

**EFFORTS OF COATING AND TESTING HIGH ASPECT RATIO  
MICROFABRICATED NICKEL GAS CHROMATOGRAPHY COLUMNS**

A Thesis

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To my mother

**Jamuna Paga**

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## **Abstract**

Gas chromatography (GC) is a widely used analytical technique, with applications in the chemical process industry, oil exploration, environmental monitoring, purification of substances, and general organic compound analysis. Although traditional GC's are widely used they have their own disadvantages like high power consumption and long times for analysis. Several laboratories are working on the miniaturization of GC's for rapid and onsite chemical analysis.

Many researchers are currently working on the development of microfabricated columns for realizing a hand held GC sensor. Microfabricated nickel columns have been manufactured by the Center for Advanced Microstructures & Devices (CAMD), Baton Rouge. The columns are attractive due to their small size, low mass and high thermal conductivity allowing for rapid temperature programming with relatively low power consumption and parallel manufacturing which results in low manufacturing costs, and robustness when compared to silicon columns. Using the LiGA process nickel columns with width dimensions of 50 microns, height dimensions of 500 microns and 1 meter of channel length are microfabricated with integrated on chip injection and detection connections. Connecting these column chips to the HP 5890 GC test bed is described. A commercial fused silica capillary column of 1 meter length, 100 microns i.d was tested to check the instrument set up and for providing background performance data. The microfabricated nickel column chips were tested with the same conditions after the PMMA (Poly methyl methacrylate) removed, after deactivation, and after coating. The test mixtures were methane, hexane, and a mixture of hexane and decane. Different methods of deactivation and coating these metal columns have been described. Columns were coated with dimethyl polysiloxane stationary phase (OV-1). Separation of methane and hexane was performed in less than 4 seconds. The preliminary experimental results on these coated high aspect ratio metal gas chromatography columns displayed promising results and future research is mainly focused on

coating methods to achieve more uniform coatings without any pooling of the solution in the column's corners and for separation of different chemical compounds.

## **1. Introduction**

Gas Chromatography (GC) is a type of chromatography in which the mobile phase is a gas, usually an inert gas such as helium or nitrogen, and the stationary phase is a micron thin layer of a non volatile liquid or polymer coated on inside wall of the glass or metal tubing, called a column. The instrument used to perform gaseous separations is called a gas chromatograph. It is a widely used analytical device, with applications in the chemical process industry, oil exploration, environmental monitoring, purification of substances, and general organic compound analysis. Apart from these traditional uses, GCs are playing a role in the detection of chemical warfare agents, and the detection of diseases [1]. Industrial process control is one of the big industrial applications of a GC, with instruments in the chemical plants continuously monitoring chemical processes and contributing to the quality control of the product.

### **1.1 History of Chromatography**

Chromatography dates to 1903 in the work of Russian scientist, Mikhail Semenovich Tswett during his research on plant pigments. He used liquid adsorption column chromatography with calcium carbonate as adsorbent and petrol ether or ethanol mixtures as eluent to separate chlorophylls and carotenoids. Archer John Porter Martin, who was awarded the Nobel Prize for his work in developing liquid-liquid (1941) and paper (1944) chromatography, laid the foundation for the development of gas chromatography and later produced liquid-gas chromatography (1950). German graduate student Fritz Prior developed solid state gas chromatography in 1947.

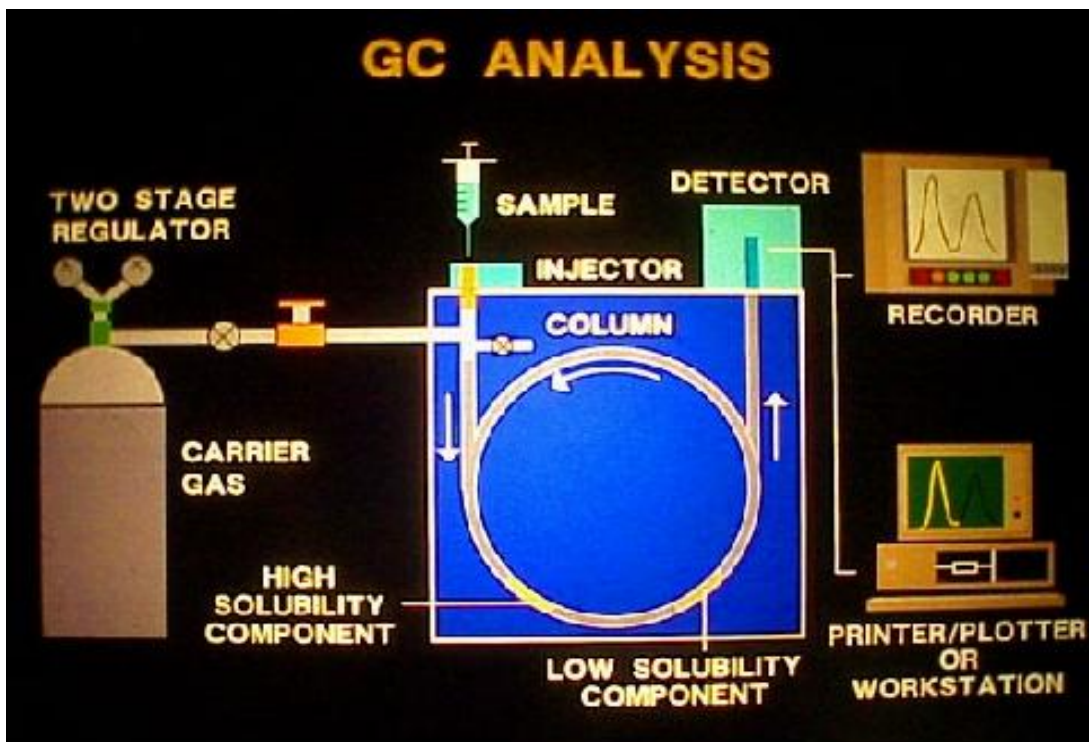
The credit for discovering gas chromatography is disputed [2], a tremendous amount of work has gone towards advancing the technique [3, 4] from the discovery of chromatography in the early 1900's to the first use of packed GC columns and the emergence of capillary GC. Martin

and Synge won the Nobel Prize in 1952 for their work in developing partition chromatography to separate amino acids. Introducing gas liquid chromatography, Martin and James performed separation on a stationary liquid phase coated on an inert support with a gaseous mobile phase, giving rise to the packed bed column. Capillary columns are currently used as separation columns which have a very small internal diameter, on the order of a few hundredths of a millimeter, and lengths between 25-60 meters are common. The inner column walls are coated with the active materials; some of them are quasi solid filled with many parallel micropores. Most modern capillary columns are made of fused-silica with a polyimide outer coating. These columns are flexible, so a very long column can be wound into a small coil.

## **1.2 Gas Chromatography Instrumentation**

A typical GC consists of an injector, a separation column, a detector, and electronics for control and data processing. A sample mixture is injected into the heated injector carried through a separating column by an inert carrier gas and detected by a detector (commonly Flame Ionized detector) and recorded as a series of peaks on a recorder as the components leave the column. The column is contained in a heated oven that is preceded by a heated injector port and followed by a heated detector which produces the electronic output signal (see figure 1-1). The peaks show different compounds present in the sample, the x-axis shows the absolute time when the compound eluted from the column, and y-axis shows the relative magnitude of the analytes present in the sample. Each component of the sample mixture reaches the detector at a different time and produces a signal at their characteristic time called the “retention time”. The area under the peak is related to the amount of that compound present in the sample. The numbers of peaks correlate to the number of compounds present in the sample and the area under the each peak correlates with the amount of the component in the sample. The standard information or data can be used to identify the compounds basing on their retention times (see figure 1-2). By calculating

the area of the peak using the mathematical function of integration, the concentration of an analyte in the original sample can be determined. Concentrations can be calculated using a calibration curve created by finding the response factor of an analyte. The relative response factor is the expected ratio of an analyte to an internal standard (or external standard) and is calculated by finding the response of a known amount of analyte and a constant amount of internal standard (a chemical added to the sample at a constant concentration, with a distinct retention time to the analyte). In most modern GC or GC-MS (GC with Mass Spectrometer detector) systems, computer software is used to draw and integrate peaks and match them to compound's library spectra in the instrument. GC analyzes the content of chemical product, for example in assuring the quality of products in the chemical industry or measuring toxic wastes in soil air or water. It is very accurate if used properly and can measure picomoles of a substance in a 1 ml liquid sample, or parts-per-billion (ppb) concentrations in gaseous samples



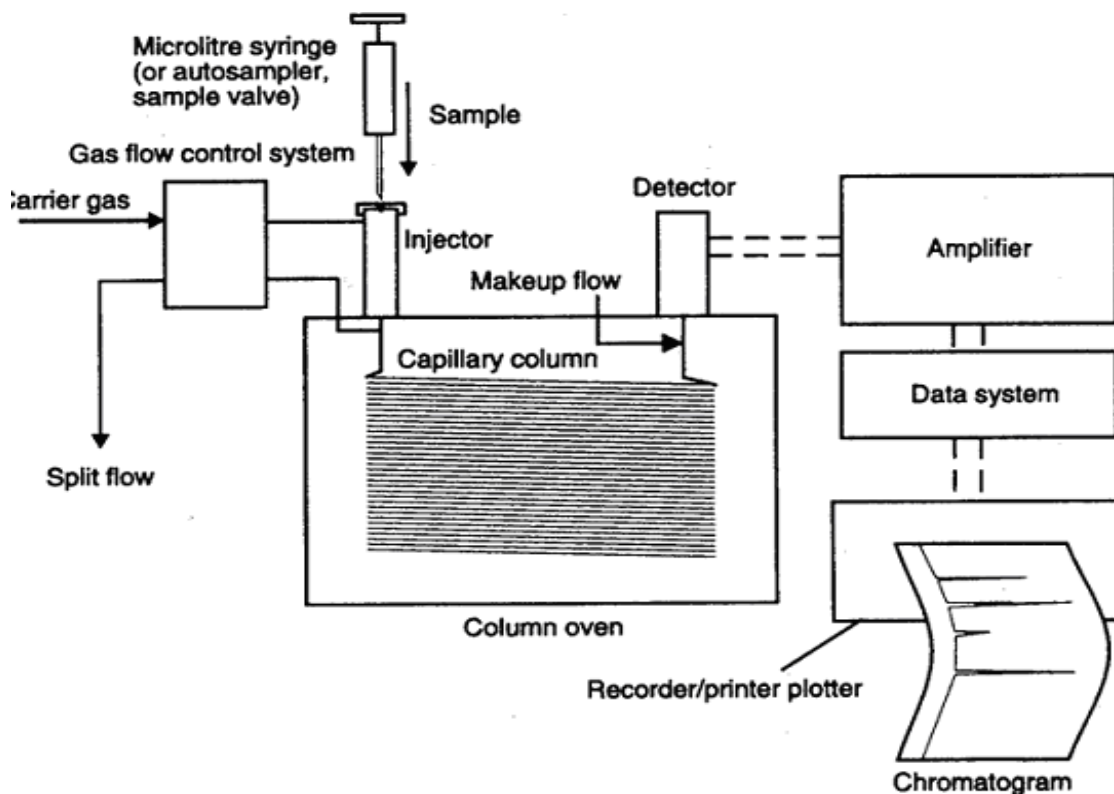
**Figure 1-1:** Typical components of GC (Source: Introduction to Gas chromatography by Betty Kreuz, University of Michigan, Dearborn 2000)

GC's are one of the most reliable and widely used analytical instruments due to their large dynamic range. They can analyze a large group of chemical compounds without much instrumental modification. The primary industrial uses of GC's are in the chemical manufacturing industry, and for environmental analysis and oil exploration. The type of GC instrument used depends on the application.

The compounds of a mixture are separated based on their boiling points and/or relative affinity for a stationary phase lining the walls of the capillary tube [6]. The schematic of a gas chromatograph system shown in figure 1-2 consists of an injector, a separation column, a detector, and fluidic manifolds composed of valves, pressure sensors, flow regulators, and electronics for data processing and overall system control. The sample can be collected by means of a pump for volatile compounds or for unattended ambient analysis, a syringe is used for manual injection of volatile or non-volatile compounds, and auto samplers such as e.g., the I-AS by Agilent Technologies, Santa Carla, CA and Cobra L/S by Central Development LLC, Baton Rouge, LA. The collected sample is usually adsorbed on an adsorbent (like Tenax) followed by thermal desorption. Common commercial GC columns are capillaries made out of fused silica, glass or metal. They range from 100-530  $\mu\text{m}$  in diameter and 1-60 m in length. The separating medium for GC columns is either a packed bed of solid adsorbents, a packed bed column, or a thin layer coated on the column wall.

With the advent of fused silica columns and wall coated stationary phases these columns are preferred over packed bed columns because of their highly efficient separations [7]. The separation in a column can occur under various operating modes: isothermally where the column temperature is held constant over the duration of the separation [6]; temperature programming, where the column temperature is raised at a constant rate from the beginning to the end of the

separation [8, 9] or by gradient through temperature programming where the column temperature varies along the length of the column and is also increased at a constant rate during separation [10]. To change the column temperature, the column is generally either installed in a convention



**Figure 1-2:** Schematic diagram of the primary components of a typical gas chromatograph oven as in the HP 5890/6890 GC's (Agilent Technologies, Santa Clara, CA) or assembled with a conductive resistive heating element as in the microFast GC (ASI Inc.,Baton Rouge ,LA).

The sample is driven through the column by a pressurized carrier gas where increasing the head pressure linearly with time during the separation improves the column efficiency [11, 12]. The analytes are transported through the column via a mobile phase, carrier gas, which typically is a low viscosity gas such as helium or hydrogen, although air is also used. There are many types of stationary phases, including polar, non-polar chiral and ionic type liquids. The choice of

a stationary phase depends on the volatilities and polarities of the analytes. The greater the interaction of a species with the stationary phase the more they are retained. The lighter the interaction of the compound, the less it will be retained and the quicker it will advance through the column. Lightly retained compounds elute from the column first. For straight chain hydrocarbons, the volatility decreases with an increasing number of carbon atoms in the molecule. Detectors, either generic, or specific to the functional groups present in the analytes, identify the eluting samples. The output of a GC is called a chromatogram. A chromatogram displays the time an analyte spends in the column and the quantity of the analyte detected by the detector, which is directly proportional to the amount of analyte present in the sample. Figure 1-3 is a chromatogram showing the analysis of several volatile compounds obtained on the HP 5973 GC (Agilent Technologies).

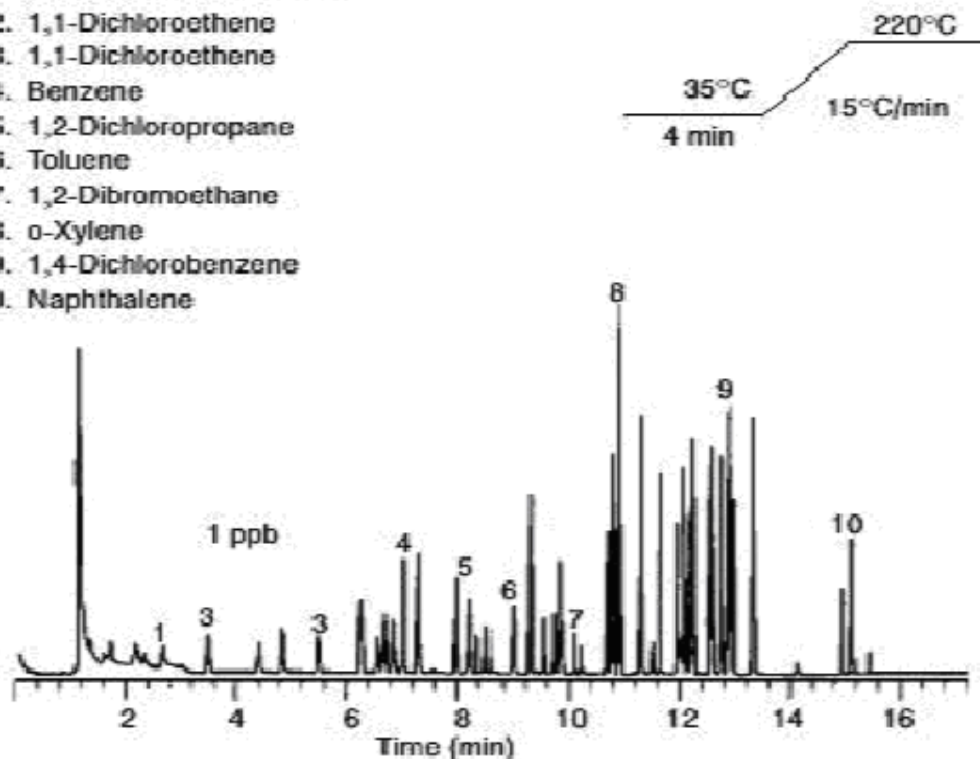
### **1.3. Types of Columns**

There are two general types of columns used in the GC. They are:

- a) **Packed columns** are 1.5 -10 meters in length with internal diameter of 2-4 mm. The tubing is usually made up of stainless steel or glass and contains a packing of finely divided, inert, solid support material that is coated with a liquid or solid stationary phase. The nature of the coating material determines what type of materials will be strongly absorbed. Numerous columns are available that are specific for separating different type of compounds. Packed columns are mostly used for analysis of volatile gaseous mixtures.
- b) **Capillary columns** have very small internal diameters on the order of a few tenths of millimeters and lengths ranging from 25-60 meters. The inner columns walls are coated with active materials such as a nonvolatile liquid or a quasi solid filled with many parallel micropores. Most capillary columns are made of fused silica with a polyimide outer coating. These columns are flexible so a very long column can be wound into a small coil.

## Fast Chromatography—60 VOC Compounds

1. Trichlorofluoromethane
2. 1,1-Dichloroethene
3. 1,1-Dichloroethene
4. Benzene
5. 1,2-Dichloropropane
6. Toluene
7. 1,2-Dibromoethane
8. o-Xylene
9. 1,4-Dichlorobenzene
10. Naphthalene



GC: 5973 GCD  
Sample: 10 ml split (ratio 40:1)  
Carrier: Helium, 0.65 ml/min constant flow  
Column: HP-624, 25 m x 200  $\mu$ m x 1.12  $\mu$ m,  
(Part No. 19091V-402)  
Injection: HP 7695 Purge & Trap  
Oven: Temperature program shown above

Pub No.: 5965-6692

**Figure 1-3:**Chromatogram showing the analysis of volatile compounds obtained on the HP 5973 GC (Agilent Technologies)

New developments are occurring in microFast GC with technology with internally heated microFast columns, where two columns, an internal heating wire and a temperature sensor, are combined with a common column sheath (microFAST GC, ASI Inc)

### 1.3.1 Coating columns- Background

In order to separate components in a sample, the Gas chromatography columns have to be

coated with a stationary phase over the inside column walls. The stationary phase coating is an essential component of the column which determines its separation performance. The inside walls of GC columns are deactivated before coating to neutralize any chemically active sites. Procedures to deactivate and coat columns have been commercialized by several manufacturers. Deactivation of capillary tubing for improved wetting is an essential step prior to coating stationary phase for most GC columns [13]. The deactivation process for commercial columns like silica or soft glass starts with an acid wash where the column is filled with 10 % weight/weight (w/w) Hydrochloric acid, the ends are sealed and the column is heated at 100° c for 1 hour [14]. It is then washed with distilled water to remove acid and dried. This procedure removes traces of heavy metal ions that can cause adsorption effects. The column is then filled with hexamethyldisilazane contained in a suitable solvent, sealed and again heated to the boiling point of the solvent for 1 hour. This procedure blocks any hydroxyl groups that were formed on the surface during acid wash. Finally the column is washed with pure solvent and then dried at elevated temperatures in a stream of nitrogen gas before it is ready for coating [14].

### **1.3.2 Coating Procedures**

GC columns can be coated internally with a liquid stationary phase or with polymeric materials that can be polymerized to form a relatively rigid, internal polymer coating. The stationary phase is typically an organic compound which forms a layer and adheres to the column walls. The retention factor is a function of the coating type and thickness, changing the type and thickness of the stationary phase alters the performance of the column [15].

Retention factor (K) is a measurement of peak which is given by,

$$K = (t_R - t_M) / t_M$$

Where  $t_R$  is the retention time, which is the time required for a peak to pass through a column.

$t_M$  is the unretained peak hold up time which is the time required for one column volume of carrier gas to pass through the column.

$t'_R$  is the adjusted retention time which is given by,

$$t'_R = t_R - t_M$$

Thick coating increases the residence time of analytes which increases the separation time and makes them suitable for analysis of more volatile compounds. A thin layer of coating may lead to fast separation but this reduces the column capacity as coating may leave some active sites uncovered resulting in the peak tailing [15]. The primary concern of the capillary column coatings is to achieve a uniform stationary phase coating on the inner surface of column walls.

There are two methods of capillary column coating. They are

1. Dynamic coating

2. Static coating

1. Dynamic coating

In this method a plug of solvent containing a stationary phase is forced through the column with gas flow. When the plug is passed through the column, gas flow is maintained for about an hour. The gas flow must not be increased because this may cause the stationary phase to displace through the column at a different speed and produces an uneven film. The column is heated above the boiling point of the solvent to remove any traces of solvent and produce a film of stationary phase. In practice 5% w/w of the stationary phase in the solvent produce a film thickness of about 0.5 mm [14]. This is only an approximation as film thickness is also determined by other factors such as physical properties of the surface, solvent speed, and the stationary phase. Commercial columns typically have film thicknesses ranging from 0.25-1.5 mm.

2. Static coating

In this method the entire column is filled with the stationary phase in a volatile liquid solvent. After filling the column with the stationary phase solution, one end of the column is sealed and the other end is connected to a vacuum pump and placed in an isothermal oven or hot water bath. The solvent evaporates leaving a thin uniform film of stationary phase on the column walls. The procedure may take several hours until all the solvent has evaporated leaving the column empty except with the stationary phase coating. The column is filled with a solution of stationary phase with concentration appropriate to produce desired film thickness. The required concentration will depend on stationary phase, solvent, condition of column walls and the temperature [14].

#### **1.4 Overview of Study**

The micromachined gas chromatographic components have been in use since 1970 when Terry et al at Stanford University originated the idea of fabricating an integrated micro GC [16] on silicon wafers. Since then many researchers have worked to develop micro GC columns. Micro GC columns in silicon were developed by Kolesar and Reston 1996[17], Hudson et al. in 1998 [18], and by Whiting et al in 2001 [19]. These microfabricated silicon columns are typically 140 $\mu\text{m}$  wide, 250  $\mu\text{m}$  deep and 1-3 m long. The columns consist of a silicon substrate micromachined using the Bosch DRIE process and a cover sheet of Pyrex. Microfabricated GC columns in parylene were developed by Noh et al in 2002, [20]. These columns use silicon as a structural base and have comparable dimensions. Due to their high thermal capacitance and low thermal conductivity these columns are suitable for isothermal operation and cannot generally be used in temperature programming operation. This limits their operation to primarily separating compounds with a narrow vapor pressure range. Microfabricated metal columns were developed by Bhushan et al in 2004, [21]. These high aspect ratio nickel columns have the advantage of high thermal conductivity, ruggedness and are suitable for temperature programming.

This study is mainly focused on methods of coating and testing microfabricated nickel columns manufactured by CAMD, Baton Rouge. The nickel columns currently used have width dimensions of 50 microns, height dimensions of 500 microns and are 1 meter in length. These columns are attractive due to their small size and low mass which allows for rapid temperature programming with relatively low power and parallel manufacturing which should result in low manufacturing costs. They are robust compared to silicon columns. For connecting to the test equipment these micro fabricated column chips are glued to small diameter stainless steel hypotubes which have 0.016" OD and 0.010" ID using JB weld epoxy glue. After drying overnight these columns were connected with their injector end to the test bed GC (HP 5890) injector end, detector end to 5890's detector with split and make up gas (Hydrogen). Using an external trigger and by injecting the sample by micro syringe the peak data is collected by an external oscilloscope (Agilent 54622D) and ultra fast Keithley 6517A electrometer. The data is then transferred to a computer and collected in the form of Microsoft excel spread sheets where the peaks are analyzed for retention times and peak widths.

The microfabricated nickel columns are tested for diagonal flow rates and leaks by passing hydrogen gas through the column. Once they have been analyzed for flow rates and potential leakage and passed these test, they are ready for further testing with specific chemical mixtures. Initial testing is done by injecting a methane sample and mixture of 1:1(v/v) hexane and decane while the chips are connected to the GC testbed (HP 5890) and the peaks are analyzed. Sharp peaks of methane indicate no leaks and an unobstructed flow path with no multiple flows through the column. Double or irregular peaks are due to leaks and multiple flows of the sample through the column. Theoretically these columns, without coating, should not give any separation when tested with a mixture of samples like hexane and decane but some chips give unwanted separation due to the presence of organic matter residue in the column channels from

manufacturing. Then these columns were deactivated with nitric acid by passing nitric acid solution through the columns in order to clean the column and to ensure that there is no organic matter in the column path. The columns are again tested in the GC testbed by the above mentioned experimental set up to ensure that the column is not giving any separation even when mixtures of organic compound samples are tested. Once the column is not giving separation it is ready for coating. In order to act as a GC separation column, the column walls have to be coated with a thin organic layer called stationary phase [22]. Molecules of different compounds diffuse in and out of the stationary phase and separate based upon their relative boiling points. The separation efficiency depends upon the column length and diameter, temperature, stationary phase thickness and uniformity. Coating solutions are prepared to give thickness in the range 0.1 - 0.2  $\mu\text{m}$ . Different methods of coating like dynamic, static and modified static in desiccator with vacuum were used to coat these columns. After coating, stationary phase is deposited on the inner channel walls. The columns are then tested for separation of organic compounds by the above mentioned experimental testbed set up.

## **2. Materials and Methods**

In this chapter fabrication of nickel columns, the deactivation process, coating methods and testing of these columns are explained.

### **2.1 Microfabricated Nickel GC Columns**

The process of microfabricating gas chromatograph columns dates back to 1970s when Terry et al at Stanford University originated the idea of fabricating an integrated micro GC [16]. The bulk micromachined system consisted of an injection valve, and a 1.5 m long, 40  $\mu\text{m}$  wide columns along with a thermal conductivity detector on a silicon wafer. The silicon columns were sealed either by epoxy or anodic bonding. Since then many researchers developed micro GC columns. Micro GC columns in silicon were developed by Kolesar and Reston in 1996 [17], Hudson et al in 1998 [18] and Whiting et al in 2001 [19]. These columns were 140 $\mu\text{m}$  wide, 250  $\mu\text{m}$  deep and 1-3 m long consisting of a silicon substrate micromachined using Bosch DRIE process and a cover sheet of Pyrex®. Microfabricated GC columns in parylene were developed by Noh et al in 2002 [20]. These columns use silicon as a structural base and have comparable dimensions. Due to their high thermal capacitance and low thermal conductivity, these columns are suitable for isothermal operation and cannot be used in temperature programming. This limits their operation to primarily separating compounds with a narrow vapor pressure range. Microfabricated metal columns were developed by Bhushan et al in 2004 [21], these high aspect ratio nickel columns have the advantage of high thermal conductivity and therefore can be used for temperature programming. The microfabricated nickel columns have been manufactured by Center for Advanced Microstructures & Devices (CAMD), Baton Rouge. The columns are attractive due to their small size, low thermal mass, ruggedness and high conductivity allowing rapid temperature programming with relatively low power consuming and parallel manufacturing

which results in low manufacturing costs, they are robust when compared to silicon columns. Coating these high aspect ratio nickel columns show promising results when compared to tubular columns [22].

Microfabricated columns can have some advantages over circular silica open tubular GC columns. Rectangular cross-section columns with aspect ratios greater than 1 have a lower height equivalent to a theoretical plate (HETP), yielding better performance than conventional capillary columns with equivalent circular cross-sectional areas [23]. The relevant dimension for determining resolution in rectangular column is the column width, as long as it is much less than the column height, while the relevant dimension for establishing sufficient volumetric flow to minimize extra column effect is the column height [24]. A narrow, high aspect ratio columns enables fast diffusion of the gas molecules in and out of the stationary phase, improving the separation efficiency, while the deeper columns allows lower pressure drops and higher gas volume in the column to offset any loss in resolution due to smaller sample volume as a result of reduced width. Improvements of the microfabricated GC and microfabricated columns have been reported by various research institutions [25-32]. The micromachined gas chromatographs are built around a column dry etched in silicon, sealed with a Pyrex cover plate and coated with a stationary phase. There are three main limitations of these designs. First, the columns are low aspect ratio structures, typically from 1-4, so the advantages of the rectangular cross section columns, mentioned by Giddings and Spangler are not fully achieved. The pooling of the stationary phase with the rectangular columns at the column corners at the interface between the column and the substrate and the column and the cover plate can be another problem [32-35]. Analytes spend a longer time in the areas with thicker coating, which degrades separation performance. The effects of pooling seems to be more in low aspect ratio columns because the pooled surface area is significant percentage of the total column surface area available for

absorbing the gases. Finally, while significant progress has been made with the anodic bonding process, there are reports of failure during high temperature operation due to thermal expansion mismatch [36], high residual thermal stresses with high temperature and high strength bonding process [37] and the dependence of bond strength on the cooling rate [38] indicate additional work before it is a reliable method of sealing columns over large areas. Additionally lack of proper leak free fluidic interconnects can result in systems with less than ideal performance.

The high aspect ratio metal columns, fabricated using the LiGA process are introduced. The LiGA process has micrometer resolution capabilities in high aspect ratio structures [39-42], good vertical side wall quality, and is scalable for high volume production through injection molding [43].

## **2.2 Microfabrication Procedure**

Microfabrication of GC columns required significant process optimization as a fairly large MEMS (Micro Electrical Mechanical Systems) design with small continuous features had to be built without any defects. The procedure includes many steps to develop workable LIGA fabrication process which is Lithography, Electroplating and Molding process in microtechnology that was developed in the early 1980's [44]. LiGA was one of the first major techniques for manufacturing of high aspect ratio structures (structures that are much taller than wide) with lateral precision below one micrometer. This is important in the fabrication of MEMS devices. The following are the steps in fabrication of high aspect ratio nickel GC columns at CAMD.

### **a) Bonding**

A PMMA (polymethyl methacrylate) wafer of 2000-3000 microns thickness is bonded to a titanium oxide coated silicon wafer using PMMA or methyl methacrylate glue. The purpose of this procedure is to prepare substrates by bonding PMMA wafers with titanium oxide in order to

fit into the synchrotron beam line scanner. The substrate also acts as a reference point during electroplating. That is why titanium oxide is added to provide conductivity where silicon alone is insufficient. (Step 1 see figure 2-1).

#### **b) Flycutting**

The purpose of this step is to achieve the desired thickness of the wafer. A silicon wafer bound by PMMA is trimmed down 50-100 microns at a time to achieve a thickness of 500 microns. Since the bonding process causes excessive strain on thin wafers it is necessary to minimize this. Thus thick wafers are bonded and then fly cutting is used to cut them down to the desired thickness. In order to preserve the stability achieved in the bonding process, bonded wafers are flycut down to the size appropriate for the column final thickness.

#### **c) Exposure**

The bonded PMMA wafers with desired thickness are then exposed to X-rays through an X-ray mask. The mask membrane consists of a 2  $\mu\text{m}$  thick silicon nitride membrane with a 10 $\mu\text{m}$  thick gold absorber (See fig 2-2). This mask provides better sidewall roughness in nickel structures ( $R_a=300\text{nm}$ ) as compared to the 125 $\mu\text{m}$  thick graphite membrane used in an earlier process [45] ( $R_a=600\text{nm}$ ) and also shows less structural defects. The silicon/PMMA wafer is placed inside the beamline scanner with the wafer's surface perpendicular to the beam. A gold plated mask of desired pattern is placed between the beam and the wafer. The PMMA wafer is then exposed to the X-ray beam using pre-calculated parameters (power, time, etc). The purpose of this step is to break bonds between the adjacent PMMA molecules by X-ray radiation. This decreases the molecular weight allowing the exposed regions to become more soluble in a developer.

#### **d) Development**

The exposed PMMA was developed in alternate cycles of the GG developer and GG rinse solutions. In this step the exposed wafer is cycled through a 20 minute stay in a developer and a

40 minute stay in a rinse for four to eight cycles. During this stay in the developer, exposed regions of the PMMA wafer are slowly dissolved, while the non-exposed regions remain intact. The rinse allows dissolved portions to be completely removed in order to expose the remaining unexposed areas underneath to the developer. (Step 2 see figure 2-1)

#### **e) Electroplating**

In this process nickel was electrodeposited in the developed PMMA mold. The Silicon-bound PMMA wafer that has been completely developed is attached to a jig that allows current to pass through the wafer. The jig is then placed in a nickel-sulfamate bath and allowed to slowly deposit nickel onto the areas of the wafer that have been completely removed by developing. Deposition continues until it reaches the height of the wafer and is allowed to completely over-plate, thus sealing the chip. This step creates the actual GC chip by depositing nickel where the PMMA has been removed with respect to the fold-plated X-ray mask.

#### **f) Polishing**

The Silicon-bound PMMA wafer that has electroplated nickel in the pattern of the X-ray mask is bound to a vacuum chuck and placed onto a polishing wheel. The over-plated nickel is polished down to a smooth, thin finish. The purpose of polishing the over-plated nickel removes excess nickel in order to decrease the mass of the chip. (Step 3 see figure 2-1)

#### **g) Etching**

The polished wafer is placed into a heated Potassium Hydroxide (KOH) bath in which KOH reacts with the silicon wafer, and the silicon dissolves. After etching, all that remains are the unfinished nickel columns bound to the PMMA wafer. Sometimes, the  $\text{TiO}_2$  layer remains on the PMMA wafer and the plated nickel is removed by polishing the bottom side of the PMMA wafer. Another method is to briefly bathe the wafer in nitric acid. The purpose of removing the silicon wafer is necessary in order to over-plate the opposite side of the nickel column.

## **h) Overplating**

The unfinished nickel columns with the PMMA columns still attached are removed from the PMMA wafer. They are then fitted into a small frame that allows them to be attached to the electroplating jig. The chips are oriented in a way that allows the non-overplated side to be exposed to the nickel sulfamate bath. Copper tape is used to restrict the current flow to only the nickel chips. The jig is placed in the bath and allowed to plate until the nickel is deposited completely over the remaining PMMA within the columns. This step seals the opposite side of the GC columns. (Step 4 see figure 2-1).

## **i) PMMA removal**

GC columns are removed from the plating jig, labeled and machined down to remove any excess nickel and expose the openings of the columns, which are still occupied by PMMA. Finally the structure forming PMMA resist was removed pyrolytically by slowly heating the chips up to 450° C over 4-6 hours and leaving them at this temperature for 4 hours. The removal of PMMA produces the hollow finished nickel tubes. (Step 5 see figure 2-1).

Using the above mentioned optimized fabrication process high aspect ratio nickel columns with typical column channel width of 50 $\mu$ m, 500  $\mu$ m height and 0.5-2 meter in length were microfabricated at CAMD, Baton Rouge. The rectangular cross-section columns are expected to perform similar to a 50  $\mu$ m diameter capillary column, but have a volumetric flow rate similar to a 90-100  $\mu$ m diameter capillary column [23]. The perfectly sealed columns are fabricated in the overplating step and perfectly sealed columns are fabricated with no leaks. The thermal capacitance of the column can be reduced allowing minimized power requirement by controlling the thickness of the overplated metal. The extremely parallel sidewalls ensure low dispersion and minimum peak broadening of the LIGA GC columns [46]. The microfabricated columns of “spiral” shape with 50  $\mu$ m column widths, 100  $\mu$ m wall thicknesses and “Serpentine” shape with

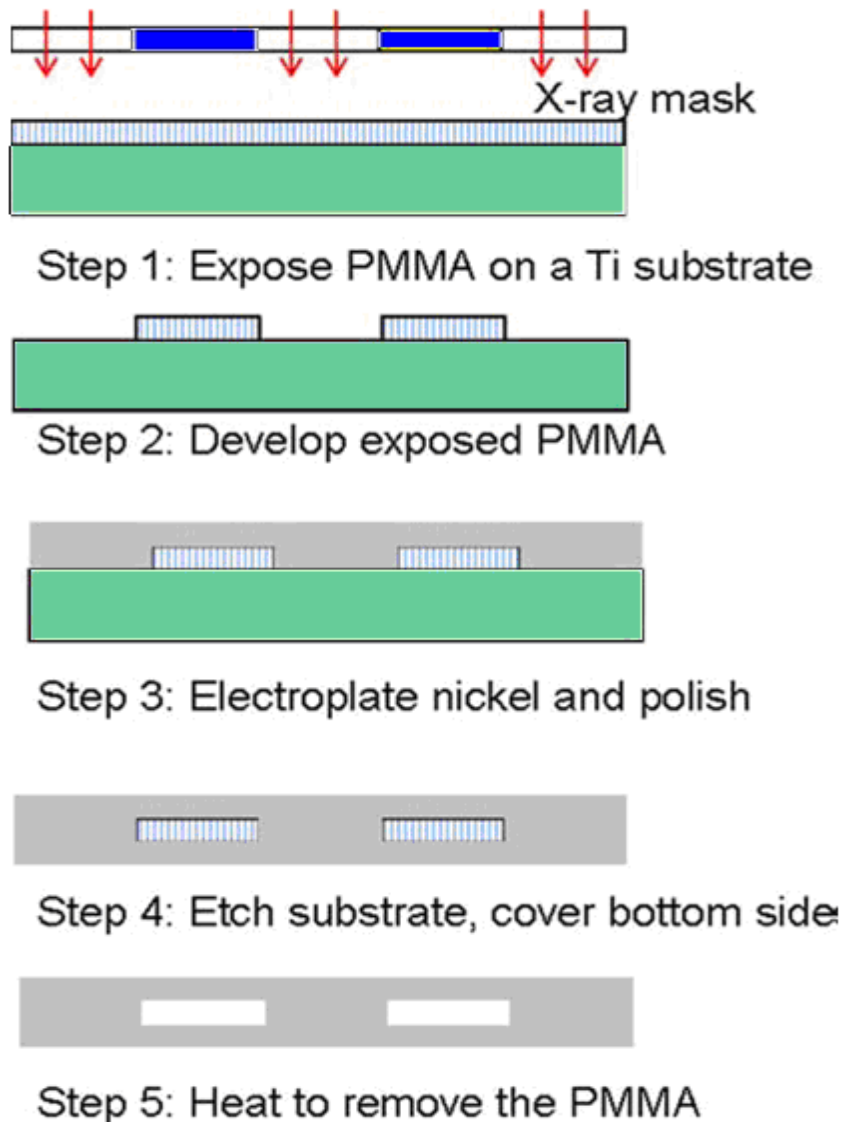
50  $\mu\text{m}$  column widths, 125  $\mu\text{m}$  wall thicknesses were used for this study. Both of the columns have inner channel length of 1 meter and heights of 500  $\mu\text{m}$ .

### **2.3 Coating Microfabricated Columns**

LIGA fabricated column tubes have to be coated with a thin organic layer called the stationary phase in order to function as a GC column [6]. Stationary phase coating is an essential step which determines the separation performance of the column. Molecules of different vapors in the sample diffuse in and out of the stationary phase and separate based on their relative boiling points. Separation efficiency of a column depends on a number of characteristic parameters like column length and diameter, and also on the function of stationary phase like its thickness and uniformity. The retention factor is a function of the coating type and thickness, changing the type and thickness of the stationary phase alters the performance of the column [15]. Thick coating increases the residence time of the analytes which increases the separation which makes them suitable for analysis of more volatile compounds, while a thin layer of coating may lead to fast separation but reduces the column capacity as a thin coating may leave some active sites uncovered resulting in the peak tailing. The interaction of the solutes with the stationary phase is due to dispersion, orientation and donor-acceptor interactions [47, 48, 49]. The primary concern of the coating is to achieve a uniform stationary phase coating in the inner surface of the columns. The type and concentration of stationary phase and the column temperature influences column sensitivity.

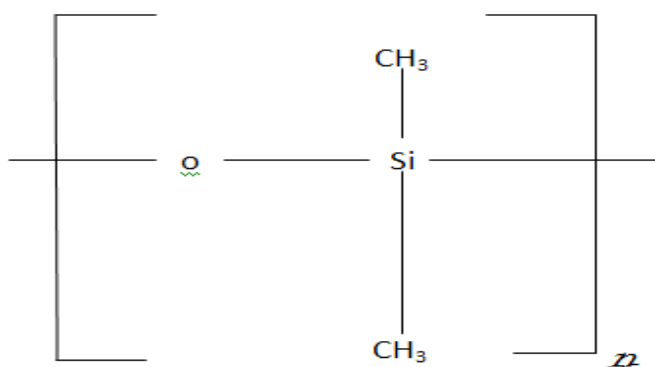
Coatings of circular capillary columns have been commercialized over the past 50 years while coatings on rectangular cross-section columns has not been satisfactorily realized and comes with its own issues. They are two main factors for consideration; adhesion of the liquid film to the metal columns, and pooling of the liquid in the corners of the microfabricated columns [22]. Metal capillary columns were used before the advent of fused capillary columns [50]. They are

more difficult to coat because of the presence of large number of active sites on the surface. Rectangular cross-section columns have the problem of pooling of the stationary phase in the corners [51]. The pooling results in an uneven stationary phase layer which causes excessive peak broadening.. Based on the literature and experience with capillary columns and meeting the requirement of fast separation times of less than 10 seconds, the stationary phase film on the LIGA columns must be between 0.05- 0.2  $\mu\text{m}$  [15] homogenously spread over the column's inner surface with no or minimum pooling.



**Figure 2-1:** Schematic of the column fabrication using the LIGA process [22]

Stationary phases are classified on the basis of their polarity as polar, non-polar, chiral and ionic. The polarity of a column can be evaluated by the McReynolds system [52, 53] in which the Kovats retention indexes of 10 solutes are computed in the stationary phase of choice and in squalane, which serves as the reference non polar stationary phase [54]. Of the 200 phases analyzed by McReynolds OV-17, OV-101, OV-225 and Carbowax 20M can provide satisfactory GC analysis for over 85% of the application [55]. The main criterion of selecting the stationary phase is the lifetime of the coating. Polar phases have shorter lifetime at elevated temperatures and are less efficient when compared to non-polar phases which are more resistant to oxidation



**Figure 2-2:** Molecular structure of polydimethylsiloxane (PDMS) molecule

and hydrolysis than polar Polysiloxane phases are most commonly used stationary phases because of their high thermal stability and coatings formed are mostly non-polar. Change of polarity will occur when methyl groups of the polysiloxanes are replaced by other functional groups. The molecular structure of the polysiloxane molecule is shown in the figure 2-2.

### 2.3.1. Methods of Coating

Microfabricated columns have to be coated on the column inner walls with a thin layer of stationary phase in order to function as a separating column in the GC. Molecules of different

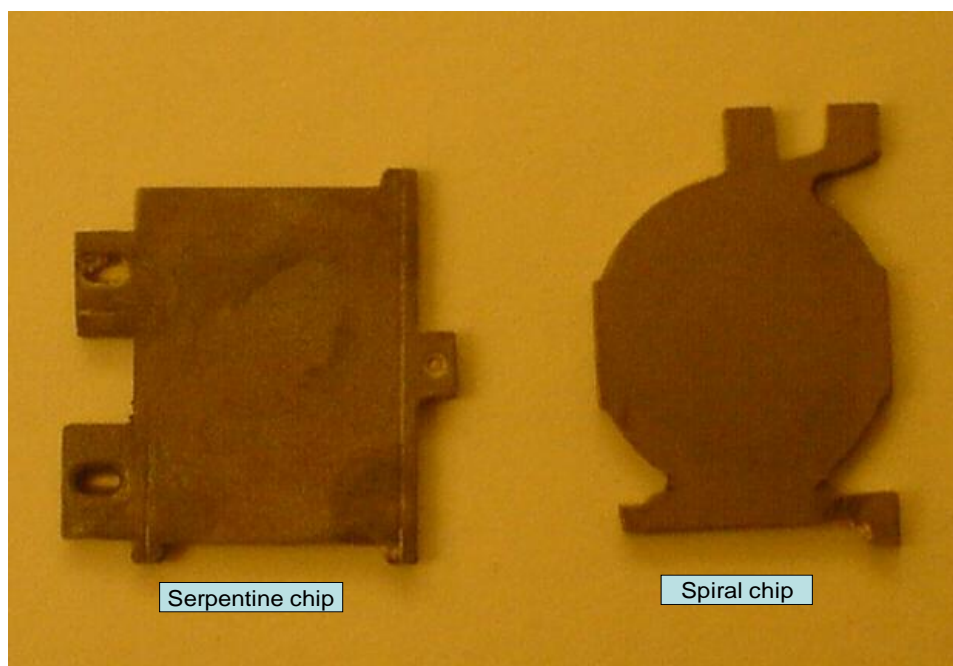
compounds diffuse in and out of the stationary phase at different rates and are separated based on their relative boiling points. The separation efficiency depends upon the column length, diameter, temperature, stationary phase thickness and uniformity. Coating solutions are prepared to give thickness in the range 0.1-2  $\mu\text{m}$ . Different methods of coating like dynamic, static and modified static method in dessicator with vacuum were used to coat these columns. After coating, stationary phase is deposited on the inner channel walls. Coating of columns involves pre coating process like deactivating the columns and coating the columns either by static or dynamic. The following are the procedures involved in coating columns.

a) Column connections and deactivation

In order to connect microfabricated column chips to the GC testbed, steel tubings with 0.016 o.d and 0.010 i.d (small parts, Miami Lakes, FL) were attached by JB Weld (JB Weld, Sulfur Springs TX). About 6-8 cms of steel tubings were cut and then attached to all the four outlets of the column chips (Injector, detector, split and make up gas ends) with JB Weld. Other epoxy glues like JB Kwik and epoxy (H77S, EPOXY Technology, Billerica, A) were tried. JB Kwik will dry with in minutes but it cannot withstand use for long times, and column chips will begin to leak at the tube connections after use. The epoxy (H77S, EPOXY technology) glue is much more temperature resistant as it can withstand temperature up to 450°C while JB Weld and Kwik can withstand up to above 300°C. This glue was used to connect the column chips with the steel tubings. After mixing the glue it was kept at 150°C in the oven so that it can be solidified and forms as a thick paste and easily glued to the columns. Then the columns are dried for 2 hours at 150°C in the oven. The main problem with this glue was after the oven treatment; some of the epoxy glue started to melt and dripped through the tubing ends which resulted in either blocking of the chips as some of the glue entered into the column outlets or leaving weak connections with a chance of leaking after use. For the above reasons, JB Weld was selected as the best glue for

the column connections, it is strong with no leaks and the glue will withstand for longer times compared to the other two glues.

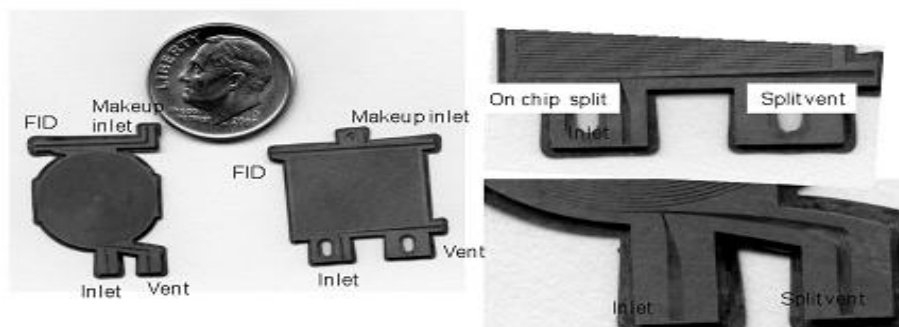
The column chips with these steel tubings after attached with JB Weld were dried overnight and then tested for the flow and leaks. The columns with these connections were placed in water with hydrogen flow through the column. Diagonal flows of the column, which is the flow of hydrogen from the injector end to detector end, was measured by digital flow meter (Restek 6000 flow meter). Any leaks in the column chip connecting tubings which can hamper the column efficiency can be identified and the column chip connections can be reglued with JB Weld.



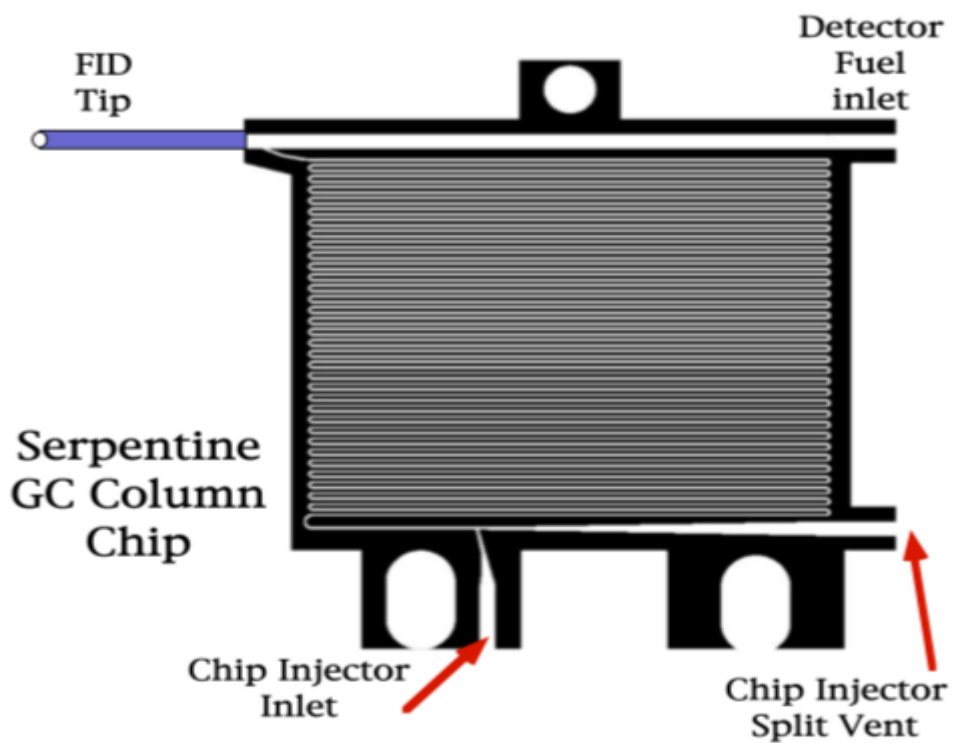
**Figure 2-3:** Spiral and serpentine column chips (without steel tubings connection)

The column is then connected to the testbed GC by the experimental set up described later, and a plug of methane gas is injected through the column where, a sharp peak of methane indicates no leaks or no multiple flows through the column. Once the column chips have no external leaks and have flow through them, they are ready for deactivation and coating.

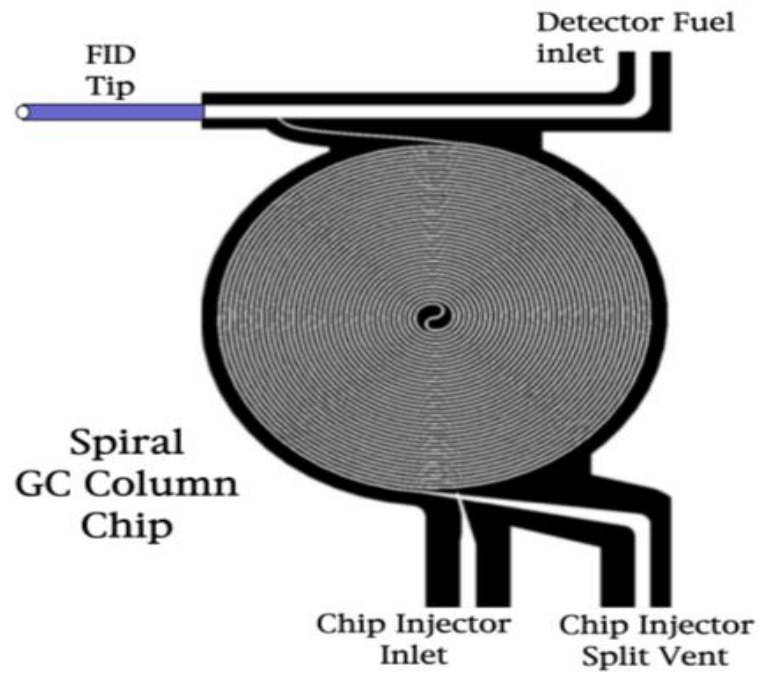
GC columns have to be deactivated before coating to neutralize any chemically active sites.



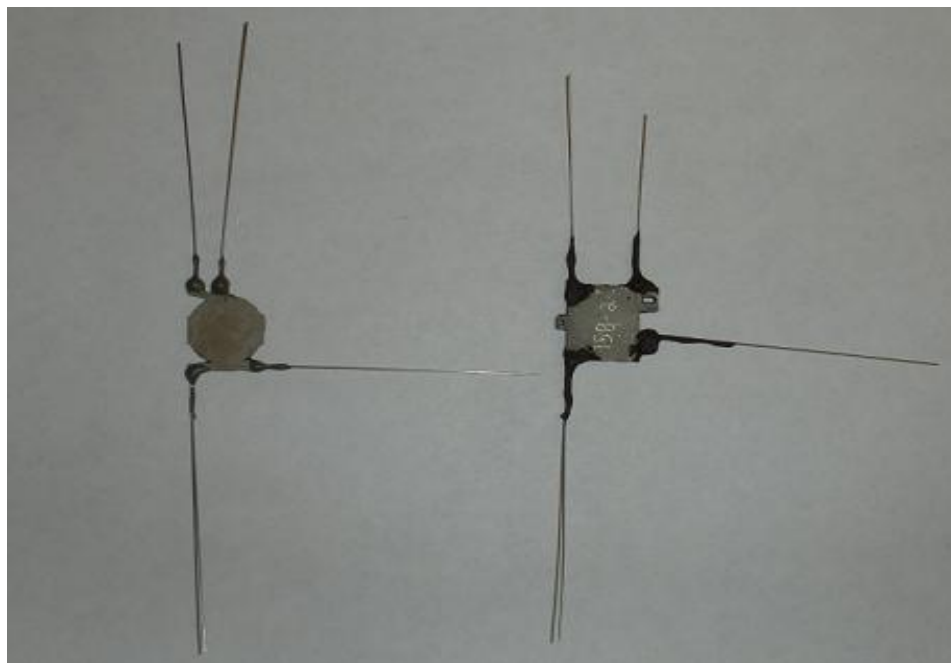
**Figure 2-4:** Spiral and serpentine column chips, before over-plating, with size compared to a 10 cent coin



**Figure 2-5:** Serpentine chip with inner column channel and Column outlets



**Figure 2-6:** Spiral chip with inner column channel and the column outlets



**Figure 2-7:** Spiral and Serpentine column chips after attaching steel tubings with JB Weld



**Figure 2-8:** Testing chip for leaks with hydrogen flow in water

Deactivation and coating procedures are done on all commercial columns. Deactivation of capillary tubing for improved wetting is an essential step before coating stationary phase for most GC columns [13]. Deactivation process for commercial silica or soft glass columns starts with an acid wash where the column is filled with 10% Hydrochloric acid, the ends are sealed and the column is heated at 100°C for 1 hour. It is then washed with distilled water to remove acid and then dried. This process removes traces of heavy metal ions that can cause adsorption effects. The column is then filled with hexamethyldisilazane in a solvent, sealed and again heated to the boiling point of the solvent for 1 hour. This process blocks any hydroxyl groups that were formed during acid wash. The column is then washed with pure solvent and dried at elevated temperatures in a stream of nitrogen gas which is ready for coating [14].

Microfabricated columns have also to be deactivated before coating to deactivate the large number of active sites present on the surface which can react with analytes, increasing their adsorption and leading to peak tailing. Deactivation will reduce the surface interactions and

cover the column surface with non active chemical or coating which, in most cases, is a form of silanol group. Polymethylhydrosiloxanes and silanol are most commonly used for deactivating fused silica columns [56]. Thermal degradation of polysiloxanes [57], poly ethylene glycols (PEGs), octamethylcyclotetrasiloxane (D<sub>4</sub>) [58, 59] and Carbowax 20M [60] were other commonly used methods for deactivation of silica or fused quartz columns. Deactivating the column and immobilizing the stationary phase is commonly practiced [6].

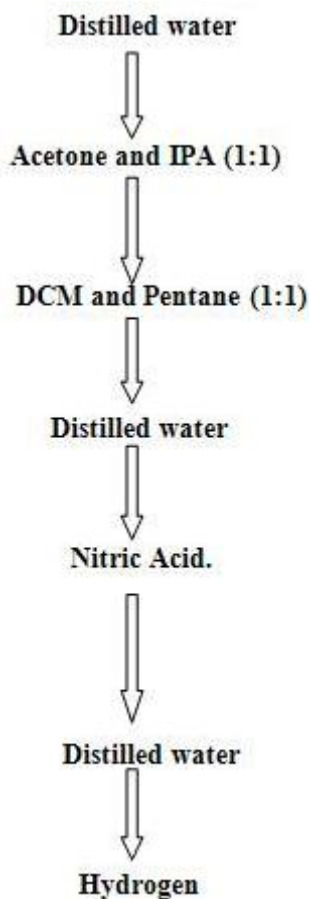
Deactivation of steel column with commercial solutions like Ultimet (Varian, Palo Alto, A), Silico-steel (Restek, Bellefonte, PA) are commonly used but these are not suitable for nickel columns [61]. Deactivations of nickel columns generally include deposition of a thin layer of silicon either in gaseous phase [62] or in aqueous phase [63]. In the gaseous phase technique, full concentrated silane is run through the column at 380°C for 3 hours which deposits a layer of silicon on the column walls. During coating, the stationary phase adheres to this silicon layer. However the chemicals used in this method are highly toxic and flammable and cannot be used in a general laboratory. Deactivating the columns using a mixture of 0.5% silane in helium instead of pure silane was commonly used for safety purposes [64]. However, this procedure requires heating the column chips to 425°C and cannot be used for the column chips glued with JB Weld as it cannot withstand this temperature.

Microfabricated LiGA columns were deactivated by methylsiloxane spin on glass (11F, Filmtronics, Butler PA), Silicate spin on glass (15A, Filmtronics) and D4 [15]. The other method to coat these columns is to deactivate the surface by using siloxanediol salt and using an OV-1 type phase to attach the toluene group of the diol salt [22]. This method should enable deposition of uniform thin layer of phase but the problem until now has been in attaching the diol salt to the nickel column. The main reason may be the presence of impurities in the form of graphite and other organic matter left behind after pyrolytic removal of PMMA changes the surface locally

and restricts a uniform deposition of the salt [22]. Deactivating the microfabricated nickel LiGA columns were not entirely successful as these methods sometimes results in the blocking of columns or lack of uniform deposition due to difference in their surface chemistry compared to commercial columns. Other method to deactivate these columns is cleaning with Nitric Acid (70%). The detailed process of nitric acid deactivation is explained below.

Microfabricated LiGA column chips with the connecting tubes were deactivated with nitric acid which involves the following steps. About 1-2 ml of distilled water is manually injected from the syringe through the column by connecting the syringe with the column by means of zero dead volume connectors (Teklab, Stainless steel 0.5mm bore) and ferrules from the injector to detector end. This is followed by injecting 1-2ml of acetone and Isopropyl alcohol (IPA) solution (1:1). Then about 1-2 ml mixture of Dichloromethane (DCM) and Pentane (1:1 ratio) is injected through the column. Once the solution passes out through the column outlets, the outlets, except injector and detector ends, are sealed by septa (Teflon 13mm diameter, Teklab, Baton Rouge). The idea is to fill these two outlets with DCM and Pentane solution which restricts the flow of Nitric acid through these outlets but allows it to flow from the injector to detector end. The purpose is to dissolve any dust or organic matter present on the column walls by DCM and Pentane solvent. This is followed by injecting distilled water from injector to detector end leaving the septa on the other two ends. Then Nitric acid (70%) is injected into the column from through the injector end to detector end. Nitric Acid is a strong acid, so it dissolves any presence of organic matter or PMMA residuals on the column walls leaving the surface clean. Then immediately distilled water is injected to wash away any nitric acid residue which can oxidize the nickel layer. Finally the column is connected to hydrogen gas flow to remove any presence of water or nitric acid and checked for any leaks. The column is then connected to the GC testbed and about 2 $\mu$ l mixture of hexane and decane (1:1) was injected manually by micro

syringe at 110°C to check for any separation. Any separation indicates the presence of active sites which needs to be cleaned again by nitric acid treatment and if there is no separation the column is ready for coating.



**Figure 2-9:** Schematic diagram of nitric acid deactivation process

## **b) Coating procedure**

There are two methods commonly used for capillary column coating. They are:

1. Dynamic coating
2. Static coating

### **1. Dynamic coating**

In this method a plug of solvent containing a stationary phase is pushed through the column with gas flow. The gas flow must not be increased which causes the stationary phase to unevenly

displace along the walls of column as the solvent plug is pushed through the column. This causes a thin film of the stationary phase adheres to the column walls. Then the column is heated above the boiling point of the solvent to remove any traces of solvent to produce a film of stationary phase. The film thickness in this process can be calculated by Fair-Brother equation (Equation 2-1) [15]

$$h_f = \frac{r C_s}{200} \left( \frac{u \eta}{\gamma} \right)^{\frac{1}{2}}$$

Where, r is the radius of the column or the hydraulic diameter for a rectangular column,  $\mu$  is the velocity, and  $\gamma$  is the surface tension between the coating solution and the column.

## 2. Static coating

In this method the entire column is filled with a solution of the stationary phase dissolved in the solvent. After filling the column with the stationary phase solution one end of the column is sealed and the other end is connected to vacuum pump and the column is placed in water bath. The solvent then evaporates under vacuum leaving a film of stationary phase. The procedure may take several hours until all the solvent is evaporated leaving the column wall coated with only stationary phase coating. The film thickness of the stationary phase is a function of the concentration of the coating solution  $C_{cs}$  determined by a simple mass balance equation (Equation 2-2) [15].

$$h_f = \frac{\text{volume of column}}{\text{surface area of column}} * C_{cs}$$

Microfabricated silicon columns of 300 $\mu$ m wide, 100 $\mu$ m tall and 0.9 m long were coated by vapor depositing a 2000 Å thick layer of  $\alpha$  phase copper phthalocyanine before sealing them with anodic bonding to serve as a solid adsorbent in separating NO<sub>2</sub> from a gas sample was first reported [25,36]. At 80°C and under head pressure of 20-40 psi, NH<sub>3</sub> and NO<sub>2</sub> were separated where the peaks showed significant broadening and tailing due to presence of dead volumes. In

another paper 100 $\mu$ m wide, 10  $\mu$ m tall and 2 m long silicon micromachined columns were coated by depositing a solid stationary phase like plasma-polymerized fluoropolymer. This column was used in environmental applications as it showed little response to water vapor [65, 66]. Depositing stationary phase on columns before sealing will not work for the LiGA columns since the columns are filled with resist until they are sealed. Static and dynamic coating procedures on 150 $\mu$ m wide, 240 $\mu$ m tall and 1-3 m long silicon DRIE columns has been reported recently [30,67]. Cavitation at the sharp corners on the microfabricated columns resulted in a non-uniform film created a problem which was partially solved by adding dicumyl peroxide which is a cross-linking agent to the stationary phase before coating. The cross linking agent stabilizes high temperature operation of the coated columns. Using static coating procedure, coating thickness of 0.1-1 $\mu$ m and by using dynamic coating 1-2 $\mu$ m was achieved. Separation of alkanes from C<sub>1</sub>-C<sub>12</sub> was obtained on 3m long column by temperature programmed operation in about 500 seconds. In another research paper carbon nano tubes grown on the bottom of 50 cm long separation channel by vapor deposition were used as stationary phase [68].The carbon nano tubes have a very high surface to volume ratio and have great potential as a stationary phase. The microchip using these single walled carbon nano tubes had integrated heaters for fast temperature programming and separation of a four compound mixture was achieved in less than one second. LiGA microfabricated columns of 0.5 and 2 m long, 50 $\mu$ m wide and up to 600  $\mu$ m high aspect ratio columns with on chip integrated sample injection and detection were fabricated [22]. A 2m LiGA nickel column coated by Restek Corporation with RTX-1 and a separation of four compounds methane, butane, pentane and hexane was achieved less than 4 seconds. Some of the peaks are broad suggesting that the stationary phase has pooled in corners and further experiments are needed to improve the efficiency. Most recently 0.5 m long, 50 $\mu$ m wide and 600 $\mu$ m tall high aspect ratio nickel columns were coated with OV-1 stationary phase by static

coating methods and a mixture of four hydrocarbons hexane, octane, decane and dodecane were separated in less than 2s at 70°C [69]. These results suggest that fast separation of compounds in a few seconds is possible with appropriate thin coatings on the microfabricated high aspect ratio nickel columns.

## **2.4 Experimental Set Up**

A HP 5890 GC was used as a testbed for experimental test as shown in the figure 2-11. Either gaseous (methane) or liquid samples were injected manually using a syringe. The pressure at the injection port purge was maintained between 5-10psi. The injected sample vaporized at 1 ml volume injector chamber where the temperature was maintained at 180°C. The column head pressure was kept at 30 psi for all the experiments. The carrier gas used was helium and the split flow rate at the column inlet was kept between 400-500 ml/min. In addition to this split an on column split from the split outlet of the column was maintained 0% by closing the split end with GC septa. By splitting the injected sample volume twice, a narrow plug of sample was ultimately injected into the column. An additional make up gas from a hydrogen source maintained constant at 15 psi was connected to the column chip make up gas end. The detector end was connected to Flame Ionized Detector (FID) of the testbed maintained at 180°C. Using an additional electronic trigger and by injecting the sample, the data was collected as an electronic signal by ultra fast Keithley 6517A electrometer and was collected and stored as peaks by external oscilloscope (Agilent 54622D). The 5890 GC testbed was activated by EZ Chrome software. Data was then transferred to a computer and collected in the form of Microsoft excel spread sheets. The retention time and peak widths of the peaks can be collected either manually in the oscilloscope or by the excel sheets.

Microfabricated high aspect ratio nickel columns are fabricated at CAMD, Baton Rouge. The Spiral chips with 50 microns wide, 500 microns height and serpentine chips with 50 microns

width and 500 microns height were used for the experiments (See figure 2-7). Both the columns were 1 meter in length. These columns are attractive due to their small size and low thermal mass which can allow for rapid temperature programming with relatively low power and parallel manufacturing which should result in low manufacturing costs. They are robust compared to silicon columns. These columns have four outlets; the injector end, the detector end, the injecting split and the make up gas end. The columns are glued to small diameter stainless steel hypo tubes which have 0.016'' o.d. and 0.010'' i.d using JB Weld epoxy glue as mentioned previously. After drying overnight these columns were connected with their injector end to GC's injector end and detector end to GC's detector. The detector end was connected by means of deactivated fused silica capillary with zero dead volume connectors (Teklab, Stainless steel 0.5 mm bore) which was tested before to ensure that it does not show any separation when a mixture of compounds like hexane and decane were tested. Any separation of the compounds must be from the chips but not from the deactivated fused silica capillary. An on chip split (provided for nickel column chip) was connected by means of deactivated fused capillary to a valve where the split is maintained at 0% by sealing the split end with GC septa and make up gas from another hydrogen source maintained at 15 psi was connected with another deactivated fused capillary. The purpose of the make up gas and on column split was to ensure the sample injected enter the column and detector directly as a sharp plug.

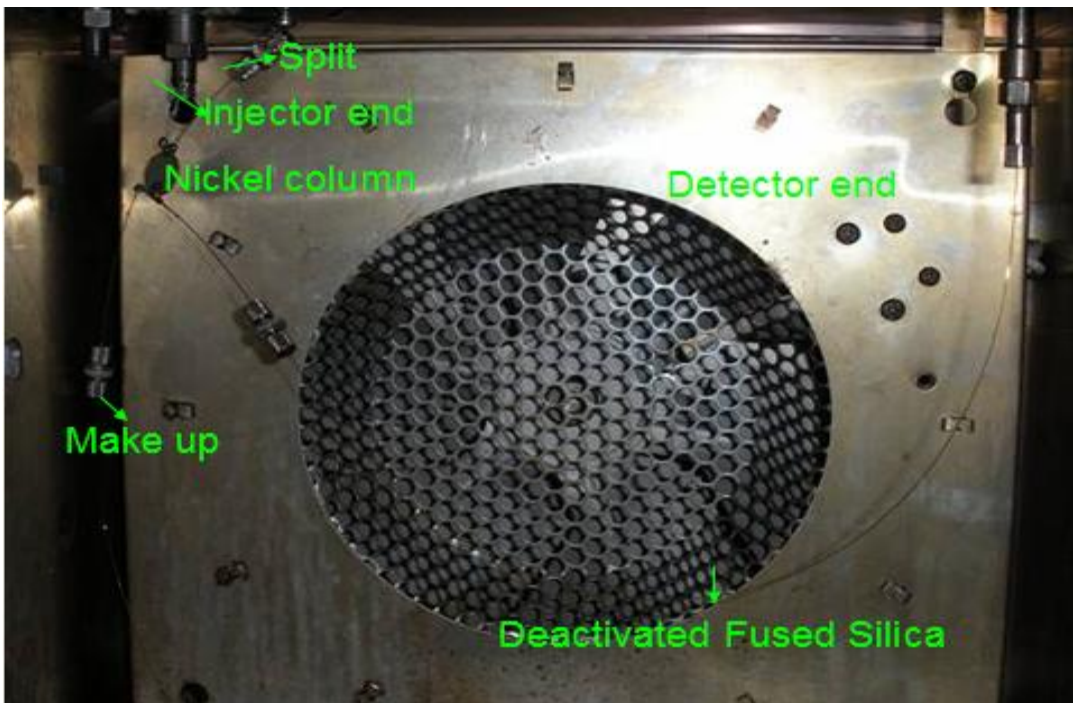
#### **2.4.1 Testing Instrument**

The GC testbed has been checked with a commercial fused silica capillary column before testing of the microfabricated high aspect ratio nickel columns to ensure that instrument is working well and to have background data on peaks with a known quality GC column. Fused silica capillary (DB-5 GC column) manufactured by Agilent J&W scientific with 0.4 film thickness and internal diameter of 100 microns was cut into a 1 meter length and connected

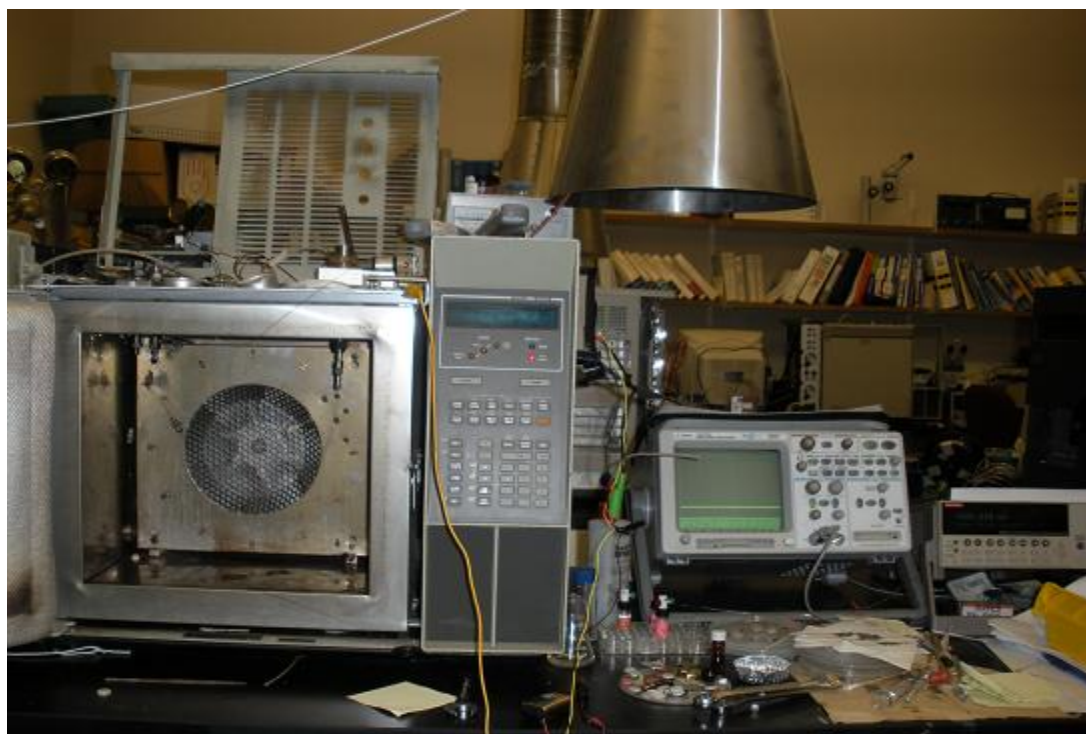
directly to the GC with one end to the injector and other end to the detector end of GC. All the conditions were same as mentioned above with injector and detector temperature at 180°C, injection pressure at 5-10 psi and oven temperature at 110°C. A plug of methane gas was injected manually from a 5 ml syringe to make sure that the column has enough flow and the data was gathered. Then about 2 µl of hexane was injected from a 10 µl micro syringe and data was gathered. About 2µl of mixture of hexane and decane (1:1) was injected and the trigger was manually activated to see the separation and the data was gathered in the excel sheets. The first spike in the data was from the electronic trigger followed by peaks. The time taken from the trigger spike to the peak represents the retention time, and the peak widths were measured at half height. Each experiment was repeated 3 times with the same amount of sample to ensure that the data gathered was nearly same in the each data set and the retention times and peak widths of the peaks were recorded in each case. Data for separation of hexane and decane was gathered at 80°C and 110°C. The data gathered shows that the instrument is working with the above mentioned set up.

#### **2.4.2 Testing Microfabricated Nickel Columns**

After connecting the steel tubings with JB Weld, the nickel column chips were then tested for leaks and then they are connected to the GC testbed. All the conditions used for testing Fused silica capillary column were maintained the same as for the Nickel columns. After connecting to GC (which was explained earlier) the column connections and column were checked for leaks with a liquid leak detector (Swagelok Snoop®, liquid leak detector, Swagelok Company, OH). Any leaks in the connections or in the column will result either in low flow from the column resulting in irregular peaks or no peaks or even multiple peaks due to multiple flows through the column. Once the column is perfectly connected to the GC testbed it is tested with methane, hexane and mixture of hexane and decane. Theoretically the column should not show any



**Figure 2-10:** Experimental set up with showing nickel column (chip) connected to GC (HP 5890)



**Figure 2-11:** GC connected to Electrometer and Oscilloscope

separation when mixture of compounds was injected as there is no coating in these columns. If the column displayed any separation it is an unwanted separation due to presence of any residual organic matter from the thermal removal of PMMA in the column. Then the column has to be deactivated.

#### **a) Deactivating nickel columns**

Microfabricated silica columns have been deactivating using silane and other techniques and some of the same techniques were employed for nickel columns. Some of the techniques proved successful but the surface chemistry of nickel was entirely different from the silica so sometimes the columns were blocked or did not show any difference. Deactivating the nickel columns with nitric acid was finally employed (which was described earlier). After deactivating with nitric acid the columns were again tested for methane, hexane and mixture of hexane and decane. The data was compared with the data before deactivation. Once the column did not show separation even for mixture of compounds, it is ready for coating.

#### **b) Coating techniques**

Static and dynamic coatings are the two most frequently used methods for production of wall-coated open tubular fused silica columns [70]. About 8  $\mu\text{l}$  of non polar polymethyldisiloxane (Ov-1, Ohio valley, Specialty chemical, Marietta, OH) is mixed with 2 ml mixture of 1:1 dichloro methane (DCM) and pentane [30]. Coating solution prepared give coating thickness in the range of 0.1-0.2  $\mu\text{m}$ . The coating solution was agitated for 30-45 minutes to ensure thorough mixing of the solution. Prior to agitation about 1-2 % of thermally activated cross-linking agent, dicumyl peroxide was added to prevent from loss of stationary phase due to thermal degradation and useful for temperature programmed operations. The cross linking agent may help to reduce the cavitation of stationary phase at sharp corners of the microfabricated columns.

### **1. Dynamic coating**

In this technique a plug of stationary phase in a suitable solvent is pushed through the column by the flow of non reactive gas. Figure 2-12 shows the apparatus for coating and figure 2-13 shows the schematic diagram of coating. A mixture of 1:1 DCM and pentane is passed through the microfabricated nickel column by the flow of nitrogen at the solvent reservoir which was connected to the column by means of deactivated fused silica tubing. Once the solution passes through the column the ends except the injector and detector ends are closed by septa. The purpose is to fill the other two ends with DCM and pentane solution but not with the coating solution. The coating solution is passed from injector to detector end of the column for about 1-2 minutes. The purpose of DCM and pentane solution is to clean the column and remove any organic matter. Then immediately a plug of stationary phase (OV-1) coating solution is passed through the column and the column is filled with the stationary phase solution. Once the column is filled with the coating solution the ends are sealed by GC septum and the nitrogen gas flow was turned off. Then the column is connected to GC and heated with a temperature ramp from 30°C to 180°C at the rate of 5°C per minute with flow of hydrogen at 10 psi for 2-3 hours to evaporate the solvent leaving behind a thin film of stationary phase.

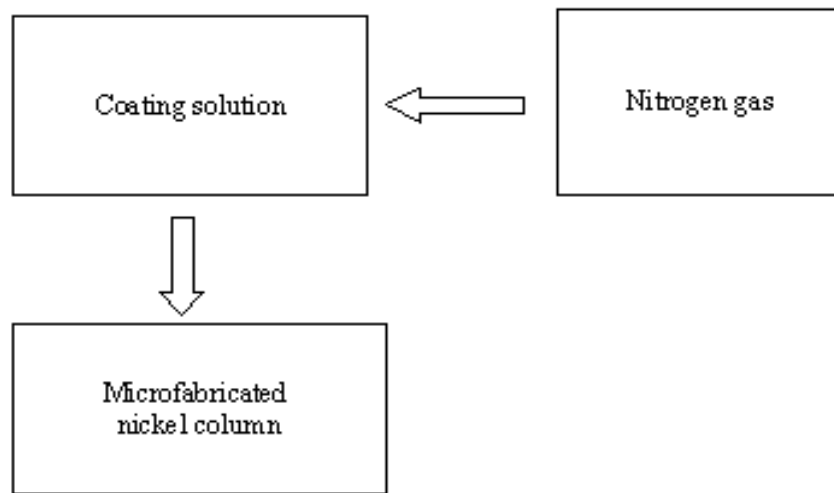
## **2. Static coating**

In static coating once the column is filled with the solution of DCM and pentane the other two ends of the column except the injector and detector ends are sealed with the GC septa and a plug of stationary phase (OV-1) is passed through the column. Once the column is filled with the coating solution, the injector end of the column is connected to a vacuum with all the other ends sealed with the septa. The column was then placed in a water bath at 40°C and the vacuum pump was maintained constant at 10 psi and left for overnight to evaporate the solvent leaving behind a thin film of stationary phase. Static coating generates thinner and more uniform layer of coating and the coating thickness can be estimated [70]. The major problem in the static coating

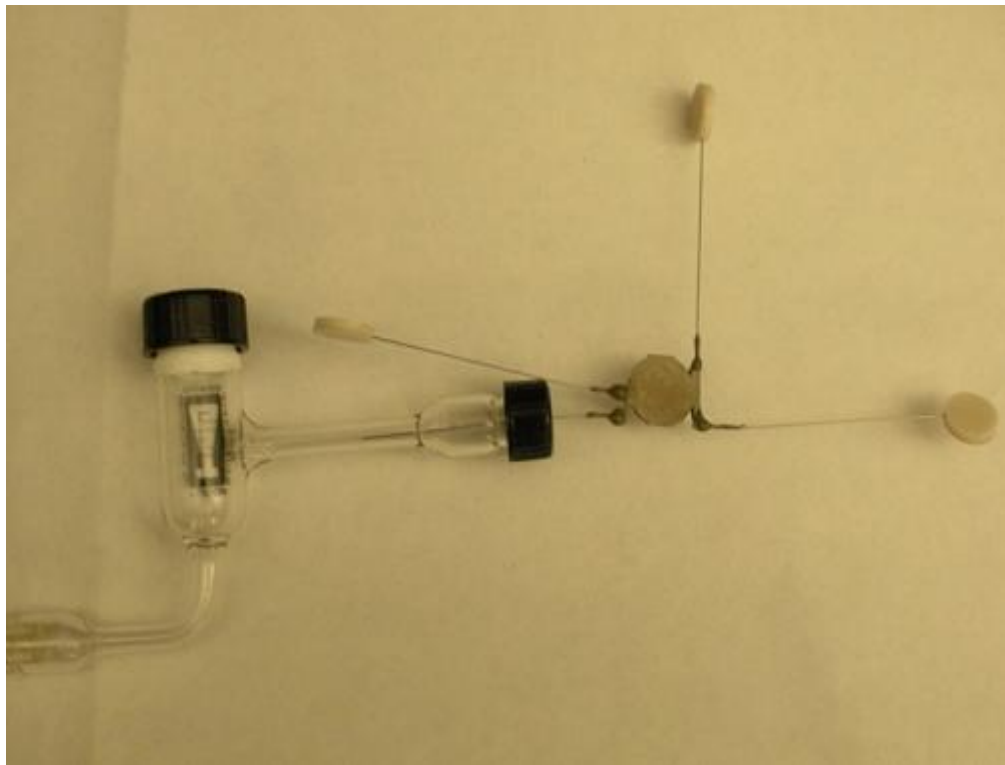


**Figure 2-12:** Apparatus for coating chips where coating solution in the test tube (reservoir) is passed through the nickel column with nitrogen flow

is the formation of bubbles (air spaces) in the connections during the coating in the tubing which causes the coating solution pulled by the vacuum leaving behind a non uniform coating or without any coating. This was proved by connecting a glass T-Tube between the column and the vacuum connection (see figure 2-14). Once the column is connected, the vacuum pulls the coating solution due to formation of any bubbles in the connecting tubing and can be seen in the glass T- tube. To prevent this, another approach of static coating was applied where the column after filling with the coating solution it is kept in the dessicator which was connected to vacuum pump, leaving all the ends open and left for overnight to evaporate the solvent leaving behind a thin layer of stationary phase. After coating, the columns were again checked for flows and leaks. Then they are tested for methane, hexane and mixture of hexane and decane in the GC with same conditions with the above mentioned experimental set up. Separation of hexane and

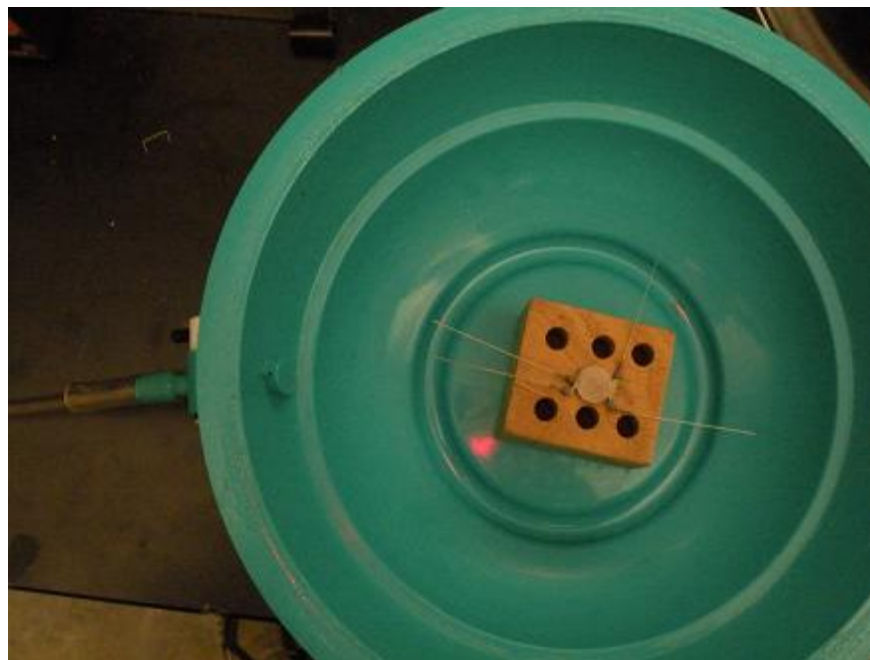


**Figure 2-13:** Schematic diagram of Coating nickel columns

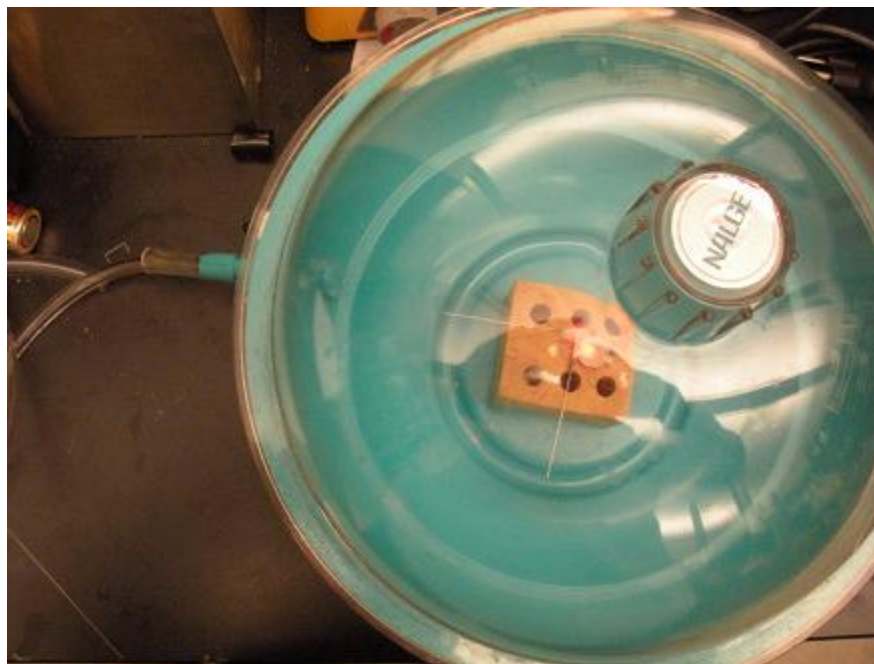


**Figure 2-14:** Nickel column with glass T-tube by connecting vacuum

decane at 80°C and 110°C were recorded. The data for microfabricated nickel column chips presented in this study is the best data achieved so far as a result of several hundreds of chips tested from past 2 years. The methodology presented here was due to the experience achieved in working with the nickel column chips. Data was gathered initially at different injecting split (0%, 25%, 50%, 75%, and 100%) by means of an adjusting valve. But the split change did not affect the data so it was kept at 0% just to add as a back pressure to the column. The column head pressure was kept at 30 psi which is the maximum pressure in the GC testbed. Data was also gathered at different pressures (10 psi, 15 psi, 20 psi, 25 psi, and 30 psi), separation of hexane and decane was achieved but the peaks are broader at low pressures, so all the experiments carried at 30 psi where the peaks are sharper when compared with the data at other column head pressures.



**Figure 2-15:** Coating nickel column in dessicator (before closing lid)



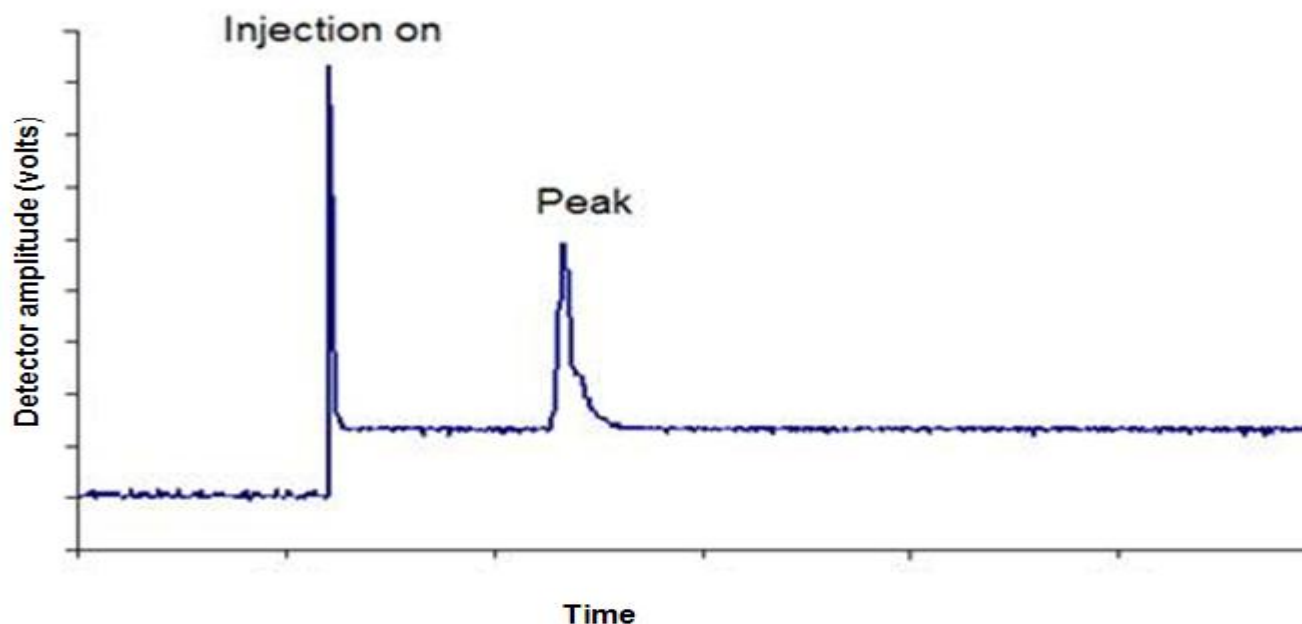
**Figure 2-16:** Coating nickel column in dessicator (after closing lid)

### **3. Results and Discussions**

A HP 5890 GC testbed was used for experimental tests connected to oscilloscope (Agilent 54622D) and ultra fast electrometer (Keithley 6517A). All of the samples are injected manually by syringes and a manual trigger was connected to GC. Sample was injected and the trigger was activated manually and simultaneously. The first spike in the oscilloscope is from the trigger which was followed by the GC peak from the sample injected. The time taken for the sample from the trigger spike to the peak represents its retention time (RT) and the width at the half height (W) was used, which are collected manually from the oscilloscope. The injector and detector temperatures were maintained at 180°C with split flow at 400-500 ml/min and oven temperature used was at 80°C and 110°C. The injection port purge pressure was between 5-10psi with helium as carrier gas. The column head pressure was kept at 30 psi for all the experiments.

#### **3.1 Results of Deactivated Fused Silica Capillary**

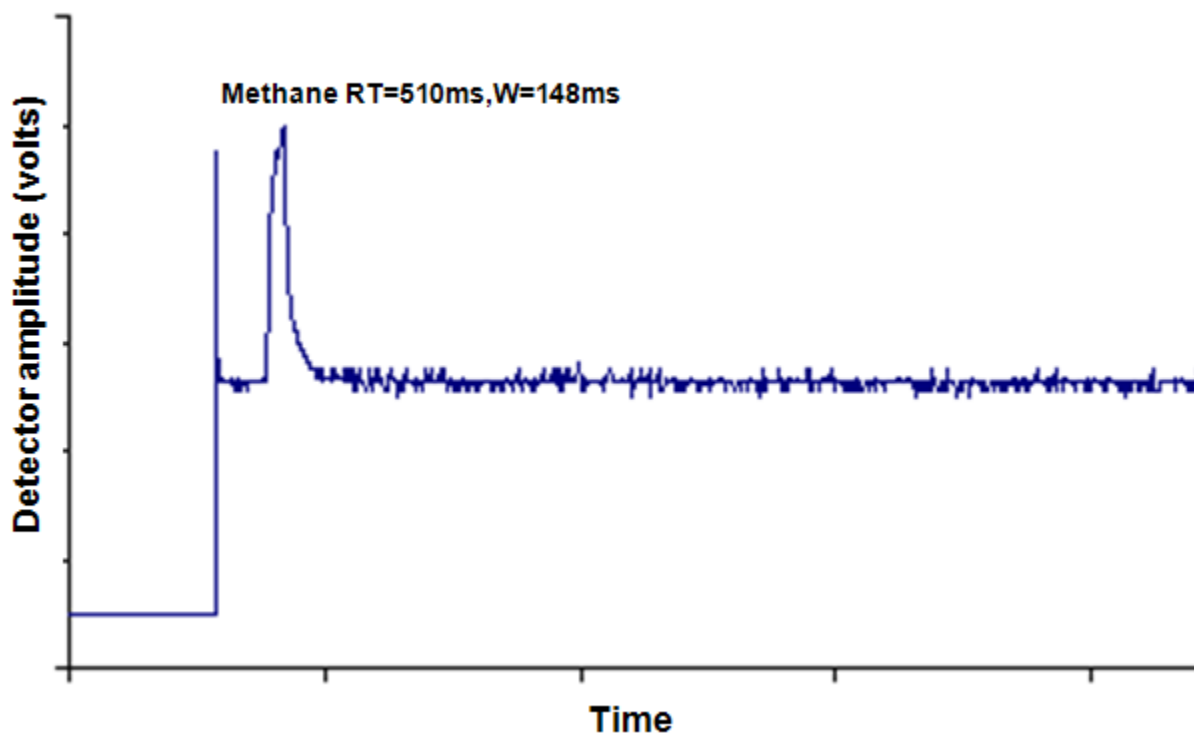
Microfabricated nickel column chips were connected to the GC testbed with deactivated silica capillary tubing. Before testing the column the deactivated silica capillary was tested with 1:1 hexane and decane for separation to ensure that the connecting tubing is not displaying any separation. The data is displayed in figure 3-1 where the first spike represents the injection time followed by the sample peak where it did not show any separation with hexane and decane. The Y-axis represents the detector amplitude in volts while the X-axis is the time in seconds in the oscilloscope. After connecting the column chips the separation of compounds should be from the column but not from the connected deactivated tubing. This experiment was done before connecting any column chip to the GC testbed. When the system does not show any separation it was ready to test the columns by connecting the deactivated silica capillary to the column and GC.



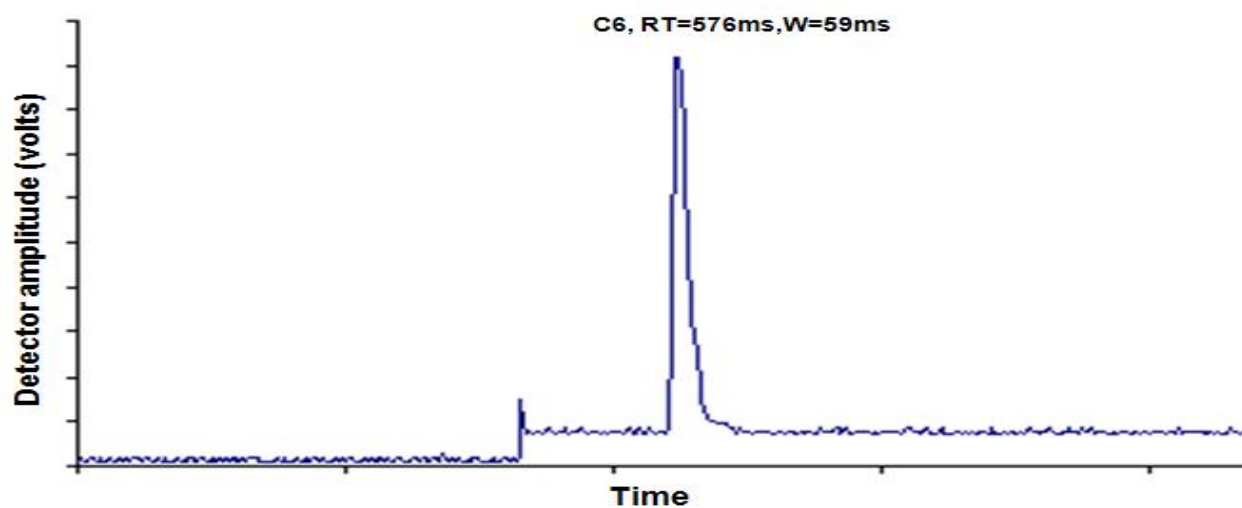
**Figure 3-1:** Data showing no separation when C6 & C10 were tested with the deactivated fused silica capillary used to connect the chip to the GC detector at 110°C and 30 psi column head pressure (CHP)

### 3.2 Results of 1 meter Commercial Fused Silica Capillary Column

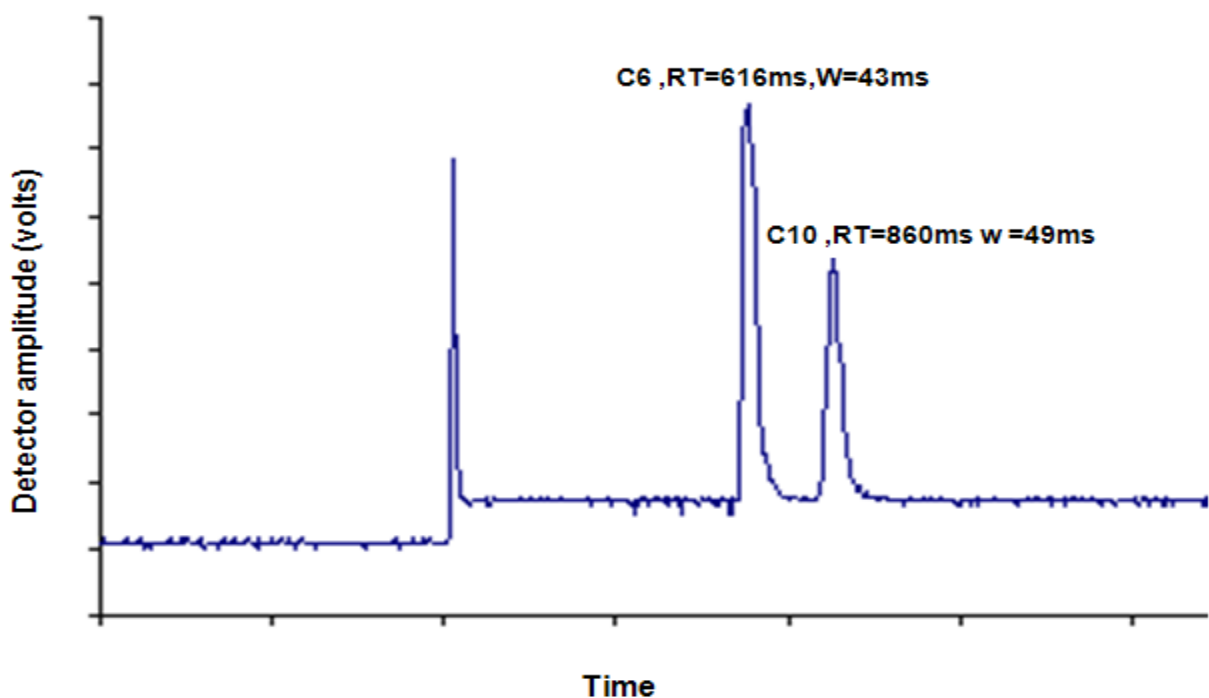
A Fused silica DB-5 capillary Open Tubular Column (OTC) of 0.4 film thickness, 100 microns internal diameter, manufactured by Agilent J&W scientific was cut into 1 meter length and tested in the GC for background data. All the conditions of the GC were maintained the same as mentioned earlier. The data was gathered for methane, hexane and mixture of hexane and decane. Figure 3-2 represents the methane peak with retention time (RT) of 510 milliseconds and peak width (W) of 148 milliseconds (ms) at 110°C. Figure 3-3 represents hexane peak with RT of 576 ms and W of 59 ms. Figure 3-4 represents the peaks for hexane and decane where hexane has RT of 616 ms and W of 43 ms while decane has RT of 860 ms and W of 43 ms. Both the peaks are sharp with separation of 244 ms. The oven temperature was 110°C and column head pressure (CHP) was 30 psi for methane, C6 and separation of C6 and C10.



**Figure 3-2:** Data displaying methane peak for 1 meter 100 microns i.d, DB-5 Open Tubular Column with film thickness of 0.4 at 110°C and CHP 30 psi



**Figure 3-3:** Data displaying hexane peak for 1 meter DB-5 capillary Open Tubular Column with film thickness of 0.4 and internal diameter of 100 microns at 110°C and CHP 30 psi



**Figure 3-4:** Hexane and decane separation in 1 meter 100 micron i.d OTC at 110°C and CHP 30 psi

### 3.3 Results of Microfabricated Nickel Column after PMMA Removed

Microfabricated nickel high aspect ratio column chips were tested for leaks and tested in the GC testbed after PMMA removal. Methane, hexane and mixture of hexane and decane (1:1) were injected and the peaks were recorded. Figure 3-5 displaying the peak for methane with RT of 3.0 seconds and W of 292 ms. Figure 3-6 displaying the peak for hexane with RT of 3.0 seconds and W of 140 ms where hexane peak has little tailing. Figure 3-7 shows the peaks for hexane and decane when a mixture of the same is injected. Theoretically the column should not show any separation when a mixture of compounds are tested as there is no stationary phase coating on the column walls. The separation is an unwanted separation due to presence of organic matter or some PMMA residue. So this column has to be cleaned and deactivated before coating.

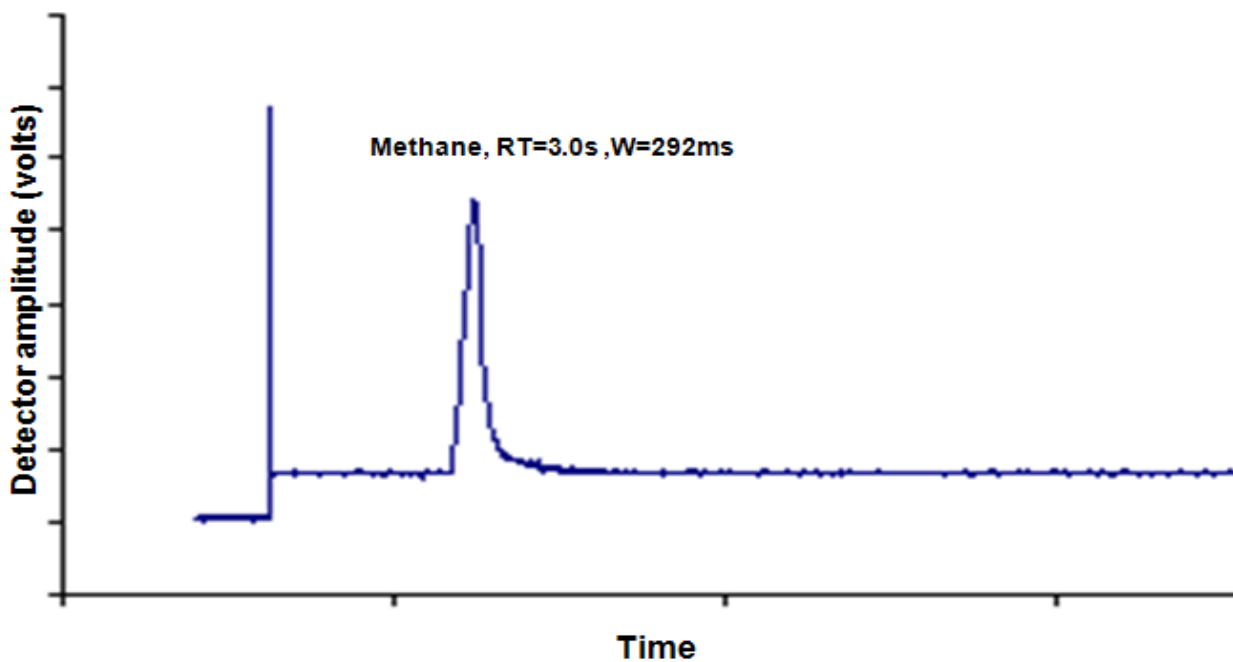


Figure 3-5: Methane peak after PMMA removed at 110°C and CHP 30 psi

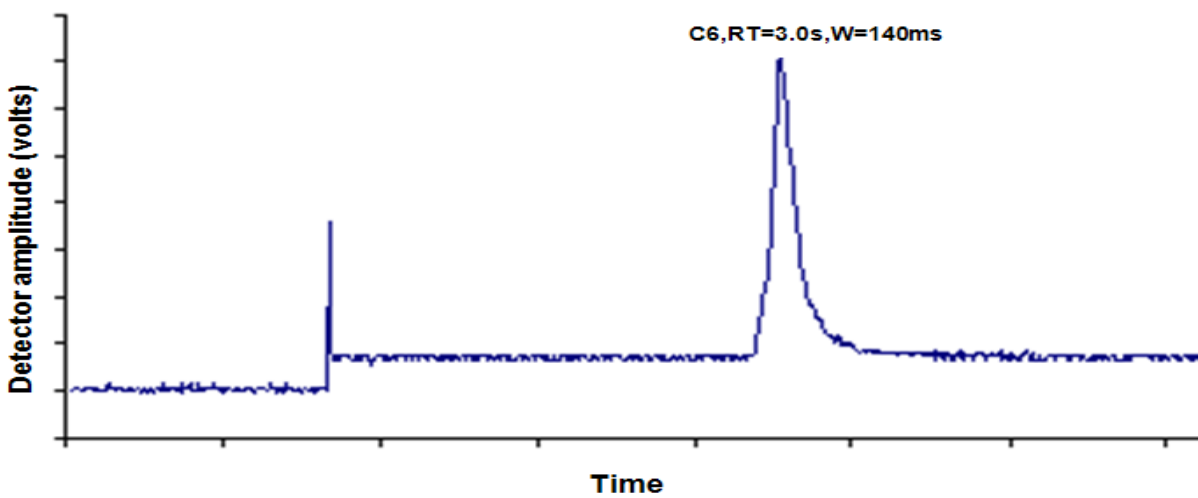
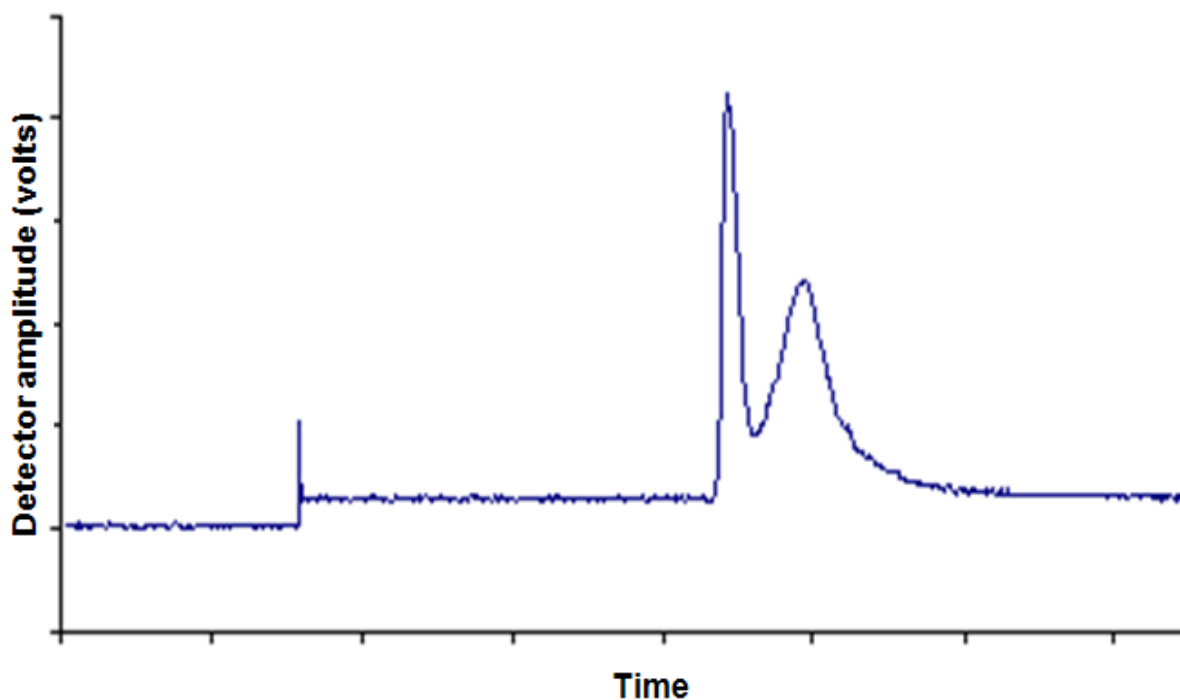


Figure 3-6: Hexane peak after PMMA removed at 110°C and CHP 30 psi



**Figure 3-7:** C6 and C10 showing separation in the column after PMMA removal at 110°C

### 3.4 Results of Column Deactivated with HNO<sub>3</sub>

Microfabricated nickel column chips deactivated with nitric acid were again tested for leaks, connected to GC and tested for methane, hexane and mixture of hexane and decane. Figure 3-8 shows the peak for methane where the RT is 1.8 seconds and W is 192 ms. The peak is sharper when compared to the same methane peak before deactivation where it has W of 292 ms. Figure 3-9 shows the peak for hexane with RT of 1.88 seconds and W of 62 ms. The retention times for methane and hexane are higher (3.0s) before deactivation may be due to presence of PMMA residue in the column chip. The peak is sharp but it has little tailing at the bottom of peak which may be due to some left over residue in the column steel tubing or may be due to connections of column to the GC. Figure 3-10 shows no separation with single peak when hexane and decane mixture was injected at 110°C. So the column was deactivated with nitric acid and it is ready for coating.

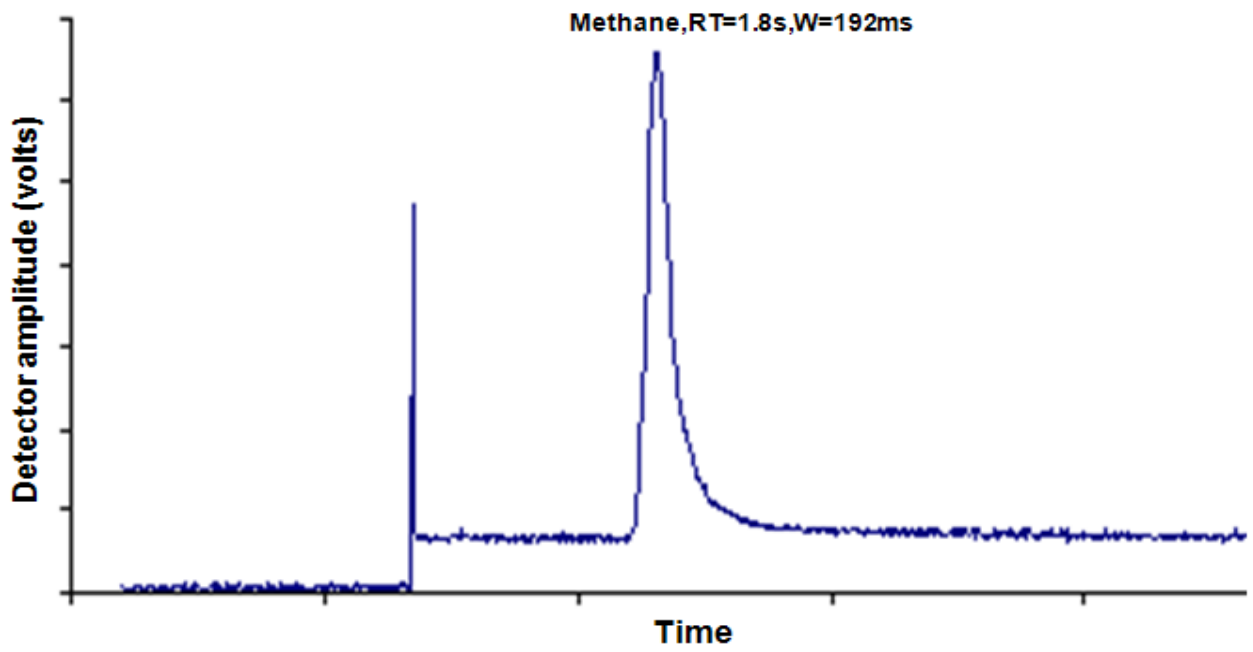


Figure 3-8: Methane peak after cleaning with HNO<sub>3</sub> at 110°C and CHP 30 psi

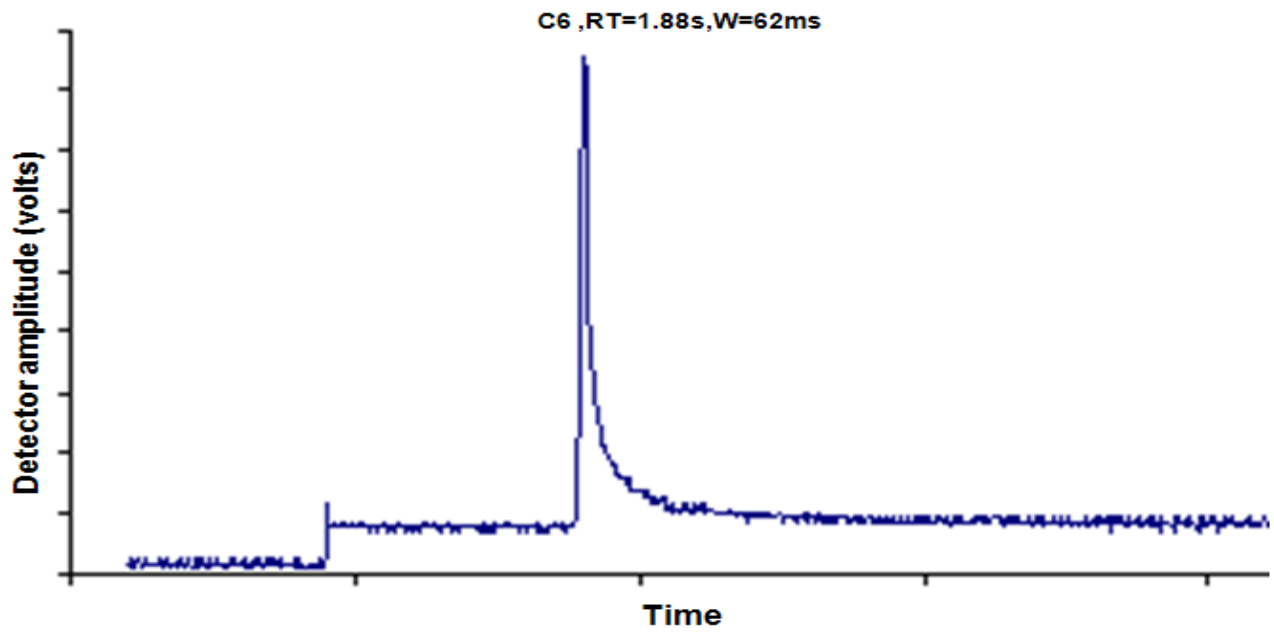
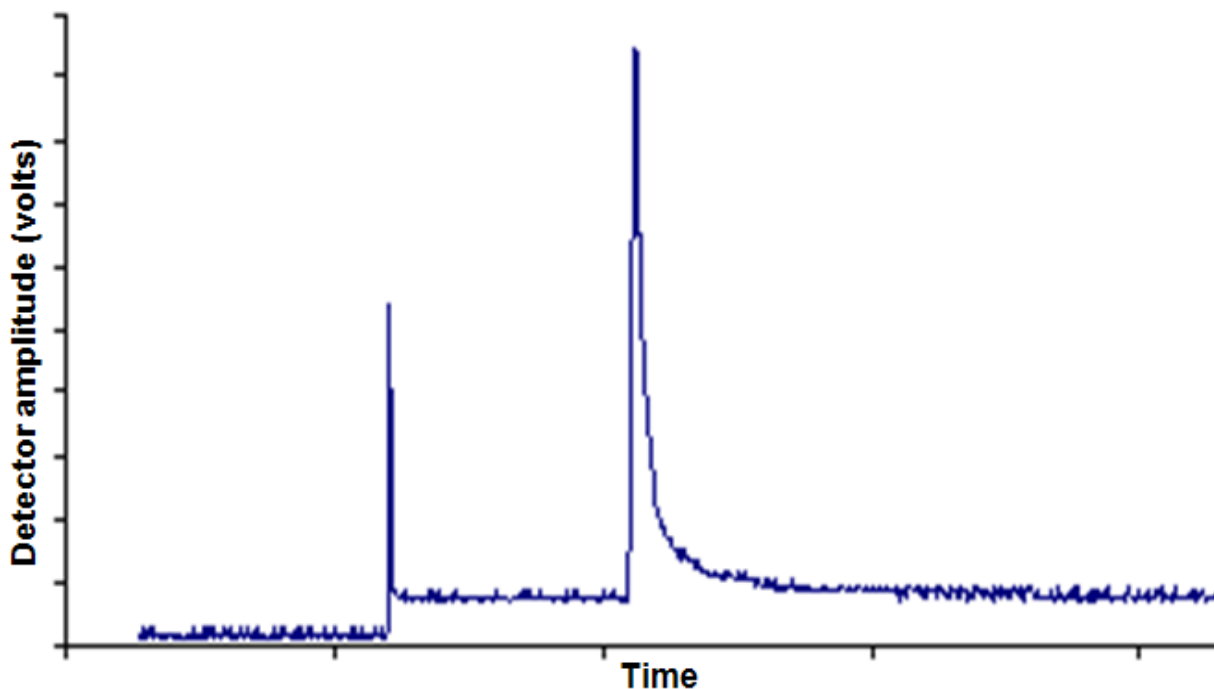


Figure 3-9: Hexane peak after cleaning with HNO<sub>3</sub> at 110°C and CHP 30 psi



**Figure 3-10:** C6 and C10 showing no separation after cleaning with HNO<sub>3</sub> at 110°C

### 3.5 Results of Column after Static Coating in Dessicator

Microfabricated nickel columns were coated with OV-1 and kept in the dessicator under vacuum overnight. About 8  $\mu$ l of OV-1 solution was dissolved in 2 ml of mixture of DCM and pentane (1:1) to prepare a coating solution of 0.4 mg/ml. A plug of methane, hexane and mixture of hexane and decane were injected and peaks were recorded. Figure 3-11 shows the peak for methane where its RT is 1.8 seconds and W is 220 ms. The peak did not have much difference in its retention time and peak width when compared to the methane peak after deactivation (RT=1.8s, W=292 ms). Figure 3-12 shows the peak for hexane with RT of 1.8 seconds and W of 79 ms. The peak is sharp with little tailing when compared to the hexane peak after deactivation with almost same retention time and peak widths (RT=1.88s, W=62 ms). Figure 3-13 shows the data for hexane and decane separation at 110°C with retention time and peak widths of hexane

are 1.7 seconds and 82 ms respectively where retention time and peak width of decane are 2.6 seconds and 320ms. The experiment was repeated again for hexane and decane separation and the retention times and peak widths of hexane and decane did not show much difference (C6, RT=1.68s, W =82 ms, C10 RT =2.58s, W =340ms). Figure 3-14 shows the peaks for hexane and decane when the same column was tested again after some days reconnecting to the GC testbed. The retention times and peak widths of hexane and decane are almost the same and did not show much difference. This shows repeatability and consistency of the data due to uniform coating. The retention times of methane, hexane and decane are higher than 1 meter open tubular capillary column; (See Figure 3-17) this may be due to additional connection of deactivated fused capillary from the column detector end to the GC testbed detector which is of nearly 50 cms of length. The peaks are sharp with good separation of 900 ms when compared with 1 meter capillary column (244ms separation). Figure 3-18 shows the comparison of retention times and peak widths at half height for 1 meter commercial capillary open tubular column (DB-5) and nickel column coated modified static in desiccator with OV-1. The separation is higher for the column chip may be due to the fact, that it has thicker coating than the open tubular capillary column as thicker the coating the higher the separation of compounds. The decane peak is a little broader when compared to the open tubular capillary column and this may be due to little pooling of solution in the column edges which was partially solved by adding dicumyl peroxide and coating in the desiccator. Separation of C6 and C10 was achieved in less than 4 seconds. Hexane and decane separation was also done at different temperatures (80°C, 90°C, 100°C, 110°C and 150°C). The lowest temperature possible for good separation and peaks is at 80°C below which the peaks are very broad. Figure 3-15 shows the separation of hexane and decane at 80°C where hexane has RT of 1.6s, W of 93 ms and decane has RT of 3.12s, W of 620ms with separation

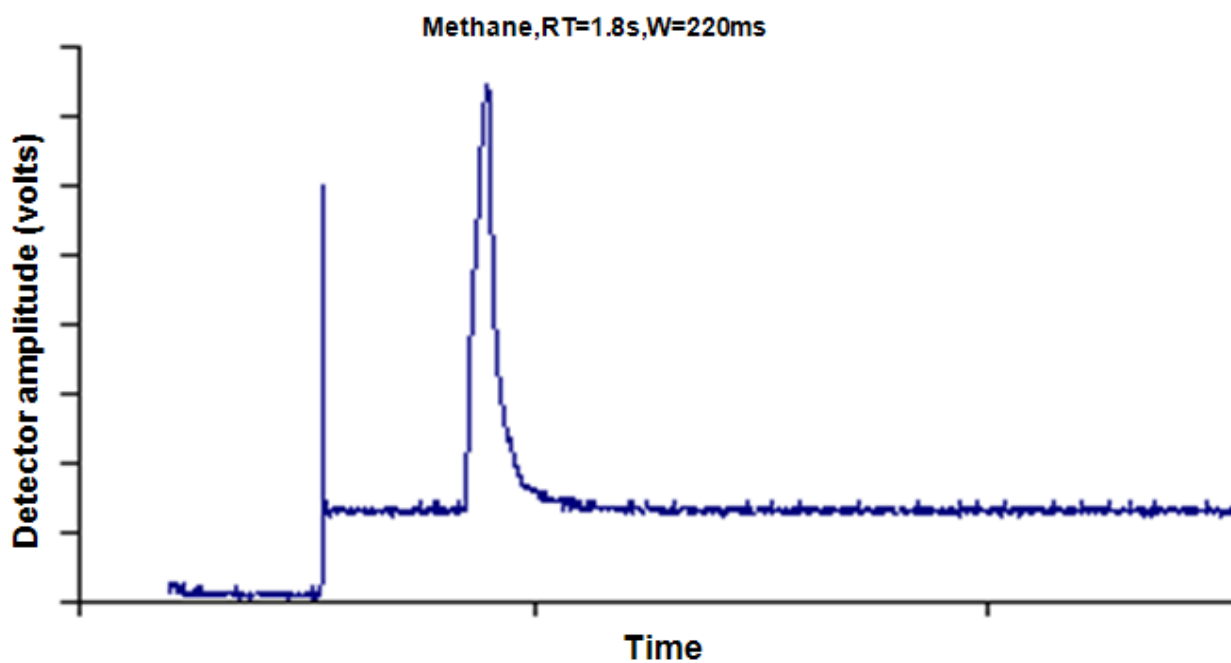


Figure 3-11: Methane peak after coating static in dessicator with 0.4 OV-1 at 110°C, CHP 30 psi

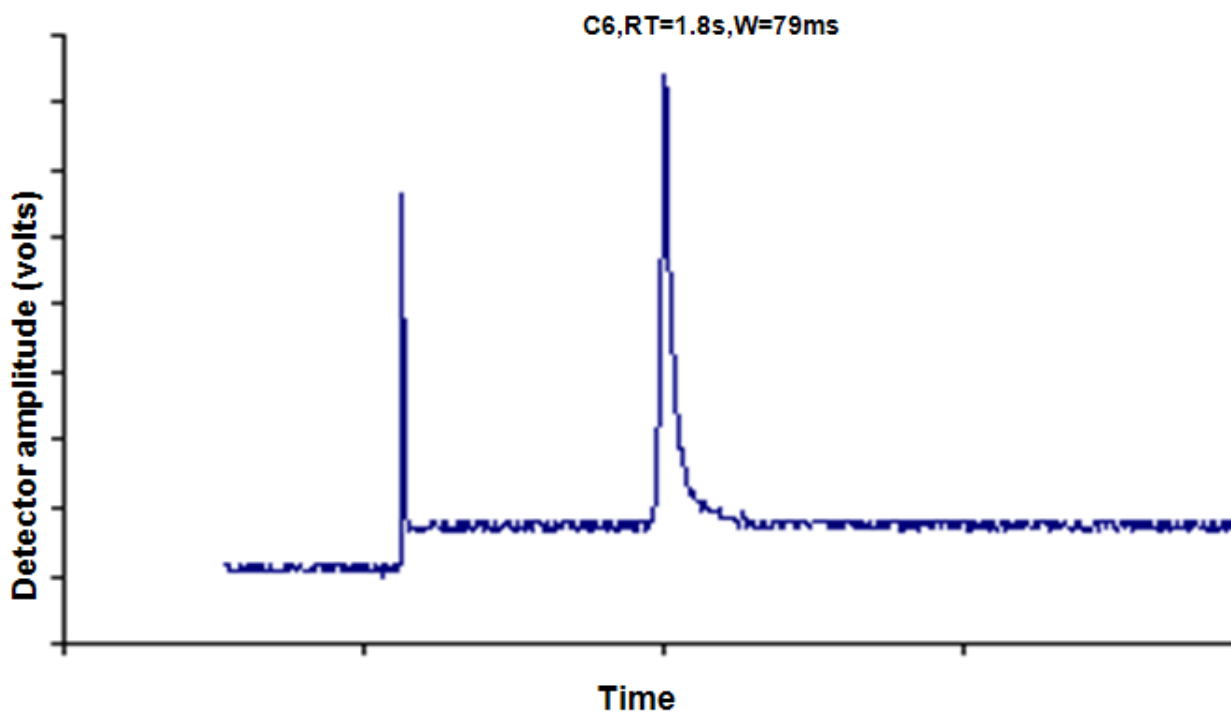
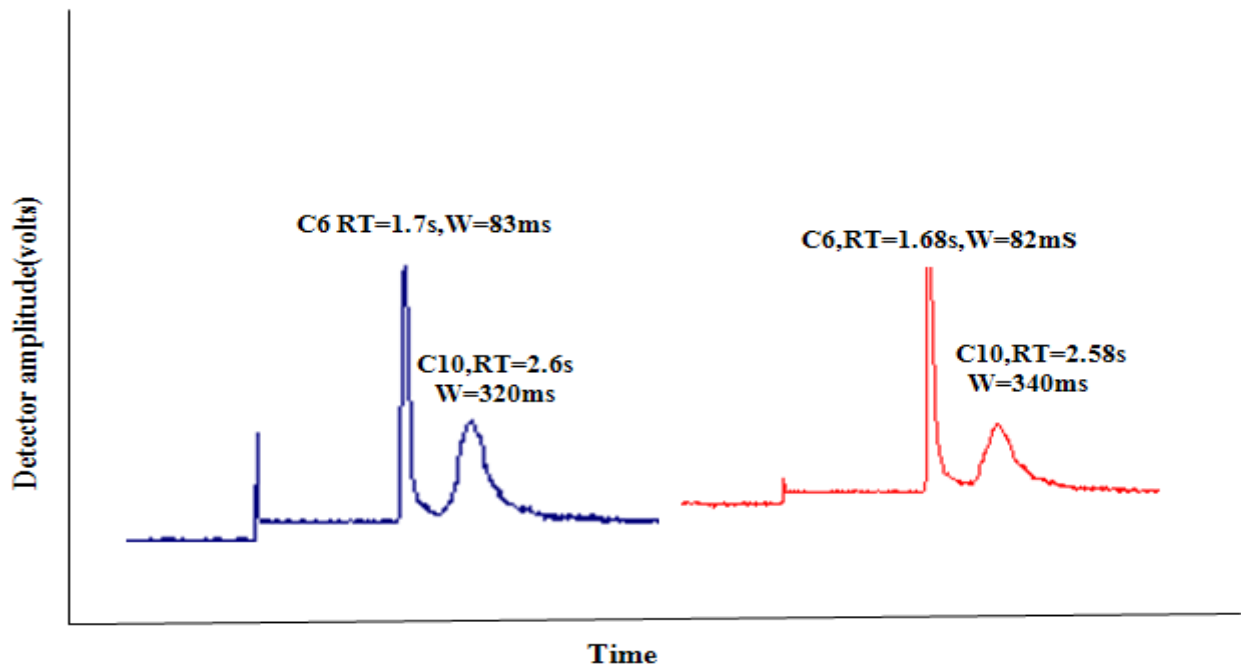
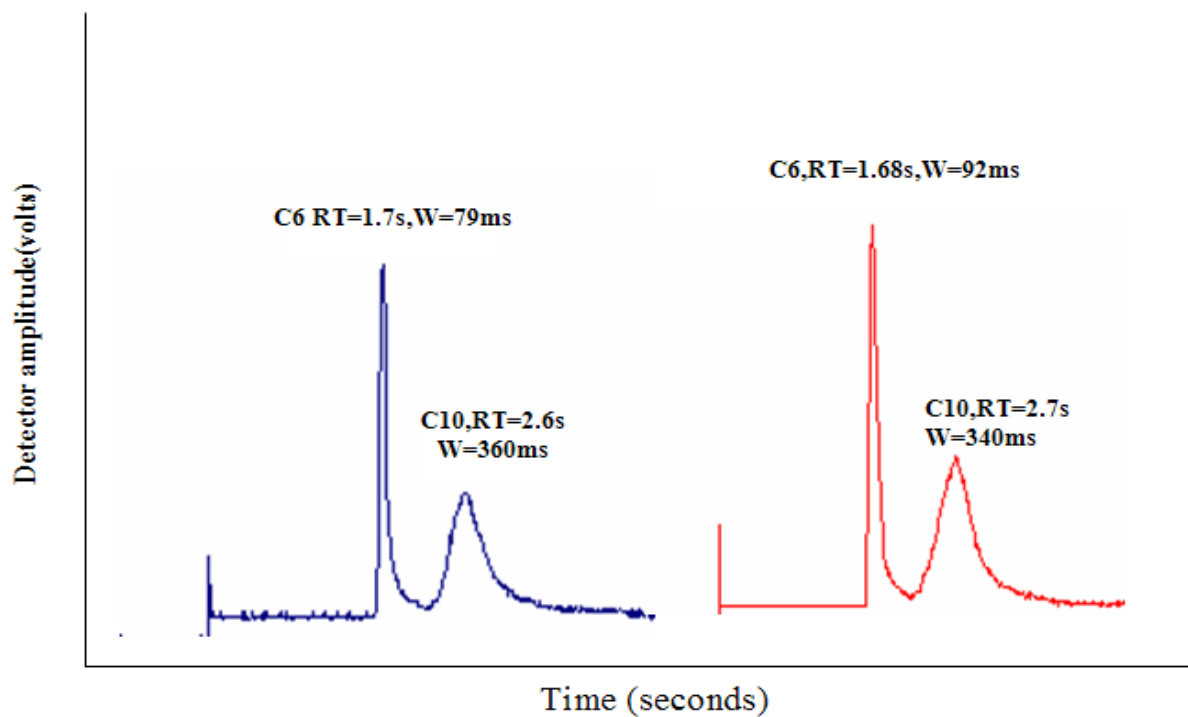


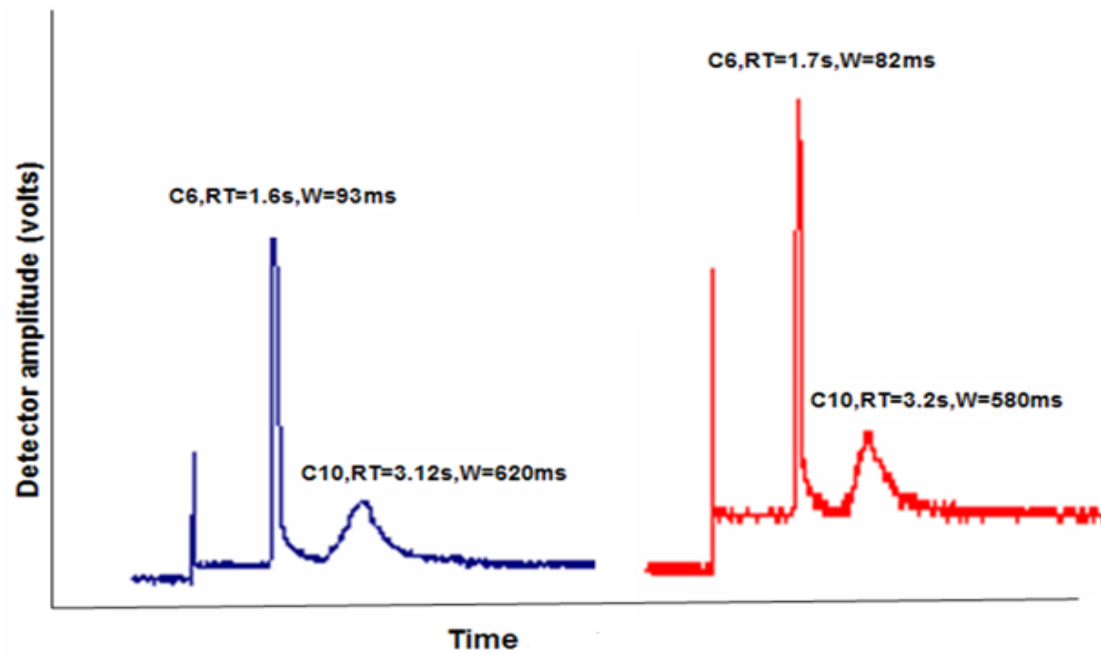
Figure 3-12: Hexane peak after coating static in dessicator with 0.4 OV-1 at 110°C, CHP 30 psi



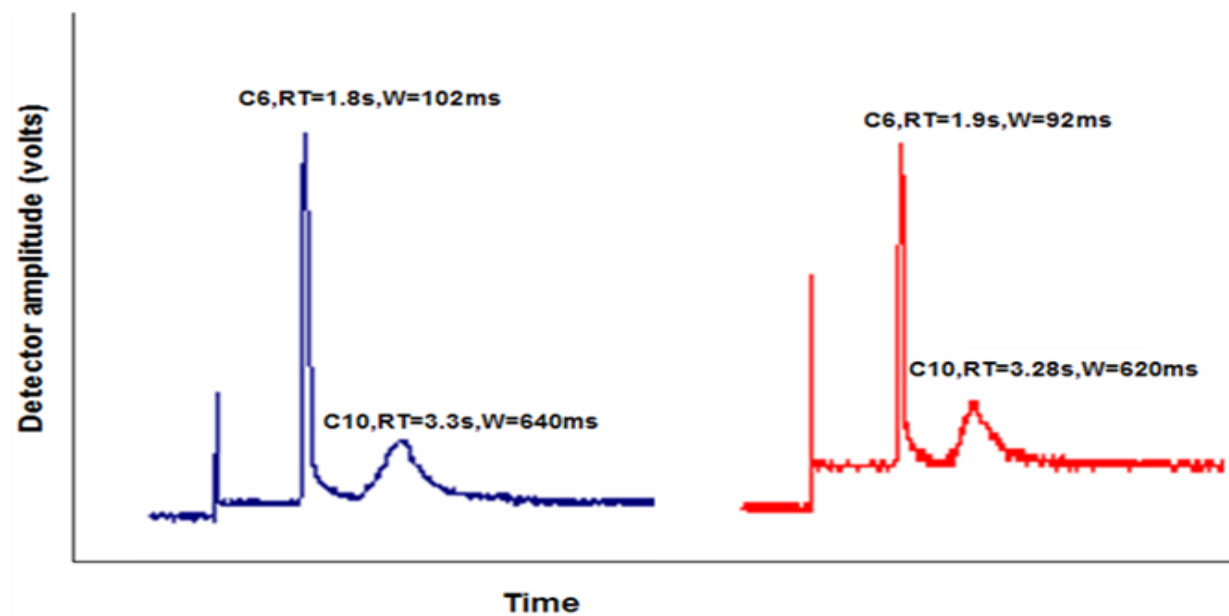
**Figure 3-13:** Data displaying separation of C6& C10 repeated twice after coating the Nickel column with 0.4 OV-1 at 110°C and CHP 30 psi



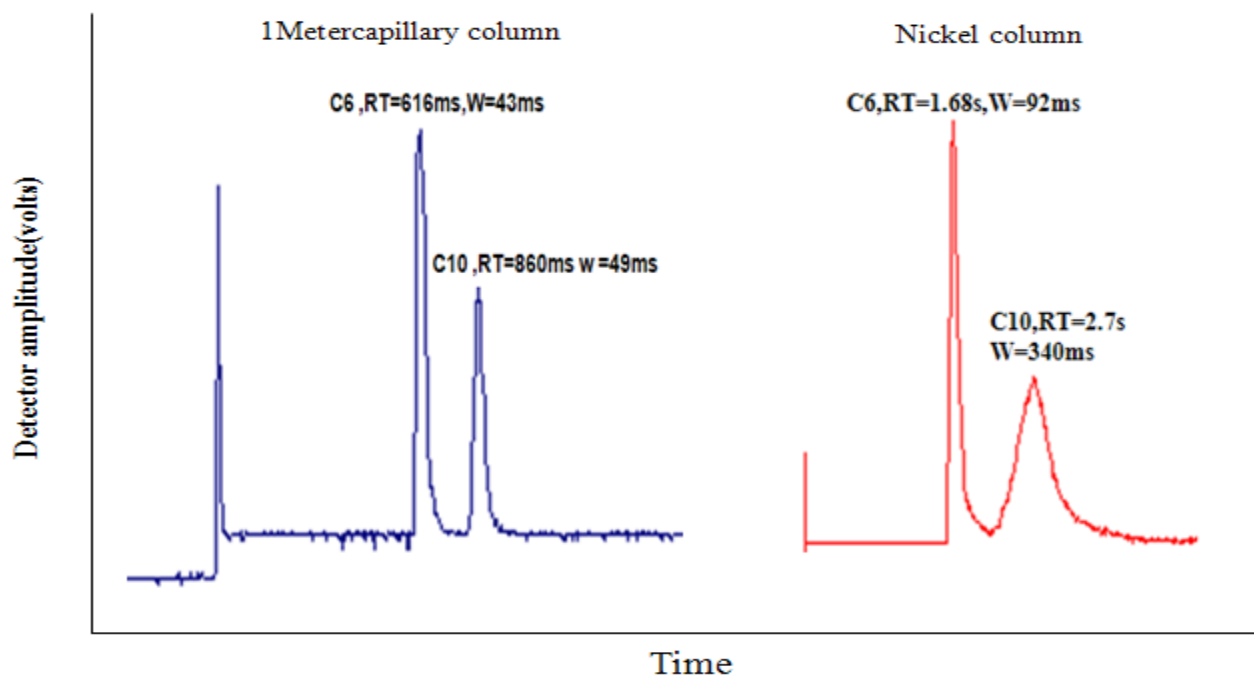
**Figure 3-14:** Data displaying separation of C6& C10 repeated twice after coating the Nickel column with 0.4 OV-1 (Retested the same column) at 110°C and CHP 30 psi



**Figure 3-15:** Data displaying separation of C6 & C10 at 80°C and CHP 30 psi after coating with OV-1



**Figure 3-16:** Data displaying separation of C6 & C10 at 80°C and CHP 30 psi (Retested the same column)



**Figure 3-17:** Data displaying comparison between 1 meter open tubular capillary column and nickel High Aspect Ratio (HAR) column in separation of C6 and C10 at 110°C and CHP 30 psi

Column	Methane		Hexane		Decane	
	RT	W	RT	W	RT	W
1 meter open tubular capillary column (DB-5)	510 ms	148 ms	576 ms	59 ms	860ms	49ms
Nickel HAR column coated with modified static in dessicator	1.8 s	220 ms	1.8 s	79 ms	2.6 s	330 ms

**Figure 3-18:** Comparison of retention times (RT) and peak width at half height (W) for 1 meter open tubular capillary column DB-5 and Nickel HAR column coated modified static in dessicator( the average values of RT and W were used when the experiment was repeated 3 times for each sample)

of 1.5s. The experiment was repeated twice and the retention time and peak widths are almost same with out much difference. Figure 3-16 shows the separation of hexane and decane when the same experiment was repeated twice after some days. The data shows repeatability showing that

the column performance has not been reduced. Separation of hexane and decane were achieved in less than 4 seconds.

The highest temperature for good separation and peaks is 110°C, above which the peaks are sharp but the separation is not good. So the data for hexane and decane at 80°C and 110°C were presented in this study. The data presented in this study is the best data achieved so far after testing and coating several nickel column chips.

#### 4. Conclusions and Summary

Using the LiGA process high aspect ratio nickel gas chromatograph column chips were fabricated with on chip integrated sample injection and detection connectivity. Different epoxy glues were tested for attaching steel connecting tubings to the nickel column chips and JB Weld has proved to be the best glue due to its resistance to high temperatures and longevity. A split injection was used to inject narrow injection plugs to the column. The connection of column chip to the detector end by using the deactivated fused silica capillary proved successful for connecting columns directly to the GC testbed (HP 5890). A fast electrometer and oscilloscope used in the experimental set up were able to expedite the data gathering within seconds. Different procedures for deactivating the column were discussed and nitric acid deactivation proved successful to some extent. Further study of deactivating the metal columns were required as all the commercial deactivation process of silicon columns cannot be applied to metal columns due to difference in their surface chemistry and presence of active sites.

The problem in static coating of metal columns was uncovered by connecting the column with a T-glass tube in between the column connection and vacuum during the evaporation process. The vacuum pulled the coating solution out leaving a non uniform coating residue. Other method of coating, leaving the column in the dessicator with all the ends open with vacuum was tried with limited success. The pooling of solution in the corners of the column was the major problem in coating the metal high aspect ratio columns. The coating process and performance of the column also depends on efficient removal of any residue from the thermal removal of PMMA, and future efforts will be focused on achieving more uniform coating inside the LiGA metal column without pooling in the corners. Separation of hexane and decane was achieved in less than 4 seconds. The retention times of methane, hexane and decane are higher than was achieved using 1 meter open tubular capillary column (See Figure 3-17). This may be

due to additional lengths of connecting tubes needed in connecting the GC chip to the injector and detector of the testbed. The decane peak is a little broader when compared to the open tubular capillary column and this may be due to pooling of solution in the column corners which was partially solved by adding dicumyl peroxide and coating in the dessicator. Coating of microfabricated high aspect ratio metal columns showed promising results. Many laboratories are working on the development of microfabricated columns for miniaturization of GC systems. Microfabricated columns provide a good source for realizing a hand held GC sensor for rapid and on site analysis of chemicals.

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