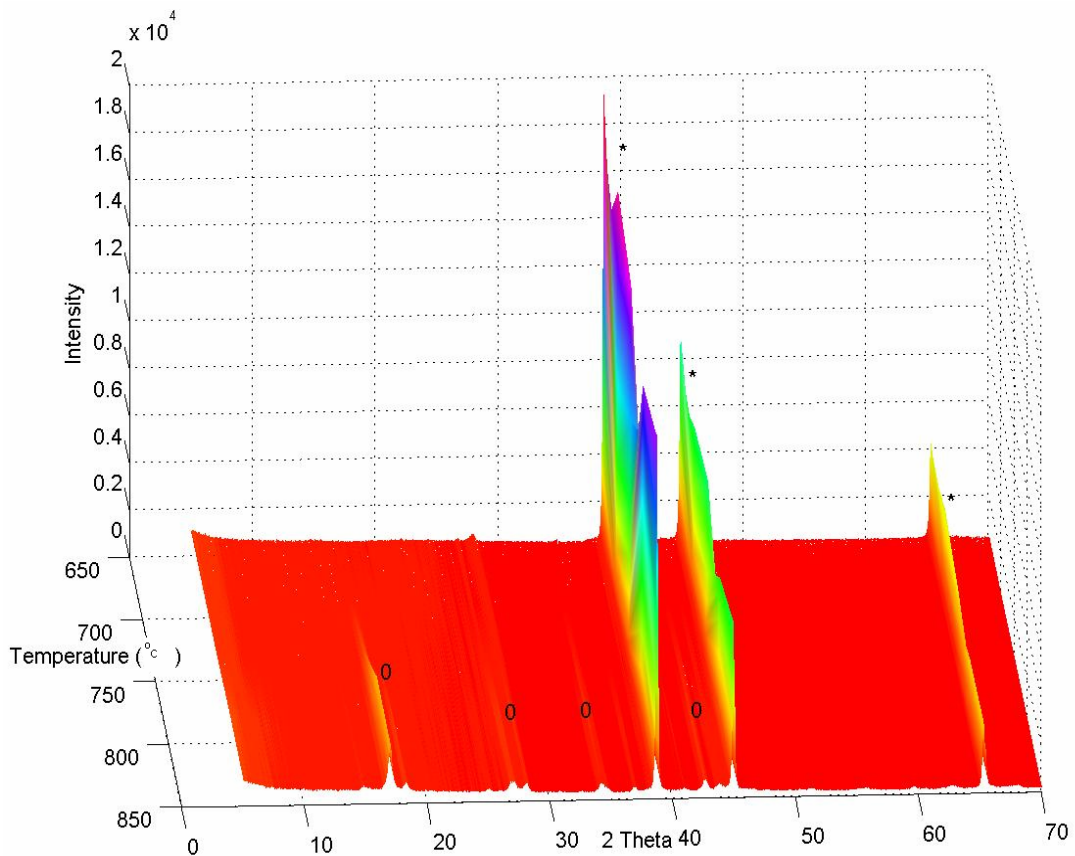


Figure 4.1. The XRD Spectra for Boron Synthesis at Different Temperatures  
 \*= Al, o = Al<sub>4</sub> B<sub>2</sub>O<sub>9</sub>

#### 4.1.1.2. Effect of Reaction Time

Samples were heated at 750 °C for various time intervals. Results show same peaks as previous experiment. Peaks heights increase with increasing time. Here, also aluminum and aluminum borate peaks are observed but elemental boron is not observed. Figure 4.2. shows these results. As seen in the Figure 4.2. while aluminum amount decreases with increasing time, aluminum borate amount increases with increasing time.

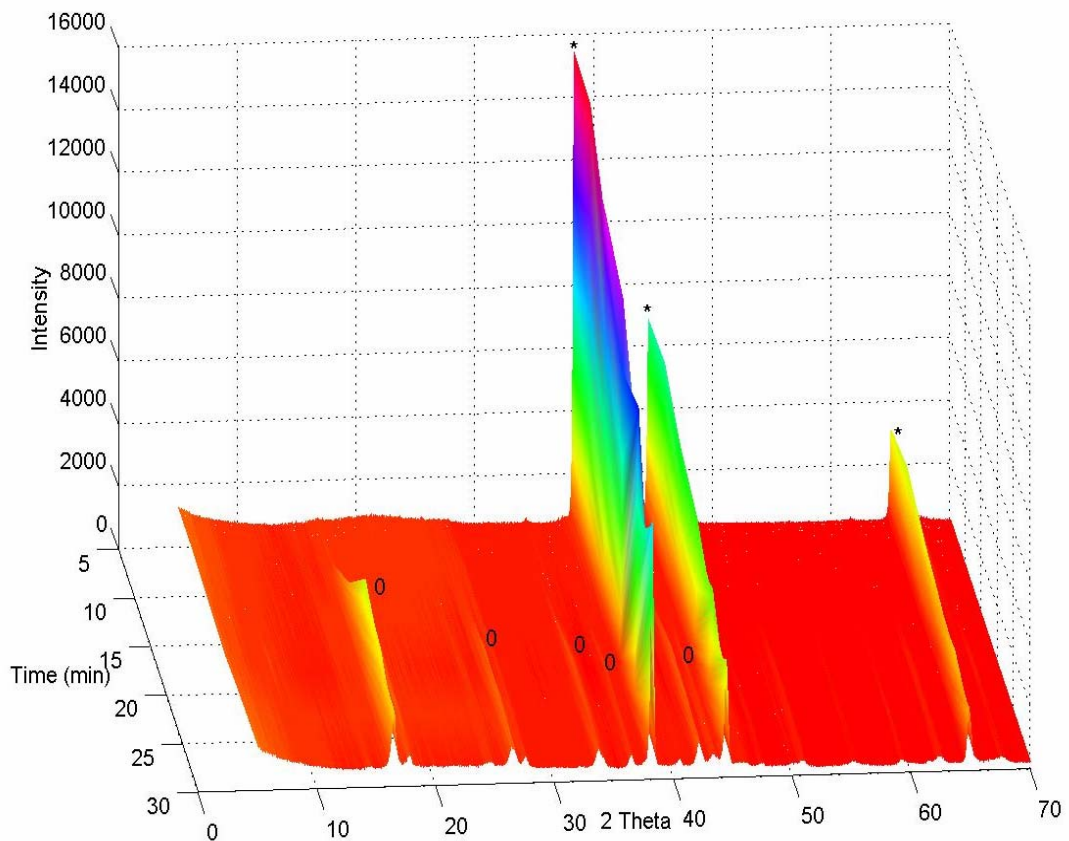


Figure 4.2. The XRD Spectra for Boron Synthesis at Different Time Intervals  
 \* = Al, 0 =  $\text{Al}_4\text{B}_2\text{O}_9$

#### 4.1.2. Microwave Oven

**a- For Finding Focal Point;** First of all, focal points of microwave oven were tried to find, so different experiments were done and fire brick was selected for support material.

**b- For Investigating Mixture Ratio Effect;** Samples in crucibles were set on the selected point. Flames was observed and samples were heated to red-hot. Samples were analyzed by XRD. Figure 4.3. shows XRD results. Results indicate that all samples produced same peaks. Samples that were prepared to the stoichiometric ratio and higher  $\text{B}_2\text{O}_3$  amount show bigger peaks than sample prepared with higher aluminum amounts. These peaks belong Al,  $\text{Al}_2\text{O}_3$  and  $\text{Al}_5(\text{BO}_3)\text{O}_6$ .

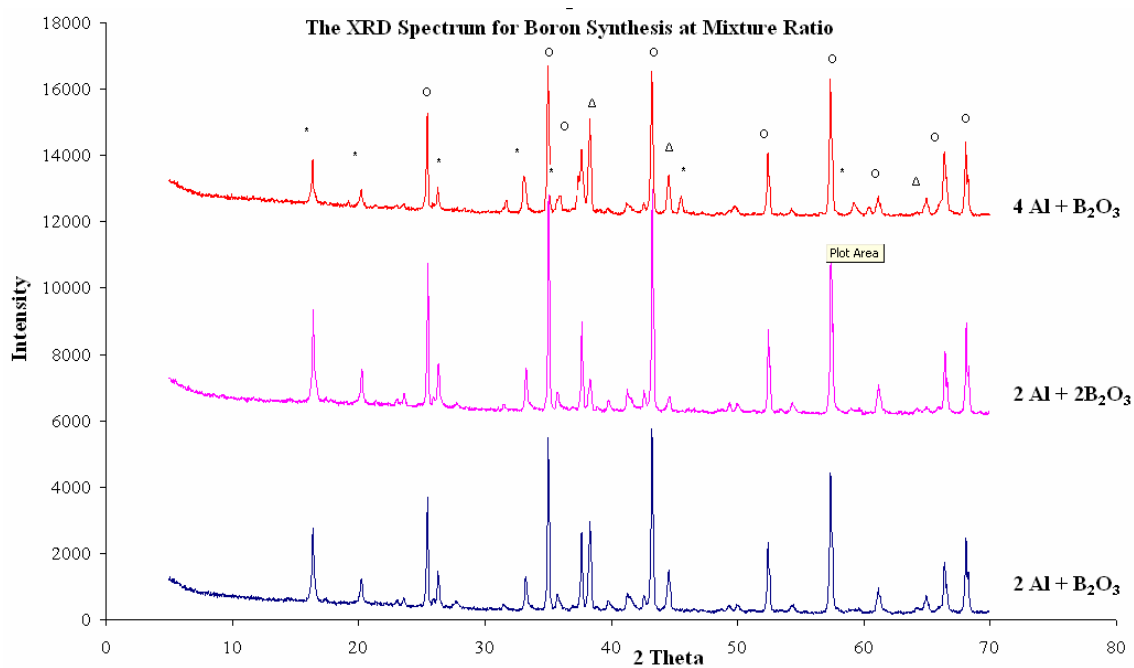


Figure 4.3. The XRD Spectra for Boron Synthesis at Mixture Ratio Effect  
 $\Delta = \text{Al}$ ,  $0 = \text{Al}_2\text{O}_3$ ,  $* = \text{Al}_5(\text{BO}_3)\text{O}_6$

### 4.1.3. Experiments Carried in the Tube Furnace

#### 4.1.3.1. Experimental Design for Boron Synthesis

Three important parameters were selected and experiments were carried out for three levels to find the optimum conditions.

Samples were analyzed by XRD and SEM-EDX. XRD results show aluminum, aluminum oxide and aluminum borate and percentage of boron, aluminum, oxygen were found by EDX. Then, these samples were leached with 6M HCl in order to remove undesirable by products from samples. Samples were again analyzed by XRD and EDX. Samples were compared but no difference was observed. Therefore, % boron amount in mixture was not found. Figure 4.4. shows the spectra for a sample before leaching and after leaching.

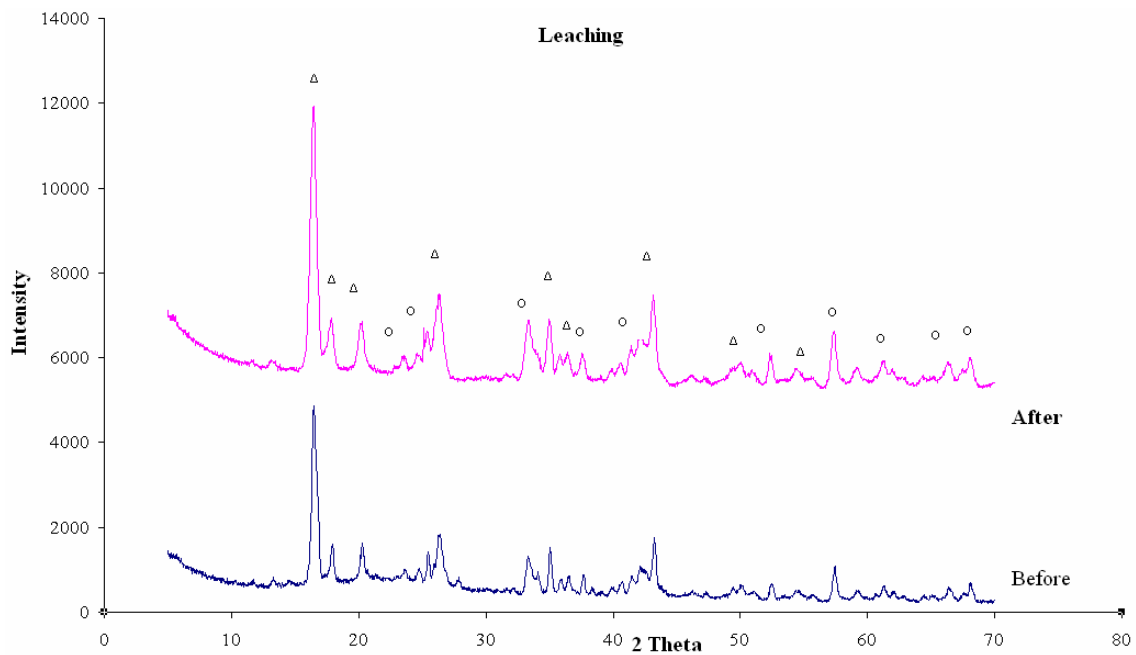


Figure 4.4. The XRD Spectrum Before and After Acid Leaching  
 $\Delta = \text{Al}_2\text{O}_3$  ,  $\text{O} = \text{Al}_{18}\text{B}_4\text{O}_{33}$

## 4.2. Further Studies in Boron Determination

### 4.2.1. Determination of Boron with DRIFTS and GILS

Since XRD and SEM-EDX techniques did not give direct results for boron determination, the new method with DRIFTS coupled with genetic multivariate calibration was tried.

In the literature, it is stated that, absorbance is present at  $1260$  and  $720 \text{ cm}^{-1}$  in the FTIR spectrum for  $\text{B}_2\text{O}_3$ . These bands are attributed to boron oxide, namely asymmetric stretching of O-B-O out of plane racking of O-B respectively (Putkonen and Niinistö 2006). But there is no information about B-B bond. Pure boron DRIFTS data was obtained and analyzed by DRIFTS. The spectrum of pure boron with KBr between  $400$  to  $1500 \text{ cm}^{-1}$  is shown in Figure 4.5.

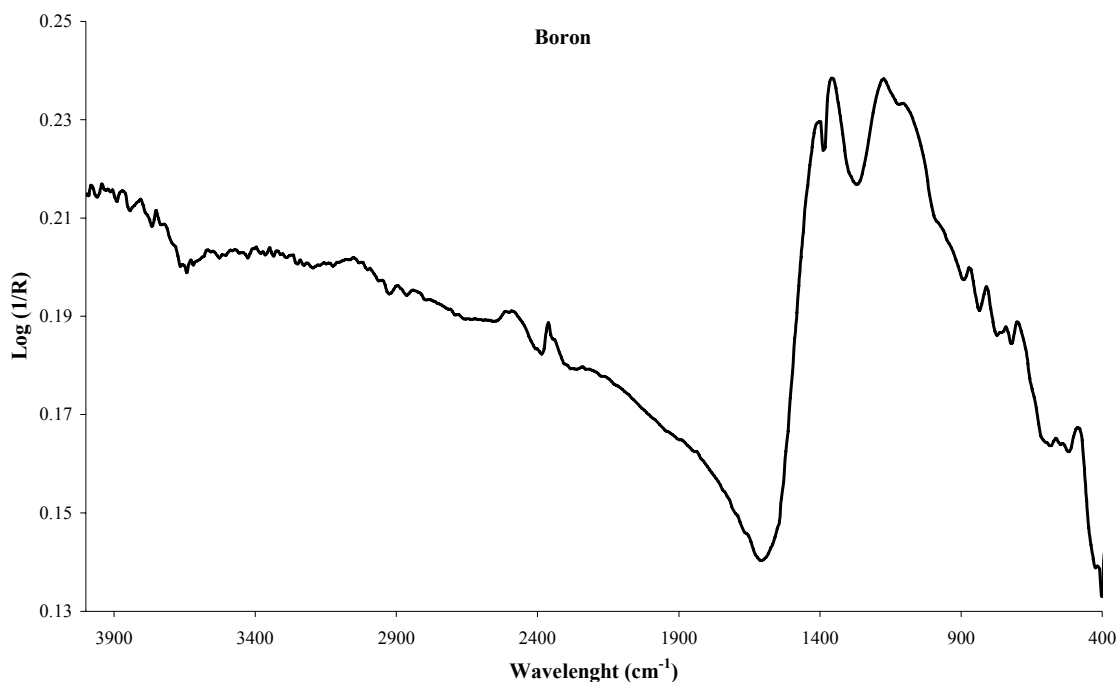


Figure 4.5. The DRIFT Spectrum for Pure Boron in KBr.

#### 4.2.1.1. Random Design

In order to prepare calibration models, 15 of 25 samples were used to build calibration set and the remaining 10 sample were reserved for validation set to test the performance of the models. The program was set to run 30 times with 50 genes and 100 iterations. That is, the GILS program was iterated 100 times in each run, full cross validation was applied during model building step to avoid possible overfitting problems.

The standard error of calibration (SEC) and the standard error of validation (SEP) results for calibration and prediction sets, respectively along with the average percent recoveries (APR) and associated standard deviation (SD) values for the data set are shown in Table 4.1. The following equations are used to calculate percent recovery (PR), APR and SD.

$$PR_i = \frac{\hat{c}_i}{c_i} \times 100\% \quad (4.1)$$

$$APR = \frac{\sum_{i=1}^m \frac{\hat{c}_i}{c_i} \times 100\%}{m} \quad (4.2)$$

$$SD = \sqrt{\frac{\sum_{i=1}^m (PR_i - APR)^2}{m-1}} \quad (4.3)$$

where  $c_i$  is the actual and  $\hat{c}_i$  is the predicted concentration of  $i^{\text{th}}$  sample for  $m$  number of samples as defined below.

Table 4.1. Parameters for Random Design of B.

Data Set	Parameters	Boron
Calibration Set	SEC (mg)	1.08
	APR	102.86
	SD	3.34
Validation Set	SEP (mg)	1.25
	APR	114.24
	SD	14.20

As seen in the Table 4.1, the SEC and SEP values ranged between 1.08 and 1.25 % by mass for boron. The APR values ranged between 102.86 and 114.24 % and SD values between 3.34 and 14.20 %.

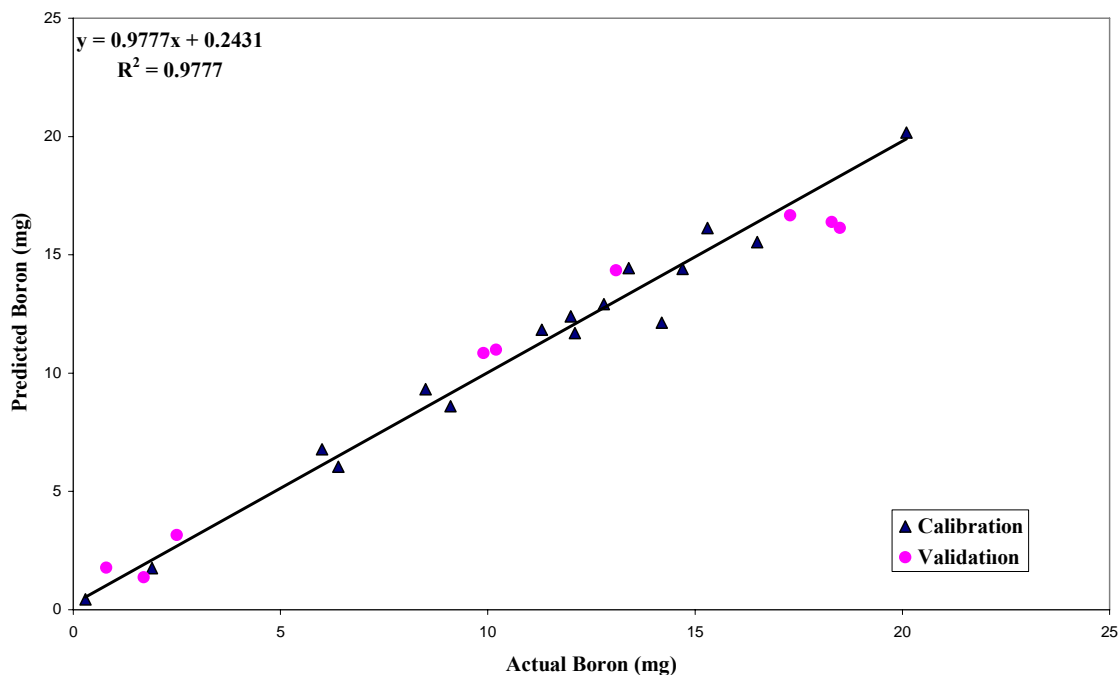


Figure 4.6. Actual versus GILS Predicted Concentration of Boron for Random Design.

The plot of actual versus DRIFTS predicted concentration for boron is illustrated in Figure 4.6. It is evident that the proposed method is able to predict boron in a wide range from 0.03 to 2.0 % by mass.

#### 4.2.1.2. Mixture Design

Binary mixtures of boron and boron oxide were used for analysis. Calibration model was prepared with 28 samples. 19 of 28 samples were used to build calibration set and the other 9 samples were reserved for validation set. The program was set to run 30 times with 50 genes and 100 iterations.

The SEC and SEP results for calibration and prediction sets, respectively along with the average percent recoveries (APR) and associated standard deviation (SD) values for the data set are shown in Table 4.2.



Table 4.2. Parameters for Mixture Design of B and B<sub>2</sub>O<sub>3</sub>.

Data Set	Parameters	Boron	Boron Oxide
Calibration Set	SEC (mg)	2.63	3.77
	APR	99.38	100.18
	SD	4.47	8.28
Validation Set	SEP (mg)	3.55	5.61
	APR	86.76	137.06
	SD	4.36	43.80

Table 4.2. shows that the SEC and SEP values ranged between 2.63 and 5.61 % by mass for both boron and boron oxide in the binary mixture. The APR values ranged between 89.76 and 137.06 %. SD values are between 4.47 and 43.8 % for both boron and boron oxide .

The plot of actual versus DRIFTS predicted concentration for boron is illustrated in Figure 4.7. Figure 4.8 shows the actual versus DRIFTS predicted concentration for boron oxide. Figure 4.7 shows that boron can be predicted in a range from 0.0 % to 2.8 % by mass.

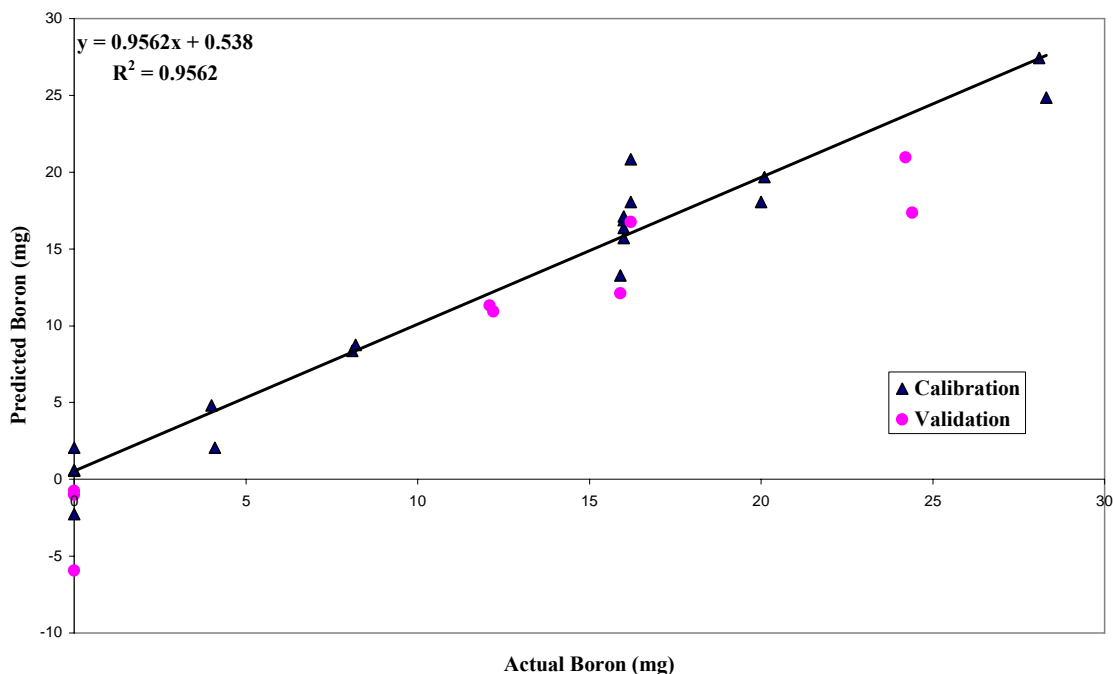


Figure 4.7. Actual versus GILS Predicted Concentration of Boron for Mixture Design.

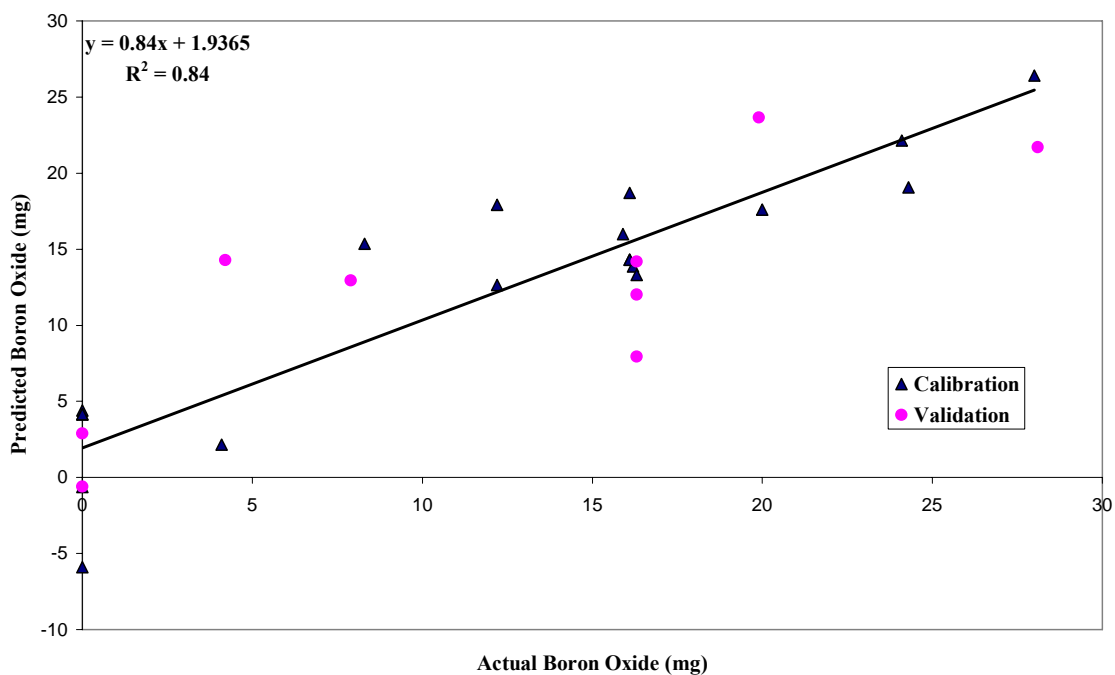


Figure 4.8. Actual versus GILS Predicted Concentration of Boron Oxide for Mixture Design.

#### 4.2.1.3. Random Mixture Design

Binary mixtures of B and B<sub>2</sub>O<sub>3</sub> were used for analysis. Calibration model was prepared with 30 samples. 20 of 30 samples were used to build calibration set and the other 10 samples were reserved for validation set. The program was set to run 30 times with 50 genes and 100 iterations.

Table 4.3. Parameters for Random Mixture Design of B and B<sub>2</sub>O<sub>3</sub>.

Data Set	Parameters	Boron	Boron Oxide
Calibration Set	SEC (mg)	1.72	2.64
	APR	101.86	104.05
	SD	3.06	4.30
Validation Set	SEP (mg)	2.29	3.19
	APR	104.83	101.21
	SD	6.45	8.80

As seen in the Table 4.3., the SEC and SEP values ranged between 1.72 and 3.19 % by mass for both boron and boron oxide in the binary mixture. The APR values ranged between 101.21 and 104.05 %. SD values are between 3.06 and 8.80 % for both boron and boron oxide .

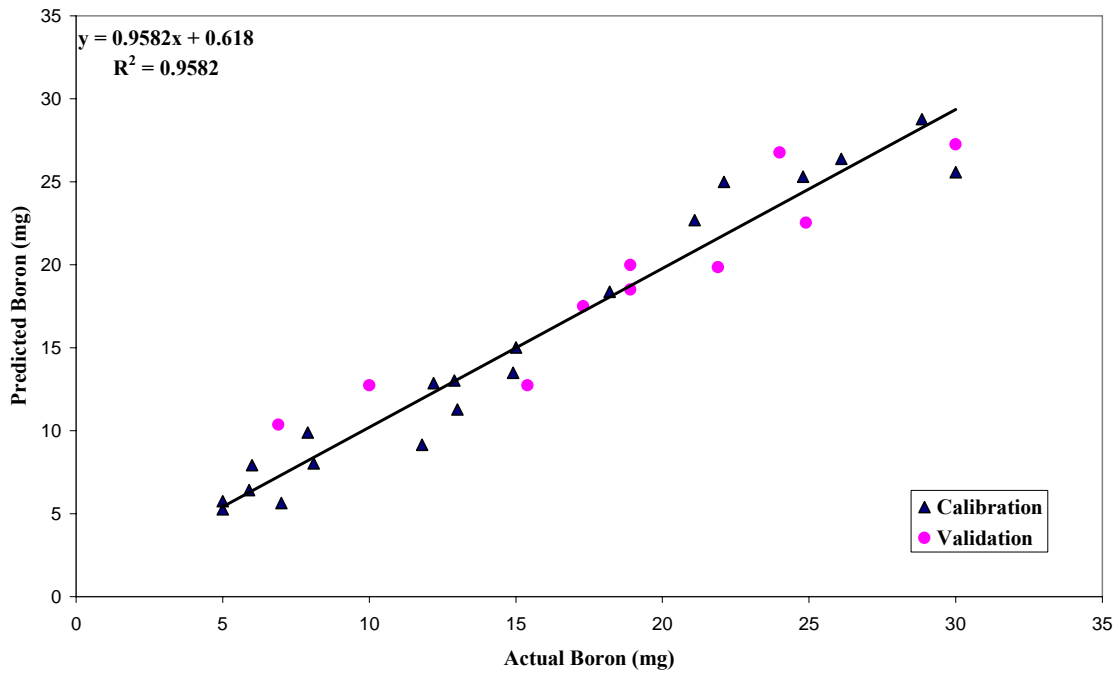


Figure 4.9. Actual versus GILS Predicted Concentration of Boron for Random Mixture Design.

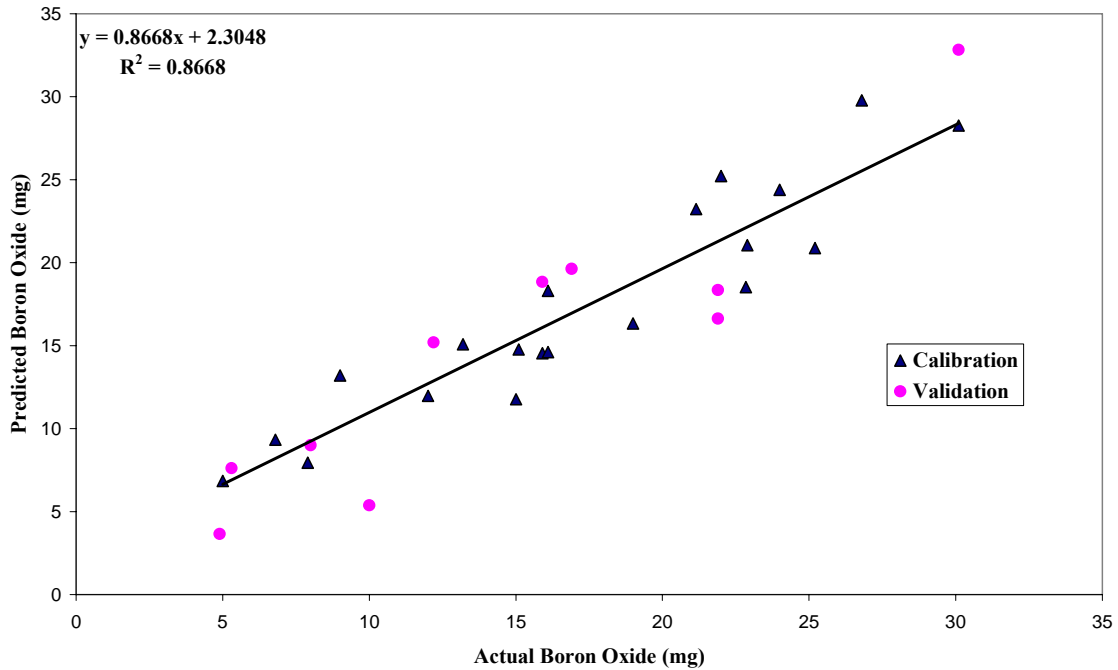


Figure 4.10. Actual versus GILS Predicted Concentration of Boron Oxide for Random Mixture Design.

Figure 4.9 shows that the actual versus DRIFTS predicted concentration for boron. The actual versus DRIFTS predicted concentration for boron oxide is illustrated in Figure 4.10. Figure 4.9 shows that boron amount can be predicted in a range from 0.5 % to 3.0 % by mass.

#### 4.2.1.4. Ternary Mixture Design

Ternary mixtures of B,  $B_2O_3$  and Al were used for analysis.

**a. For Fifty Samples;** In order to prepare calibration models, 30 of 50 samples were used to build calibration set and the remaining 20 sample were reserved for validation set to test the performance of the models. The program was set to run 30 times with 50 genes and 100 iterations.

Table 4.4. Parameters for Ternary Design of B, B<sub>2</sub>O<sub>3</sub> and Al for Fifty Samples.

Data Set	Parameters	Boron	Boron Oxide	Aluminum
Calibration Set	SEC (mg)	4.03	4.11	6.85
	APR	102.78	104.09	107.75
	SD	4.37	4.56	6.32
Validation Set	SEP (mg)	5.13	5.54	6.28
	APR	103.03	99.15	114.09
	SD	4.59	7.29	11.86

Table 4.4 shows that the SEC and SEP values ranged between 2.63 and 5.61 % by mass for both boron, boron oxide and aluminum in the ternary mixture. The APR values ranged between 99.15 and 114.09 %. SD values are between 4.37 and 11.86 % for ternary mixture

The plot of actual versus DRIFTS predicted concentration for boron is illustrated in Figure 4.11. Figure 4.12 shows that the actual versus DRIFTS predicted concentration for boron oxide and Figure 4.13 indicates that the actual versus DRIFTS predicted concentration for aluminum. Figure 4.11 shows that boron can be predicted in a range from 0.5 % to 5.0 % by mass.

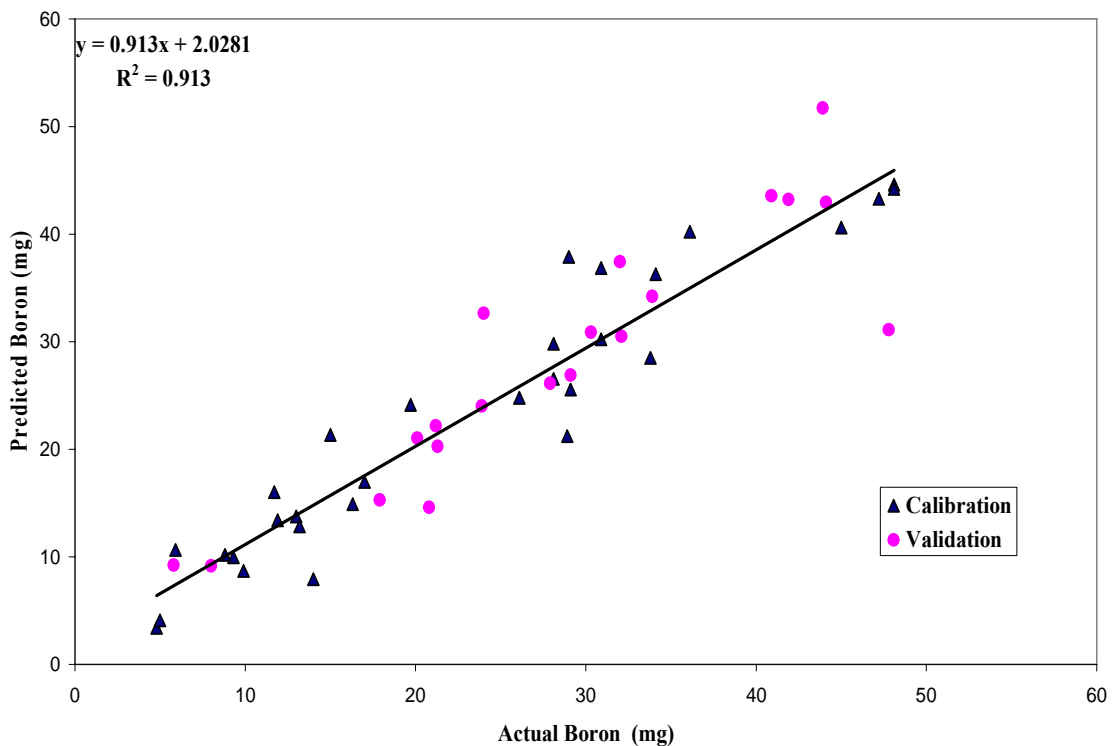


Figure 4.11. Actual versus GILS Predicted Concentration of Boron for Fifty Samples.

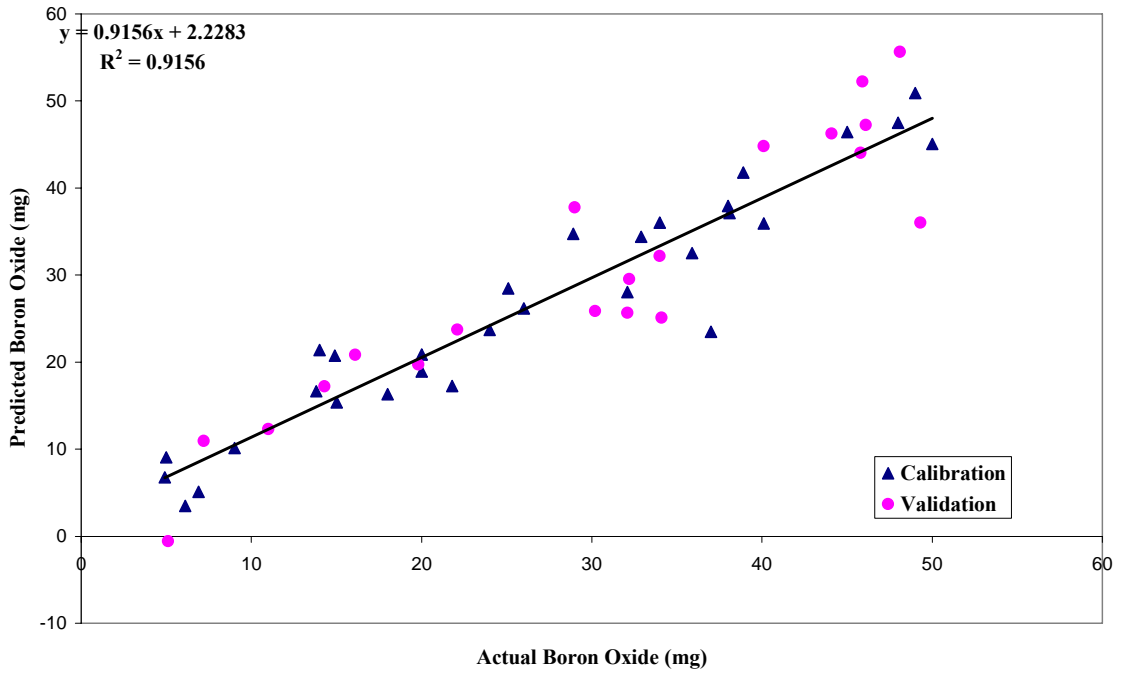


Figure 4.12. Actual versus GILS Predicted Concentration of Boron Oxide for Fifty Samples.

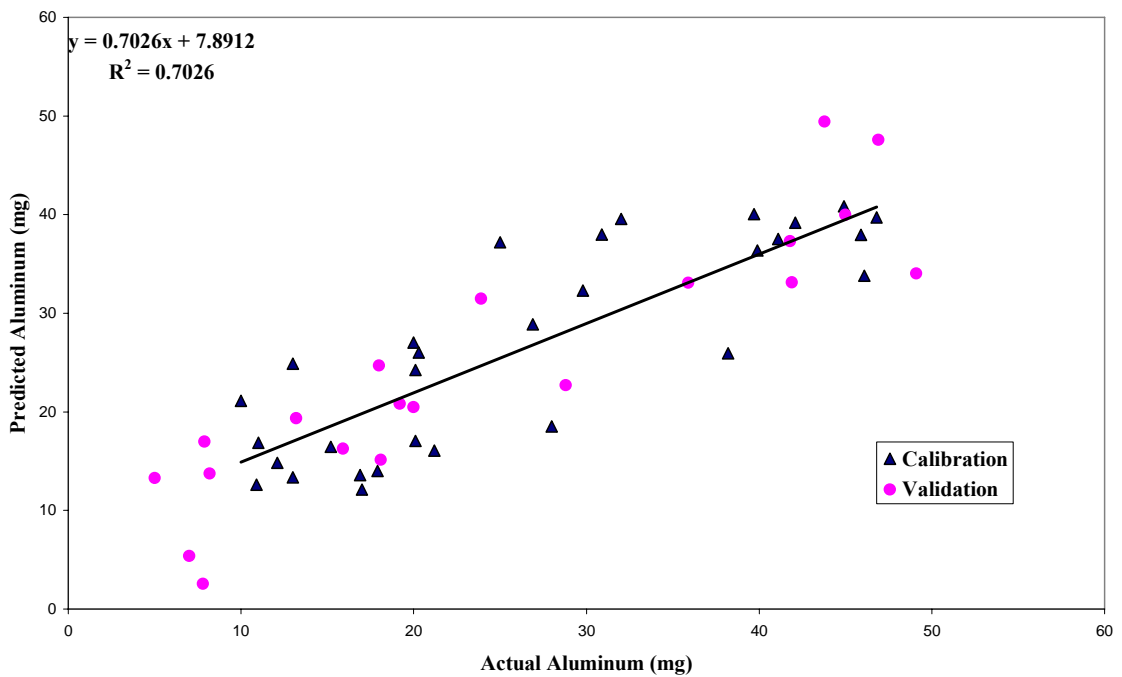


Figure 4.13. Actual versus GILS Predicted Concentration of Aluminum for Fifty Samples.

**b. For a Hundred Samples;** Two sets in step a were combined, because GILS gives better results when there is more data. Calibration model was prepared with 100 samples. 55 of 100 samples were used to build calibration set and the other 45 samples were reserved for validation set. The program was set to run 30 times with 50 genes and 100 iterations.

Table 4.5. Parameters for Ternary Design of B, B<sub>2</sub>O<sub>3</sub> and Al for Hundred Samples.

Data Set	Parameters	Boron	Boron Oxide	Aluminum
Calibration Set	SEC (mg)	0.15	2.21	3.77
	APR	100.01	100.51	103.30
	SD	0.10	1.70	2.88
Validation Set	SEP (mg)	3.21	4.29	5.23
	APR	105.57	100.23	104.62
	SD	4.01	3.06	4.44

As seen in the Table 4.5, the SEC and SEP values ranged between 0.15 and 35.23 % by mass for boron, boron oxide and aluminum in the ternary mixture. The APR values ranged between 100.01 and 105.57 % . SD values are between 0.10 and 4.44 % for boron, boron oxide and aluminum.

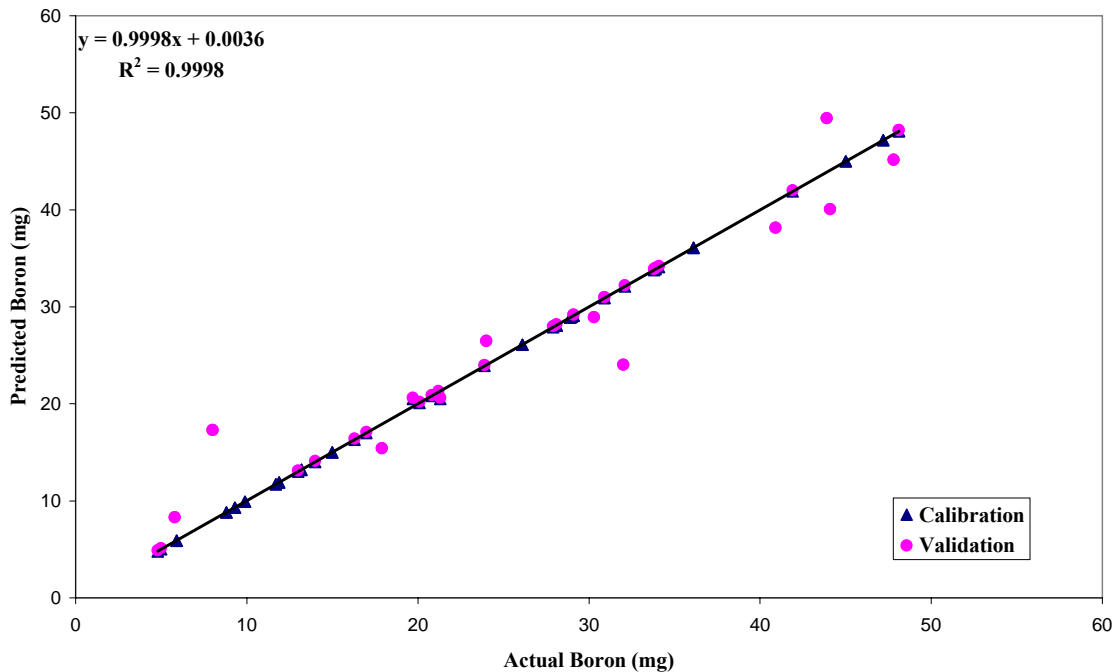


Figure 4.14. Actual versus GILS Predicted Concentration of Boron for Hunred Samples.

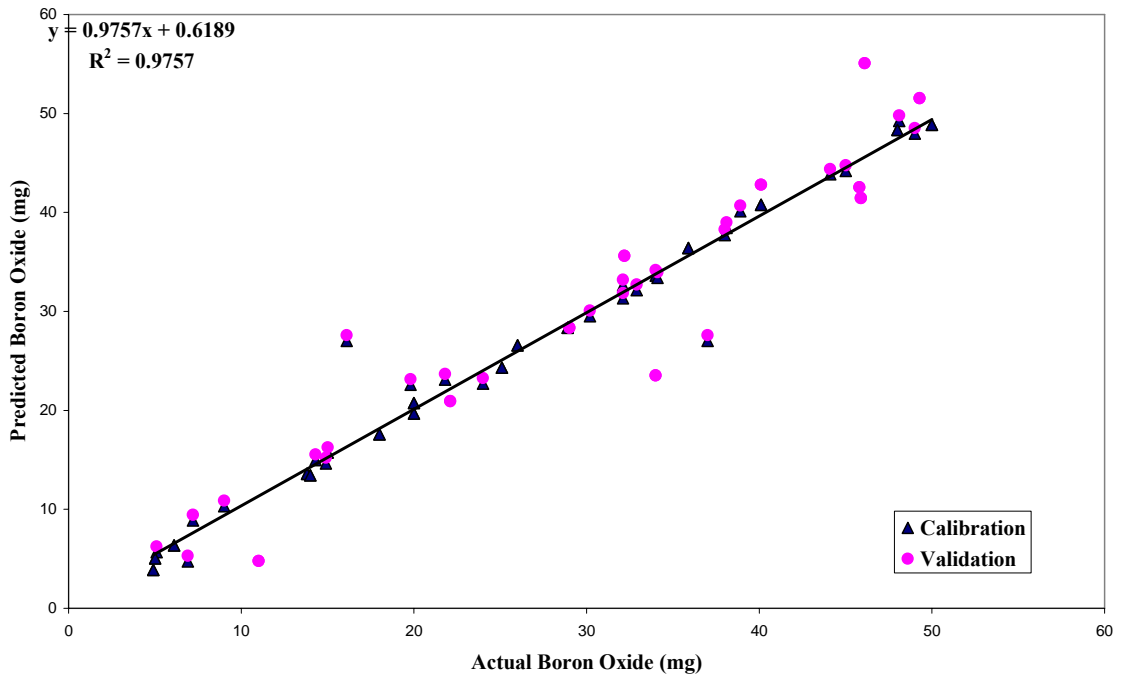


Figure 4.15. Actual versus GILS Predicted Concentration of Boron Oxide for Hundred Samples.

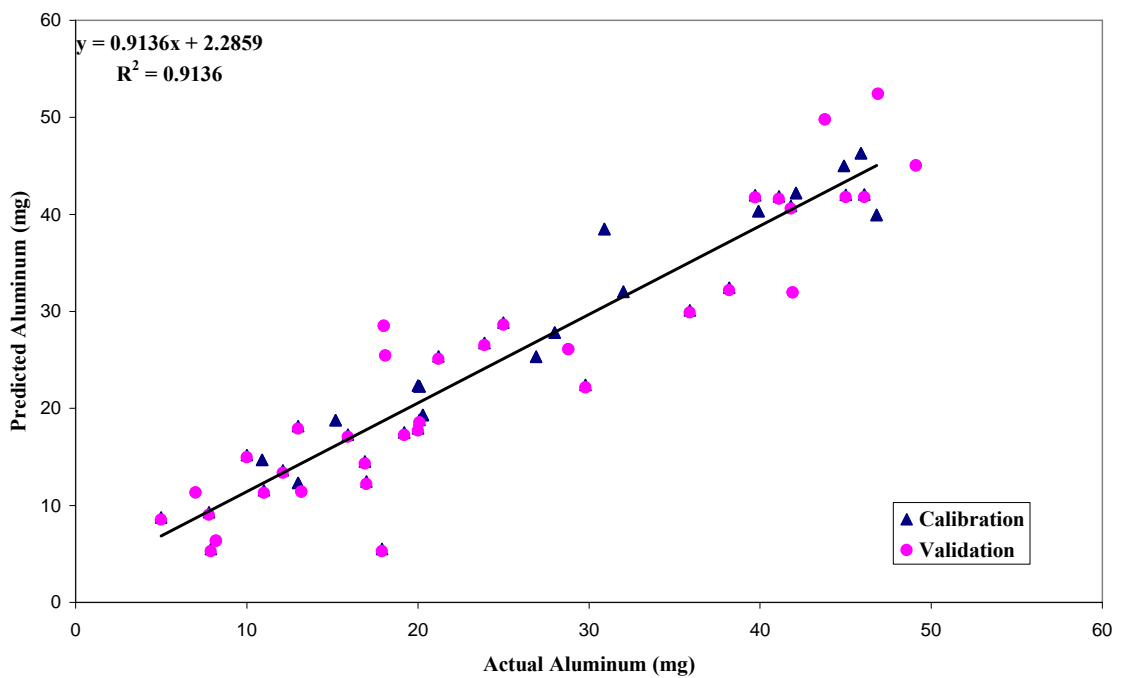


Figure 4.16. Actual versus GILS Predicted Concentration of Aluminum for Hundred Samples.



Figure 4.14 shows the actual versus DRIFTS predicted concentration for boron. The actual versus DRIFTS predicted concentration for boron oxide is illustrated in Figure 4.15 and 4.16 show that the actual versus DRIFTS predicted concentration for aluminum. Figure 4.14. shows that boron can be predicted in a range from 0.5 % to 5.0 % by mass.

**c. For Twenty Five Samples;** In this step, KBr amount was increased and transmittance was enhanced by this way. Calibration model was prepared with 25 samples. 17 of 25 samples were used to build calibration set and the other 8 samples were reserved for validation set. The program was set to run 30 times with 50 genes and 100 iterations.

Table 4.6. Parameters for Ternary Design of B, B<sub>2</sub>O<sub>3</sub> and Al for Twenty-five Samples.

Data Set	Parameters	Boron	Boron Oxide	Aluminum
Calibration Set	SEC (mg)	2.99	0.32	2.81
	APR	100.49	100.39	101.49
	SD	3.92	0.45	3.72
Validation Set	SEP (mg)	4.04	3.25	5.21
	APR	108.83	101.40	98.82
	SD	7.83	8.22	11.08

As seen in the Table 4.6, the SEC and SEP values ranged between 2.99 and 35.21% by mass for both boron, boron oxide and aluminum in the ternary mixture. The APR values ranged between 98.82 and 108.83 % . SD values are 0.45 and 11.08 % for boron, boron oxide and aluminium

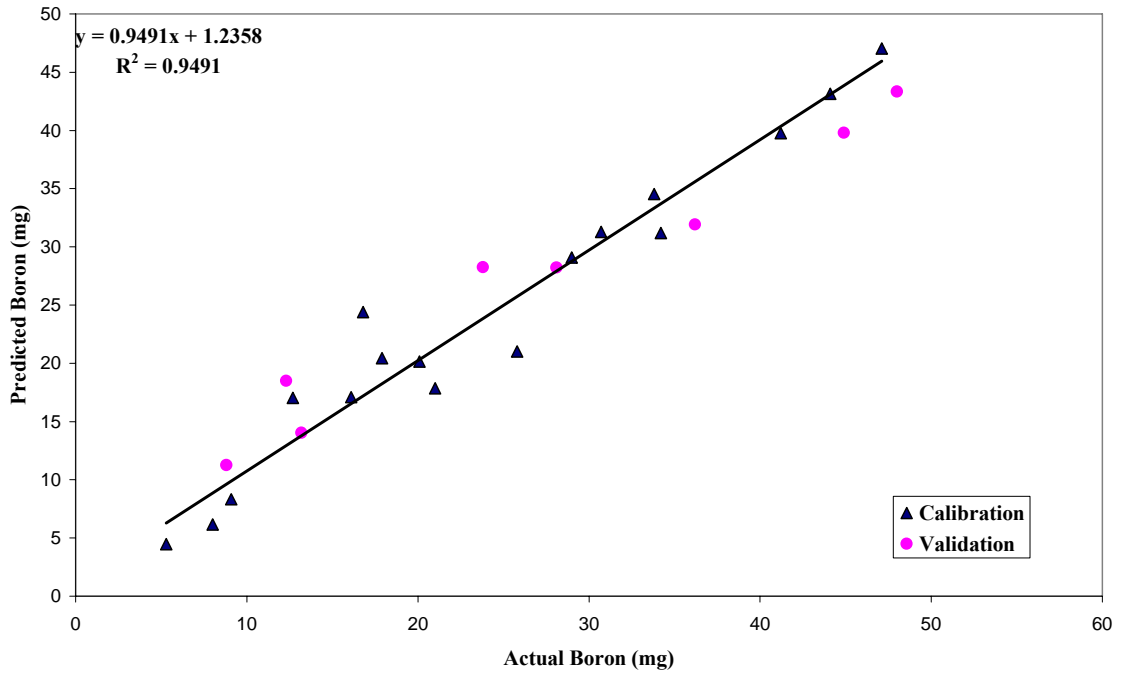


Figure 4.17. Actual versus GILS Predicted Concentration of Boron for Twenty-five Samples.

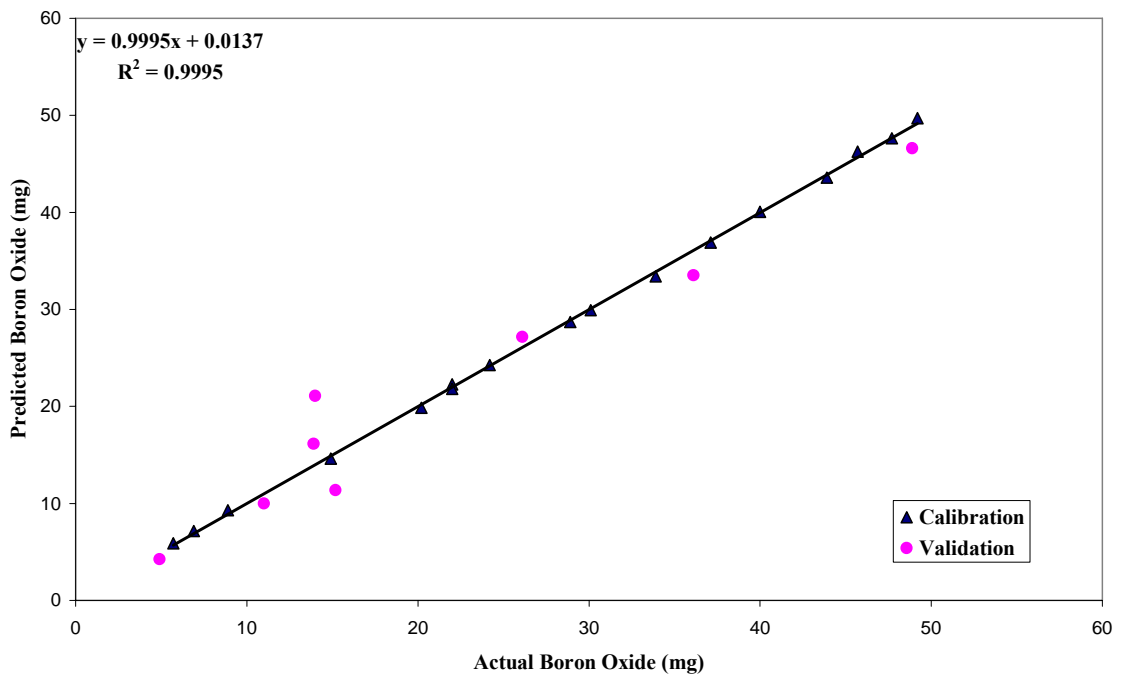


Figure 4.18. Actual versus GILS Predicted Concentration of Boron Oxide for Twenty-five Samples.

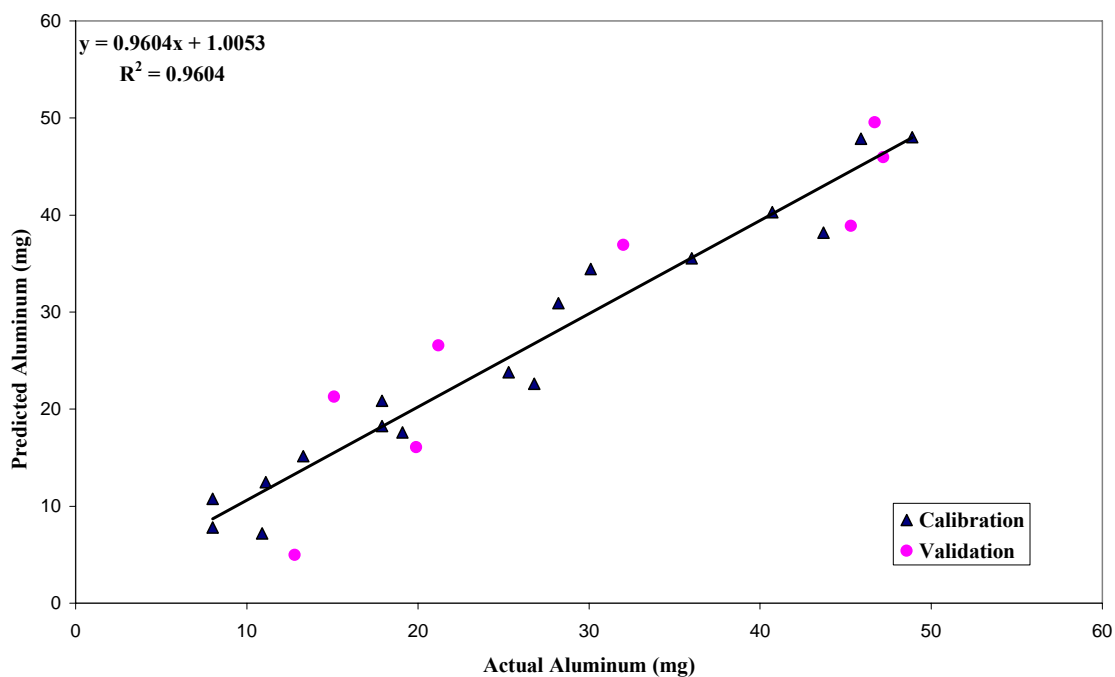


Figure 4.19. Actual versus GILS Predicted Concentration of Aluminum for Twenty-five Samples.

Figure 4.17 shows the actual versus DRIFTS predicted concentration for boron. The actual versus DRIFTS predicted concentration for boron oxide is illustrated in Figure 4.18. Figure 4.19 shows the actual versus DRIFTS predicted concentration for aluminum. Figure 4.17 shows that boron can be predicted in a range from 0.5 % to 5.0 % by mass in the ternary mixture.

**d. For Produced Samples;** 25 samples were prepared for calibration model. Original sample data were checked with calibration set data, and boron presence in the original samples were investigated. However no meaningful results could be obtained.

Figure 4.20 indicates that the DRIFTS spectrum of calibration sample and the DRIFTS spectrum of produced sample illustrated in Figure 4.21. As is seen from both spectra, visual control of the peaks do not yield meaningful results either. Therefore presence of boron could not be identified in this way either.

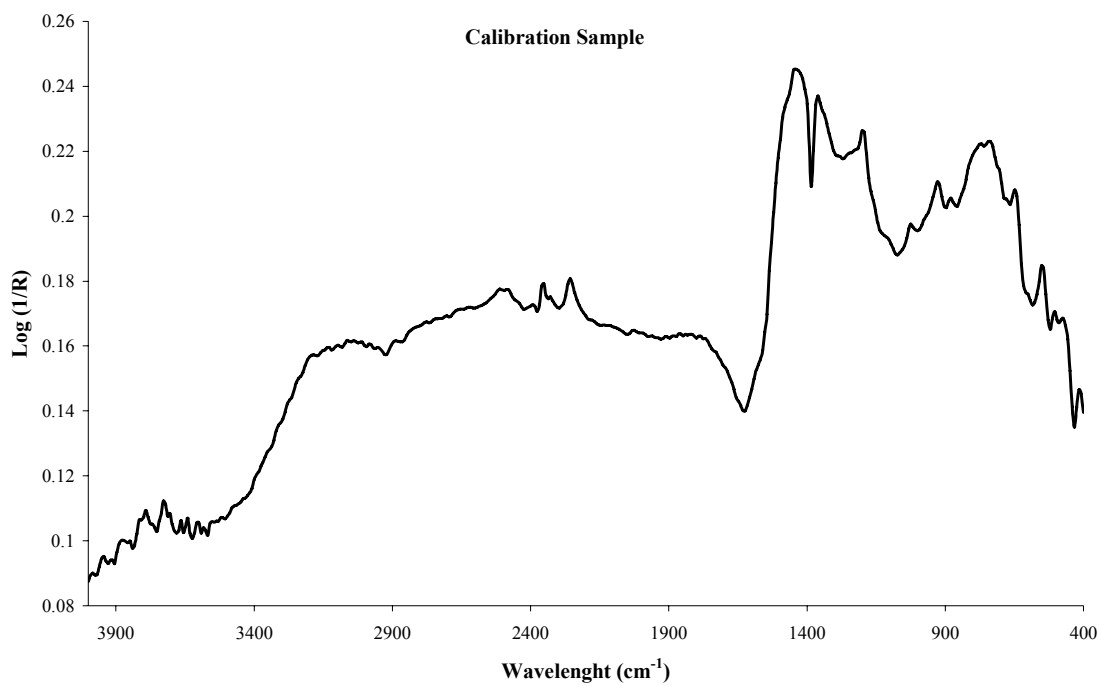


Figure 4.20. The DRIFT Spectrum of Calibration Sample.

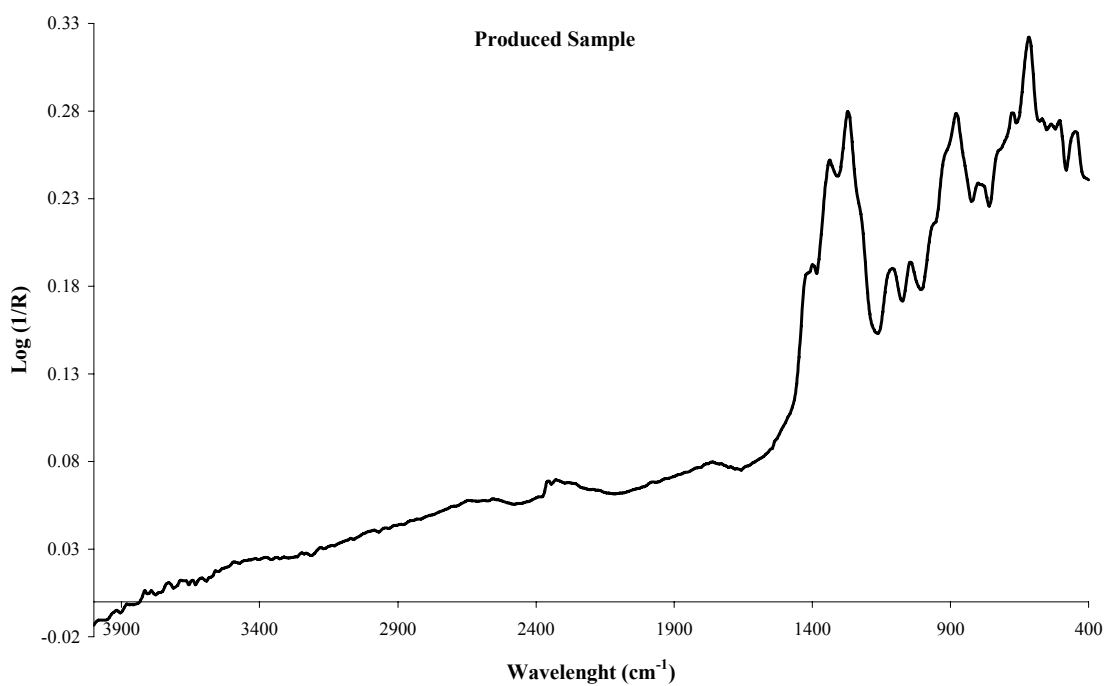


Figure 4.21. The DRIFT Spectrum of Produced Sample in Tube Furnace.

## CHAPTER 5

### CONCLUSION

In this study, mainly the reaction of boron oxide with aluminum was investigated to obtain elemental boron. A new method to determine boron purity directly in the mixture was also developed.

Studies progressed in two stages.

1) Experiments were carried out for the investigation of the reaction of boron oxide with aluminum. For this purpose, different furnaces were used and temperature, time and reaction stoichiometry effect were investigated.

\* When working with the muffle furnace no distinct change was observed. It was found that this type of furnace was not suitable for the reaction. The temperature was controlled but heating rate was slow. The main drawback is the absence of inert gas medium, therefore open to extra reaction with air oxygen.

\* In the study with the microwave oven, heating and reaction rate is fast but with our facilities we had an inadequate oven set up. We could not maintain temperature control and inert atmosphere in the oven. Therefore undesirable aluminium borate compounds formed in the reaction. Moreover, these compounds could not be removed from the mixture and analysis of boron could not be fulfilled.

\* In the tube furnace, different temperatures, different reaction times and different mixtures were investigated but could not be optimized for boron synthesis. Undesirable compounds could not be removed from the reaction mixture by leaching, so boron presence could not be evidenced. If any boron formed in reaction mixture, boron percentage could not be measured. The experiments with the tube furnace can be improved and better results can be obtained.

2) In the second part of study, the new method with DRIFTS coupled with genetic multivariate calibration was tried for the determination of boron in the reaction mixture. Different calibration models were designed.

\* In the first stage, calibration model was build for only boron. Results show that model works well for determination of boron.

\* In the second stage, determination of boron and boron oxide was investigated. Boron amount could be determined fairly well, but same improvement could not be achieved for boron oxide.

\* In the study for the ternary data set, the GILS method is also successful in the prediction of boron content in the mixture and random mixture design set.

\* When there is more data, model gives better results. In addition, when samples are mixed with more KBr, results are better because of high transmittance.

For boron synthesis with aluminum reduction, thermochemical data is not so much in favour of the reaction of boron oxide with aluminum ( $\Delta H = -402.7$  kJ/mol). Therefore direct reduction of boron oxide with aluminum does not seem so feasible. In our studies, we tried to change the experimental conditions (mixture ratio, inert atmosphere, etc.) to obtain boron. However we could not achieve the desired conditions as we expected, and boron oxide reduction did not proceed to a measurable extent. If better facilities and satisfactory conditions can be fulfilled, we think that satisfactory results can be obtained.

The success of this study was achieved by setting up a new method for the direct determination of boron in solid samples.

## REFERENCES

- Beebe, K.R., and Kowalski, B.R., 1987. "An Introduction to Multivariate Calibration and Analysis", *American Chemical Society*, Vol. 59, No. 17.
- Brereton, R.G. 2000. "Introduction to Multivariate Calibration In Analytical Chemistry", *The Royal Society of Chemistry*, Vol. 125, pp. 2125-2154.
- Budavari, S. et al., 1989. *The Merck Index*, (Rahway, Merck and Co., Inc., 11<sup>th</sup> Edition).
- Butterwick, L., De Oude, N., Raymond, K., 1989. "Safety Assessment of Boron in Aquatic and Terrestrial Environment", *Ecotoxicology and Environmental Safety*. Vol.17, pp. 339-371.
- Cueilleron, J., and Viala, J.C., 1979. "The Chemical and Pyrometallurgical Purification of  $\beta$ -Rhombohedral Boron", *Journal of the Less-Common Metals*, Vol. 67, pp. 333-337.
- European Centre for Ecotoxicology and Toxicology of Chemicals, 1995. "Ecotoxicology of Some Inorganic Borates" Special Report, SrNo.11.
- Haaland, D.M., and Thomas, E.V., 1988 "Partial Least-Squares Methods for Spectral Analyses. 1. relation to Other Quantitative Calibration Methods and The Extraction of Qualitative Information", *Analytical Chemistry*, Vol.60, No. 11.
- Hibbert, D.B., 1993. "Genetic Algorithms in Chemistry", *Chemometrics and Intelligent Laboratory Systems*, Vol.19, pp. 277-293.
- Houmes, J.D., and Loye, H.C. 1997., "Microwave Synthesis of Ternary Nitride Materials", *Journal Of Solid State Chemistry* , Vol. 130, pp. 266-271.
- Jesus, D.P., Saito, R.M., Lago, C.L., 2004. "Determination of Boron in Natural Water and Products Derived from Grape Using an Automated Flow Injection Analysis System with Piezoelectric Detection ", *J. Braz. Chem. Soc.* Vol. 15, pp.754-718.
- Kalafatoğlu, İ.E., and Örs, S.N., 2003. "21. Yüzyılda Bor Teknolojileri ve Uygulamaları" BAÜ Fen Bil. Enst. Derg. 5.1
- Kar, Y., Şen, N., Demirtaş, A., 2006. "Boron Minerals in Turkey, Their application Areas and Importance For The Country's Economy ", *Minerals & Energy*. Vol. 3-4, pp. 2-10.
- Kılıç, A.M., 2004. "Importance of Boron Mine for Turkey and Place in the Future" Proceedings of the 2nd International Boron Symposium, Eskişehir, (23-25 September 2004) p. 34.
- Lucasius, C.B., and Kateman, G., 1991. "Genetic Algorithms for Large-Scale Optimization in Chemometrics an Application", *Trends in Analytical Chemistry*, Vol. 10, No. 8.

- Lucasius, C.B., and Kateman, G., 1993. "Understanding and Using Genetic Algorithms Part 1. Concepts, Properties and Context", *Chemometrics and Intelligent Laboratory Systems*, Vol.19, pp. 1-33.
- Lyday, P.A., 2004. "Boron", US Geological Survey Minerals Yearbook.
- Mark, F.H., Mcketta, J.J., Othmer, D.F., 2001. "Boron Alloys", in *Kirk-Othmer Encyclopedia of Chemical Technology*, pp.602-612.
- Mendez, U.O, Kharissova, O.V., Rodriguez, M., 2003. "Synthesis and Morphology of Nanostructures Via Microwave Heating", *Rev. Adv. Mater. Sci.*, Vol. 5, pp. 398-402.
- Greenwood, N.N., 1973. "Boron, " in J. C. Bailar (ed.): *Comprehensive Inorganic Chemistry*, Pergamon Press, Oxford-New York, Vol. 1, pp. 680-689.
- Özdemir, D., 1999. PhD Thesis: "Multi – Instrument Calibration Using Genetic Regression in UV-Visible and Near Infrared Spectroscopy", *Clemson University* pp. 55-79.
- Özdemir, D., And Öztürk, B., 2007. "Near Infrared Spectroscopic Determination Of Olive Oil Adulteration with Sunflower and Corn Oil ", *Journal of Food and Drug Analysis*, Vol.15, No. 1.
- Ragno, G., Ioele, R., Risolli, A., 2004. "Multivariate Calibration Techniques Applied to the Spectrophometric Analysis of One-to-Four Component Systems", *Analytica Chimica Acta*, Vol. 512, pp. 173-180.
- Rodriguez, M., Kharissova, O.V., Mendez, U.O., 2004. "Formation of Boron Carbide Nanofibers and Nanobelts From Heated by Microwave", *Rev. Adv. Mater. Sci.*, Vol. 7, pp. 55-60.
- Putkonen, M., and Niinistö, L., 2006. "Atomic Layer Deposition of B<sub>2</sub>O<sub>3</sub> Thin Films at Room Temperature", *Thin Solid Films*. Vol. 514, pp. 145-149.
- Sah, R.N., and Brown, P.H., 1997. "Techniques for boron determination and their application to the analysis of plant and soil samples", *Plant and Soil*. Vol. 193, pp. 15-33.
- Sarıca, D.Y., and Ertuş, N., 2001. "Flow Injection Analysis for Boron Determination by Using Methyl Borate Generation and Flame Atomic Emission Spectrometry", *Turk J Chem*. Vol. 25, pp.305 - 310.
- Shapiro, A.I., 2003. "The Role of Epithermal Neutrons in AGB stars: Boron Synthesis", *Astronomy Letters*. Vol. 30, No. 6.
- Sugaya, T., 1976. "Preparation and Crystal Structure of Solid Boron Grown from the BBr<sub>3</sub>-H<sub>2</sub> Mixture", *Journal of the Less-Common Metals*, Vol. 47, pp. 49-54.
- Thomas, E.V., 1994. "A Primer on Multivariate Calibration", *American Chemical Society*, Vol. 66, No. 15.



- Thomas, E.V., and Haaland, D.M., 1990. "Comparison of Multivariate Calibration Methods for Quantitative Spectral Analysis", *Analytical Chemistry*, Vol.62, pp. 1091-1099.
- Tsagareishvili, G.V., Oganezov, K.A., Bairamashvili, I.A., Khvedelidze, G.A., Mazmishvili, G.A., Chepelev, V.V, tabutsidze, M.L., 1979. " The Relationship Between the Concentrations of Hydrogen, Nitrogen, and Oxygen in Melted Boron", *Journal of the Less-Common Metals*, Vol. 67, pp. 419-424.
- Vandenbulcke, L., and Vuillard, G., 1979. " Polymorphismin Boron Deposited by the H<sub>2</sub> Reduction of BCl<sub>3</sub>", *Journal of the Less-Common Metals*, Vol. 67, pp. 65-78.
- WEB\_1, 2006. Nationmaster web site, 08/03/2006.  
<http://www.nationmaster.com/encyclopedia/Boron>
- WEB\_2, 2007. Webelements web site, 22.03.2007.  
<http://www.webelements.com/webelements/elements/text/B>
- WEB\_3, 2006. Wikipedia, 11/5/2006.  
<http://en.wikipedia.org/wiki/x-ray-crystallography>
- WEB\_4, 2006. Surface Science Western web site, 11/5/2006.  
<http://www.uwo.ca/ssw/services/sem.html>
- WEB\_5, 2007. Wikipedia, 2/4/2007.  
<http://en.wikipedia.org/wiki/Aluminium>
- WEB\_6, 2007. Northwestern web site, 3/4/2007.  
<http://www.nuance.northwestern.edu/KeckII/ftir1.asp>
- WEB\_7, 2007. Northwestern web site, 3/4/2007.  
<http://www.nuance.northwestern.edu/KeckII/ftir7.asp>
- WEB\_8, 2007.Safetyemporium web site, 3/4/2007.  
<http://www.nuance.Synthetic Equipment Furnaces.htm>
- WEB\_9, 2007.WCAS web site, 26/5/2007.  
<http://www.wcaslab.com/tech/tbftir.htm>
- WEB\_10, 2006.David Reid web site, 28/10/2006.  
<http://www.home.c2i.net/metaphor/mvpage.htm>
- Wopenka, B., Freeman, J.J., Grew, E., 1999. "Raman Spectroscopic Identification of B-Free and B-Rich Kornerupine (Prismatine) ", *American Mineralogist*, Vol. 84, pp. 550-554.
- Ullmann's Encyclopedia of Industrial Chemistry, 2002. Sixth Edition, WILEY-VCH, Boron Compounds.