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Hydrogen Storage with Trilithium Aluminum Hexahydride

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Abstract

Hydrogen-oxygen fuel cells are the source for primary electrical power in manned space flight. The largest obstacle for these fuel cells is their ability to store hydrogen. The nature of the hydrogen molecule does not lend itself to achieving high densities in its pure form. In addition to low hydrogen densities, storing hydrogen in its pure form has safety considerations. Better hydrogen densities have been achieved by using metal hydrides to absorb hydrogen but these materials suffer from the high density of the metals used. In space, the high density of the total material is too great a cost. By chemically bonding hydrogen with light metals, a higher density can be achieved.

Trilithium aluminum hexahydride (Li_3AlH_6) is a chemical hydride that has emerged as a candidate for hydrogen storage. Using water as a reagent, the reaction is extremely rapid and extremely exothermic. The sole gaseous product of the reaction is hydrogen. To control the reaction rate, the trilithium aluminum hexahydride was mixed with polydicyclopentadiene (DCPD). Upon addition of water, the Li_3AlH_6 /DCPD matrix reacted much more slowly than the pure Li_3AlH_6 . However, contaminants from the polymer were found in the gaseous products.

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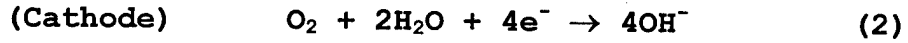
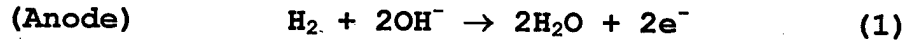
Background

Fuel cells have good potential to replace batteries for many applications requiring moderate, portable electric power. Applications being researched can range from cellular telephones and radios to power generators for large camps. The primary advantages of fuel cells include high power density, low temperature operation, silent operation, no poisonous exhausts, high electric efficiency, and fast start-up capability. While many commercial industries are just beginning to look at the opportunities fuel cells present, the space program has driven the development of fuel cell technology.

According to the International Fuel Cells Corporation, the batteries that would replace the space shuttle fuel cells are 10 times the weight of the alkaline H_2-O_2 fuel cells.¹ The use of fuel cells for space shuttle missions is undisputed. The shuttle carries three of the most advanced alkaline fuel cells available. These fuel cells have a rated power output of 12.0kW providing 436A at 27.5 volts. The overall weight of each unit is 112kg giving a specific power of 100W/kg.¹

An alkaline fuel cell generates electricity by combining hydrogen and oxygen to form water. Fuel cells can convert 70-90% of the energy release from this reaction directly into

electricity.² A KOH solution near 30% is used to maximize the conductivity of the electrolyte.² The half-cell reactions are:



A schematic of an alkaline $\text{H}_2\text{-O}_2$ fuel cell is shown below in Figure 1.

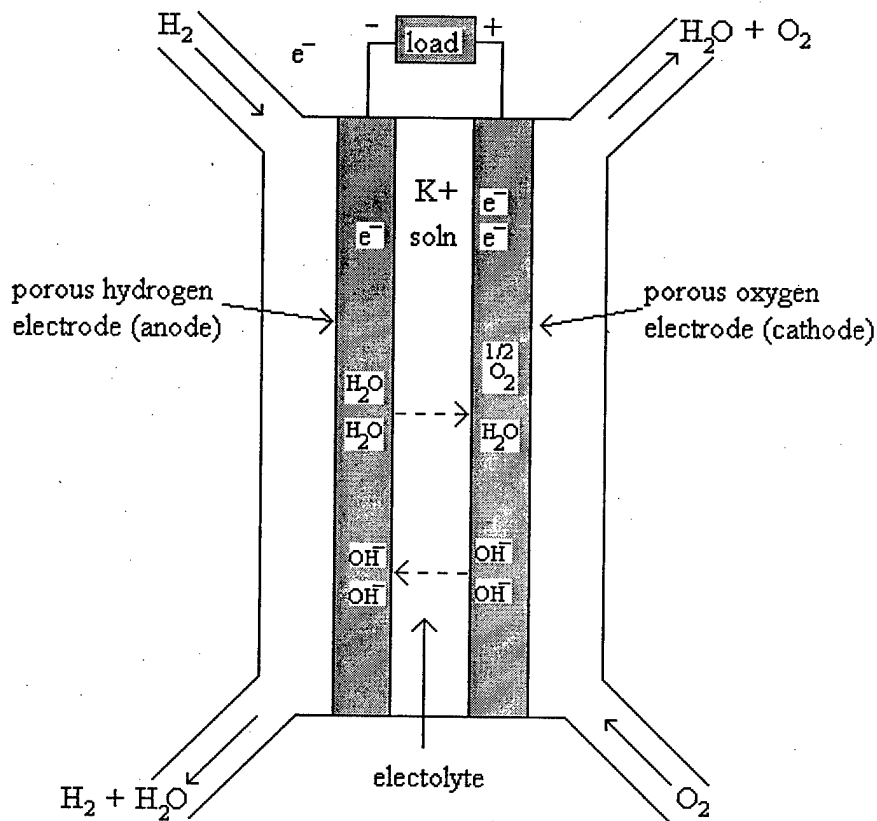


Figure 1. Principles of operation of alkaline fuel cells²

An important difference between batteries and fuel cells is the ability to refill a fuel cell. A fuel cell will work as long as it is continuously provided with fuel and oxygen. Thus, a large part of the specific power and energy density of the cell depends on the storage method of the fuel and oxidizer.

Introduction

There are three main ways of storing hydrogen. The first way is in its elemental state as a gas, liquid or solid. Another increasingly popular method to store hydrogen is in metal hydrides where the hydrogen is absorbed into a metal. The third way to store hydrogen is by chemically bonding the hydrogen to another material. These materials are known as chemical hydrides. Table 1 shows representative hydrogen densities that can be achieved with each method of hydrogen storage. Calculations for Table 1 can be found in Appendix A.

Form	Example	Material ρ (g/cm ³)	Hydrogen ρ (gH/cm ³)
H ₂ Gas	P=1atm, T=20°C	0.00008385	0.00008385
H ₂ Gas	P=2000psi, T=20°C	0.0114	0.0114
H ₂ Gas	P=14000psi, T=20°C	0.0470	0.0470
H ₂ liquid	P=1atm, T=19K	0.070	0.0700
H ₂ solid	P=0.07atm, T=13.8K	0.087	0.0870
Metallic H ₂	P=1.4atm, T=3000K	0.5*	0.5*
Metal Hydride	FeTiH _{1.95}	5.47	0.0983
Metal Hydride	LaNi ₅ H _{6.7}	6.59	0.1013
Metal Hydride	MgH ₂	1.4	0.1072
Metal Hydride	TiH ₂	3.75	0.1504
Chemical Hydride	LiAlH ₄	0.917	0.0974
Chemical Hydride	Li ₃ AlH ₆	1.13	0.127
Chemical Hydride	LiBH ₄	0.66	0.1222

Table 1. A comparison of hydrogen storage mechanisms.^{3,4}

The primary advantage to storing hydrogen in its pure state is that there are no by-products or substances left behind after the hydrogen is used. Depending on the state in which it is stored, pure hydrogen does have some disadvantages. In the

gaseous state, the only way to achieve a significant density is by using high-pressure systems, which implies serious safety considerations. For storing hydrogen as a solid or a liquid, cryogenic temperatures are required. Special pumps are also required for liquid and slush hydrogen distribution systems.

The reason hydrogen has such a poor density in its pure form is associated with the molecule itself. On an atomic level, hydrogen is very small with one proton in the nucleus. However, the electron density of the atom is still much larger than the nucleus. Localizing the electron in a bond allows great improvements in the hydrogen density.

Metallic hydrogen has been produced at Lawrence Livermore National Laboratory. It is not a practical method for storing hydrogen on earth but its estimated density serves as reasonable upper limit for the hydrogen density in any material. It is interesting to note that hydrogen, even as a metal only achieves half the density of water.

Metal hydrides achieve a better density because the H_2 is absorbed into the interstices between metal atoms at high pressure and low temperature.⁵ The hydrogen then desorbs out of the metal at low pressure and high temperature. Advantages of metal hydrides include reversibility, high hydrogen density, and low operating pressure. The important properties of metal hydrides are absorption/desorption rate, dissociation

temperature and pressure, material density, hydrogen density, reversibility, expansion coefficient, and durability and can vary greatly between materials.

These properties can have a great impact on the efficiency of the metal hydride. MgH_2 has one of the best combinations of material and hydrogen densities for metal hydrides. However, the amount of heat required to raise the temperature of the material to the dissociation temperature is more than can be provided by combusting all of the hydrogen stored within the material.⁵ One material that is used in batteries today is the lanthanum nickel-5 compound that appears to have a poor combination of densities. This compound is chosen because its dissociation temperature and pressure are near atmospheric conditions and for the materials' high durability.

Durability is a property that refers to how many times the material can be charged and discharged. Metal hydrides expand and contract during absorption and desorption of hydrogen. After several cycles, the material is reduced to a powdered, flour-like form with about 10-micron particles. The material can still absorb and desorb hydrogen in this state. Preventing this powder from leaving with the hydrogen is one of the challenges that faces applications. The property that virtually eliminates metal hydrides from consideration in space applications is the high material density. While a metal

hydride can hold more hydrogen than liquid hydrogen on a volume basis, the liquid hydrogen holds as much as 100 times the hydrogen on a weight basis.

The third method of storing hydrogen is by chemically bonding it to form a compound. Compounds that readily release this hydrogen by addition of another reactant such as water or ammonia are called chemical hydrides. Using light metals such as lithium and aluminum, high hydrogen densities can be achieved while also keeping the material density reasonably low. The primary drawback to this method of storage is that it is not reusable. The materials cannot be charged and discharged like metal hydrides because it is a chemical reaction that releases the hydrogen.

The chemical properties of the reactions used to generate the hydrogen in chemical hydrides are similar to the numerous physical properties of the metal hydrides. An example is reacting LiAlH_4 with water. This is such an exothermic reaction that it decomposes the LiAlH_4 before the reaction is complete. There are many ways to deal with the storage and generation of hydrogen by using different reactants or moderating the reaction. The use of chemical hydrides for hydrogen storage is a relatively new idea. The potential of many materials with high hydrogen densities has not yet been explored. For many

materials rich in hydrogen, it is only a matter of finding the correct catalyst to release the hydrogen.

The purpose of this investigation is to determine if the properties of a particular chemical hydride, trilithium aluminum hexahydride (Li_3AlH_6) are favorable for hydrogen storage and generation. The reaction of Li_3AlH_6 with water will be examined. A mixture of Li_3AlH_6 and polydicyclopentadiene and its reaction with water is also examined. Properties such as density, expansion, and stability are considered.

Specific Topics of Review

Trilithium Aluminum Hexahydride

A quantity of approximately 60 grams of Li_3AlH_6 was available that had been prepared according to the procedure published by Chini et al.⁶

Procedure

The reaction of the lithium aluminum hexahydride was carried out in the experimental setup depicted in Figure 2 below.

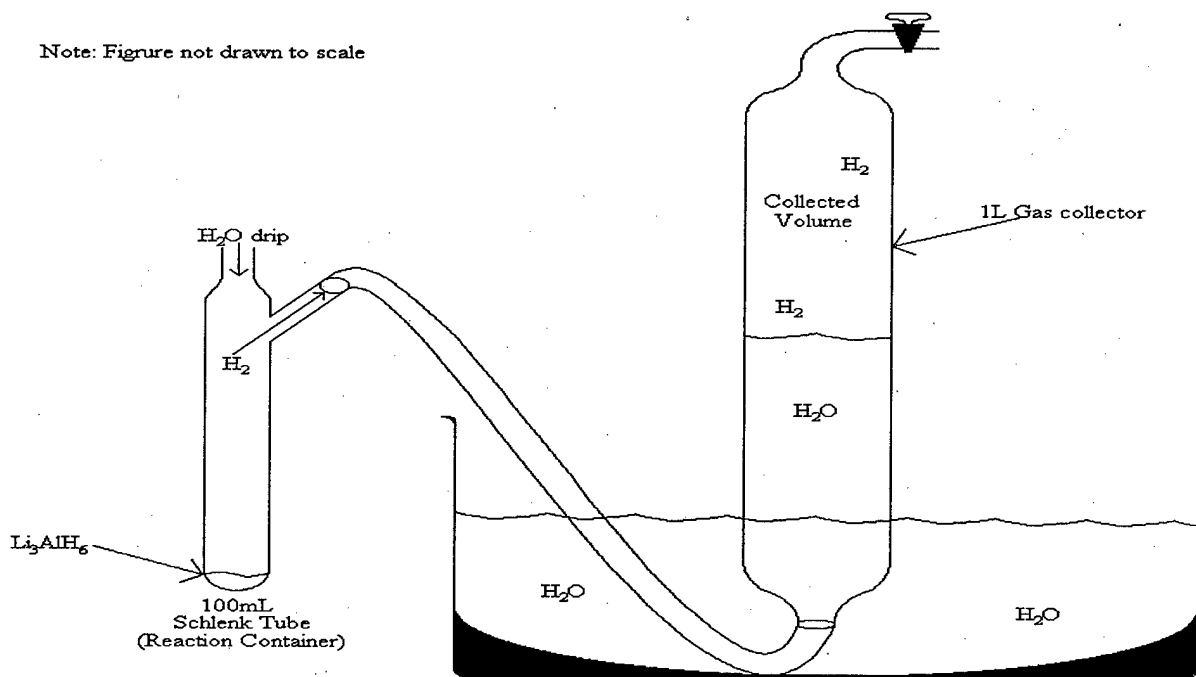
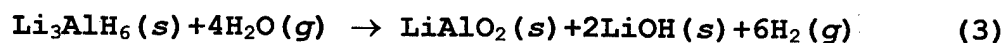


Figure 2. Reaction container and gas collector

The reaction that takes place upon addition of water to Li_3AlH_6 is given in Equation 3.



Approximately 200mg of Li_3AlH_6 was measured and sealed into the reaction container in an inert atmosphere. The system lines were flushed with nitrogen before the schlenk tube was connected. Approximately 10ml of 18M Ω deionized H_2O was added to the Li_3AlH_6 . Measurements of atmospheric temperature and pressure were made after the hydrogen generation was complete. The height of the water in the collection tube above the water pool and the water temperature were measured to account for the water vapor pressure.

Observations

The Li_3AlH_6 was a gray powder with a density measured at 0.405g/mL. The density reported in Table 1, 1.13g/cm³, is the density found in the literature. This higher density is achieved by packing the material near its crystal density. Li_3AlH_6 must be kept under an inert atmosphere at all times. If left in air, the material will react with water vapor and carbon dioxide according to Equation 4:



The hydrogen generation occurred so rapidly that the plunger in the syringe would be blown out if pressure were not constantly applied. The reaction was observed to be extremely exothermic. If water were added all at once instead of being dropped in, the Li_3AlH_6 would glow red-hot. The hydrogen generation from

approximately 200mg of Li_3AlH_6 lasted less than one minute. From Equation 3, part of the hydrogen generated comes from the water. When the total hydrogen generated is accounted for, the hydrogen density of Li_3AlH_6 is 0.254 gH/cm^3 , twice the hydrogen density reported in Table 1. The rationale for omitting the water density will be explained in the discussion of applications.

Results

Amount of Li_3AlH_6 (mg)	Gas collected (cm^3)	Yield
198	707	94.1%
199	705	95.0%
200	704	90.6%

Table 2. Results from Li_3AlH_6 trials

The percentage yields in Table 2 come from the calculations located in Appendix B; adjustments were made for water vapor pressure and the pressure differential inside the collection tube.

After the reaction had gone to completion, the gas inside the schlenk tube was analyzed using a HP 5890A gas chromatograph coupled with a HP 5970 mass selective detector. The parameters used for this analysis are located in Table.3.

Parameters for Gas Chromatograph/Mass Spectrometer (GC/MS)	
Column	Helliflex AT-1 25m x 0.25mm x 0.2 μm
Mass Range	10 to 400
Scans/sec	0.9
Oven Setpoint	70°
Injector Temperature	225°
Detector Temperature	280°

Table 3. Gas chromatograph and mass spectrograph parameters

The mass spectrometer is not able to detect the presence of hydrogen because of its low mass. To demonstrate the presence of hydrogen, the gas from the collection tube was collected in a small soda bottle and combusted. Condensation was observed after the combustion was complete.

The first sample to be run through the GC/MS showed signs of nitrogen and oxygen. It is believed that the septum on the schlenk tube was old and dried out, allowing air to enter the tube after sitting overnight. The septum was replaced on the second trial and the spectra appeared much cleaner. The second trial spectra showed only water, the only material that was expected. The third trial also had predictable GC/MS data, showing only water present. The actual spectra from the gas analysis are presented in Appendix C. The data files were named for the trial number, trial 1 is HYDRID1.D, trial 2 is HYDRID2.D, and trial 3 is HYDRID3.D.

Trilithium Aluminum Hexahydride and Polydicyclopentadiene

While the reaction between Li_3AlH_6 and water gave high percentage yields, the reaction would be more desirable if it occurred at a slower rate. A slower reaction rate would allow time for the heat to be carried away. By coating the Li_3AlH_6 , it may be possible to slow the reaction. The material selected to coat the Li_3AlH_6 was polydicyclopentadiene.

Dicyclopentadiene (DCPD) forms a rubber like substance upon polymerization. By mixing in Li_3AlH_6 during the polymerization, the Li_3AlH_6 would be coated with this rubber-like substance and significantly slow the reaction between Li_3AlH_6 and water, without affecting the reaction.

Synthesis

To create this mixture, 35g of DCPD was heated to approximately 35°C , while being magnetically stirred. Next, a small scoop (5-30mg) of the inhibitor triphenol phosphene was added followed by a small scoop (5-30mg) of the catalyst Bis-tricyclohexylphosphene benzylidene ruthenium dichloride. 1-2 minutes after the catalyst was added, the solution changed color from rose to brown, indicating the start of the polymerization. Li_3AlH_6 was mixed in until the solution reached a mortar-like consistency and required hand stirring. After approximately 20 minutes, the material was completely stirred. Because of the material's consistency, the material may not be homogeneous. The material was packed into glass tubes, sealed in a plastic container, and left in a helium atmosphere dry box. 29.682g of Li_3AlH_6 stirred into the polymerization, creating a material that was 45.9% by weight Li_3AlH_6 .

Procedure

The initial experiments on DCPD/Li₃AlH₆ were done on a smaller setup than depicted in Figure 2, using only a 100ml graduated cylinder. Instead of a schlenk tube, a glass bottle and a rubber stopper were used for the reaction container. This technique did not allow for the analysis of the gas generated. This technique was subject to more error than the technique previous described so it was abandoned and the same procedure already described for the pure Li₃AlH₆ was adopted.

Observations

The matrix of DCPD/Li₃AlH₆ was a very hard substance. In order to obtain samples for hydrogen generation experiments, pieces were broken off with a hammer. Upon removing the material from the tubes, the density was measured at 0.0877g/cm³. The density of the material could vary significantly based on the packing technique. There were gas pockets in the glass tubes suggesting either H₂ from the Li₃AlH₆ or DCPD vapors. The material had the same gray color as the pure Li₃AlH₆.

After approximately 10 days in the helium dry box, the material was removed because the filters in the dry box were filling. Upon removal of the DCDP/Li₃AlH₆, the strong, unmistakable odor of DCPD was detected. A possible explanation for this is that not enough inhibitor was added to the

polymerization. This theory would also explain the hardness of the material. By adding more inhibitor, more polymer chains would have been formed, thus lowering the average molecular weight and allowing more mobility to each chain. Allowing more mobility to polymer chains causes fewer monomer units to be left behind and causes more ductility in the material.

After the material was removed from the dry box, it was stored in the plastic container in a vacuum desecator and handled only in a plastic glove bag. Before opening the container, the bag was purged for at least 15 minutes and kept under positive pressure with nitrogen the entire time the material was out of the container. This precaution preserved the material reasonably well. After several weeks of being in the container, the ends of the tubes had experienced color change while the material inside the tubes appeared stable. The decomposition of the material from air was very noticeable. The DCDP/ Li_3AlH_6 went from a gray, extremely hard material to an off-white powder. The life of the material in the atmosphere varied with the size of the piece. After only one hour, samples smaller than 200mg had undergone noticeable decomposition. For larger samples, the core of the sample would remain intact and hard while the outside decomposed into a powder and flaked off.

This decomposition is expected to follow Equation 2 just like pure Li_3AlH_6 , the air having no effect on the DCPD.

However, when a gravimetric analysis was attempted, percentage yields were consistently over 100%. A possible explanation is products of Equation 4 forming hydrates. The decomposition of the material in air is inconclusive because the number of H₂O molecules attached to each product was not predictable.

Upon handling the material for the initial experiments, a strong DCPD odor was present. After dropping the sample into the water, the sample floated for approximately 30 minutes. The hydrogen coming from the inside of the material was keeping it afloat. After being in the water for an extended period, the material became swollen and spongy. When the material was fully reacted, it lost the gray color and turned white. Parts of the material had turn to a tan or brown color. This may have been from the heat of the reaction charring the polymer or from the products of the reaction such as LiOH reacting with the polymer.

Results

DCPD/Li ₃ AlH ₆ Results					
Trial #	Sample Mass	Gas Collected	% yield	Time in water	Filename
1	37 mg	86 ml	140.6	3 min	N/A
2	27 mg	59 ml	132.5	1.5 hr	N/A
3	203 mg	285 ml	86.0	24 hr	N/A
4	283 mg	408 ml	89.5	24 hr	HYDRID4.D
5	413 mg	670 ml	103.5	24 hr	HYDRID5.D
6	386 mg	670 ml	111.0	24 hr	HYDRID6.D

Table 4. Results from DCPD/Li₃AlH₆ trials

The calculations for Table 4 are located in Appendix D. Trials 1 and 2 were performed on the smaller setup and therefore

the gas could not be analyzed. The 40% excess yield is attributed to the DCPD fumes and the larger amount of error possible in the experimental setup. The initial trials were not left in the water as long because it was not thought the reaction would last more than one hour. The third trial was performed one week after the sample had been weighed and sealed in the schlenk tube. It appears that the DCPD, when left in a large enough space, vents the remaining monomer units from the polymerization. By letting the material sit in an inert atmosphere, the monomer was allowed to escape while CO_2 and H_2O were not allowed to decompose the Li_3AlH_6 . This also explains the percentage yield in trials 4, 5, and 6. The sample for trial 4 was taken from the end of a tube, where the DCPD could dry. A color change to a lighter gray in sample 4 indicated some exposure to the atmosphere. Sample 5 was taken near the end of a tube where some drying may have been allowed. Sample 6 was taken from the middle of the tube and had not experienced any color change.

The gas left in the schlenk tube was analyzed using the same parameters listed in Table 3 that were used to analyze the gas of the pure Li_3AlH_6 . The GC/MS data from each trial supports the theory that DCPD is allowed to escape given space. The spectra from each trial are found in Appendix E according to the filenames given in Table 4. The only predominant peak in the

gas chromatograph from HYDRID4.D is water; no trace of cyclopentadiene was evident. The gas chromatograph from HYDRID5.D has three peaks. The first and predominant peak was identified as water. The second peak, a small shoulder on the first, was identified as dichloromethane. This material is assumed to have come from the inhibitor in the polymerization process, catalyst Bis-tricyclohexylphosphene benzyldene ruthenium dichloride. The third peak was identified as 4,7-Methano-1H-indene,3a,4,7,7a-tetrahydro. This is the IUPAC name for what is commonly known as dicyclopentadiene (DCPD). The structure for DCPD is shown in Figure 3.

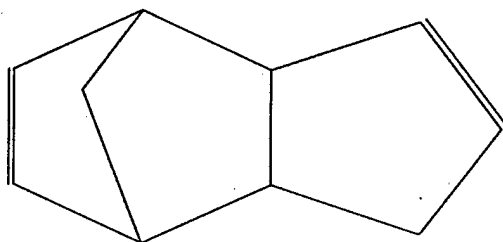


Figure 3. The structure of dicyclopentadiene

The purpose of coating Li_3AlH_6 with the polymer was to slow the reaction of the Li_3AlH_6 . The reaction time of 200mg Li_3AlH_6 was approximately 1 minute. Results are presented in Figure 4.

Based on the data in Figure 4, the DCPD did a good job of slowing the reaction rate of Li_3AlH_6 . The size of the pieces that made up the sample appears to have an affect on the time it takes for the reaction to go to completion. The trial that produced the most gas the fastest was trial 5. The sample for

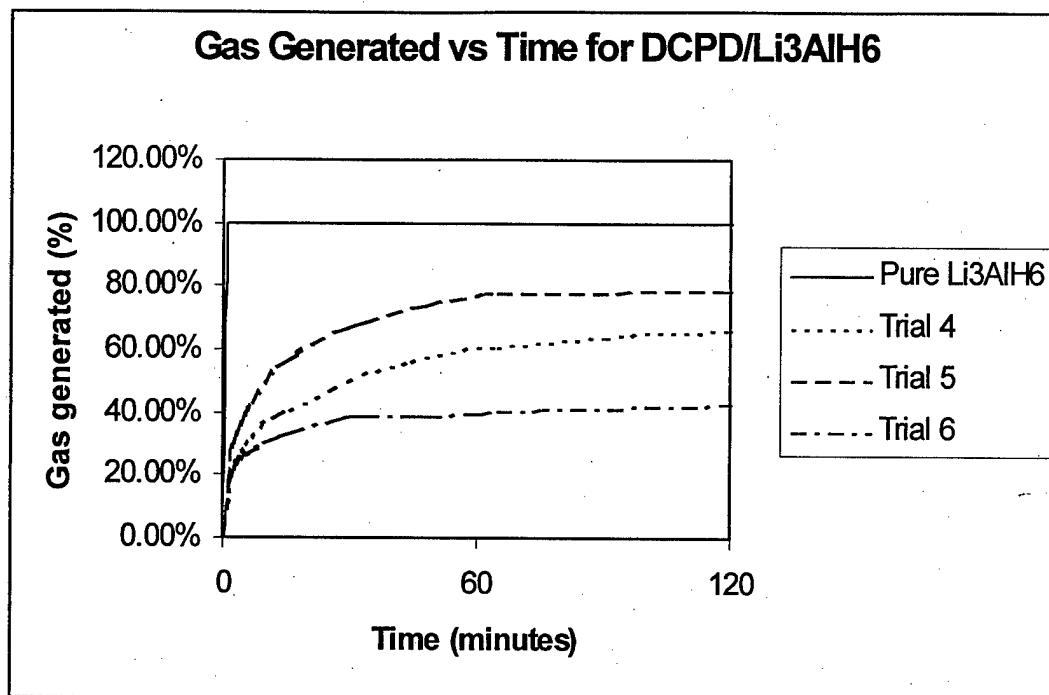


Figure 4. Gas generation from DCPD/Li₃AlH₆

this trial was broken up into many pieces. Trial 6 had one large piece that was used. This logic suggests that a powdered sample of the DCPD/Li₃AlH₆ matrix may generate hydrogen as fast as the pure Li₃AlH₆.

Depending on the application, the amount of swelling the material does in water may play an important role. To measure the swelling of the material, a rough cube was cut, measured and dropped in water. After the reaction had gone to completion, the cube was taken out and measured again. The volume after swelling the reaction was found 110% of the volume before the reaction. This swelling may affect the design of applications for this material.

Suggestions and Recommendations

The use of DCPD as a coating to slow the reaction of Li_3AlH_6 and water worked well. These preliminary findings suggest that the polymerization process plays an important role in determining speed of the hydrogen generation. Carefully controlling the properties of the polymer may also eliminate the excess gaseous products. Advanced Polymer Technologies Inc. has developed methods to carefully control the properties of the polymer. However, this information was proprietary and could not be accessed.

Discussion of Limitation

The limitations of Li_3AlH_6 deal primarily with the chemical properties of the reaction. One of the most obvious limitations is that the reaction is not reversible. Once the material is used, it cannot be recharged. The kinetics and the amount of heat given off by the reaction between Li_3AlH_6 and water may pose an obstacle for some applications.

The solution to slowing the reaction of Li_3AlH_6 may or may not be DCPD. One of the largest problems identified with the mixture of these materials is that the gas given off was not pure hydrogen. Most fuel cells today require a hydrogen purity of 99.99%.⁷ The details of the polymerization process remains the largest unknown. If the polymer can be engineered for Li_3AlH_6 in a manner that does not produce a gaseous by-product, it could play a large part in applications using Li_3AlH_6 for hydrogen storage.

Discussion of Applications

The applications of Li_3AlH_6 will depend on the development of a reliable storage and generation system. Once a lightweight, dependable storage system has been developed, Li_3AlH_6 can be used in fuel cells for terrestrial and space applications. A hydride storage method would be ideal for the fuel cell developed by Ball Aerospace that requires an external source of hydrogen regulated to less than 250psi. The Ball fuel cell is about the size of a small lunch box, weighs 6.5 pounds, and can provide 100W of continuous power at 12 or 24 volts, as long as it is supplied with hydrogen.⁸

A simple hydrogen generator could be constructed with a quantity of Li_3AlH_6 , the water required to carry out the reaction, and a balloon to collect the hydrogen. For practical applications, a less clumsy approach will probably be used. The reaction between Li_3AlH_6 and water may be governed by Le Chatelier's principle which states that when an external stress is applied to a system at equilibrium, the system adjusts itself to partially offset the stress.⁹ If Le Chatelier's principle does apply to equation 2, a high-pressure container with a regulator could be developed to store the Li_3AlH_6 and the water. This design would serve as an instantaneous feedback system, with an on-demand supply of hydrogen. As the hydrogen

generation builds pressure in the system, the reaction slows until equilibrium is reached and hydrogen generation stops. When the fuel cell is turned on, the pressure drops inside the container, and the reaction generates more hydrogen. This instantaneous feedback system may be the ideal hydrogen generator for fuel cells similar to the one developed by Ball.

A consideration for using Li_3AlH_6 over another type of hydrogen storage system is that the second reactant, water, is also required for the system to work. As previously stated, the hydrogen density of Li_3AlH_6 based on the reaction in Equation 2 is 0.091 gH/cm^3 . The water is not accounted for in this calculation because water is a product of the fuel cell reactions from Equations 1 and 2. Therefore, designing for water required to complete the reaction rather than water required to initiate the reaction would not be efficient. A possible hydrogen generator based on the $\text{Li}_3\text{AlH}_6/\text{H}_2\text{O}$ reaction would take the water produced from the fuel cell and feed the hydrogen generator. This design would only require a minimal amount of water to initiate the reaction.

Conclusion

The storage of hydrogen for use in fuel cells used as portable electric power generators is important. The development of high energy and power density electrical generators is directly tied to the ability to store fuel at a high density. Chemical hydrides offer the ability to store hydrogen at a higher density than liquid hydrogen without the high material densities of metal hydrides. For these reasons, chemical hydrides are the best means of hydrogen storage for lightweight portable power sources.

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APPENDIX A

- H₂ Gas at 1atm and 20°C

$$MW = 2.016 \frac{g}{mol} \quad PV = nRT \quad V = \frac{(1 \text{ mol})(0.0820575 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(293 \text{ K})}{1 \text{ atm}} = 24.04 \text{ L}$$

$$\rho = \frac{2.016 \text{ g}}{24.04 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.0008385 \frac{g}{\text{cm}^3}$$

- H₂ Gas at 2000psi and 20°C

$$MW = 2.016 \frac{g}{mol} \quad PV = nRT \quad V = \frac{(1 \text{ mol})(0.0820575 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(293 \text{ K})}{(2000 \text{ psi})(\frac{1 \text{ atm}}{14.696 \text{ psi}})} = 0.176665 \text{ L}$$

$$\rho = \frac{2.016 \text{ g}}{0.176665 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.0114 \frac{g}{\text{cm}^3}$$

- H₂ gas at 14,000psi and 20°C

$$MW = 2.016 \frac{g}{mol} \quad PV = nRT \quad V = \frac{(1 \text{ mol})(0.0820575 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(293 \text{ K})(1.7^*)}{(14,000 \text{ psi})(\frac{1 \text{ atm}}{14.696 \text{ psi}})} = 0.0429 \text{ L}$$

$$\rho = \frac{2.016 \text{ g}}{0.0429 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.0469 \frac{g}{\text{cm}^3}$$

* term accounts for non-ideal behavior (from Vander Waals equation)

- FeTiH_{1.95} Metal Hydride

$$MW = 105.88 \frac{g}{mol} \quad \rho = \frac{5.47 \text{ g FeTiH}_{1.95}}{\text{cm}^3} \times \frac{1.95 \text{ g H}}{105.68 \text{ g FeTiH}_{1.95}} = 0.0983 \frac{g}{\text{cm}^3}$$

- LaNi₅H_{6.7} Metal Hydride

$$MW = 439.05 \frac{g}{mol} \quad \rho = \frac{6.59 \text{ g LaNi}_5\text{H}_{6.7}}{\text{cm}^3} \times \frac{6.75 \text{ g H}}{439.05 \frac{g}{mol}} = 0.1013 \frac{g}{\text{cm}^3}$$

- MgH₂ Metal Hydride

$$MW = 26.326 \frac{g}{mol} \quad \rho = \frac{1.4 \text{ g MgH}_2}{\text{cm}^3} \times \frac{2.016 \text{ g H}}{26.326 \text{ g MgH}_2} = 0.1072 \frac{g}{\text{cm}^3}$$

-TiH₂ Metal Hydride

$$MW = 49.88 \text{ g/mol} \quad \rho = \frac{3.75 \text{ g TiH}_2}{\text{cm}^3} \times \frac{2.016 \text{ g H}_2}{49.88 \text{ g TiH}_2} = 0.1504 \text{ gH/cm}^3$$

-LiAlH₄ Chemical Hydride

$$MW = 37.953 \text{ g/mol} \quad \rho = \frac{0.917 \text{ g LiAlH}_4}{\text{cm}^3} \times \frac{4.032 \text{ g H}}{37.953 \text{ g LiAlH}_4} = 0.09743 \text{ gH/cm}^3$$

-Li₃AlH₆ Chemical Hydride

$$MW = 53.851 \text{ g/mol} \quad \rho = \frac{1.13 \text{ g Li}_3\text{AlH}_6}{\text{cm}^3} \times \frac{6.048 \text{ g H}}{53.851 \text{ g Li}_3\text{AlH}_6} = 0.127 \text{ gH/cm}^3$$

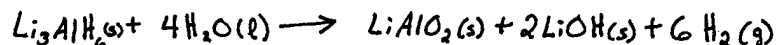
-LiBH₄ Chemical Hydride

$$MW = 21.783 \text{ g/mol} \quad \rho = \frac{0.66 \text{ g LiBH}_4}{\text{cm}^3} \times \frac{4.032 \text{ g H}}{21.783 \text{ g LiBH}_4} = 0.1222 \text{ gH/cm}^3$$

-Li₃AlH₆ + 4H₂ (g) → LiAlO₂ (s) + 2LiOH (s) + 6H₂ (g)

$$\rho = \frac{1.13 \text{ g Li}_3\text{AlH}_6}{\text{cm}^3} \times \frac{1 \text{ mol Li}_3\text{AlH}_6}{53.851 \text{ g Li}_3\text{AlH}_6} \times \frac{6 \text{ mol H}_2}{1 \text{ mol Li}_3\text{AlH}_6} \times \frac{2.016 \text{ g H}}{\text{mol H}_2} = 0.254 \text{ gH/cm}^3$$

APPENDIX B



- 0.198g Li₃AlH₆ sample

$$0.198\text{g Li}_3\text{AlH}_6 \times \frac{1\text{mol Li}_3\text{AlH}_6}{53.851\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{1\text{mol Li}_3\text{AlH}_6} = 0.02206\text{mol H}_2 \quad \text{theoretical}$$

Total Volume actually produced = 0.707L

atmospheric pressure = 580 mmHg temperature = 23°C

height of H₂O = 278mm temperature = 20°C

278mm H₂O = 20,428 mmHg P_{vap H₂O} = 17,54 mmHg

PV = nRT

$$n = \frac{(580\text{ mmHg} - 20,428 - 17,54) (0.707\text{ L})}{760\text{ mmHg/atm}} = \frac{0.02076\text{ mol actual}}{(0.0820575\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (296\text{ K})}$$

$$\% \text{ yield} = \frac{0.02076}{0.02206} \times 100\% = 94.1\%$$

GC/MS data Hybrid 1.D

- 0.199g Li₃AlH₆ sample

$$0.199\text{g Li}_3\text{AlH}_6 \times \frac{1\text{mol Li}_3\text{AlH}_6}{53.851\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{1\text{mol Li}_3\text{AlH}_6} = 0.02217\text{mol H}_2 \quad \text{theoretical}$$

Total volume produced = 0.705L

PV = nRT

$$n = \frac{(580\text{ mmHg} - 10,728 - 17,54) (0.705)}{760\text{ mmHg/atm}} = \frac{0.02107\text{ mol actual}}{(0.0820575\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (296\text{ K})}$$

n = 0.02107 mol actual

$$\% \text{ yield} = \frac{0.02107}{0.02217} \times 100\% = 95.0\% \text{ yield}$$

GC/MS data HYDRID 2.D

atmospheric pressure = 580.0 mmHg

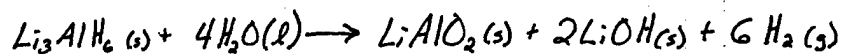
atmospheric temperature = 23°C

water column height = 146mm

water temperature = 20°C

146mm H₂O = 10,728 mmHg

P_{vap @ 20°C} = 17,54 mmHg



- 0.200g Li₃AlH₆ sample

$$0.200\text{g Li}_3\text{AlH}_6 \times \frac{1\text{mol Li}_3\text{AlH}_6}{53.851\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{1\text{mol Li}_3\text{AlH}_6} = 0.022284\text{mol H}_2 \text{ theoretical}$$

Total volume produced = 0.704L

atmospheric pressure = 575.6 mmHg

room temperature = 21.5°

Water column = 6.0° = 11.1987 mmHg

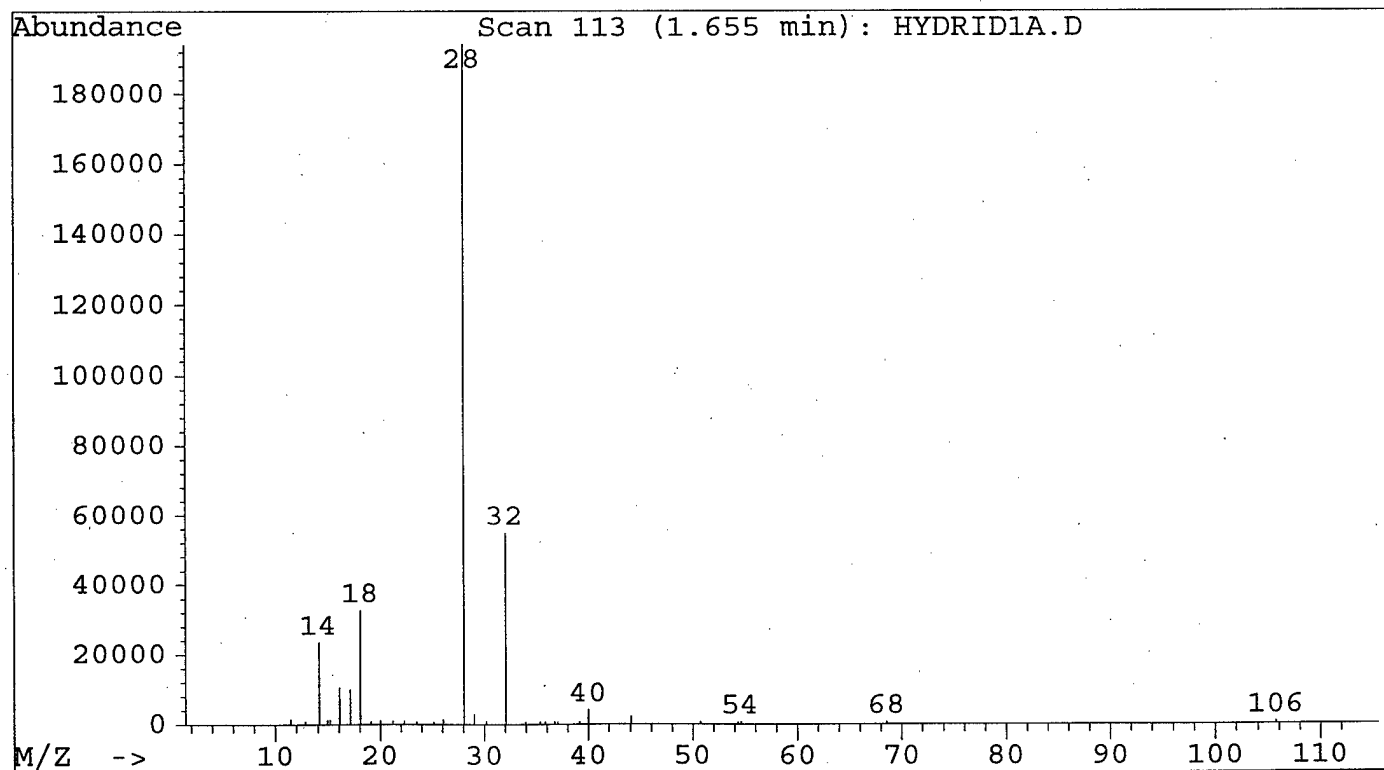
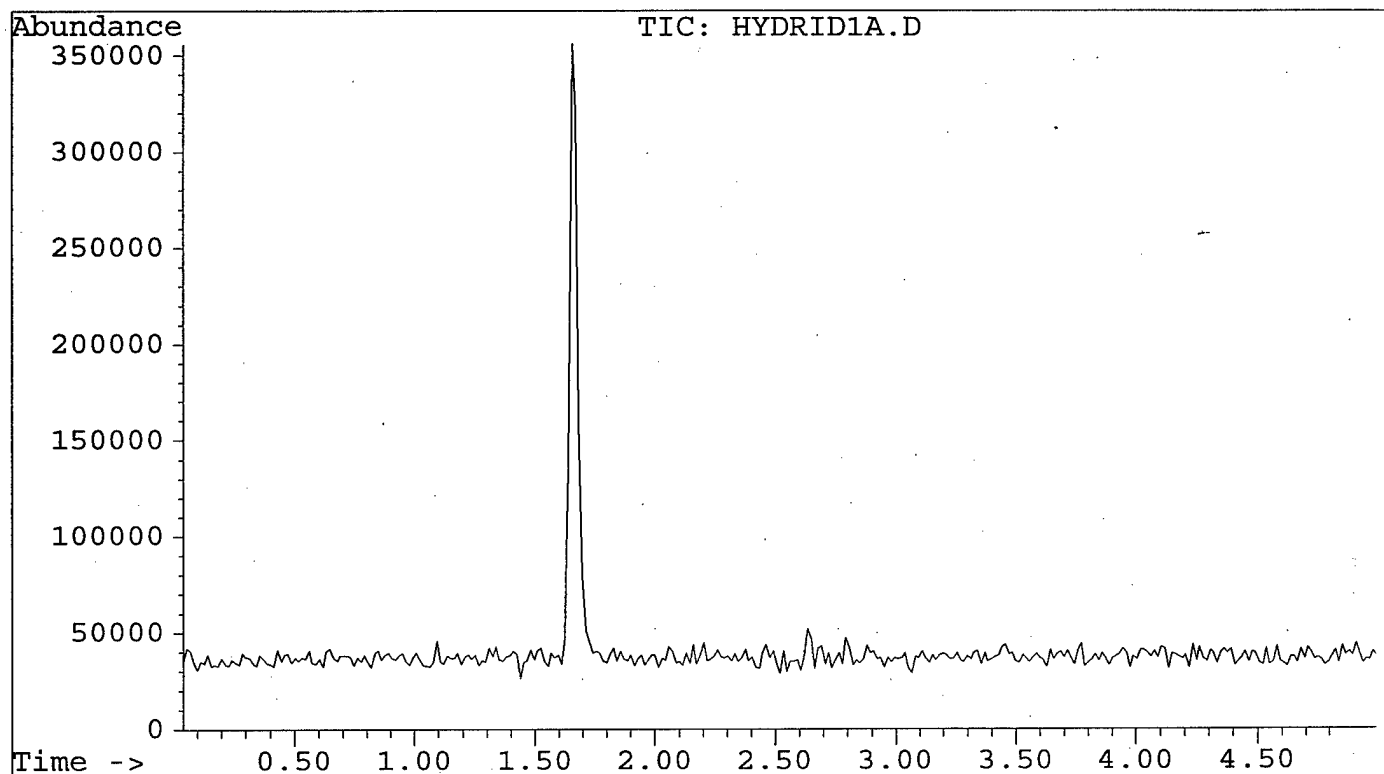
water temperature = 19.5°C ; P_{vap} = 17.07 mmHg

$$PV = nRT \quad n = \frac{\left(\frac{575.6\text{mmHg} - 11.20\text{mmHg} - 17.07\text{mmHg}}{760 \frac{\text{mmHg}}{\text{atm}}} \right) (0.704\text{L})}{(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}) (294.5\text{K})} = 0.02018\text{mol actual}$$

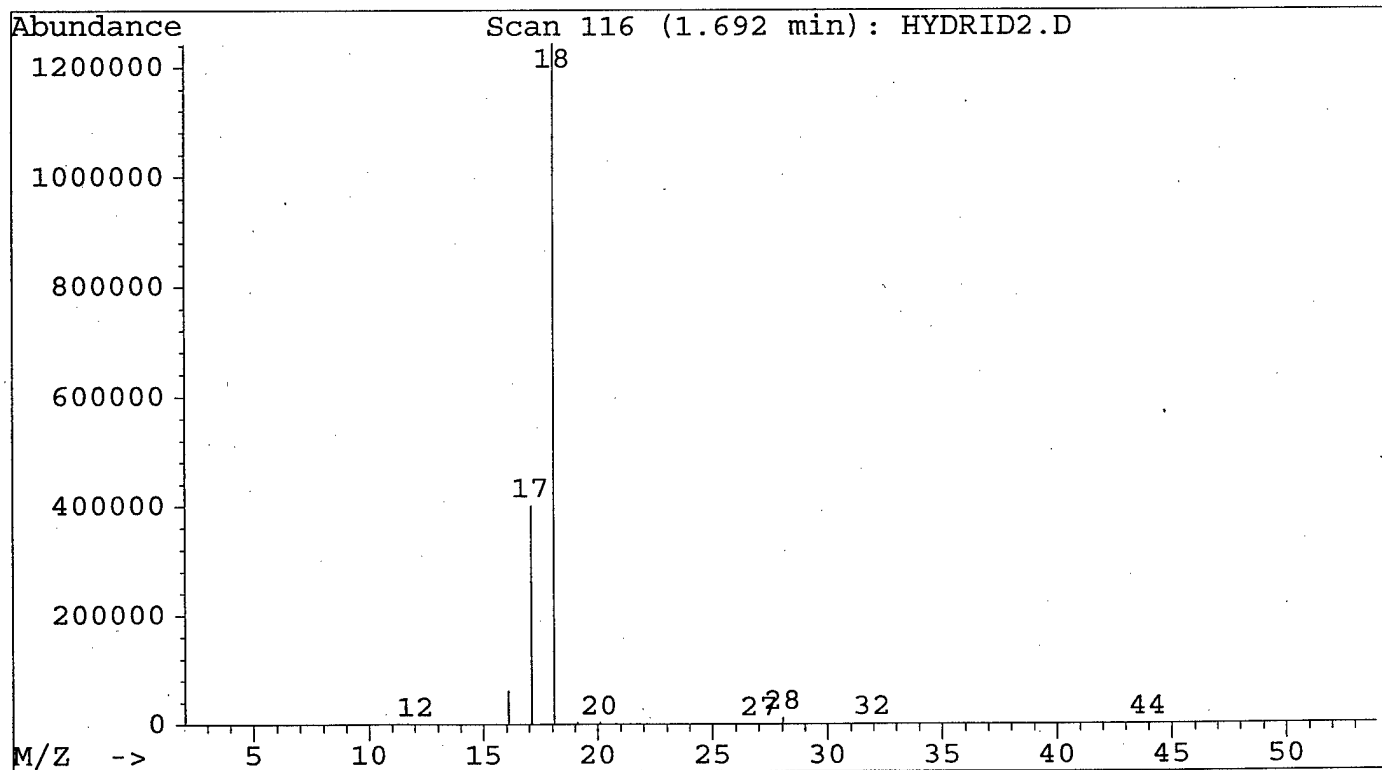
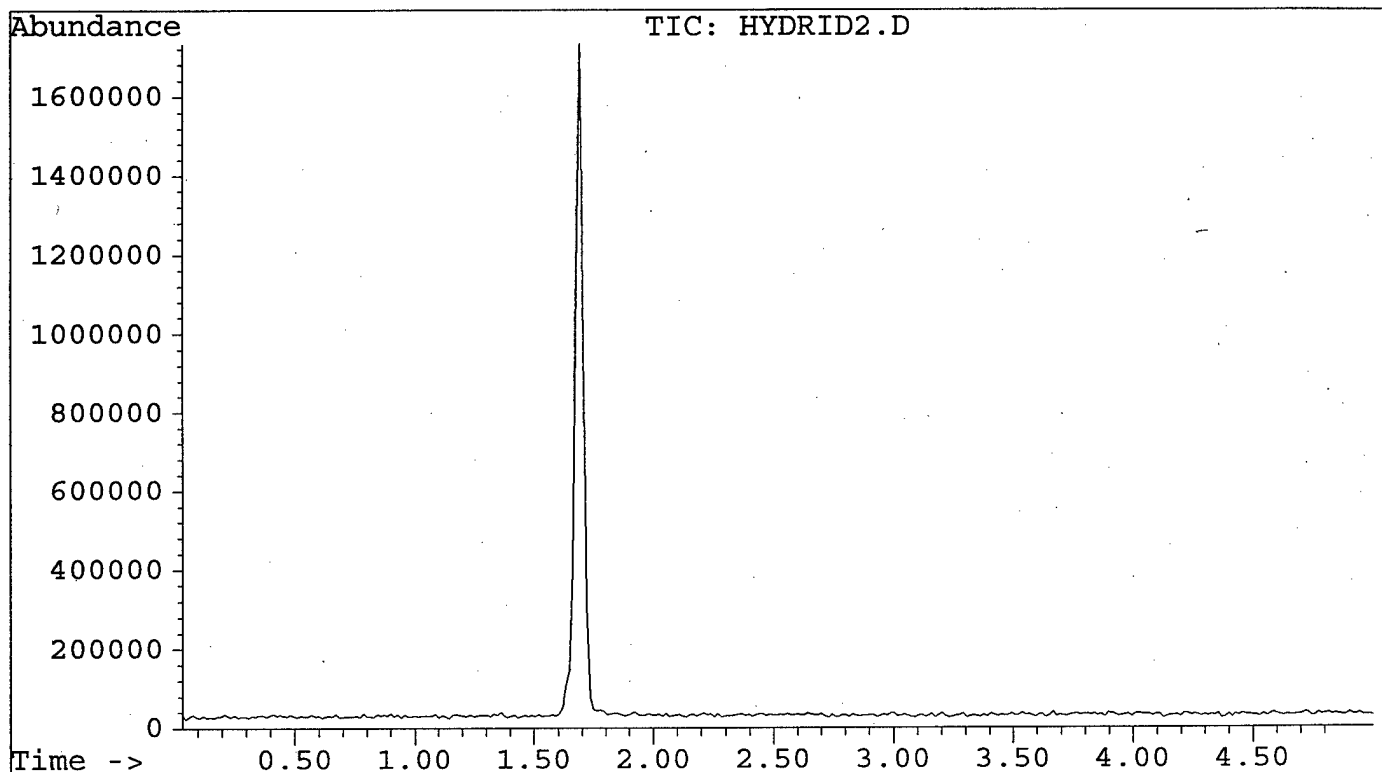
$$\% \text{ yield} = \frac{0.02018}{0.02228} \times 100\% = 90.6\% \text{ yield}$$

APPENDIX C

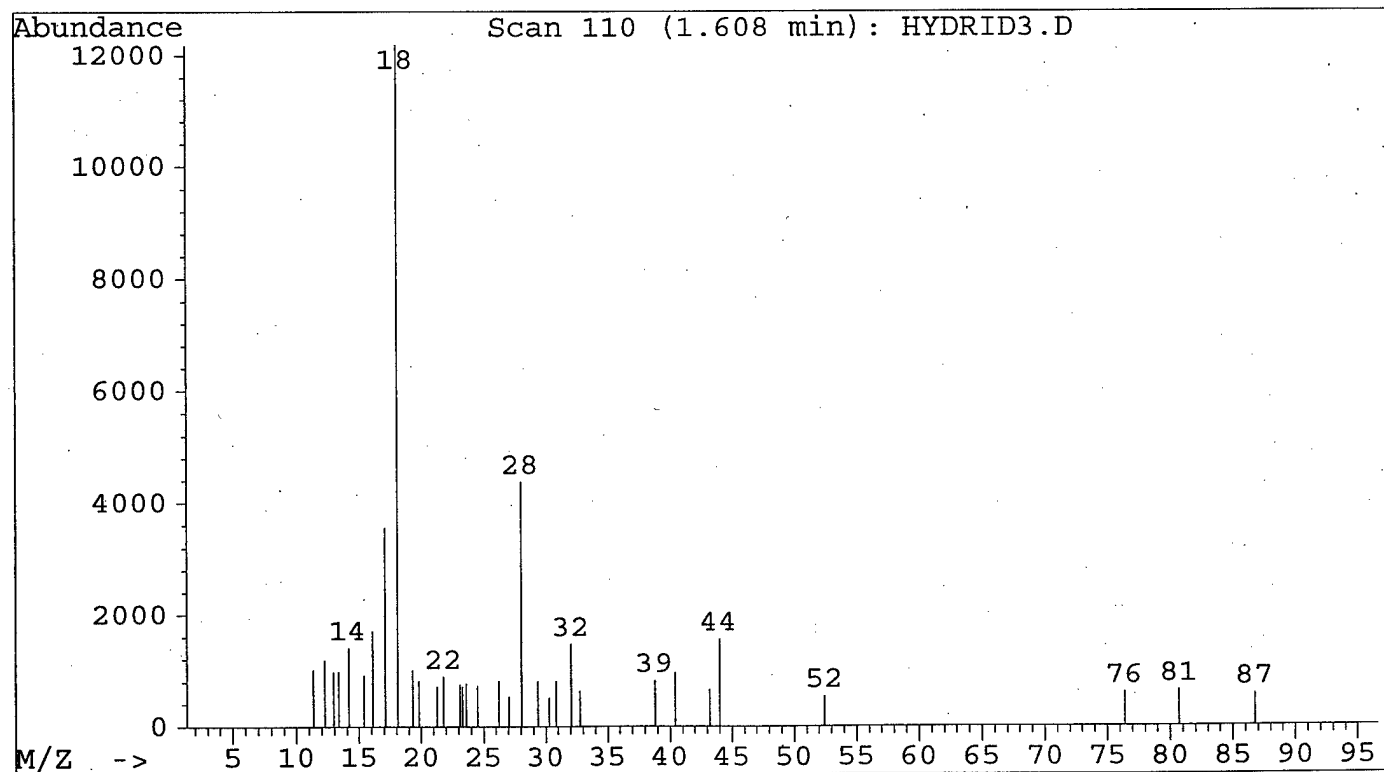
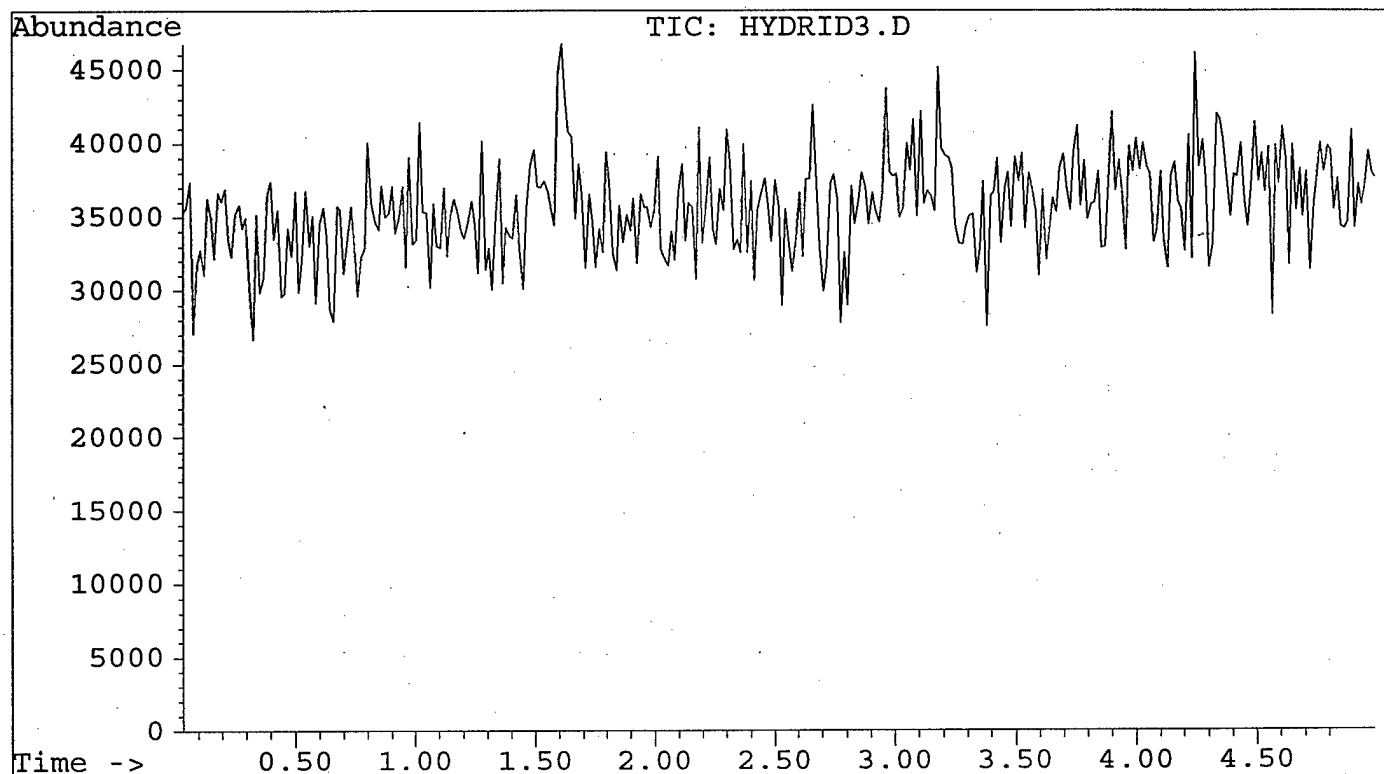
File: C:\CHEMPC\DATA\HYDRID1A.D
Operator: TAN
Date Acquired: 23 Feb 98 12:48 pm
Method File: HYDRIDE1.M
Sample Name: hydrogen gas from Li3Al H6
Misc Info:
ALS vial: 1



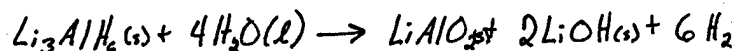
File: C:\CHEMPC\DATA\HYDRID2.D
Operator: TAN
Date Acquired: 23 Feb 98 2:22 pm
Method File: HYDRIDE1.M
Sample Name: hydrogen gas from Li3Al H6
Misc Info:
ALS vial: 1



File: C:\CHEMPC\DATA\HYDRID3.D
Operator: TAN
Date Acquired: 24 Feb 98 1:05 pm
Method File: HYDRIDE1.M
Sample Name: hydrogen gas from Li3AlH6
Misc Info:
ALS vial: 1



APPENDIX D



- 0.037g sample of 45.9% by weight Li₃AlH₆

Total gas produced = 86 mL
 atmospheric pressure = 586 mmHg
 atmospheric temperature = 21°C
 water temperature = 21°C ; P_{vap} = 18.62 mmHg
 water column height = 0

$$0.037\text{g DCPD/Li}_3\text{AlH}_6 \times \frac{0.459\text{g Li}_3\text{AlH}_6}{1\text{g DCPD/Li}_3\text{AlH}_6} \times \frac{1\text{mol Li}_3\text{AlH}_6}{53.85\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{1\text{mol Li}_3\text{AlH}_6} = 1.892 \times 10^{-3} \text{ mol H}_2 \text{ theoretical}$$

$$PV = nRT \quad n = \frac{\left(\frac{586 - 18.62}{760} \frac{\text{mmHg}}{\text{atm}}\right)(0.086\text{L})}{\left(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(294\text{K})} = 2.661 \times 10^{-3} \text{ mol H}_2 \text{ actual}$$

$$\% \text{ yield} = \frac{2.661 \times 10^{-3}}{1.892 \times 10^{-3}} \times 100\% = 140.6\% \text{ yield}$$

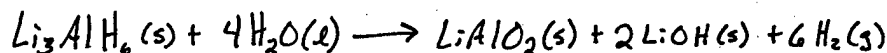
- 0.027g sample of 45.9% by weight Li₃AlH₆

Total gas produced = 59 mL
 atmospheric pressure = 588.6 mmHg
 atmospheric temperature = 21°C
 water temperature = 21°C ; P_{vap} = 18.62 mmHg
 water column height = 0 mm

$$0.027\text{g DCPD/Li}_3\text{AlH}_6 \times \frac{0.459\text{g Li}_3\text{AlH}_6}{1\text{g DCPD/Li}_3\text{AlH}_6} \times \frac{1\text{mol Li}_3\text{AlH}_6}{53.85\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{1\text{mol Li}_3\text{AlH}_6} = 1.3838 \times 10^{-3} \text{ mol theoretical}$$

$$PV = nRT \quad n = \frac{\left(\frac{588.6 - 18.62}{760} \frac{\text{mmHg}}{\text{atm}}\right)(0.059\text{L})}{\left(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(294\text{K})} = 1.834 \times 10^{-3} \text{ mol actual}$$

$$\% \text{ yield} = \frac{1.834 \times 10^{-3}}{1.3838 \times 10^{-3}} \times 100\% = 132.5\% \text{ yield}$$



- 0.203g sample DCPD/Li₃AlH₆

Total gas produced = 285 mL
 atmospheric pressure = 587.9 mmHg
 atmospheric temperature = 20°C
 water temperature = 18°C; P_{vap} = 15.64 mmHg

$$0.203\text{g sample} \times \frac{0.459\text{g Li}_3\text{AlH}_6}{1\text{g sample}} \times \frac{\text{mol Li}_3\text{AlH}_6}{53.851\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{\text{mol Li}_3\text{AlH}_6} = 1.03816 \times 10^{-2} \text{ mol H}_2 \text{ theoretical}$$

$$PV = nRT \quad n = \frac{\left(\frac{(587.9 - 15.64)\text{ mmHg}}{760\text{ mmHg/atm}}\right)(0.285\text{ L})}{\left(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(293\text{ K})} = 8.9256 \times 10^{-3} \text{ mol H}_2 \text{ actual}$$

$$\% \text{ yield} = \frac{8.9256 \times 10^{-3}}{1.03816 \times 10^{-2}} \times 100\% = 86.0\% \text{ yield}$$

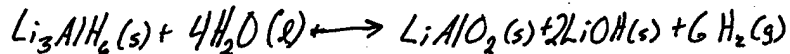
- 0.283g sample DCPD/Li₃AlH₆

Total gas produced: 408 mL
 Atmospheric Pressure: 578.1 mmHg
 Atmospheric Temperature: 20°C
 Water Temperature: 18.5; P_{vap} = 16.115 mmHg
 Water column height: 320 mm = 24.25 mmHg

$$0.283\text{g sample} \times \frac{0.459\text{g Li}_3\text{AlH}_6}{1\text{g sample}} \times \frac{\text{mol Li}_3\text{AlH}_6}{53.851\text{g Li}_3\text{AlH}_6} \times \frac{6\text{mol H}_2}{\text{mol Li}_3\text{AlH}_6} = 0.614473 \text{ mol H}_2 \text{ theoretical}$$

$$PV = nRT \quad n = \frac{\left(\frac{(578.1 - 24.25 - 16.115)\text{ mmHg}}{760\text{ mmHg/atm}}\right)(0.408\text{ L})}{\left(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(293\text{ K})} = 0.012074 \text{ mol H}_2 \text{ actual}$$

$$\% \text{ yield} = \frac{0.012074}{0.614473} \times 100\% = 89.5\% \text{ yield GC/MS data: HYDRID4.D}$$



- 0.413 g sample DCPD/Li₃AlH₆

Total gas produced: 670 mL

Atmospheric pressure: 583.7 mmHg

Height of water column: 16.5 mm H₂O = 12.125 mmHg

Atmospheric Temperature: 20°C

Water Temperature: 18.5°C; P_{vap} = 16.115 mmHg

$$0.413 \text{ g sample} \times \frac{0.459 \text{ g Li}_3\text{AlH}_6}{1 \text{ g sample}} \times \frac{1 \text{ mol Li}_3\text{AlH}_6}{53.851 \text{ g Li}_3\text{AlH}_6} \times \frac{6 \text{ mol H}_2}{1 \text{ mol Li}_3\text{AlH}_6} = 0.019685 \text{ mol H}_2 \text{ theoretical}$$

$$PV = nRT \quad n = \frac{\left(\frac{583.7 - 12.125 - 16.115}{760} \text{ mmHg/atm} \right) (0.670 \text{ L})}{\left(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (293 \text{ K})} = 0.020367 \text{ mol H}_2 \text{ actual}$$

$$\% \text{ yield} = \frac{0.020367}{0.019685} \times 100\% = 103.5\% \text{ yield} \quad \text{GC/MS data} = \text{HYDRID5.D}$$

- 0.386 g sample DCPD/Li₃AlH₆

Total gas produced: 670 mL

Atmospheric Pressure: 585.2 mmHg

Height of H₂O column: 170 mm ⇒ 12.492 mmHg

Atmospheric Temp: 20°C

Water Temperature: 18°C ⇒ P_{vap} = 15.64

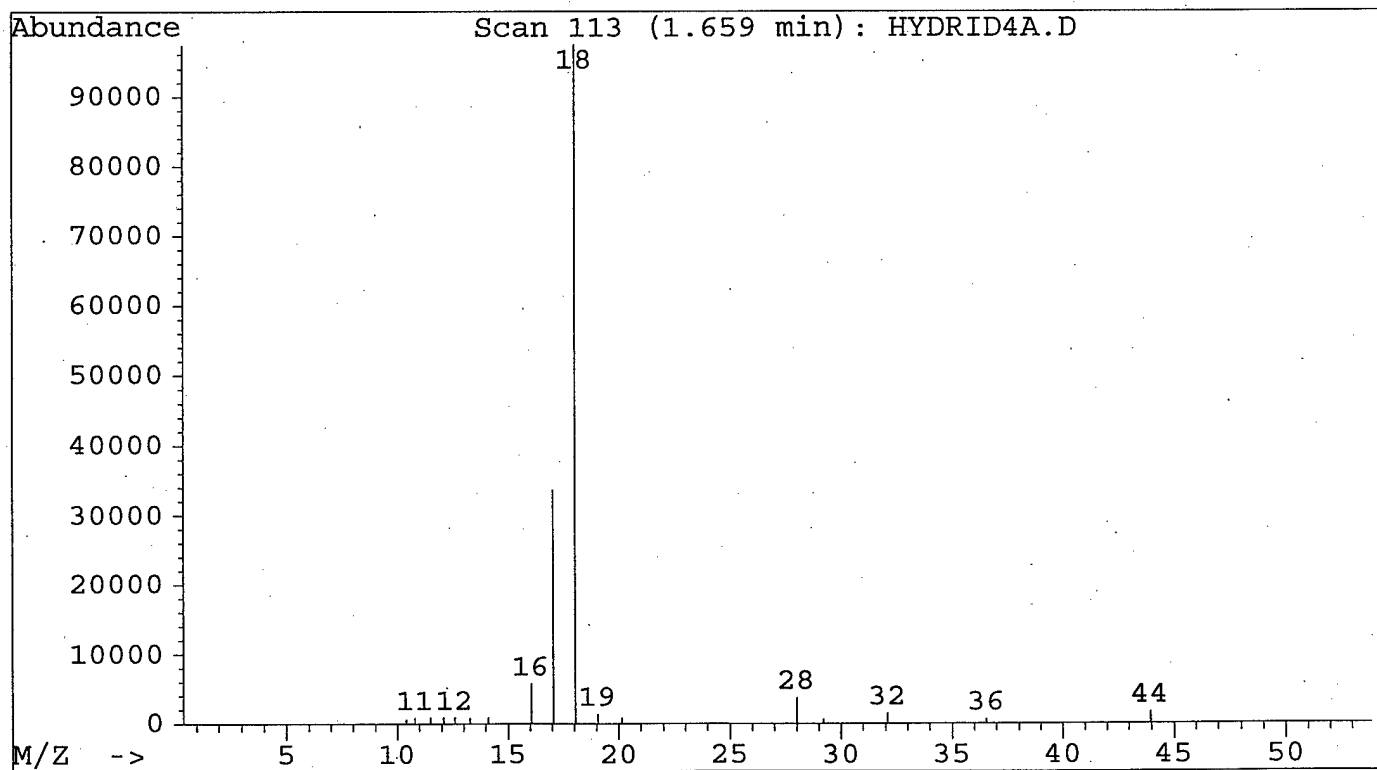
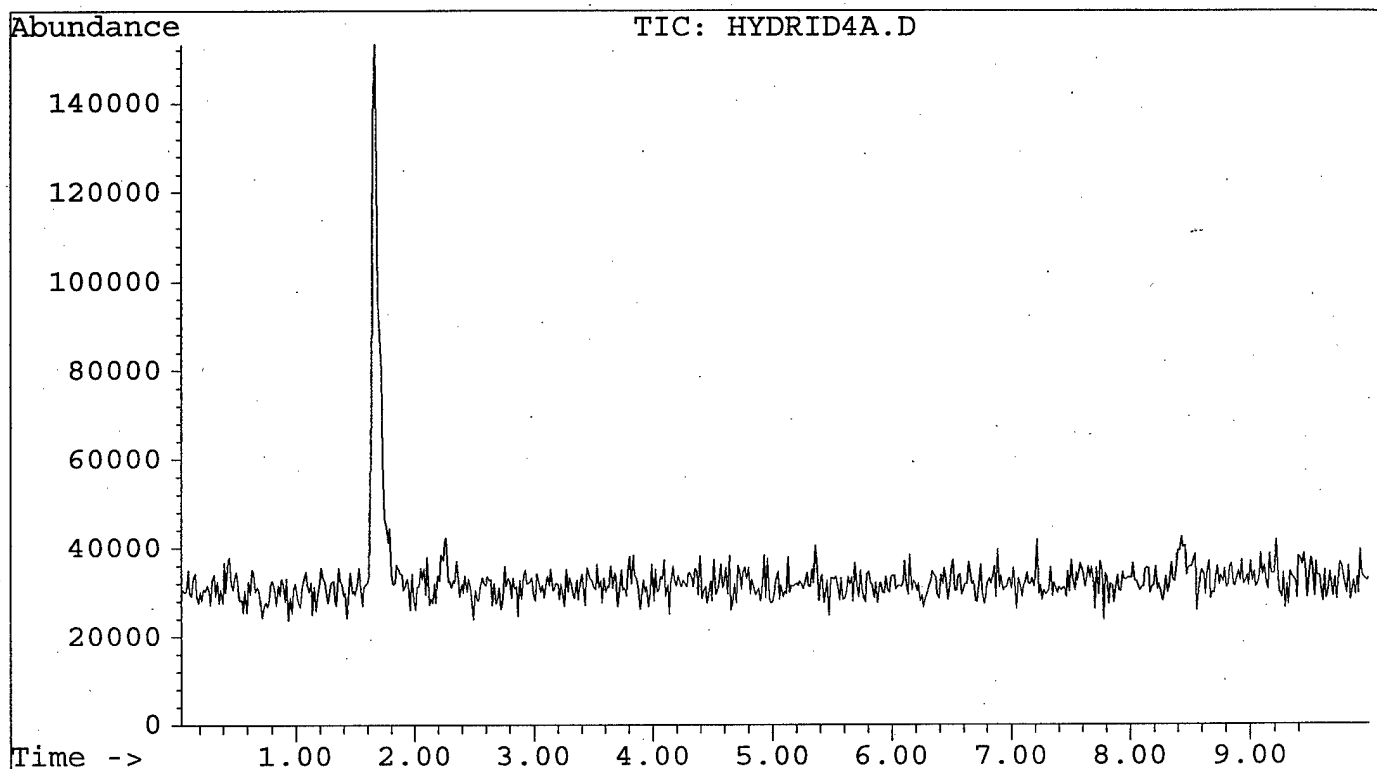
$$0.386 \text{ g sample} \times \frac{0.459 \text{ g Li}_3\text{AlH}_6}{1 \text{ g sample}} \times \frac{1 \text{ mol Li}_3\text{AlH}_6}{53.851 \text{ g}} \times \frac{6 \text{ mol H}_2}{1 \text{ mol Li}_3\text{AlH}_6} = 0.018398 \text{ mol H}_2 \text{ theoretical}$$

$$PV = nRT \quad n = \frac{\left(\frac{585.2 - 12.492 - 15.64}{760} \text{ mmHg/atm} \right) (0.670 \text{ L})}{\left(0.0820575 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (293 \text{ K})} = 0.020426 \text{ mol actual}$$

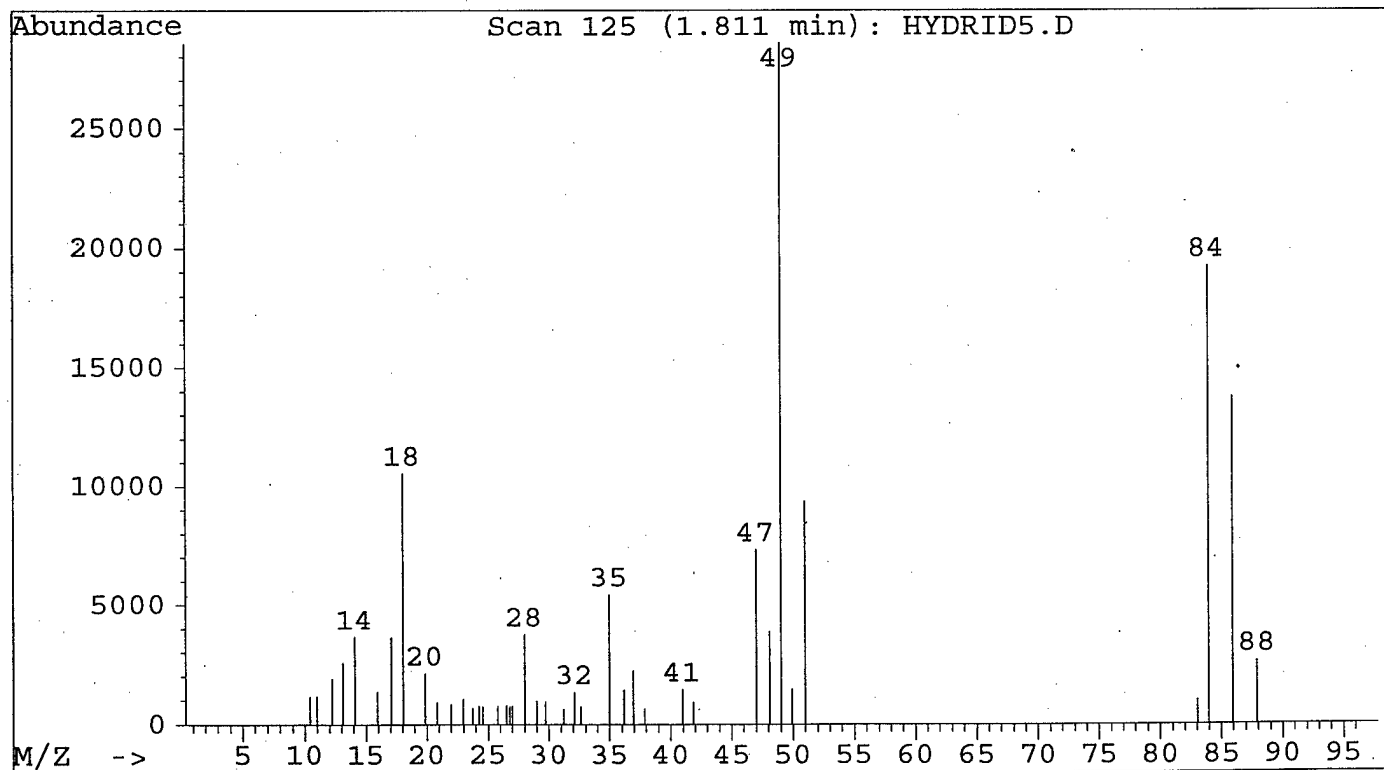
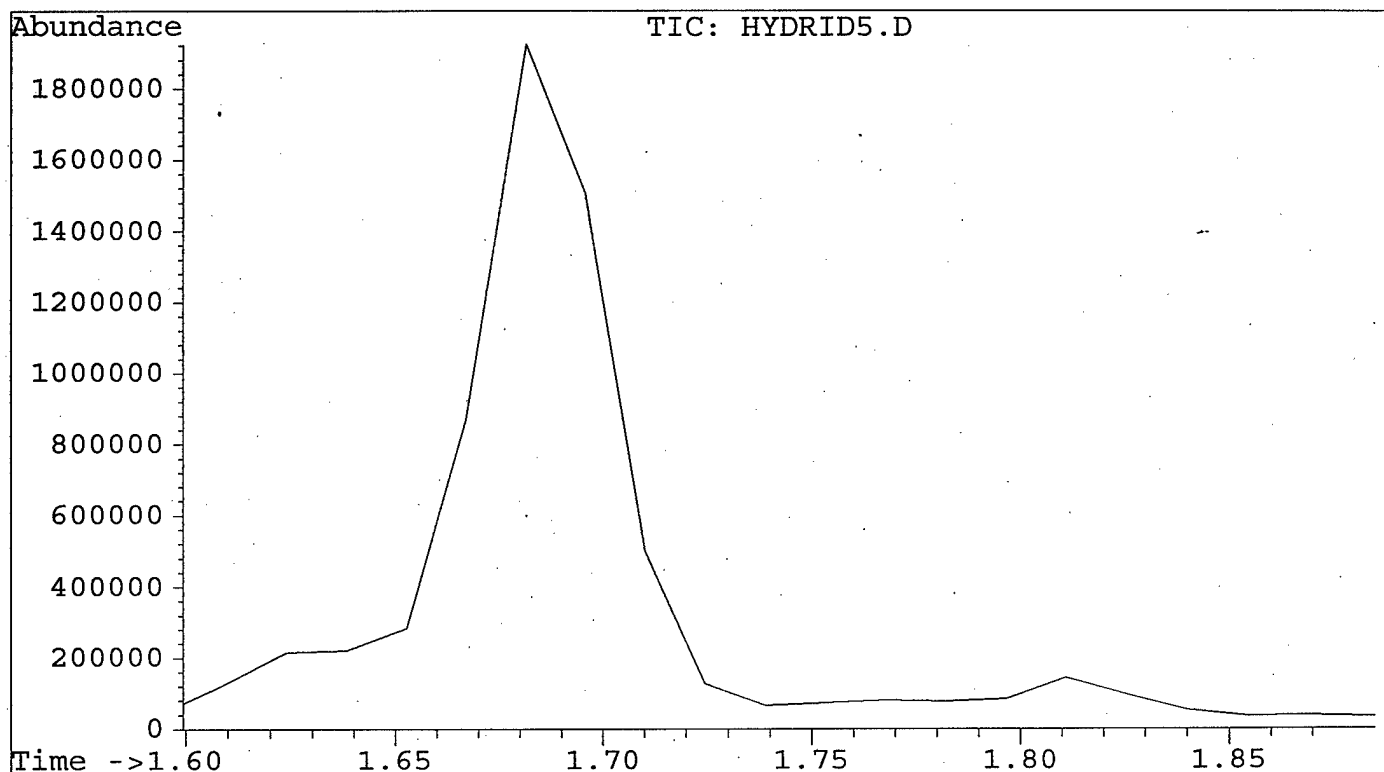
$$\% \text{ yield} = \frac{0.020426}{0.018398} \times 100\% = 111.0\% \quad \text{GC/MS data} \Rightarrow \text{HYDRID6.D}$$

APPENDIX E

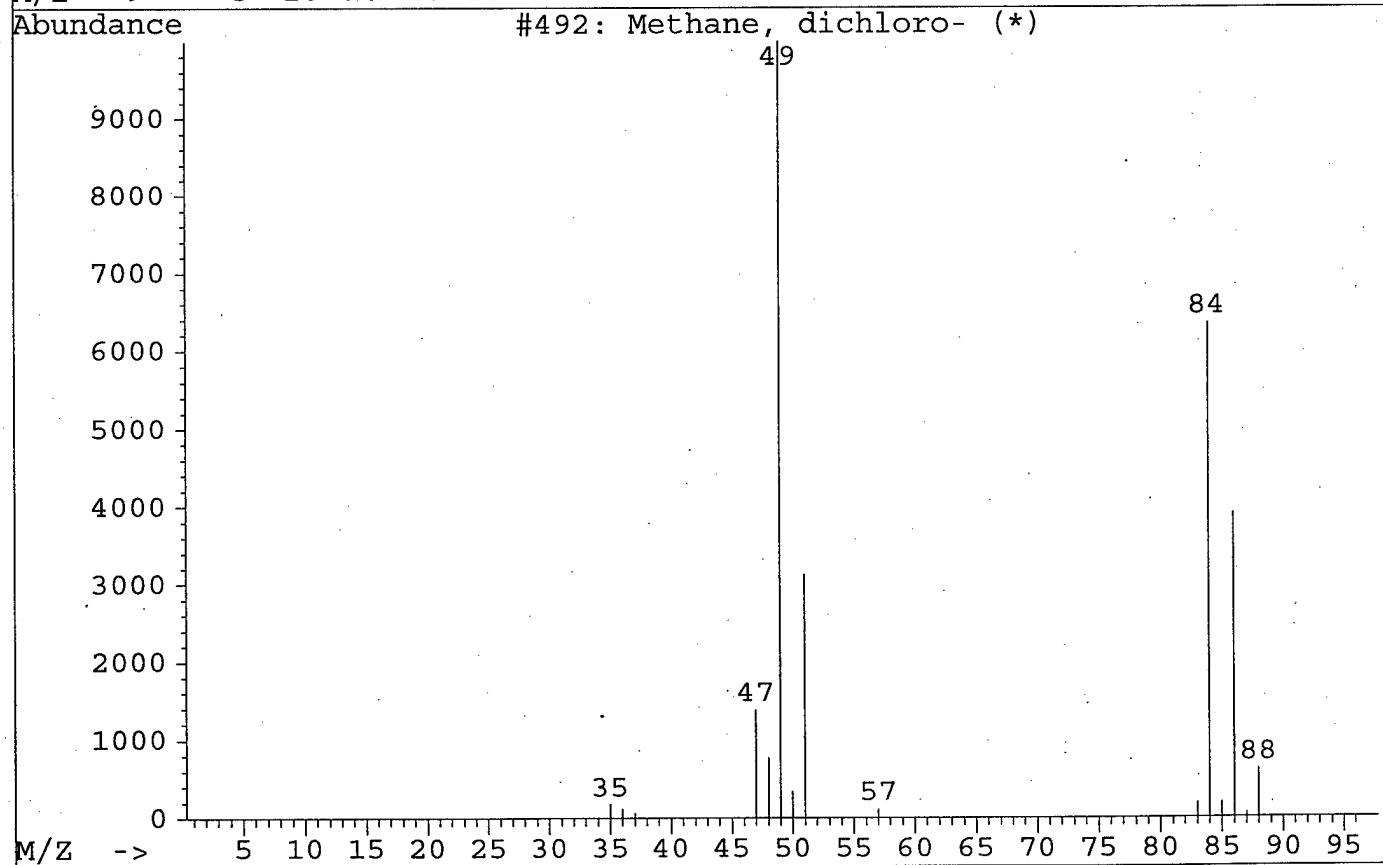
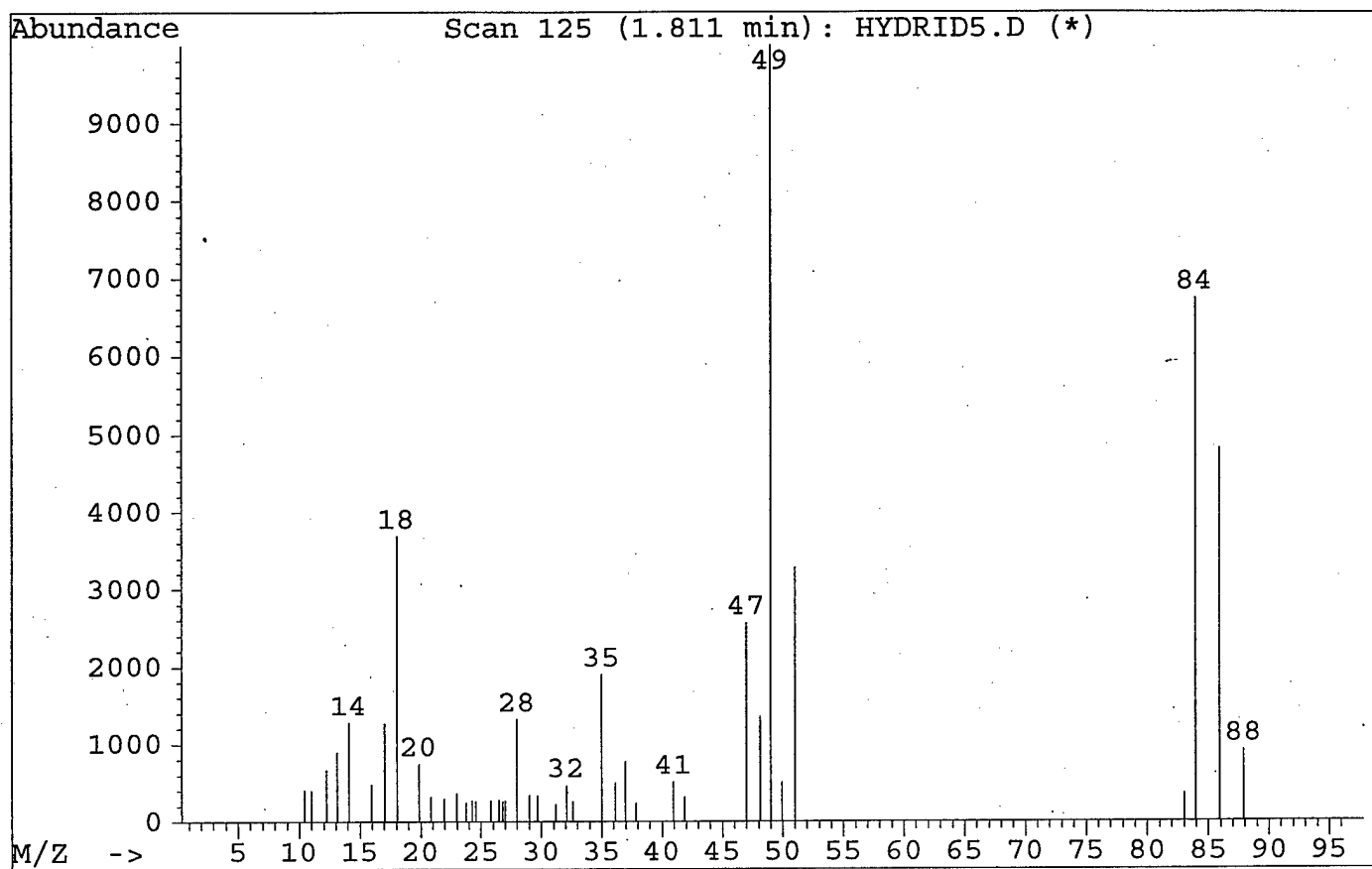
File: C:\CHEMPC\DATA\HYDRID4A.D
Operator: TAN
Date Acquired: 7 Apr 98 12:57 pm
Method File: HYDRIDE1.M
Sample Name: 283mg DCPD/Li3AlH6
Misc Info: Possibly exposed to air prior to the run
ALS vial: 1



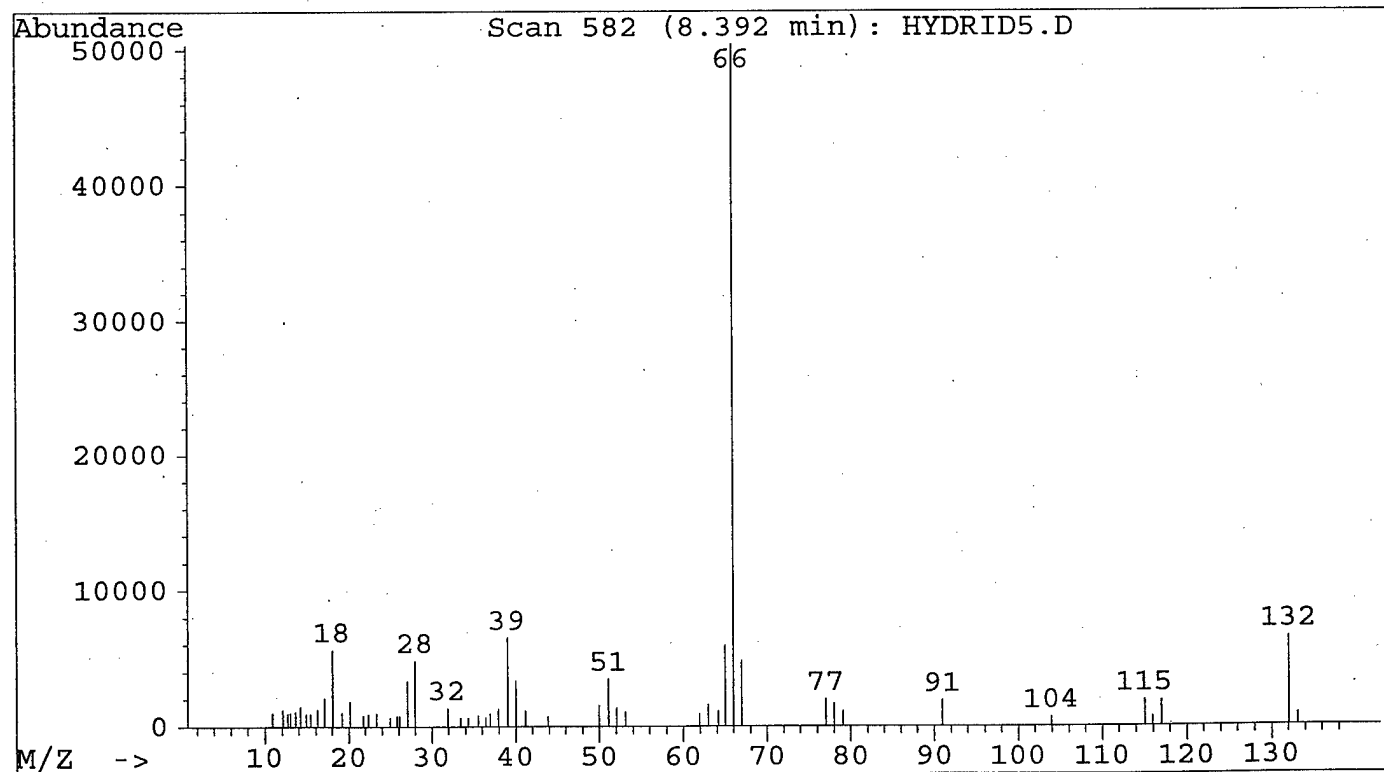
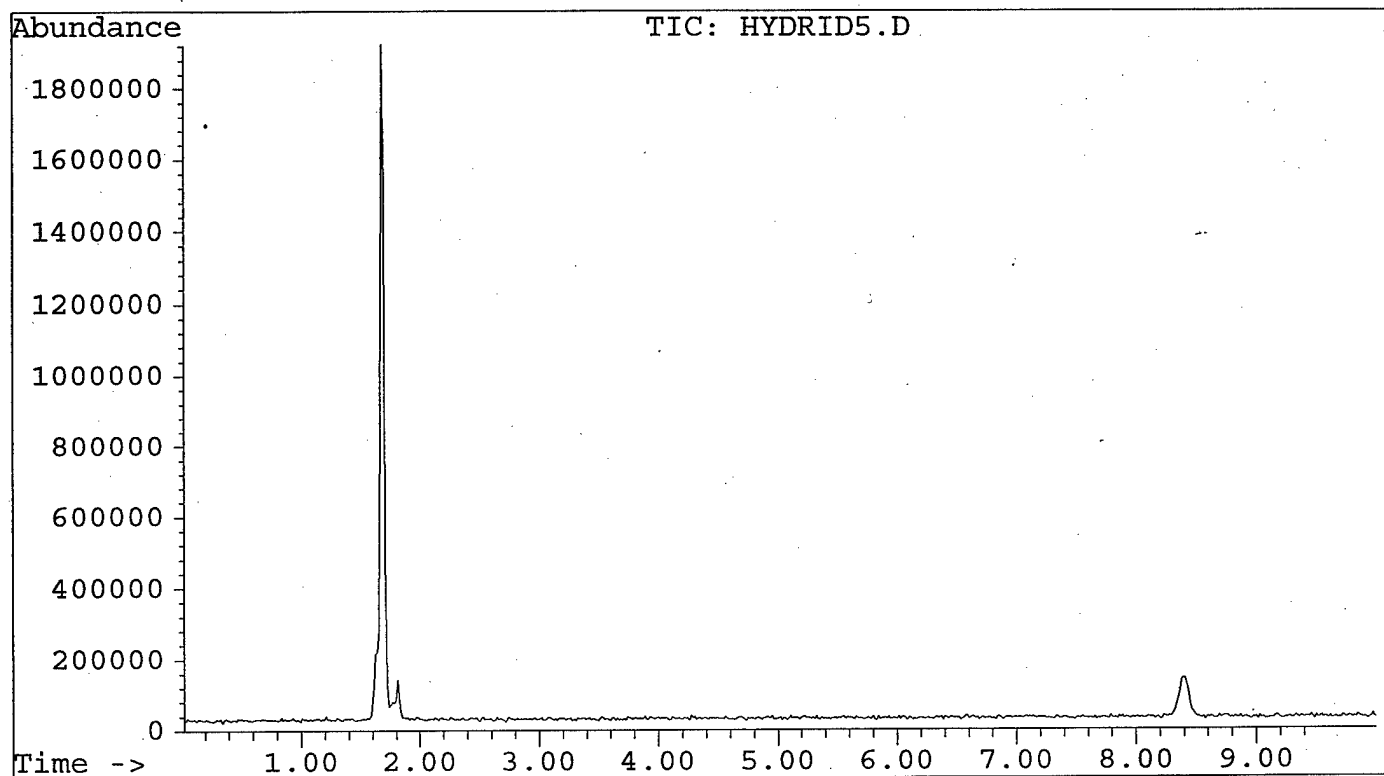
File: C:\CHEMPC\DATA\HYDRID5.D
Operator: TAN
Date Acquired: 9 Apr 98 1:04 pm
Method File: HYDRIDE1.M
Sample Name: DCPD and Li3AlH6
Misc Info: Sample may have been exposed to air
ALS vial: 1



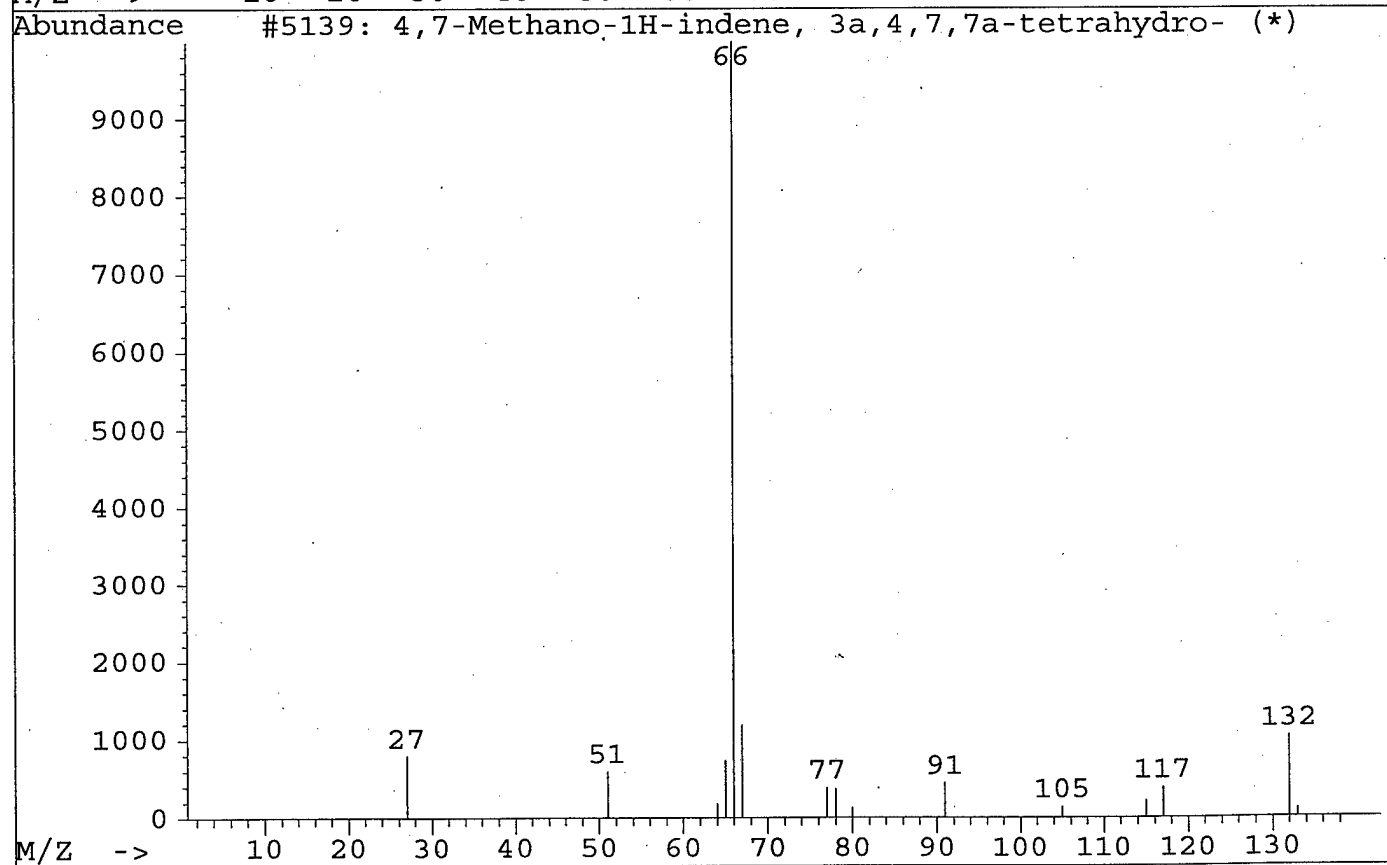
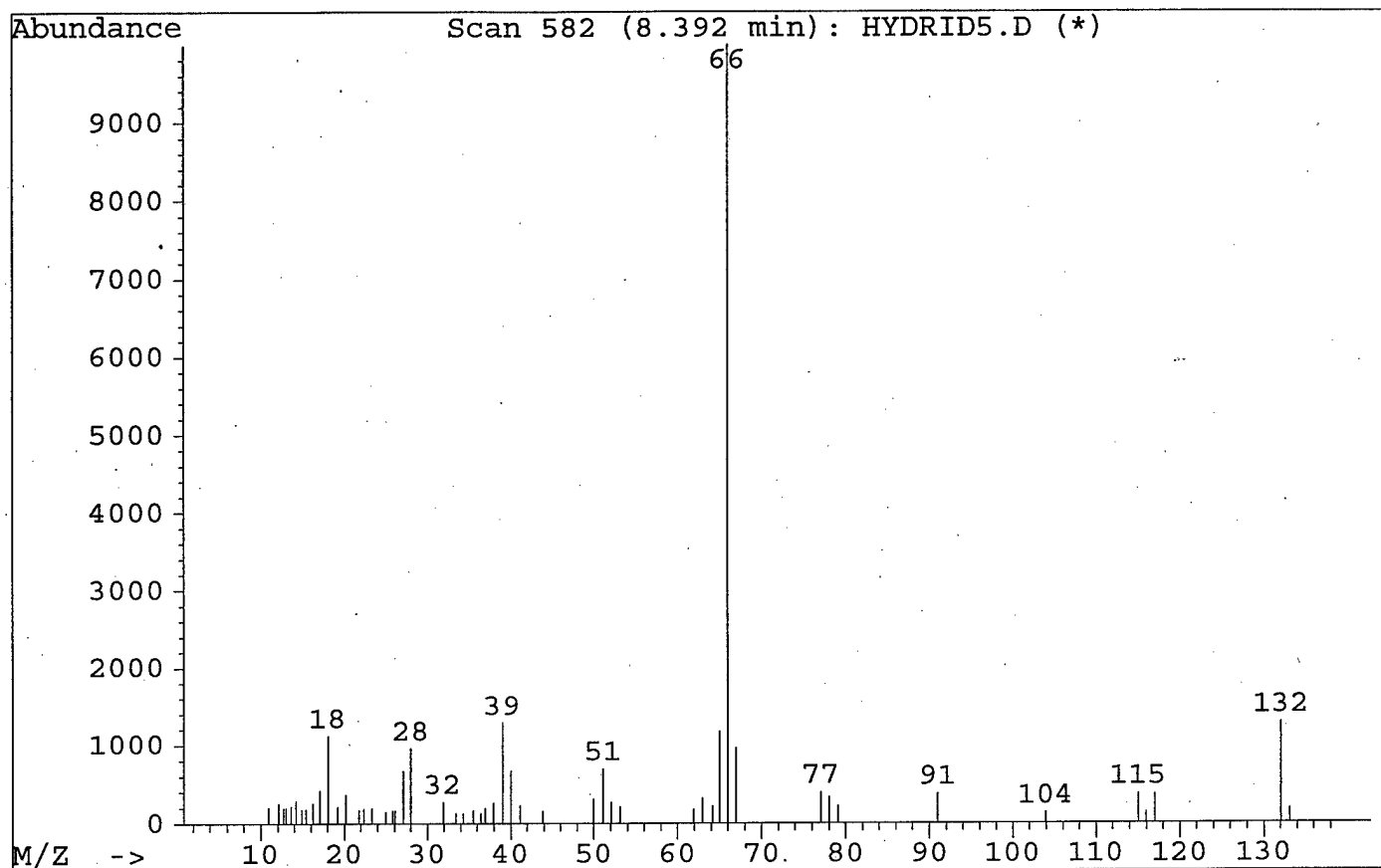
Library Searched : NBS54K.L
Quality : 74
ID : Methane, dichloro-



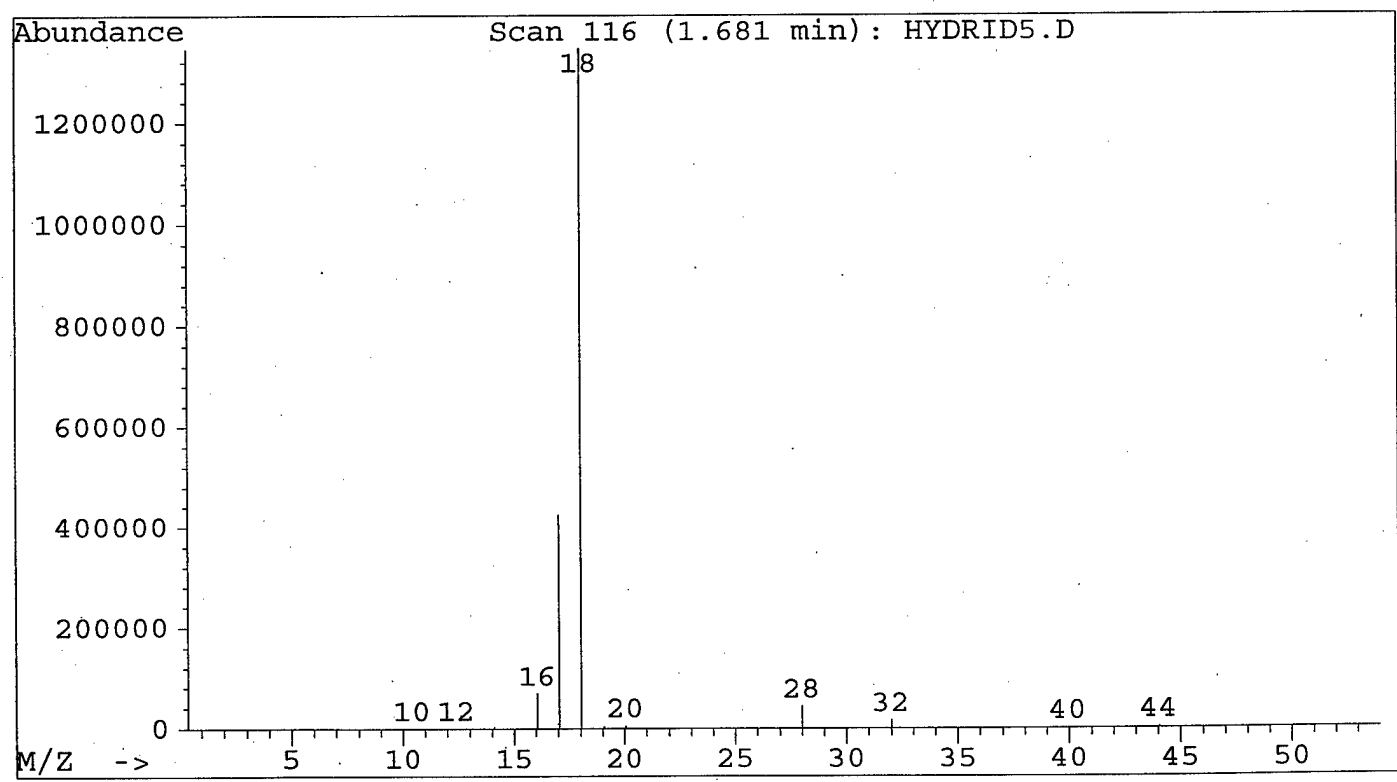
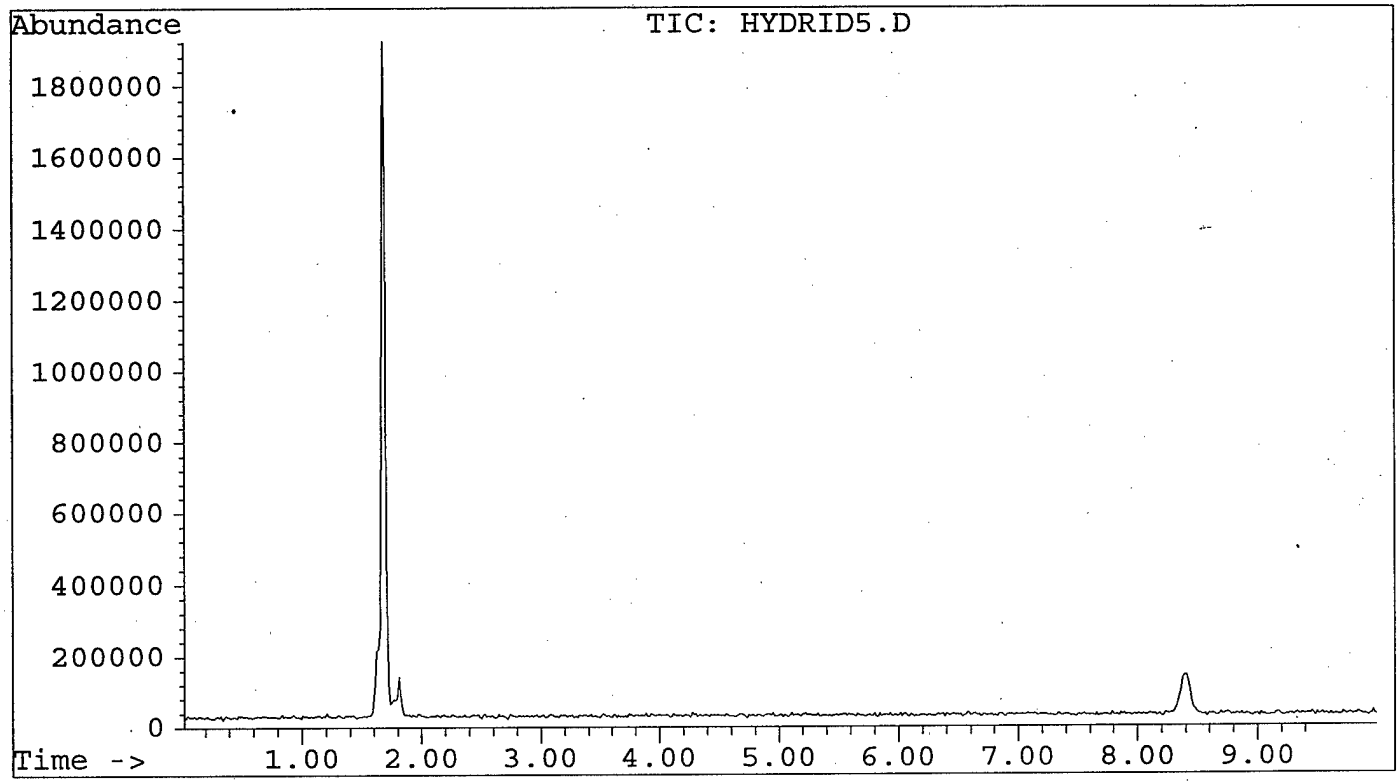
File: C:\CHEMPC\DATA\HYDRID5.D
Operator: TAN
Date Acquired: 9 Apr 98 1:04 pm
Method File: HYDRIDE1.M
Sample Name: DCPD and Li3AlH6
Misc Info: Sample may have been exposed to air
ALS vial: 1



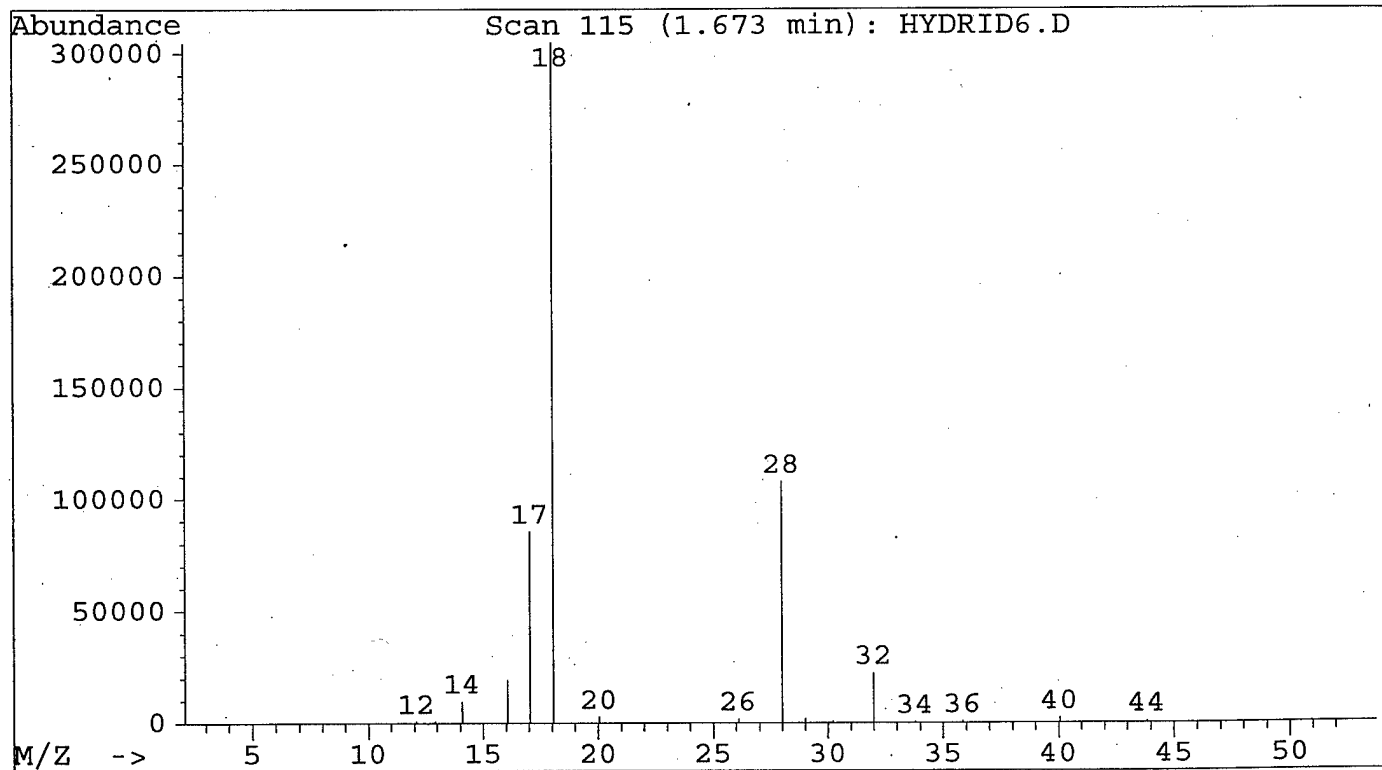
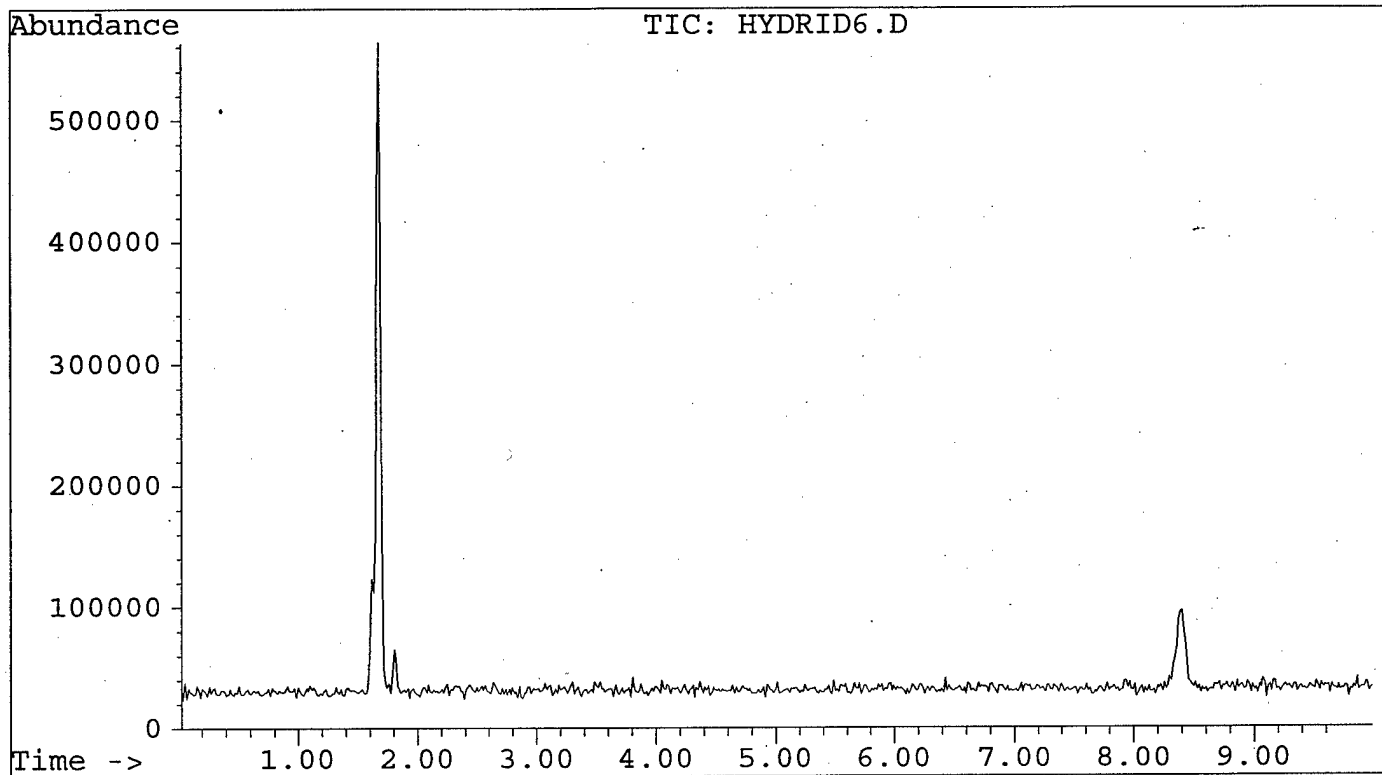
Library Searched : NBS54K.L
Quality : 91
ID : 4,7-Methano-1H-indene, 3a,4,7,7a-tetrahydro-



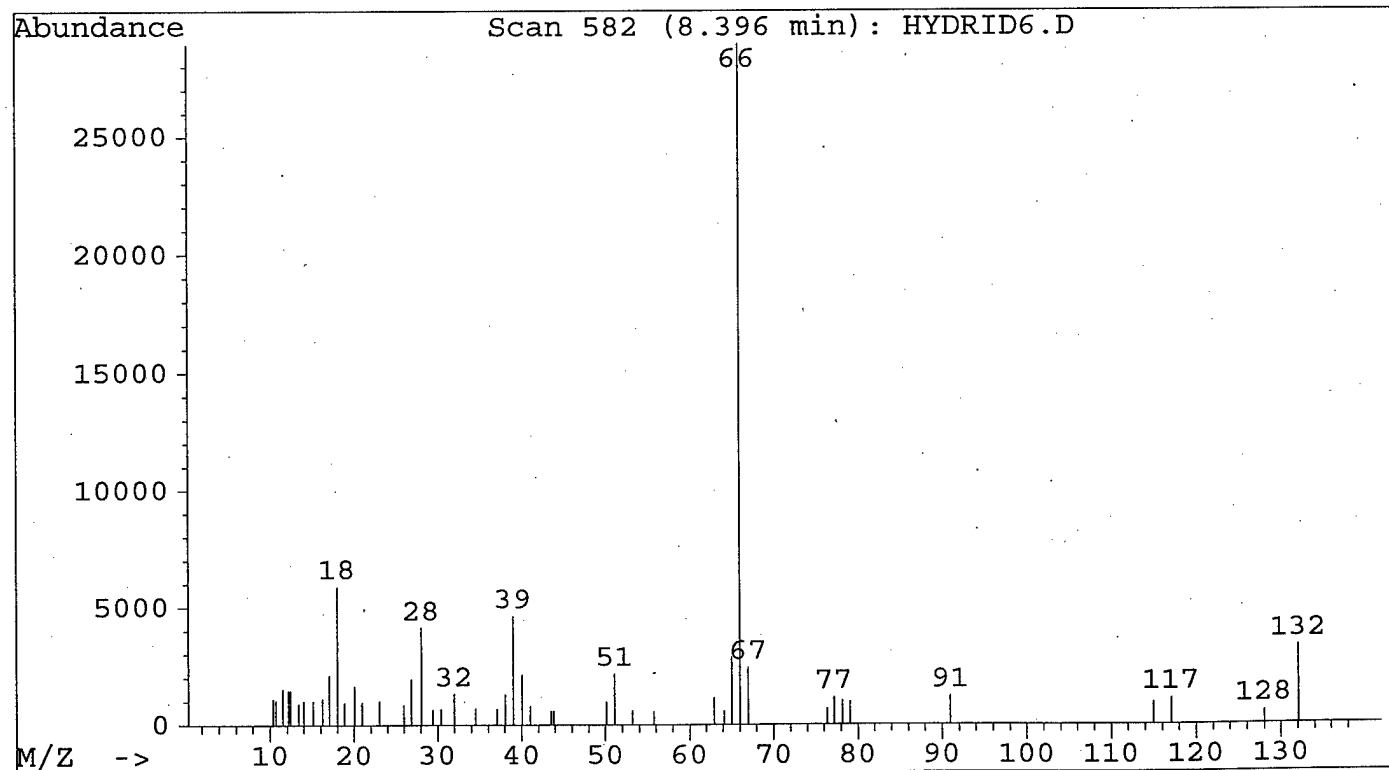
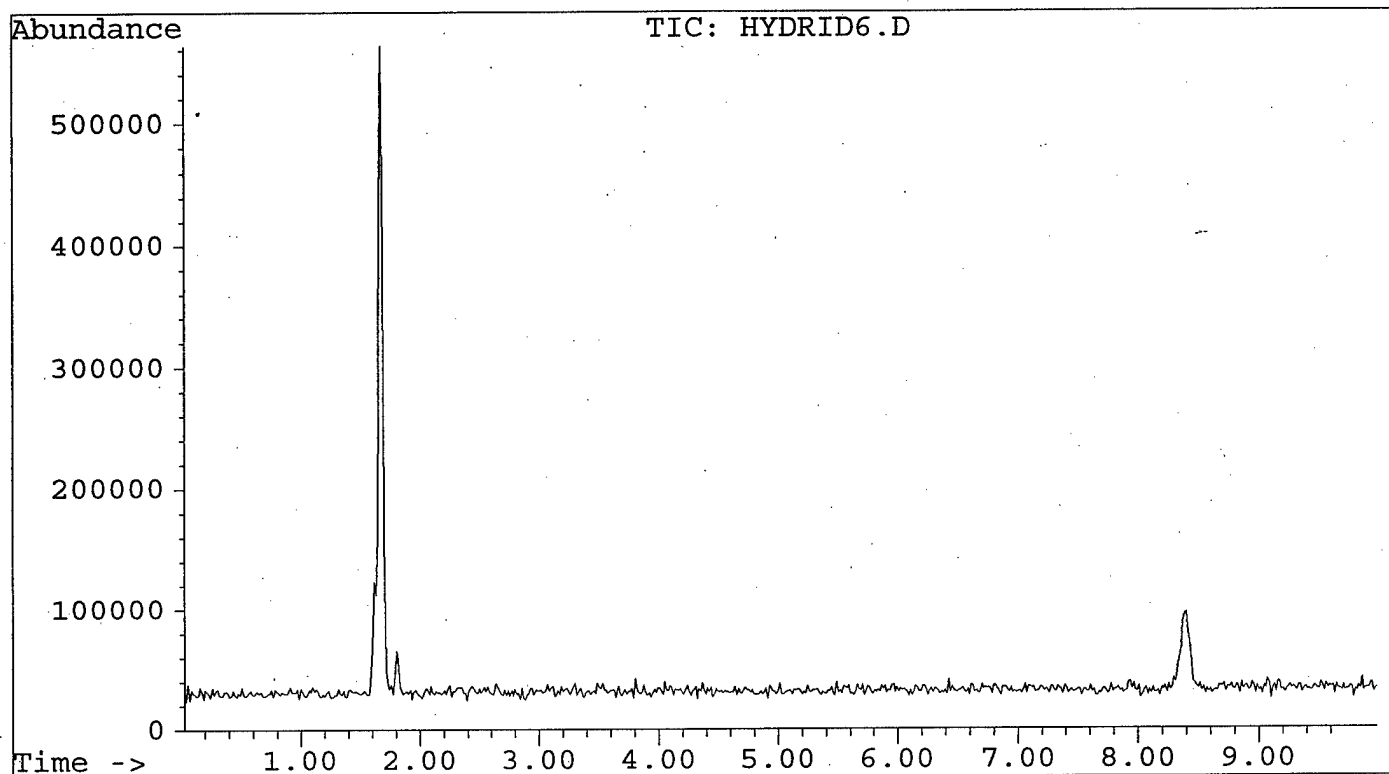
File: C:\CHEMPC\DATA\HYDRID5.D
Operator: TAN
Date Acquired: 9 Apr 98 1:04 pm
Method File: HYDRIDE1.M
Sample Name: DCPD and Li3AlH6
Misc Info: Sample may have been exposed to air
ALS vial: 1



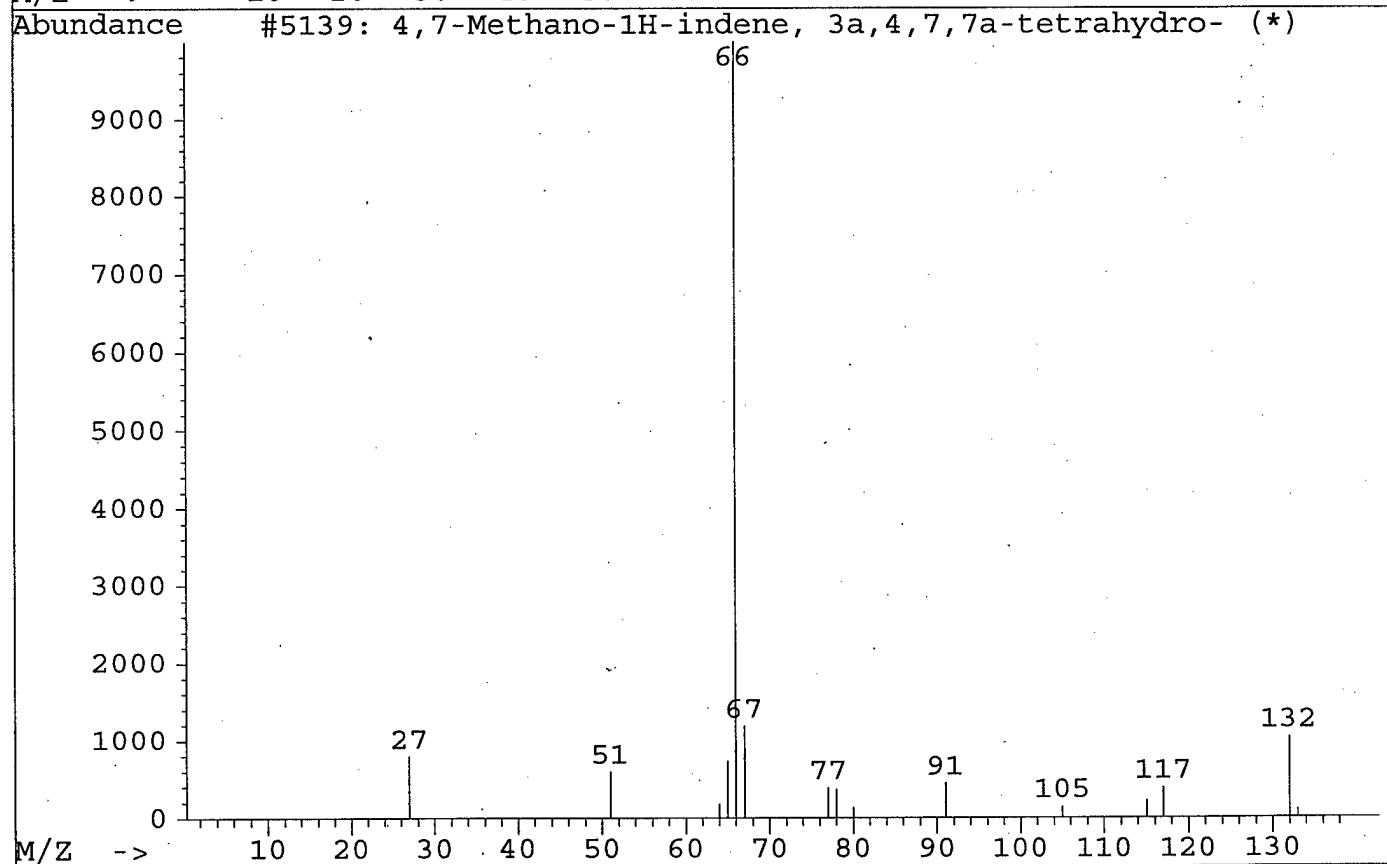
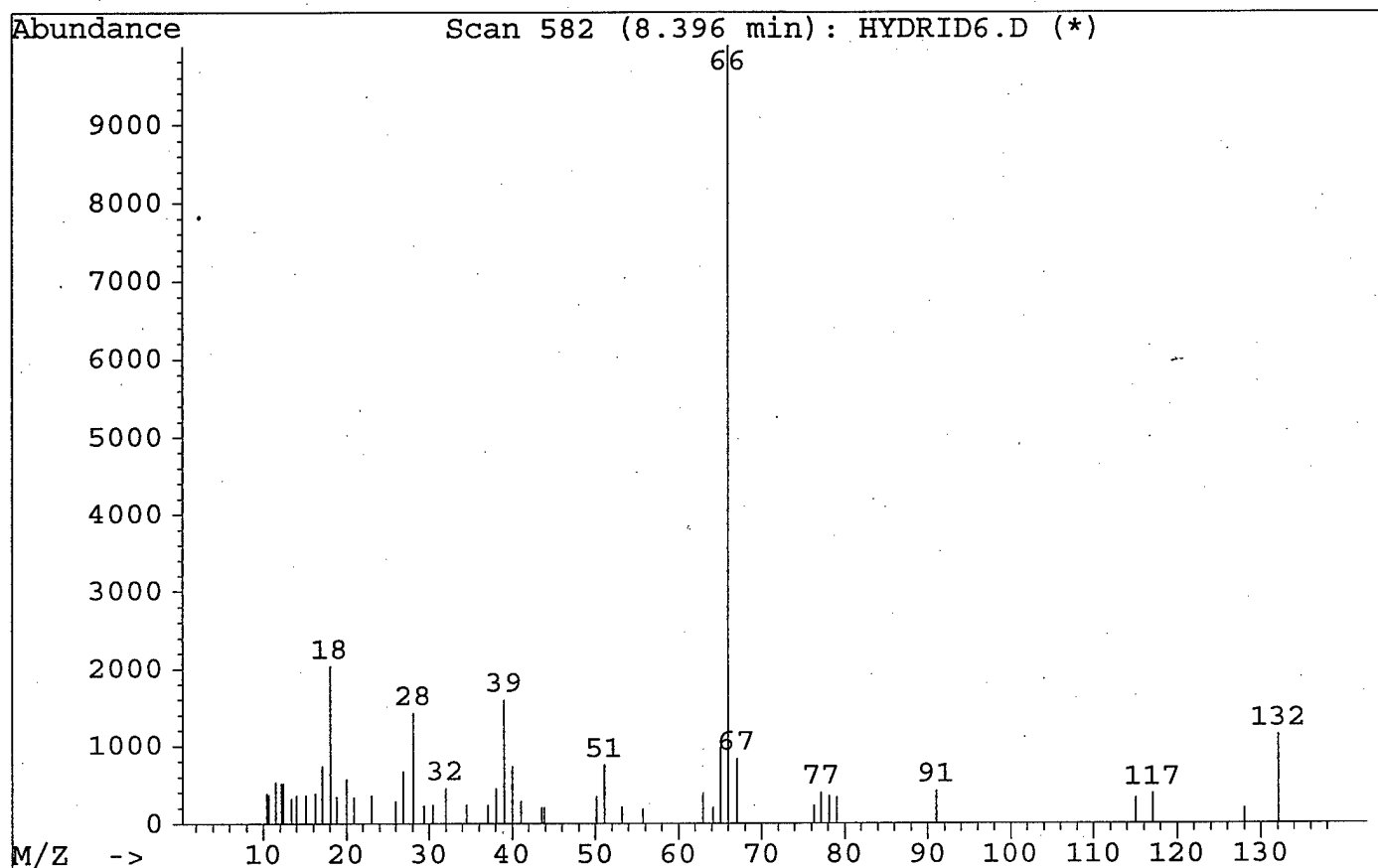
File: C:\CHEMPC\DATA\HYDRID6.D
Operator: TAN
Date Acquired: 9 Apr 98 1:48 pm
Method File: HYDRIDE1.M
Sample Name: DCPD and Li3AlH6
Misc Info: Sample was taken from the middle of a tube
ALS vial: 1



File: C:\CHEMPC\DATA\HYDRID6.D
Operator: TAN
Date Acquired: 9 Apr 98 1:48 pm
Method File: HYDRIDE1.M
Sample Name: DCPD and Li3AlH6
Misc Info: Sample was taken from the middle of a tube
ALS vial: 1



Library Searched : NBS54K.L
Quality : 91
ID : 4,7-Methano-1H-indene, 3a,4,7,7a-tetrahydro-



File: C:\CHEMPC\DATA\HYDRID6.D
Operator: TAN
Date Acquired: 9 Apr 98 1:48 pm
Method File: HYDRIDE1.M
Sample Name: DCPD and Li3AlH6
Misc Info: Sample was taken from the middle of a tube
ALS vial: 1

