

IDENTIFICATION OF SODIUM BOROHYDRIDE FROM SOLID REACTION PRODUCTS

Sevgi FETTAH

R&D Engineer

Mustafa Deniz KOZLU

Prof. Dr. Beycan IBRAHIMOGLU

Prof. Dr. Sadig KULIYEV

VESTEL Defense Industry, R&D Department, Ankara, TURKEY

OUTLINE

- Introduction
- Advantages of Sodium Borohydride
- Usages of Sodium Borohydride
- Our Aim Is...
- Sodium Borohydride Synthesis and Identification Process
- Methods
- Experimental Apparatus
- Quantitative Identification of Sodium Borohydride
- Results

INTRODUCTION

Hydrogen usage as an alternative energy source to fossil fuels has been winning ground in the last few years.

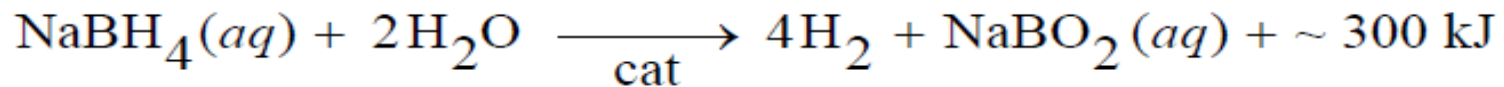
For widespread use of hydrogen energy it is necessary to develop hydrogen storage systems which are safe, capable of storing large amounts in small volumes.

The **storage of hydrogen** is obtained by various methods:

- pressurized tanks,
- liquefaction at low temperatures,
- metal hydrides or with chemicals, etc.
- Sodium borohydride (NaBH_4) has been demonstrated as an **effective, safe, efficient** hydrogen storage material.

INTRODUCTION

- NaBH₄ contains 10,5% hydrogen by weight & in order to release the hydrogen, it is necessary to be **hydrolyzed with water**.



- The hydrolysis of NaBH₄ is an exothermic reaction that releases **hydrogen** gas.
- 1 gr of NaBH₄ releases **~2,6 L of H₂** at room temperature.
- A hydrolysis reaction takes place only when an alkaline NaBH₄ solution is in contact with certain **catalysts** such as ruthenium, platinum, palladium, nickel, cobalt, carbon nanotubes etc.

INTRODUCTION

- NaBH₄ does not occur in nature; therefore it has to be synthesized.
- Generally NaBH₄ is produced by **ball milling** and **mechano-chemical** methods with the participation of H₂ and other reducing agents.
- Commercial chemical methods for NaBH₄ synthesis are; **Brown-Schlesinger process**, **Bayer process** and **Japan-Toyota process**.
- Identification of synthesized NaBH₄ from reaction products is also very important for controlling processes.
- In this presentation, identification of **mechano-chemically** synthesized sodium borohydride from the solid reaction products will be presented.
- **X-Ray Diffraction** technique has been used for the **qualitative** identification; **cyclic** and **linear voltammetry** techniques have been used for **quantitative identification** of the synthesized product from solid reaction mixture.

ADVANTAGES OF SODIUM BOROHYDRIDE

The advantages of hydrogen storage using NaBH_4 are:

- Sodium borohydride solutions in alkali medium are **stable** for a long time,
- Sodium borohydride solutions are **non-flammable**,
- The volumetric and gravimetric hydrogen storage capacity of NaBH_4 is **high**,
- The hydrogen **production from** NaBH_4 can be controlled easily,
- The by-product NaBO_2 (sodium metaborate) can be **recycled back** to NaBH_4 .

USAGES OF SODIUM BOROHYDRIDE

Sodium borohydride is used in various **industrial** applications:

- paper,
- textile,
- ceramic,
- porcelain,
- drugs,
- perfume,
- rocket and jet fuels, etc.

which makes it a **precious** industrial chemical.

OUR AIM IS...

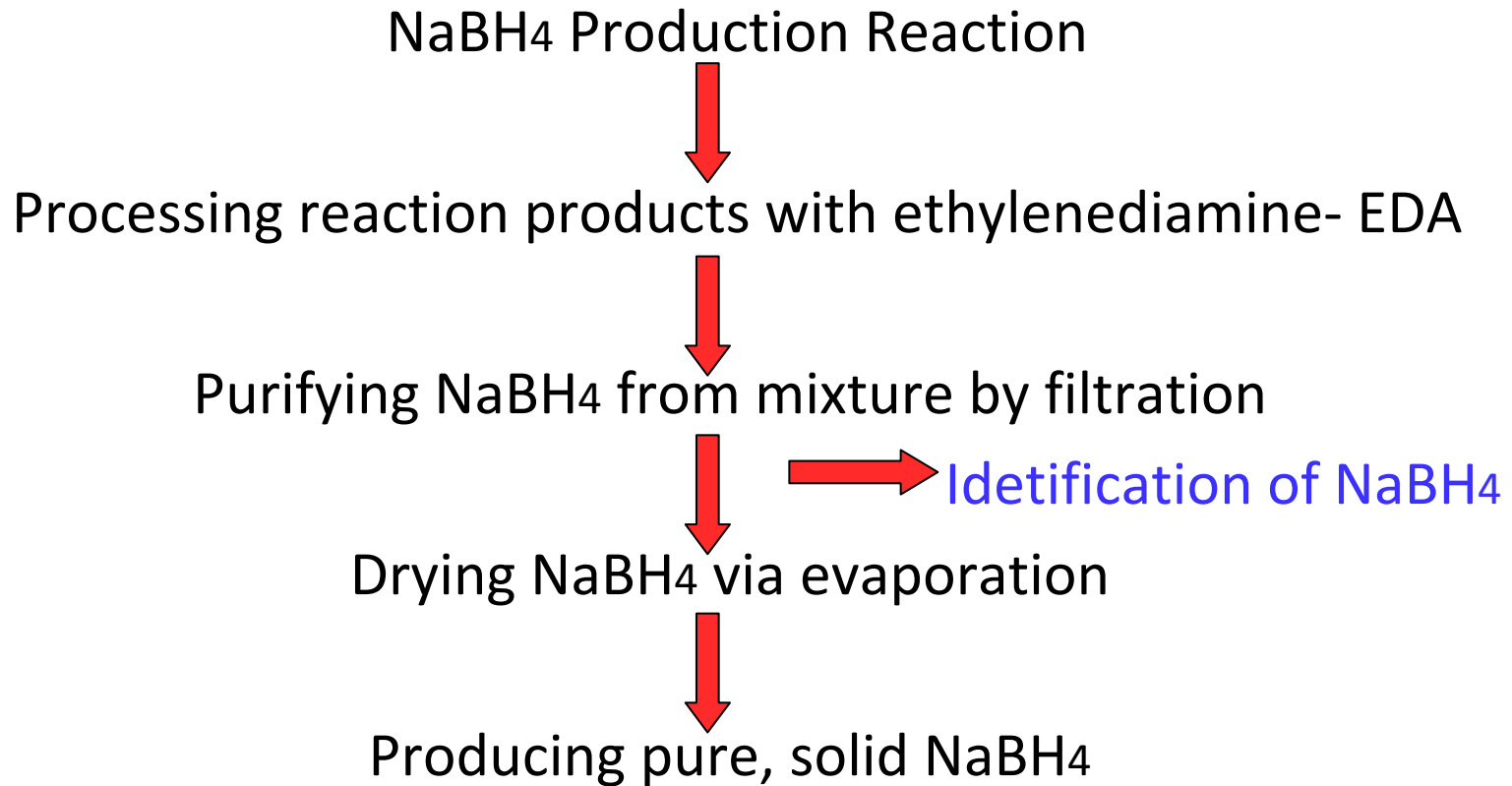
We made an analyze method based on literature survey:

- Oxidation of NaBH_4 in Au electrode between a specific potential range in an alkaline solution.
- Experimental results for identification of NaBH_4 in an alkaline solution.

From this information we want to:

- Investigate electrochemical behaviour of the NaBH_4 in etylenediamine (EDA) medium using linear and cyclic voltammetry.
- Develop analysing method for identification of NaBH_4 .

SODIUM BOROHYDRIDE SYNTHESIS And IDENTIFICATION PROCESS



METHODS

- Electrochemical experiments done by IVIUMStat potentiostat and BAS C3 cell stand.
- All the experiments made with 3 electrode electrochemical cell at 25 oC temperature.
- Surface of the Au electrode cleared with special pastes, then washed with pure alcohol and distilled water.
- Electrochemical activation of electrodes done before experiments.

EXPERIMENTAL APPARATUS



SODIUM BOROHYDRIDE SYNTHESIS And IDENTIFICATION PROCESS

- For removing the sodium borohydride from reaction product, **etylenediamine** was used as a solubiliser.

First step of the investigation was;

- Development of potentiometric method using some metals and glassy carbon indicator electrode.
- Investigation of electrode potentials in EDA-NaBH₄ medium.

QUANTITATIVE IDENTIFICATION of SODIUM BOROHYDRIDE

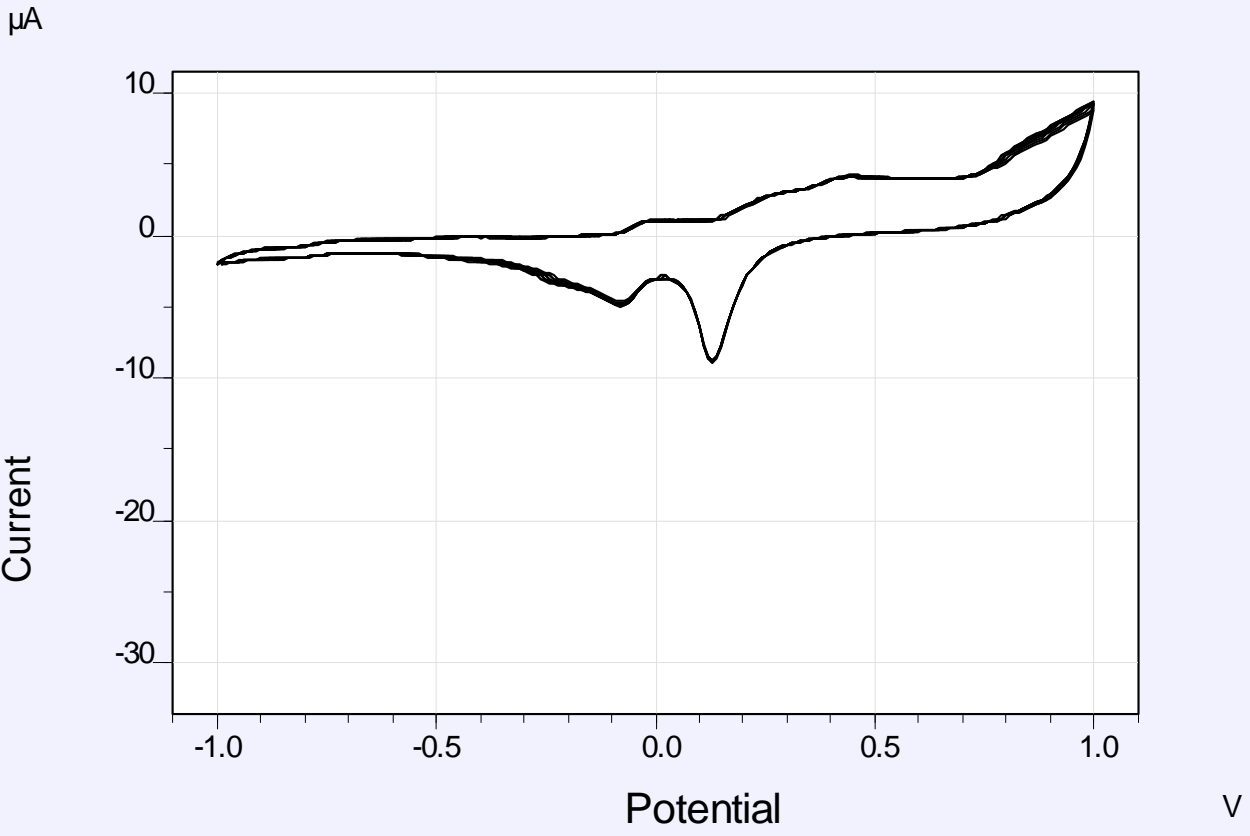


Figure 1. Cyclic voltammetry of Au electrode in 1 N NaOH solution
 ● E= -1.0/ +1.0 V, Scan rate : 0.05 V/s

● Between -1.0/+1.0 V potential range, (for reference electrode Ag/AgCl) in the **anodic semi-cycle** surface oxidation can occur, after that oxygen leaves the surface approximately at 1.0 V potential.

● On the **cathode semi-cycle**, easily seen that at least two oxides can be.

Two peaks shows that oxides reduction can occur at E= 0.1 V and = - 0.1 V potentials.

THE EFFECT OF ETHYLENDIAMINE (EDA)

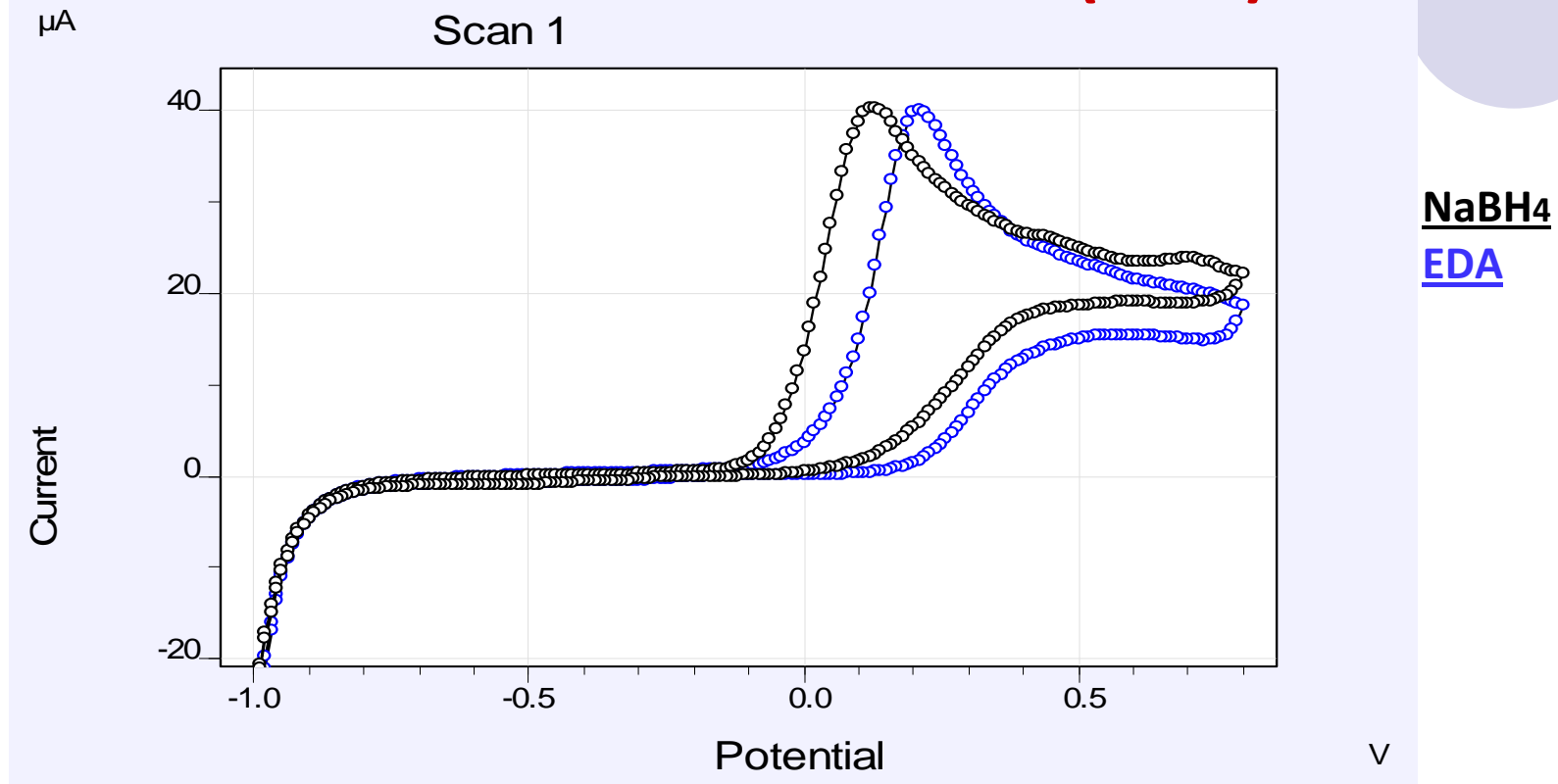


Figure 3. The Effect of EDA quantity to oxidation of NaBH₄ on Au electrode

- I_{max} of the potential shifted from 0.13 V to 0.21 V.
- Max value of the currents are same. So, we can say that, the needed current for the electrooxidation is same.

THE EFFECT OF BORAX ($\text{Na}_2\text{B}_4\text{O}_7$)

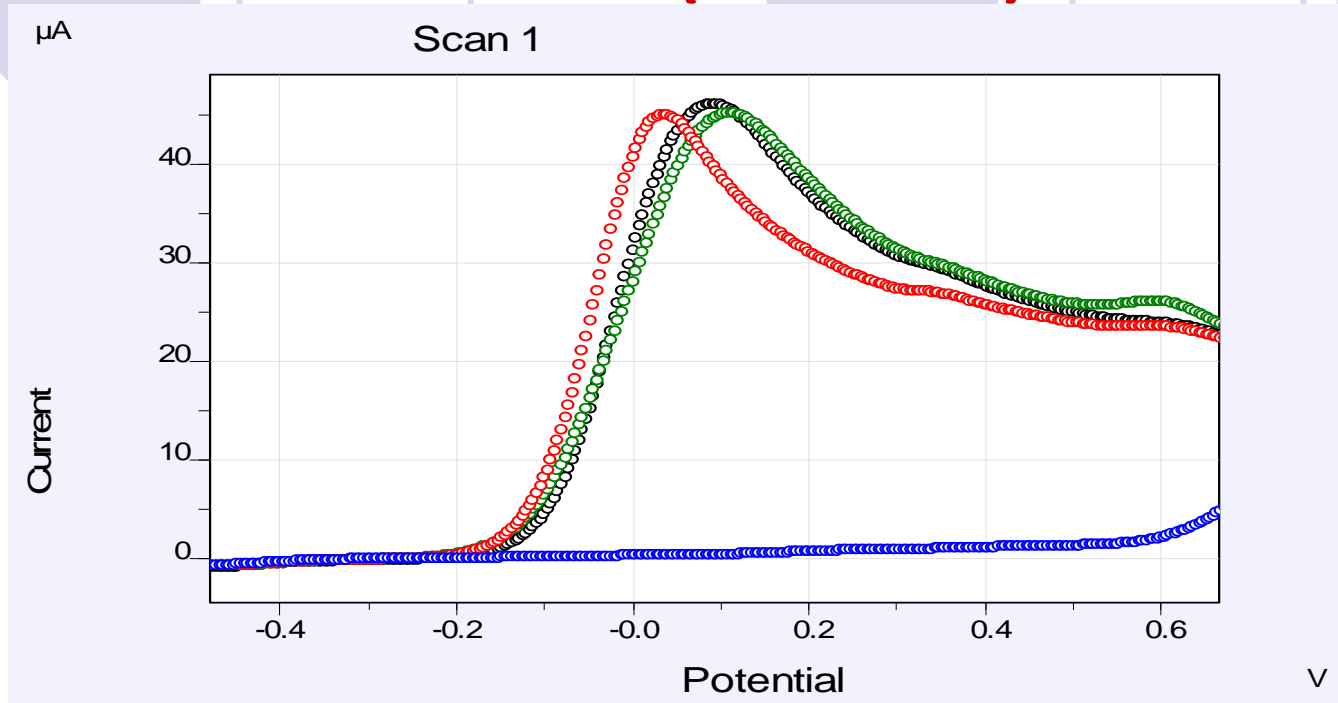


Figure 4. Effect of Borax ($\text{Na}_2\text{B}_4\text{O}_7$) linear voltamperometric diagrams (adding some solutions to 10^{-3} M NaBH_4 solution)

Blue 1 M NaOH ;

Red 10^{-3} M $\text{Na}_2\text{B}_4\text{O}_7$

Black 1 M NaBH_4

Green 0.29 M EDA

The behaviour of NaBH_4 electrooxidation in 10^{-3} M borax; is similar within 0.29 M behaviour of EDA solution

THE EFFECT OF METABORATE (NaBO₂)

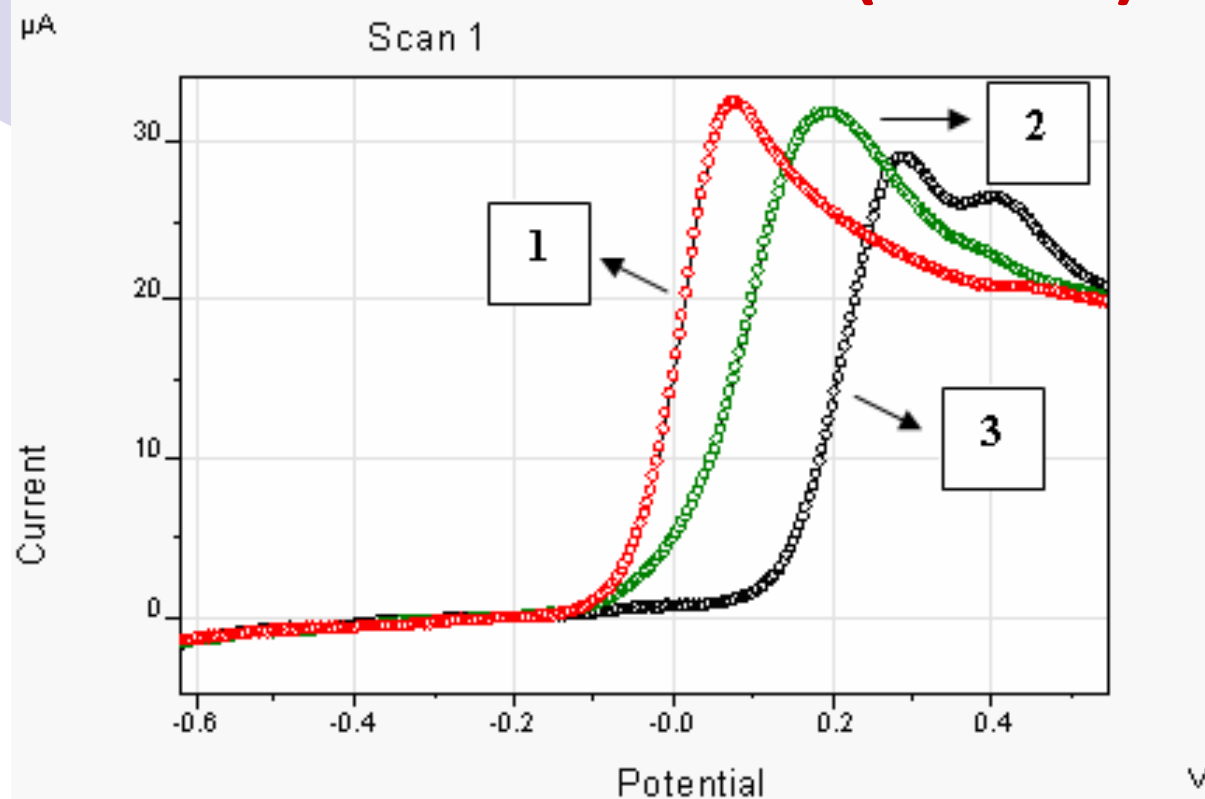


Figure 5. Effect of NaBO₂ on electrooxidation of NaBH₄

(1) 1 M NaOH + 10⁻³ M NaBH₄

(2) 1 M NaOH + 10⁻³ M NaBH₄ + 10⁻³ M NaBO₂

(3) 1 M NaOH + 10⁻³ M NaBH₄ + 10⁻³ M NaBO₂ + 0.29 M EDA

Effect of metaborate is similar with the effect of EDA.

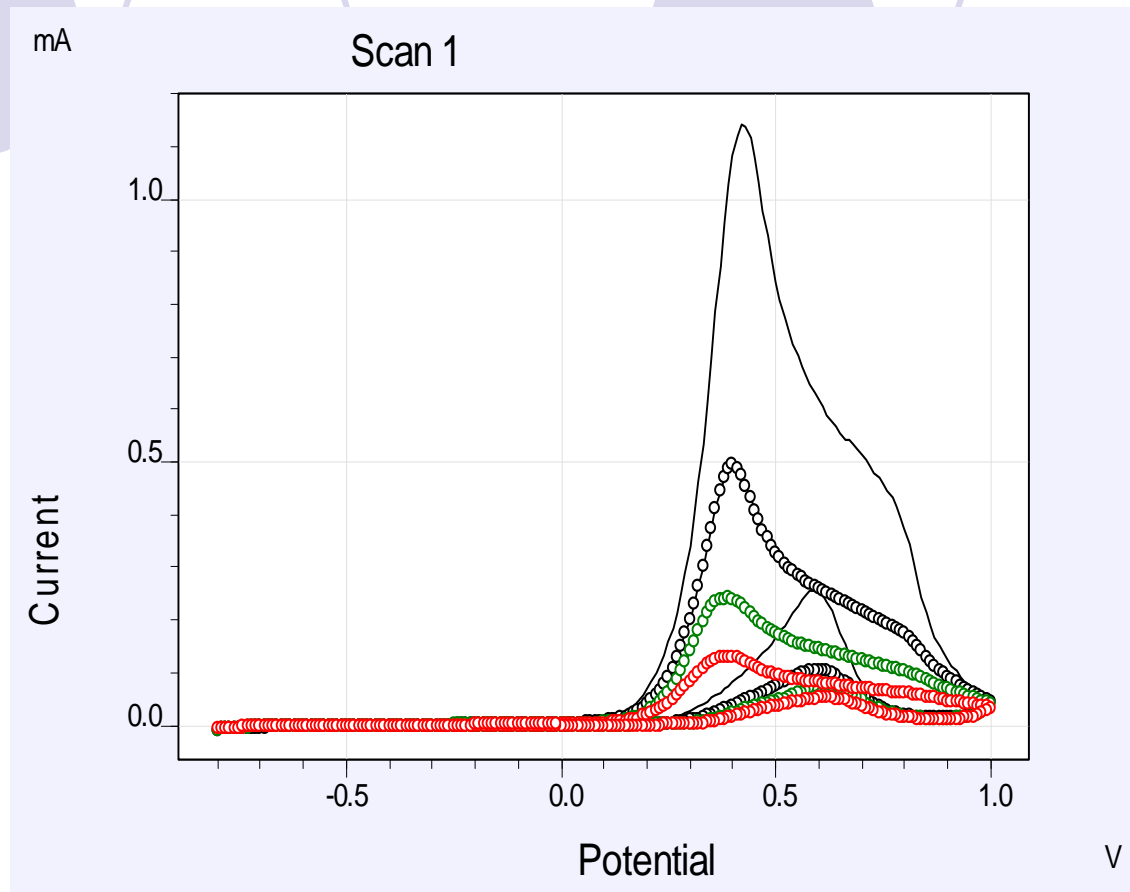
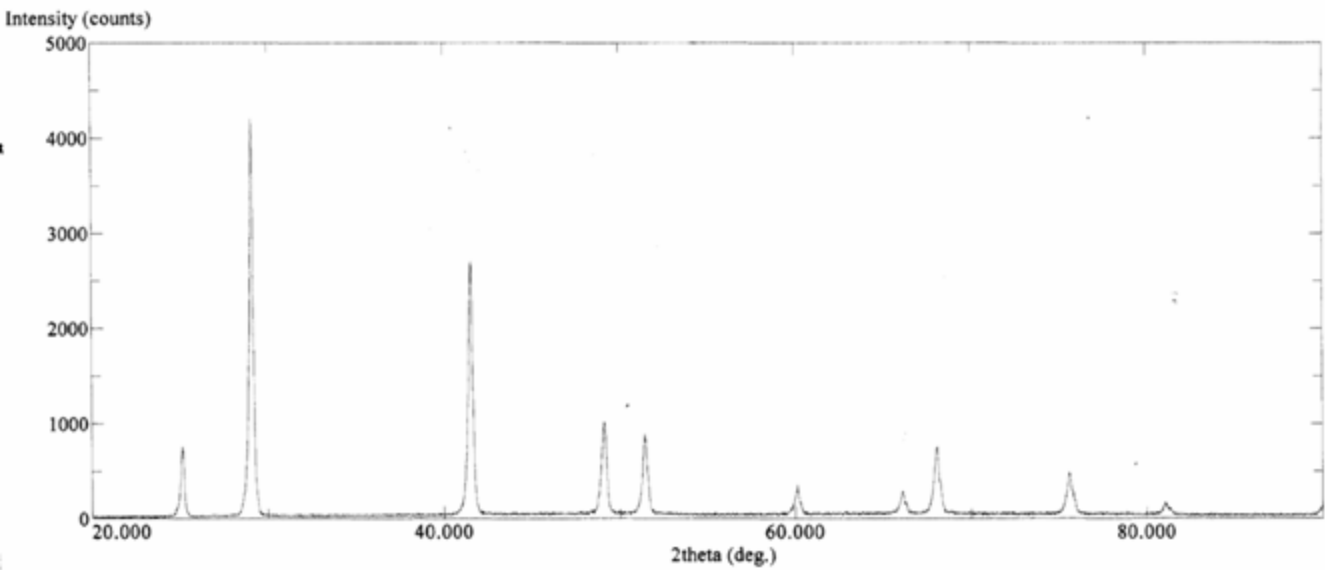
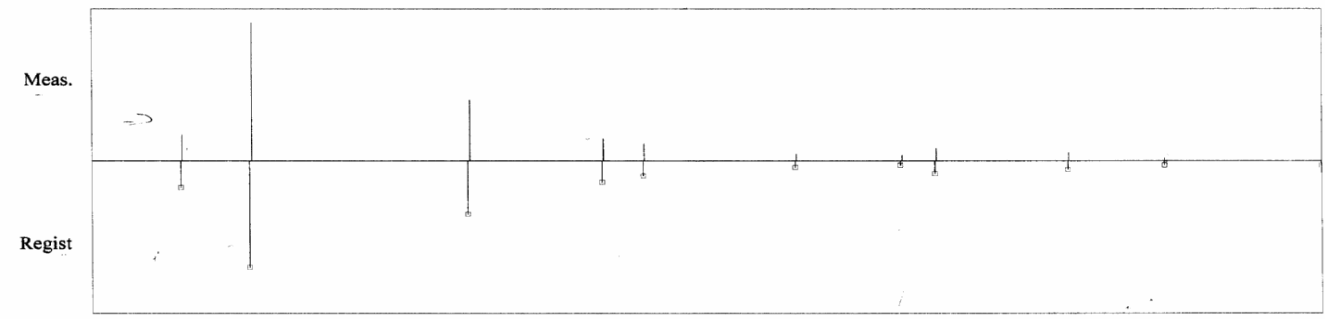
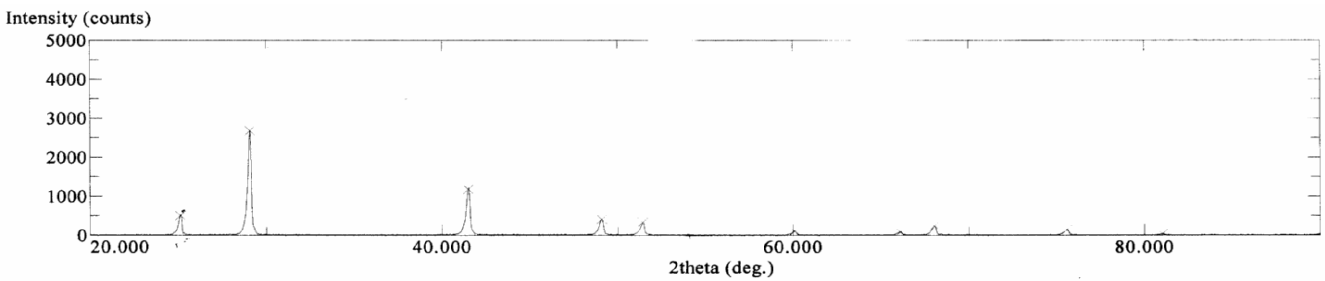


Figure 6. Cyclic voltammogram of some synthesised samples in our laboratory

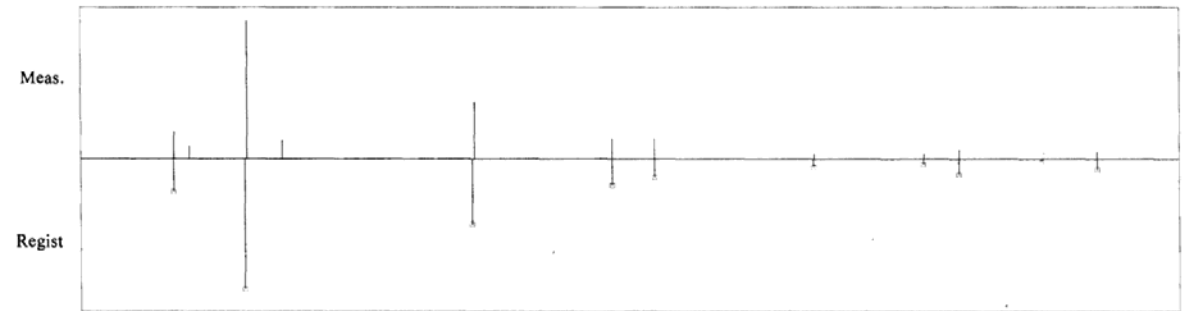
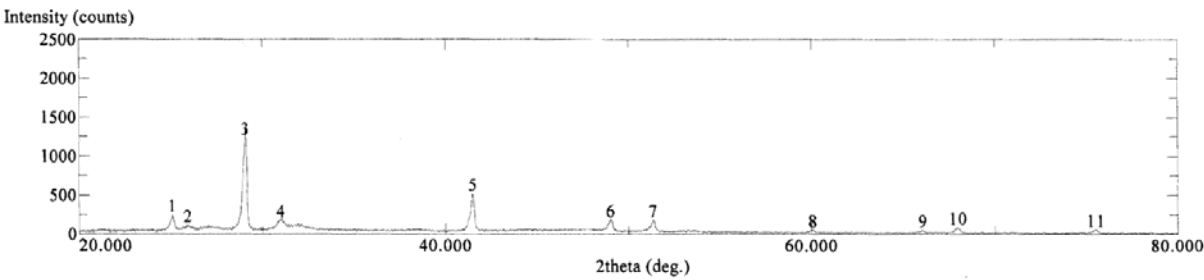
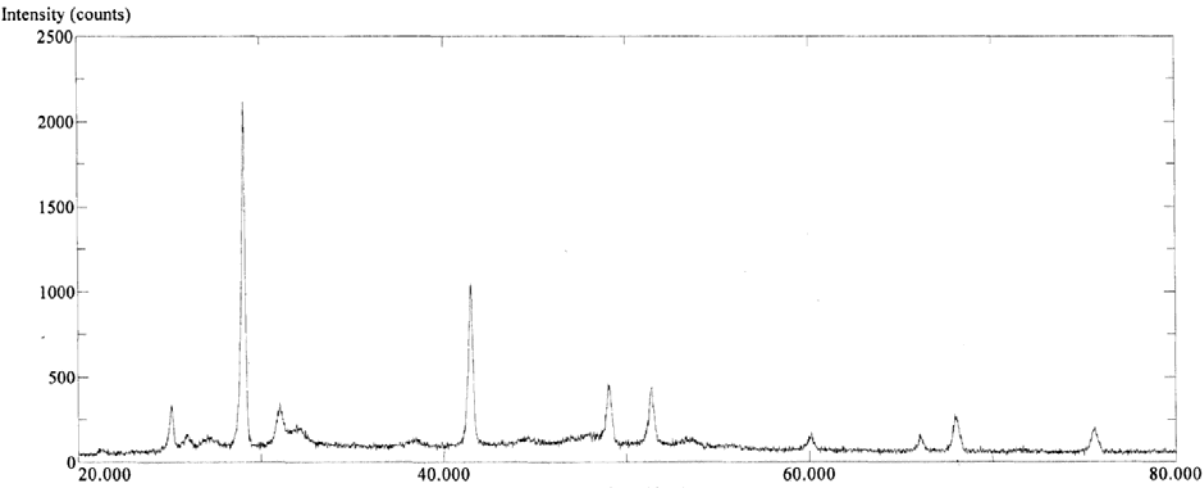
QUALITATIVE IDENTIFICATION of SODIUM BOROHYDRIDE



XRD pattern of Merck mark (%99 purity) NaBH₄



09-0386 Na B H4 Sodium Boron Hydri I 100%



09-0386 Na B H4 Sodium Boron Hydri 1 100%

NaBH₄ synthesised at
our laboratory

RESULTS

- Experimental results have shown that **both techniques** are complementary to each other and have significant importance in identification of product.
- **Au** electrode gives repeatable results on the oxidation of NaBH_4 , cleanliness of the used electrode must be checked prior to the determination process.
- Presence of **NaBO_2** and **$\text{Na}_2\text{B}_4\text{O}_7$** compounds have **small effect** on the electro-oxidation of NaBH_4 on **Au** electrode but this does not create an obstacle to determine NaBH_4 concentrations even at very low values such as 10^{-4} M.
- This method is effective when **ethylenediamine** is used as solvent to remove NaBH_4 from reaction products.



THANK YOU...