# ADSORPTION PROPERTIES OF CARBON NANOPARTICLES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EASTERN TECHNICAL UNIVERSITY

BY

SINAN OK

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
OF
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

AUGUST 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Nurcan Baç
Head Of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science**.**

| | |
|---|---|
| Assoc. Prof. Burhanettin Çiçek<br>Co-Supervisor | Prof. Dr. H.Önder Özbelge<br>Supervisor |

**Examining Committee Members**

Prof. Dr. Tülay Özbelge (METU, CHE)

Prof. Dr. H. Önder Özbelge (METU, CHE)

Prof. Dr. Suna Balcı (Gazi Üniv., CHE)

Assoc. Prof. Dr. Burhanettin Çiçek (Ankara Üniv., CHE)

Asst. Prof. Dr. Halil Kalıpçılar (METU, CHE)

**I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.**

Name, Last name : Sinan Ok

Signature :

# ABSTRACT

## ADSORPTION PROPERTIES OF CARBON NANOPARTICLES

OK, Sinan
M.s., Department of Chemical Engineering
Supervisor: Prof. Dr. H. Önder Özbelge
Co-Supervisor: Doç. Dr. Burhanettin Çiçek

August 2005, 114 pages

Carbon can be in several forms. Amorphous, graphite and diamond. Fullerenes are accepted as the fourth form of solid carbon. They are basically, large carbon cage molecules. By far the most common one is $C_{60}$. Nanotubes are actually longer forms of fullerenes.

If a voltage is applied between two carbon rods, an arc will develop between them. If the arc is maintained in helium or argon (instead of air) clouds of black carbon powder is produced. Although many studies have been performed on cathodic deposits, (i.e. nanotubes first seen in this section) very few studies on the carbon sooth are found in the literature. Only around 10% of the black soot is fullerene, the composition of the remainder varies depending on the working conditions. But it is assumed to contain parts of various fullerene particles even higher fullerenes up to $C_{300}$. This fraction is abbreviated as FES through the thesis.

This work comprises the production of FES (fullerene extracted soot), soot, cathodic deposit produced under nanotube conditions and cathodic deposit produced under fullerene conditions and characterization of these in terms of their specific surface areas; pore volume distribution, porosity and as a second part, adsorption capacity of gases $H_2$ and $NH_3$ have been found.

Both physical and chemical adsorption analyses were done using Quantichrome Autosorb 1-C surface analyzer. Obtained isotherms for nitrogen adsorption were found to be in between type II and type IV. BET surface areas for the samples of FES and soot prepared under nanotube conditions and cathodic deposit prepared under fullerene and nanotube conditions were found 240, 180, 14.6 and 29.7 $m^2$/g of surface area respectively. Micropore volumes were calculated from Horwath – Kowazoe and Saito – Foley methods were found 0.045, 0.034, $2.38*10^{-3}$ and $1.19*10^{-3}$ cc/g respectively. Active surface areas for $NH_3$ adsorption were found for FES, soot and Norit active carbon sample are found to be 39.2, 49.6, 32.5 $m^2$/g at $30^0$ C and 6.35, 14.65, 6.59 $m^2$/g at $300^0$ C respectively.

As a result of this work, it is concluded that although not superior to NORIT CN1 active carbon sample, FES is as active as that material and able to adsorb as much hydrogen as active carbon. This is important because FES is already a side product of the arc-evaporation fullerene production technique and has no known uses at all.

Keywords: Nanotechnology, Carbon Particles, Adsorption

# ÖZ

## KARBON NANOPARÇACIKLARIN ADSORBSİYON ÖZELLİKLERİ

OK, Sinan
Yüksek Lisans, Kimya Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. H. Önder Özbelge
Ortak Tez Yöneticisi: Doç. Dr. Burhanettin Çiçek

Ağustos 2005, 114 sayfa

Karbon elementi amorf, grafit ve elmas olmak üzere birkaç farklı form alabilmektedir. Fullerenler ise karbonun dördüncü formu olarak kabul edilebilirler. Fullerenler temel olarak büyük kafes yapılı karbon molekülleridir. Şimdiye kadar en çok bilineni ve üzerinde en çok çalışma yapılanı $C_{60}$ dır. Nanotüpler gerçekte fullerenlerin uzamış halinden başka birşey değildirler.

Iki karbon çubuğun arasında bir voltaj uygulandığında aralarında bir ark oluşacaktır. Eğer ark hava yerine helyum yada argon ortamında oluşturulursa, ince karbon kurumu elde edilir. Araştırmaların büyük çoğunluğu bu aşamada oluşan katodik depozitler hakkında olsa da kurum kısmın özelliklerini kapsayan oldukça az çalışma vardır. Karbon kurumunun yaklasık % 10 u fullerenlerden oluşmakta, arta kalan kısım ise üretım koşullarına bağlı olarak farklı bileşimlerde olmaktadır. Artık kısmın fulleren parçacıkları ve $C_{300}$ e varan boyutlarda fullerenlerden oluştuğu kabul edilmektedir. Tez boyunca bu kısımdan FES (fullerenden ayrılmış kurum) olarak bahsedilecektir.

Bu çalışmada, bu parçacıkların üretimi, yüzey alanı, porozite, gözenek hacim dağılımı olarak karakterizasyonu ve hidrojen ve amonyak gazları için adsorpsiyon kapasitelerinin bulunması konularını kapsamaktadır.

Fiziksel ve kimyasal adsorpsiyon analizleri Quantichrome Autosorb 1 C yüzey analiz cihazı ile gerçekleştirilmiştir. Azot adsorbsiyon izotermleri Tip II ve Tip IV arasında bulunmuştur. FES, kurum, fulleren şartlarında hazırlanan katodik depozit ve nanotüp şartlarında hazırlanan katodik depozit yüzey alanları sırasıyla 240, 180, 14.6, 29.7 $m^2/g$ ve mikro gözenek hacimleri de Horwath – Kowazoe/Saito – Foley metodları kullanılarak sırasıyla 0.045, 0.034, $2.38*10^{-3}$ and $1.19*10^{-3}$ cc/g olarak hesaplanmıstır. Amonyak adsorpsiyonu sonucu FES, kurum, Norit aktif karbon örneklerinin aktif yüzey alanları da sırasıyla $30^0$ C de 39.2, 49.6, 32.5 $m^2/g$ ve $300^0$ C de 6.35, 14.65, 6.59 $m^2/g$ bulunmuştur.

Bu çalışma sonucunda FES in aktifliğinin aktif karbon örneğinden çok üstün olmasa da en az onun kadar yüzey aktivitesi olduğu ve gene en az onun kadar hidrojen adsorblama yeteneği olduğu sonucuna varılmıştır. Bu sonuç, FES in halihazırda bir atık ürün olması ve herhangı bir kullanım alanının olmaması bakımından önemlidir.

Anahtar Kelimeler: Nanoteknoloji, Karbon Parçacıklar, Adsorpsiyon

# ACKNOWLEDGEMENTS

I wish to express my deepest gratitude to my supervisors Prof. Dr. H. Prof. Dr. H. Önder Özbelge, Assoc. Prof. Dr. Burhanettin Çiçek and Prof. Dr. Suna Balcı for their support, guidance and patience throughout this work. And also their guidance with the equipment i have used that gave me invaluable experience.

I also would like to thank Berker, Canan, Başak, Onur, Ceylan, Esin, Özge, Sinan, Burcu and Deniz for their support and patience for the weeks i was wandering in panic. Thank you all for being there...

Finally i would like to thank my family for their patience and support through this study. Sorry for the sleepless nights i have caused wandering in the corridors :)

# TABLE OF CONTENTS

CHAPTER

APPENDICES

# LIST OF TABLES

# LIST OF FIGURES

## LIST OF SYMBOLS AND ABBREVIATIONS

C : BET equation constant

C# : # Indicates the number of carbon atoms that forms the particular fullerene

Cµ : Monolayer concentration of one monomolecular layer of gas

Cµs : Maximum amount that can be adsorbed by the layer

FES : Fullerenes Extracted Soot

n : Moles of gas adsorbed on the solid surface

nm : Mole of one monomolecular layer of gas

P : Pressure of the gas in adsorption equilibrium with the surface

P0 : Saturation pressure of adsorbate gas at the experimental temperature

q1: Heat of adsorption on the first layer

qL: Heat of liquefaction of adsorbed gas on all other layers

R: Gas constant

$S_g$ : Surface area of one monomolecular layer of gas

T : Temperature

V : Volume of gas at STP conditions $V_m$ (22400 cm3/mole)

V0 : Volume of adsorbate gas at the experimental temperature

$V_m$ : Volume of one monomolecular layer of gas

Greek letters

$\alpha$ **:** Projected area of one adsorbed gas molecule

σ : Layer thickness

Θ : Fraction of the surface occupied by adsorbed molecules

# CHAPTER 1

# INTRODUCTION

Since the discovery of fullerenes in mid eighties and nanotubes in nineties, a whole range of studies have been conducted on these particles. The most important impact of the discovery of fullerenes was its lead to nanotubes. Everyday, new application areas for these novel particles are being found. For now, although in theoretical or laboratory production scale, they are used in electronics to medical researches. If not now, probably in ten or fifteen years researchers will be able to use electronical devices with fullerene and nanotube transistors in them or certain drugs that are dissolved only in the desired area of the body with no side effects. By now, there is no known way to produce types of nanotubes (such as same length, same diameter or same crystal order). But it is totally different story for fullerenes, using different solvents or treatment methods, it is possible to separate fullerenes having different number of carbon atoms in their structure. And also they are easier to produce.

Fullerenes are basically soccer-ball shaped cage molecules made up of entirely carbon. Other fullerene types were reported that made up of silica, boron and even gold which have totally different properties than their carbon-made counterparts and not as stable as carbon made ones. Main production method of producing these particles depends on vaporization of a carbon source, such as graphite or a carbon-containing medium, and then extracting the formed black powder known as soot. A widely used method which also have been used in this work is the Kratschmer method that uses DC current in an oxygen free atmosphere to evaporate a graphite rod. Produced soot is then extracted with toluene to separate fullerenes ($C_{\#}<70$). After fullerenes are removed, remaining fraction is abbreviated as FES, Fullerenes Extracted Soot, which is a side product.

Aim of this thesis is to produce fullerene and characterization of the fullerene by products by means of physical and chemical adsorption techniques by comparing results with a commercial active carbon sample.

# CHAPTER 2

# CARBON NANOPARTICLES

## 2.1. HISTORY

Carbon nanoparticles are mainly composed of folded sheets of layers formed from 5 and 6 membered rings of carbon (that can form either fullerenes or nanotubes), amorphous carbon, graphite layers and folded/unfolded bits of these structures with diameters not exceeding 100 nm.

Discovery of fullerenes is such an interesting example of both the scientific method and scientists at work. Towards the end of 1960`s, Eiji Osawa in Japan, while playing football with his son, realized that a molecule made up of $sp^2$ – hybridized carbons could have the football structure. He therefore made the first proposal for $C_{60}$. At the same time football enthusiasm of I. V. Stankevich of the topology group of the Nesmeyanov Institute in Moscow, caused independently to propose the $C_{60}$ structure. The paper published in 1973 by his group not only predicted some properties of $C_{60}$ but also of $C_{20}$ (the smallest fullerene possible) as well.

First spectroscopic evidence for fullerenes was published in 1984 by Rohlfing, Cox and Kaldor from Exxon laboratories while vaporizing graphite by laser using a supersonic beam apparatus, built from the design of Richard Smalley of Rice University-Teksas. Species in their soot-like mixture showed a maximum intensity at $C_{60}$ and $C_{70}$. Researchers concluded that new compound must have a cage-like structure depending on previous theoretical studies. But in that time these compounds are thought to be produced only in laboratory conditions. A year later Harold Kroto et. al. from Sussex University being interested in the manner in which carbon chains might be produced by carbon stars reproduced the earlier Exxon results using the same cluster beam apparatus of Rice Smalley[8]. In addition research student James Heath was able to find $C_{60}$ forming conditions. The paper describing his work was submitted to *Nature* on 12th September 1985. They named $C_{60}$ as Buckminster Fullerene because of the similarity to the structures created by the architect Buckminster Fuller. For this work they are awarded with the Nobel Prize in 1996.

The 1990 announcement of the Kratschmer-Huffman technique[7] for the simple production of large quantities of $C_{60}$ (buckminsterfullerene), has precipitated an enormous, world-wide interest in the properties of this elegant, soccer-ball-shaped molecule. Hundreds, if not thousands, of laboratories are engaged in fullerene research, with the emphasis of the work ranging from biochemistry to molecular theory to solid-state physics. Nanotubes first discovered by a coincidence in 1991 by the Japanese electron microscope operator Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes[9]. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nano-particles and nanotubes, of a type which had never previously been observed.

A short time later, Thomas Ebbesen and Pulickel Ajayan, from Iijima's lab, showed how nanotubes could be produced in bulk quantities by varying the arc-evaporation conditions[10].

Nine years later, research team led by Cheng Huiming of the Institute of Metal Research in China, produced single-walled carbon nanotubes that can store and release hydrogen in significant quantities at room temperature.

Table2.1.: Chronological order of carbon nanoparticle history

| **Time** | **Team** | **Progress** |
|---|---|---|
| **1970`s** | Harry Kroto & Dave Walton | Identification of $C_{60}$ in interstellar dust |
| **1980`s** | Smalley et. Al. | $C_{60}$ synthesized |
| **1991** | Sumio Iijima | Discovery of nanotubes |
| **1993** | Sumio Iijima et. al. | Synthesis of single walled nanotubes |
| **1996** | Robert F. Curl, Harry Kroto, Richard Smalley | Nobel prize in chemistry for the discovery of $C_{60}$ |
| **1999** | Samsung | Monitor panel made up from nanotubes |
| **2000** | IBM | First circuit using single walled nanotubes |

## 2.2. ALLOTROPY IN CARBON

A chemical element is said to have allotropy when it can be found in two or more molecular structure in the physical state. These individual forms are called allotropes. Allotropes generally differ in physical properties such as color and hardness as well as chemical activity. Oxygen ($O_2$) – ozone ($O_3$), phosphorus and sulfur are general elements that show allotropy. Many metals have allotropic crystalline forms that are stable at different temperatures.

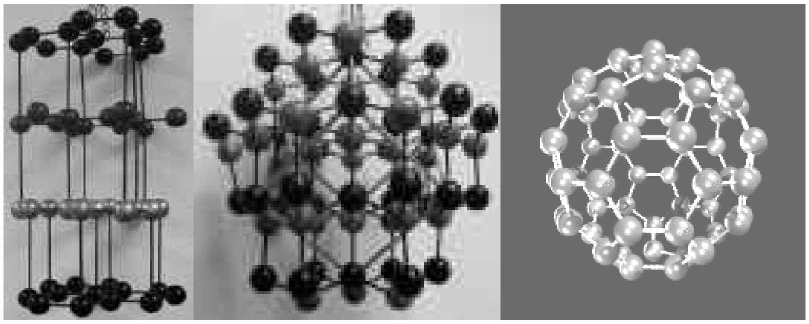

Graphite Diamond Fullerene ($C_{60}$)

Figure 2.1: Allotropes of carbon [21]

The allotropes of carbon include diamond, graphite and fullerene. Diamond is the hardest and most dense of the three (actually it is the hardest known material on earth). It has no color and it is the least reactive. Each atom has a coordination number of four so the atoms are arranged in a tetrahedral structure. The carbon atoms are linked with single bonds leaving to place for flexible electrons therefore making diamond an insulator.

Graphite is formed by the hybridization of carbon atoms forming pi orbital, enabling this form to conduct electricity. Graphite consists of 2-D layers of giant hexagonal structured molecules arranged in parallel form bonded each other through Wan der Vaals forces, just like a network of benzene formations bond each other. Weak bonding results in a sliding between the layers making it possible to use it as lubricant or in pencils.

Third type of carbon was found by Kroto and Smalley, which they called fullerenes after Richard Buckminster Fuller. Fullerenes can be described as

2-D graphite layers folded to a 3-D form with additional pentagonal structures in between. Fullerenes can be composed of 20 to several hundred carbons.

## 2.3. FULLERENES

Although fullerene related studies are relatively new, they are known to exist in interstellar dust as well as in geological formations on earth. Fullerenes are basically, large carbon cage molecules. By far the most common one is $C_{60}$. Other relatively common fullerene types are $C_{70}$, $C_{76}$, and $C_{84.}$

$C_{60}$`s shape is called a truncated isacohedron, with 20 hexagons and 12 pentagons. (It's also the exact shape of a soccer ball). A $C_{60}$ molecule or "buckyball" is about 7 angstroms in diameter (7 times as large as a hydrogen atom) and is the most common fullerene, and thus the most-studied. [29] [16]

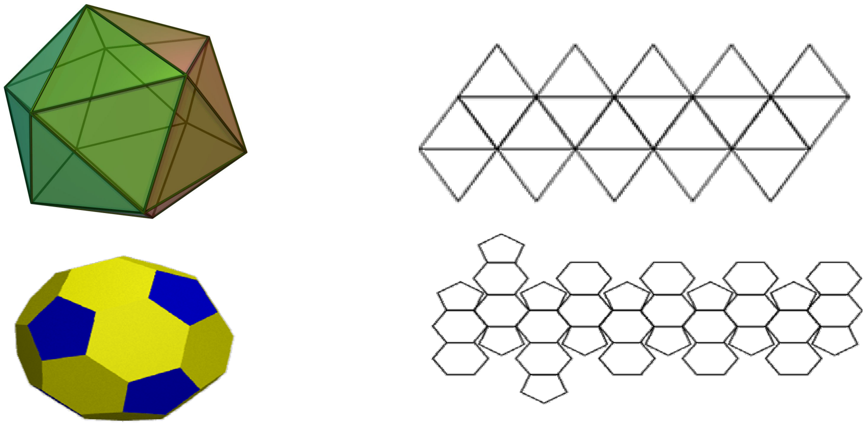


Figure 2.2.: Icosahedron (top) and truncated icosahedron figures with their 2-D form [22]

### 2.3.1. PROPERTIES OF FULLERENES

Here the properties related to this study will be given in detail. Other properties related to thermodynamics [7] [16] [29], oxidation and reduction [32], spectroscopic [8] and catalytic [4] [30] [31] [32] can be found elsewhere.

#### 2.3.1.1. SEPERATION OF FULLERENES FROM SOOT

Fullerenes are soluble in benzene and toluene. The solubility of fullerenes decreases with increasing size (carbon number). They are insoluble in acetone, ethers and alcohols. The first available purification method for the C60 fullerene was by HPLC from which small amounts could be generated at large expense. Below is a list of solvents that can be used in extraction of fullerenes.

Table 2.2: Solubility of $C_{60}$ in various solvents [16]

| **The solubility of $C_{60}$ in room temperature (mg/ml)** | |
|---|---|
| Hexane | 0.04 |
| Carbon Tetrachloride | 0.4 |
| Benzene | 1.7 |
| Toluene | 2.8 |
| 1,2-dichlorobenzene | 27 |
| 1-methylnaphtalene | 33 |

In order to separate the contents of the soot, fullerene formations have to be extracted as much as possible, this is mainly done by extraction methods with various organic solvents. Toluene is used mainly for the extraction of $C_{60}$ and $C_{70}$ from soot but this solvent is insufficient for dissolving higher fullerenes. In recent studies, some organic solvents were found to be efficient for extraction of higher fullerenes. Quinoline, for example, has been reported to extract between 80-carbon fullerenes to several hundred effectively[5]. Also hydrotreatment prior to extraction have been reported to increase efficiency both for $C_{60}$ - $C_{70}$ mixture and higher fullerenes. But these higher fullerenes and un extracted $C_{60}$ percentage is  about 1% of the soot and are neglected in this study.

A recent kilogram scale fullerene purification strategy was demonstrated by Nagata et al. [1]. In this method $C_{60}$ was separated from a mixture of $C_{60}$, $C_{70}$ and higher fullerene compounds by first adding the amidine compound DBU to a solution of the mixture in 1,2,3-trimethylbenzene. DBU as it turns out only reacts to $C_{70}$ fullerenes and higher which reaction products separate out and can be removed by filtration. $C_{60}$ fullerenes do not have any affinity for DBU and are subsequently isolated.

Fullerene-free fraction is treated as a byproduct of the Kratscmer Technique and has been rarely researched this far. The most important study was accomplished by S. Silva and coworkers from Brazil[6]. As this is the part after fullerenes are extracted, the remains are purely dependent to the operation conditions and a definite percentage of the contents are not possible to determine. Fullerenes extracted soot (FES) fraction is the focus of this study. Although the percentages are indefinite, FES mainly consists of half-formed fullerene molecules, nanohorns and nanotubes in small percentage  This fraction gives promising results for high yield adsorbent for various chemicals and high surface area compared to activated carbons.

### 2.3.3. PRODUCTION OF FULLERENES

Productions of fullerenes mainly depend on evaporation of a carbon source (graphite, hydrocarbons etc) and purification. Evaporation techniques experimented so far are by electric arc, by laser, by sunlight, by microwaves and by combustion. Combustion technique is the most advanced technique for large scale production that requires minimum amount of purification. This method was patented by Jack Howard from MIT in 1991 and an enhanced version of this method is still been experimented [2]. For laboratory scale productions, the cheapest and most efficient system is the arc method. It requires relatively less components, and not complicated like laser evaporation. Therefore arc evaporation technique is considered for fullerene production for this study.

Fullerenes have been effectively produced in gram quantities since 1990 by the Kratschmer technique. Many other production methods have also been tested; however, this graphite-arc technique still proves to be the most efficient way of producing fullerenes in laboratory scale productions. Due to problems faced in scaling up, an industrial scale process feasible for the bulk production of these novel molecules has yet to be found. But a new technique including combustion of hydrocarbons gives promising results for industrial scale production of fullerenes.

Three efficient methods for producing fullerenes have been used this far, they are listed below in chronogical order:

1. Individual graphite rods are vaporized with electrical current in low pressure gas (used in this work). Solvents are needed in order to separate fullerenes from byproducts. A kilogram of pure $C_{60}$ is around 25.000 $.

2. Continious flow of hydrocarbon fuel is vaporized at low pressure in a flat surface. Solvents are needed in order to separate fullerenes from byproducts. A kilogram of pure $C_{60}$ is around 16.000 $.

3. Continious high flow of hydrocarbon fuel is vaporized at a low pressure in a 3D chamber. No solvents needed, and a kilogram of pure $C_{60}$ is around 200 $.

If a voltage is applied between two carbon rods under inert atmosphere and vacuum, an arc will develop between them. If the arc is maintained in helium or argon (instead of air) clouds of black smoky carbon soot are produced. This technique is known as the Kratschmer technique [7]. Graphite arc technique can be applied mainly in two ways:

1. Fullerene conditons:

A low vacuum pressure (around 100 Torr) and non-flow helium atmosphere are used. Products are a cathodic deposit along with soot consisting of 15 - 20% wt $C_{60} – C_{70}$ mixture. Nanotube content is very low if any in the soot and in cathodic deposit core.
Typical set of experimental parameters are as follows

Table 2.3.: Range of important parameters for fullerene conditions in this work

V: 25-28 v
A: 65-69 A
P: 100 torr
In: Flow He atmosphere

Main products:

Soot 1: Although soot composition varies drastically with production parameters such as current, temperature and pressure it is found that soot composes mainly of graphitic structures along with various half-formed fullerene structures, nanohorns, amorphous carbon and shapeless/deformed carbon cage structures along with nanotube formations on higher pressures. Soot consists of 15-20 % $C_{60}$ and $C_{70}$ fullerenes rest being amorphous carbon, higher fullerenes and very small amounts of nanotubes.

This product can be extracted by toluene to separate fullerenes and fullerene extracted soot (FES) can be obtained. FES has been one of the substances which was subject to this study.

2. Nanotube conditions:

A relatively higher vacuum pressure (around 500 Torr) and under flowing helium atmosphere. Products are again cathodic deposit along with soot but with differences, in the soot a small percentage of multi walled nanotubes along with cathodic deposit containing multi walled nanotubes in the center.

Table 2.4.: Range of important parameters for nanotube conditions in this work

V: 25-28 v
A: 65-69 A
P: 400 - 500 torr
In: Non-flow He atmosphere

Main Products:

Soot 2: consists of amorph and graphitic carbon and a few nanotubes.

Cathodic deposit: at first sight, it consists of an outer shell (amorph and graphitic carbon) and an inner core (consists mainly of multiwalled nanotubes)

In this study soot 1 and cathodic deposit core obtained in fullerene conditions and cathodic deposit core obtained in nanotube conditions are studied.

Some interesting properties of fullerenes

- The $C_{60}$ molecule is known to rotate very rapidly at room temperature while it is in the solid state. This presents a liquid like behavior that is very strange for a solid.

- The rehybridization that occurs during the formation of the molecule creates an enhanced electron affinity measured at 2.65eV and has higher electro negativity than most hydrocarbons. It also exhibits conductor properties at higher temps and superconductor properties at 19K.

- Fullerenes dissolved in non-polar solvents create unique colors like a red-wine color to deep purple for C60 and C70 molecules such as benzene and toluene.

Table 2.5.: Application area, possible products and researching companies [2]

| Application Area | Products | Status/Activity |
|---|---|---|
| **Biopharmaceuticals** | Neuroprotectants (i.e. Alzheimer`s, Parkinson`s diseases and strokes) | Amjor pharmaceutical indistries since 1994<br>Merck & C-Sixty inc. since 2003 |
| | AIDS protease inhibitors | Pre-clinical state |
| **Personal care** | Cosmetics including anti-aging creams and wrinkle creams | Mitsubishi corp. and ITO announced joint venture by 2005 |
| | After burn creams | C-Sixty inc. |
| **Polymers** | Photodedectors | Dupont displays, Siemens |
| | Solar cells | Siemens, Philips, Agfa, Konarka, Nanosolar |
| | EMI shielding | Carbon Nano-Electronics |
| | Transistors | Philips, Agfa |
| | Membranes for hydrogen fuel cells | Sony |
| | Quick-set fiberoptic cable | Alcatel |
| | Polimides for electronic packaging | Riken |
| | Low friction ultra high molecular weight polyethylene | IMS plastics |
| | Anticorrosion coatings | Nanofullerene corp. |
| | Fluoropolymers | Dupont |
| **Diamond like carbon coatings** | Hard-disk drives | Seagate |
| **Electronics** | Capacitor electrodes | Mitsubishi |

## 2.4. NANOTUBES

Nanotubes are actually nothing but longer forms of fullerenes. By rolling up a single layer 3D graphite crystal to a cylinder and adding both ends a half-fullerene molecule, a nanotube can be made. Electric conducting property of a single walled nanotube depends on how is folded. It can be conductor, semi-conductor or non-conductor.

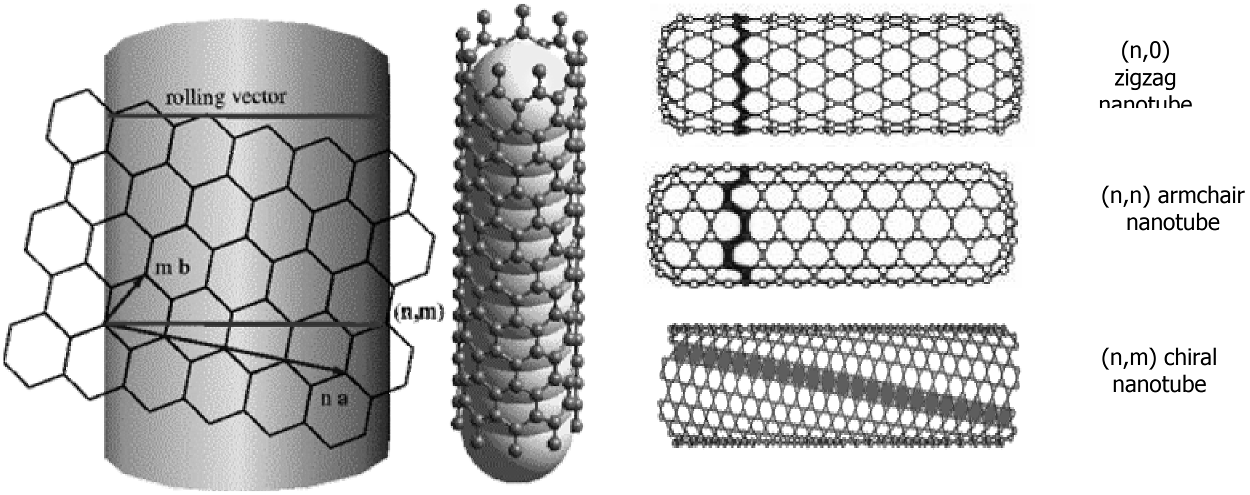


Figure 2.3.: Three main types of nanotubes that forms as a result of folding angle [23]

Two main types of nanotubes can be produced depending on the method; single walled nanotubes (SWNTs) and multi walled nanotubes (MWNTs).

### 2.4.1. MULTIWALLED NANOTUBES

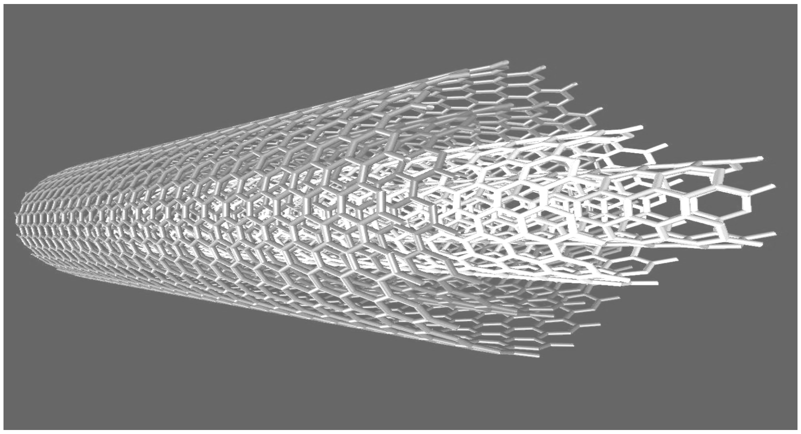


Figure 2.4.: A multi walled carbonnanotube with four walls [24]

Making MWNTs are fairly simple, they can be produced by Kratschmer Technique, which is arc vaporization of a graphite rod. Wall numbers may vary from 2 up to 90-100. There is no way to obtain a MWNT with desired number of layers or diameter yet. Produced sample is a mixture of MWNTs with different layers; therefore there are no characteristic properties. Researches on MWNT are mainly focused on their adsorption capacities.

### 2.4.2. SINGLE WALLED NANOTUBES

SWNTs can be produced also by graphite-arc method in the presence of metal catalysts such as Fe, Ni, Co. in this case, cathodic deposit contains MWNTs and the powder formed contains SWNTs. Drawback of this technique is the purification of SWNTs from metal.

A second common way to produce is the carbon vapor deposition method (CVD) where a hydrocarbon. In CVD technique, basically a carbon containing gas ($CH_4$, $C_2H_2$ etc...) is passed through hot doped catalyst metal (Pt or Fe in many cases) on a support surface, under $O_2$ free vacuum atmosphere. SWNTs can be produced under laboratory conditions with this method.

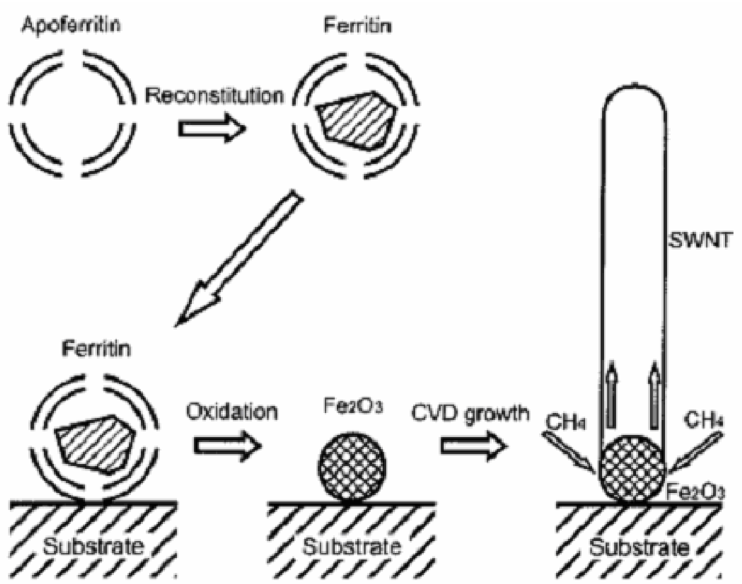


Figure 2.5.: CVD forming mechanism of a single walled nanotube over a metal catalyst [11]

Main disadvantages of this method are:

- Diameter of produced SWNTs depends on size of the attached metal particle on the surface. Therefore a standardized production is not possible unless particle sizes are strictly controlled.
- Amorphous carbon covers the metal surface after some time reducing its active area.

What makes SWNTs special is their extraordinary ability of conducting electricity. Depending on their shapes or molecules attached, they can become perfect conductors or perfect insulators. They are also elastic almost like carbon fibers. We can think them as carbon fibers in very small diameters. They are about 1000 times stronger and 6 times flexible than steel, very strong against strong acid and high temperature because of their perfect conjugated system. Acid and heat are often applied to purify carbon nanotubes.

Nanotubes can be seen in the soot depending on pressure and current of da arc reactor, but they are mainly found in cathodic deposit. And multi-walled nanotubes are produced mainly by this method.

# CHAPTER 3

# LITERATURE SURVEY

Purpose of this study aimed to find surface characterization of FES powder, and its comparison to a widely used acvite carbon. Unfortunately there was only one work that was directly related to this thesis [6]. First purpose of the literature survey was to find as much information as possible about FES. For the second part of the study, that is surface characterization, starting point had been the characterization techniques by adsorption and interpreting the data.

Descriptions of publications used in literature survey were presented below. Only summaries of these articles were given as they were explained in detail in relevant chapters.

## 3.1. PRODUCTION OF FULLERENES AND NANOPARTICLES

Kroto and Smalley reproduced the same results about a cage structured carbon molecule which they found in interstellar dust with Heath, O`Brien and Curl from Exxon laboratories produced under laser vaporisation of graphite. First publication in which the word "Buckminster Fullerene" or "buckyball" is used to describe the molecule. Almost all of the carbon nanoparticle and nanoparticle studies on non-carbon materials were started with this paper printed on Nature. [8]

First laboratory scale production of carbon nanoparticles using carbon arc technique. In which the parameters for production of these particles were first discused. [7]

A review of fullerene production and most popular methods for production. Also techniques for producing fullerenes larger than $C_{60}$, endohedral fullerenes and safety issues during production were first discussed. [17]

A brief study on fullerene soot powder characterization with TEM images. Particle distribution of single particles and macroparticles were discussed. Macroparticle range is found to be between 0.5 and 5 µm. [18]

A brief description of carbon nanoparticle history along with some information about these particles` chemical properties and possible application areas for the future. [19]

First article that has focused on fullerene contanining soot along with fullerenes excracted soot. Surface characteristics for chemical properties, electrochemical properties of these fractions were studied and compared with an active carbon sample (Vulcan XC-72) [6]

## 3.2. SEPERATON OF CARBON NANOPARTICLES

Seperation of higher fullerenes ($C_{\#}$>90) from fullerene is acchieved by extracting soot (FES) using Quinoline. Soot can be seperated into four fractions: toluene soluble, toluene insoluble, toluene insoluble-quinoline soluble and touene insoluble-quinoline insoluble. [20]

Extraction of higher molecules with low boiling point solvents such as xylenes, 1,3,5-trimethylbenzene, 1.2.4-trichlorobenzene have been discussed. This work is pretty much same as the above one. It has been taken into consideration in order to have information on $C_{60}$ and higher fullerene solvents. [5]

### 3.3. SURFACE CHARACTERIZATION

Theory and experimental methodsrelated to surface characterization by physical adsorption and chemical adsorption are given in Appendix G.

# CHAPTER 4

# EXPERIMENTAL

## 4.1. PRODUCTION

### 4.1.1. CARBON ARC TECHNIQUE

The carbon arc is a convenient way to generate a variety of carbon materials because of the high temperature of the plasma, which approaches 3700 $^0$C. It has been used to produce carbon whiskers (multi walled, onion-like structures), soot and fullerenes. One of the critical parameters that determines the products that can form is the type and pressure of the gas surrounding the arc. When it is used to produce multishell carbon nanotubes at 400 – 500 Torr, the main by-product is nanoparticles. They are mainly composed of folded sheets of layers formed from 5 and 6 membered rings of carbon (that can form either fullerenes or nanotubes), amorphous carbon, graphite layers and folded/unfolded bits of these structures with diameters not exceeding 100 nm. The size are roughly the same as the diameter of multiwall nanotubes.

The closed morphology of graphitic particles is brought about by developed graphitic layers which are flat except at the corners and edges. When a pentagon is introduced into a graphite layer (composed of hexagons), the sheet curves and the strain is localized around the pentagon. Therefore forcing to structure to form a cage structured network. As a result, the carbon cages produced look like giant fullerenes.

The structure and morphology of nanoparticles grown on an electrode are quite similar to the heat treated (above 2500 K) carbon blacks. On formation; first, natural C and ions ($C^+$) deposit and condense to form small clusters on the surface of the cathode. The structure of the particles at this stage is probably amorphous and have a low viscosity as a result of the high temperature. As if carbon atoms act as agglomerating particles in a solvent. As the cooling starts to occur from surface to the center of the particle, graphitization starts to occur from surface to center. Since the density of the graphitized carbon (≈2.2 g/cm$^3$) is higher than amorphous carbon (≈1.4 g/cm$^3$) solidification (therefore cooling) speeds and eventually stop.

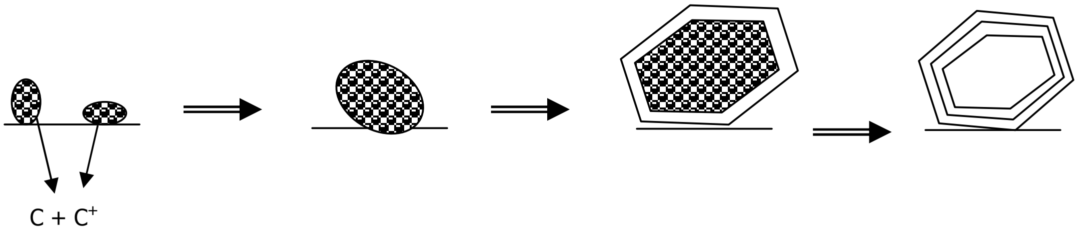


Figure 4.1..: Mechanism of multiwalled nanotube and fullerene formation

## 4.2. EQUIPMENT

### 4.2.1. NANOPARTICLE PRODUCTION EQUIPMENT

System used for fullerene production is similar to Kratschmer Chamber, with main two differences that it is cylindrical, not spherical but most important difference is the arc maintained is controlled by an electric motor. The carbon arc apparatus has a water cooling coat surrounding the chamber (drawn in pink). The electrodes are placed on both hands of the apparatus, which can be detached in order to clean chamber and replace electrodes. An ampere stabilised  AC/DC power supply was used. The whole apparatus is attached to a vacuum pump and an inert gas line. A pressure gauge allows constant monitoring of the pressure in the chamber. Graphite anode is fed to the system by an application-controlled electric motor in order to maintain arc gap between the electrodes. (i.e if the electrodes are too close motor drives back is too far motor driver forth). Graphite is used for both electrodes.

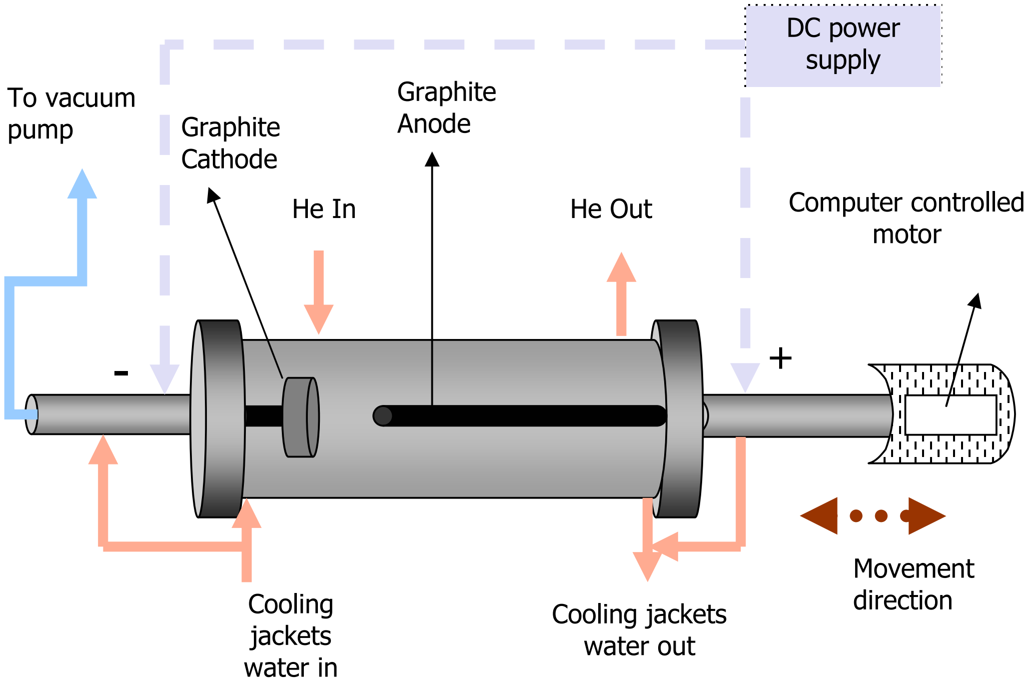


Figure 4.2.: Modified Kratschmer Chamber used in the study

**Operation of the Modified Kratschmer Chamber**

Before generating the plasma a mask must be worn in order to avoid breathing of the soot while and after operating the machine. Any deposits on cathode part and any soot powder in the chamber must be cleaned before operating the system. After that a new positive electrode can be attached. It is important that the two electrodes must not touch each other during or before the process in order to avoid short circuiting. After closing the system and opening the cooling system the apparatus is checked with a resistance meter. If conductivity appears between parts that should not be electrically connected, then the machine must be re opened and checked. If there's no short circuit, next step is to open vacuum pump in order to empty the chamber from air. The chamber is then filled with the inert gas, helium, in our system. System can be operated in two conditions, non-flow or under flow. The inert gas line valve and the vacuum line valve are left slightly open to obtain a continuous flow at given pressure. Once the pressure is stabilized, the power supply is turned on and the program on the computer is started. The moving positive electrode is brought closer to the negative one until arc begins. After the arc stabilizes, process lasts around 20 mins. During process, a deposit on cathode and roughly a handful of soot powder is formed. Once the electrode is consumed, power supply is turned off and chamber is left to cool. It is then opened and products taken. After clean up, whole process is repeated.

For optimum fullerene yield, chamber is operated under flow conditions at around 100 Torr pressure and 0.5 - 1 $cm^3$/min flow rate. For optimum nanotube conditions, chamber is operated under non-flow conditions at around 400-500 Torr pressure. Cathodic deposits up to 8-10 cm has been produced under fullerene conditions and deposits up to 25 cm has been produced under nanotube conditions. For the longest deposits that were formed is found to be at a consumption rate of 25 minutes for a run (around a cantimeter in a minute)

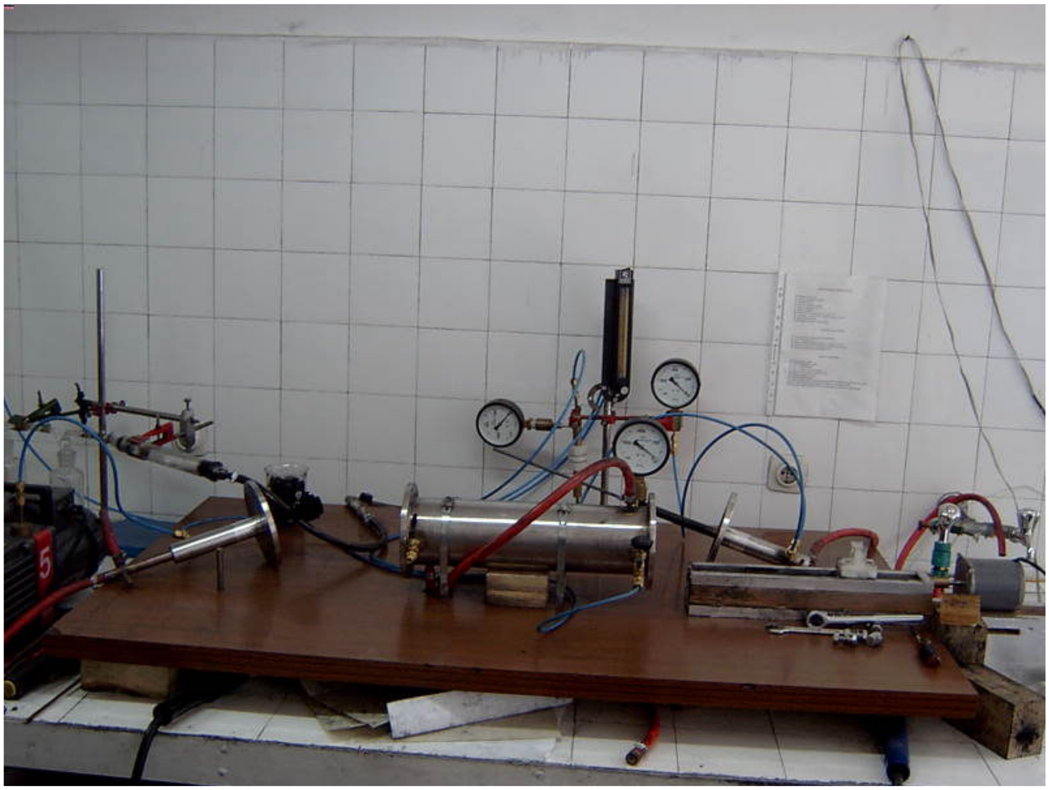
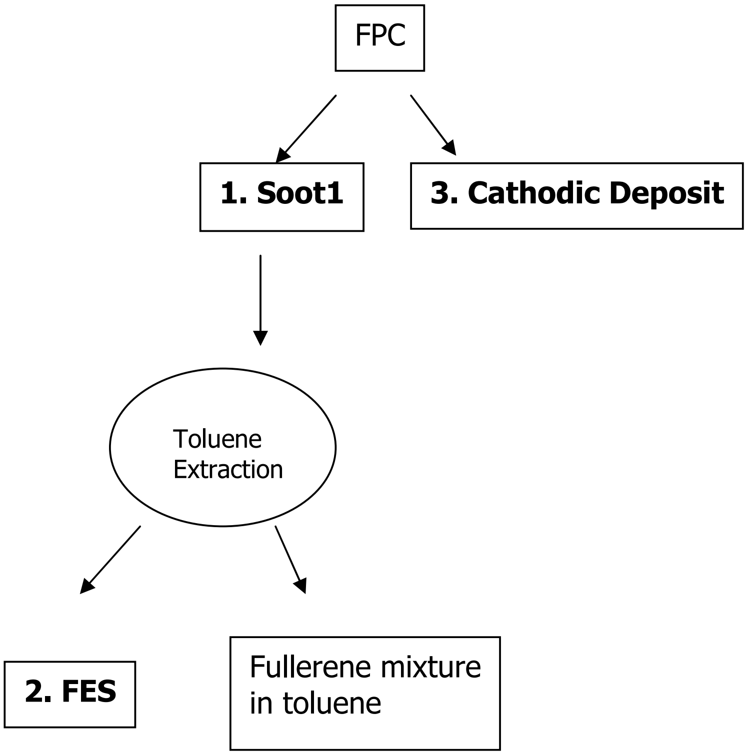


Figure 4.3.: A picture of modified Kratschmer Chamber used in study, detached

## Materials Studied in This Work

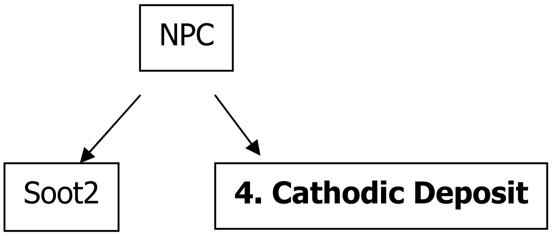
Material from fullerene producing conditions (FPC):

1. Soot 1
2. FES
3. Cathodic Deposit



Materials from nanotube production conditions

4. Cathodic deposit



The products that are not shown in bold fonts were not studied in this work.

### 4.2.2. SURFACE CHARACTERIZATION EQUIPMENT

Surface characterization have been done by Quantichrome Autosorb 1-C equipment which is capable of both low-normal pressure physisorption and chemisorption analysis.

1. Elemental analysis

   Elemental composition of the rods used to produce samples along with FES and soot samples were analyzed with an elemental analyzer (see Appendix G).

2. He pycnometer

Void volume data were taken by a He pycnometer. Pycnometer works on a pressure/volume change principle. First, calculations without sample has been done in order to get exact empty volume of the chamber and then volume of the sample – filled chamber have been taken. From the $P_1V_1 = P_2 V_2$ equation, void volume of the sample could be found. From there by dividing this value to its mass, density of the sample can be found.

3. Sorption experiments

Physisorption and chemisorption data obtained from Quantichrome Autosorb 1-C analyzer. Equipment is capable for low pressure measurement up to 1.3 atm. Device has also a mass spectrometer and a liquid sorption equipment attached.

Figure 4.4.: Quantichrome Autosorb 1-C surface analyzer

4. Titration

Titrations have been done in order to have a rough idea about surface active sites of the produced samples. Certain grams of FES and soot were put into 0.1 N NaOH mixture (40 ml each time), thoroughly mixed and titrated with 0.1 N $H_2SO_4$ solution. Miliequivalent gram amounts of each solution (NaOH and $H_2SO_4$ + sample) were found and by taking the difference, miliequivalent gram per sample is calculated. Then that value was converted for 100 gram of sample.

# CHAPTER 5

# RESULTS AND DISCUSSION

## 5.1. PRODUCTION OF NANOPARTICLES

Nanoparticles were produced in the modified chamber. The optimum values of the parameters given in table 4.2.1.1. were found experimentally to produce the highest possible amount of product during each run. After each run, cathodic deposit and soot formed on the walls of the arc reactor are collected. For the experiments under fullerene conditions soot is treated with toluene and the darkness of the solution indicated the higher amounts of fullerene production. Toluene mixtures were prepared with the soots produced under different conditions. When $C_{60}$ dissolves in toluene, the color of the mixture turns into dark-red/brown much like red wine. The darker the color, larger the fullerene amount in the mixture for a rough estimation. Therefore the most fullerene producing parameters were selected and given in Table 4.2.1.1

In order to specify optimum parameters such as current, pressure, flow rate and motor movement parameters in DOS control program, a set of experiments have been conducted.

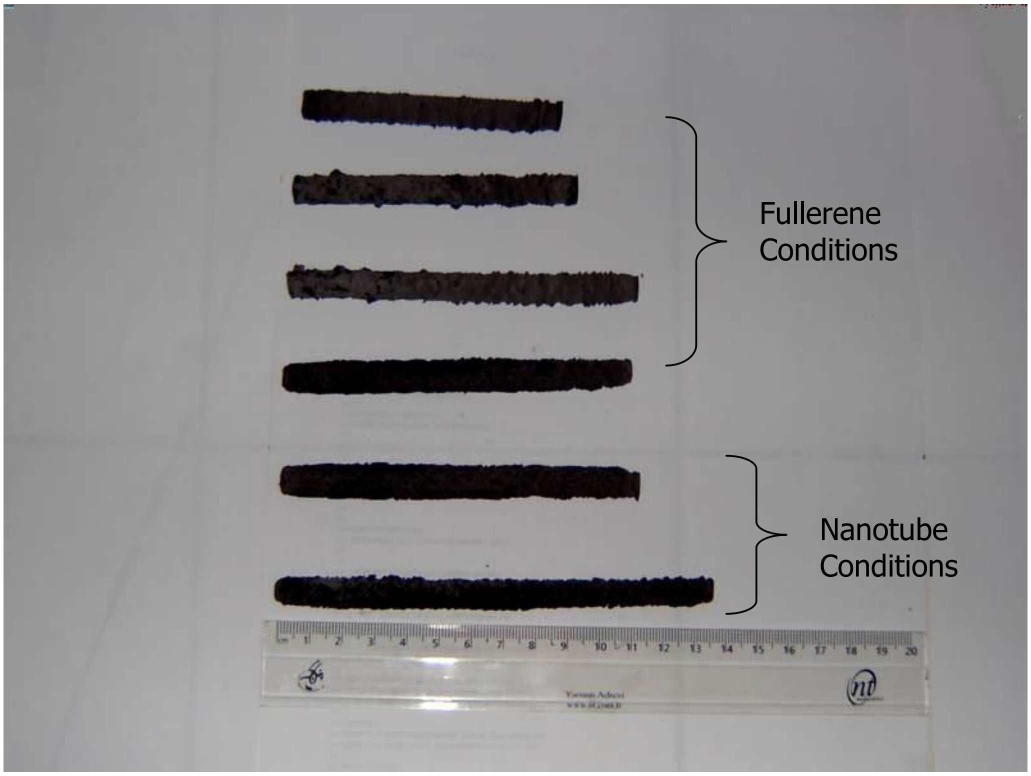


Figure 5.1.: Cathodic deposits produced under nanotube and fullerene conditions

Although these six cathodic deposits look the same on the first sight, their interior composition is quite different. They all have a hard graphitic shell outside and a softer core in the middle. The difference between them is the composition of this inner layer. They contain multiwalled nanotubes if produced under nanotube conditions and contain particles similar to soot but none or very small amounts of nanotubes if produced under fullerene conditions.

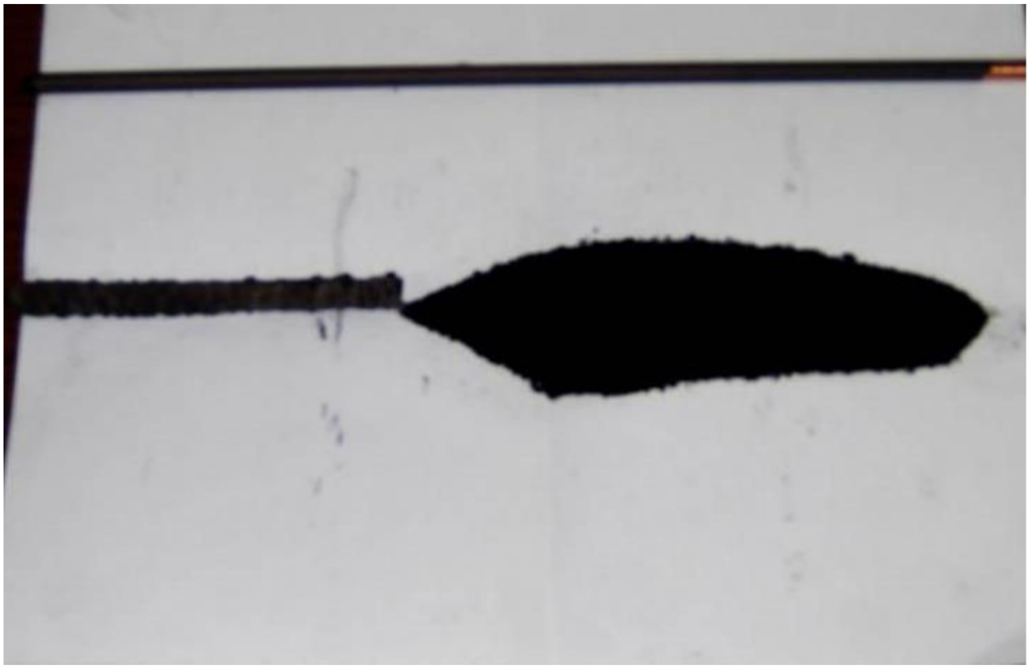


Figure 5.2.: Cathodic deposit, soot powder and graphite rod used

The graphite rod (above) which is 30 centimeter long and 6 mm in diameter, vaporizes to form cathodic deposit (below left) and soot powder (below right). It can be seen that around half of it turns into cathodic deposit while other half forms the soot powder.

## 5.2. PHYSICAL ADSORPTION RESULTS

Given in Figure 5.3., the pore structure data obtained from FES, soot cathodic deposit produced under nanotube conditions and cathodic deposit produced under fullerene conditions isotherms are summerized in Table 5.3..

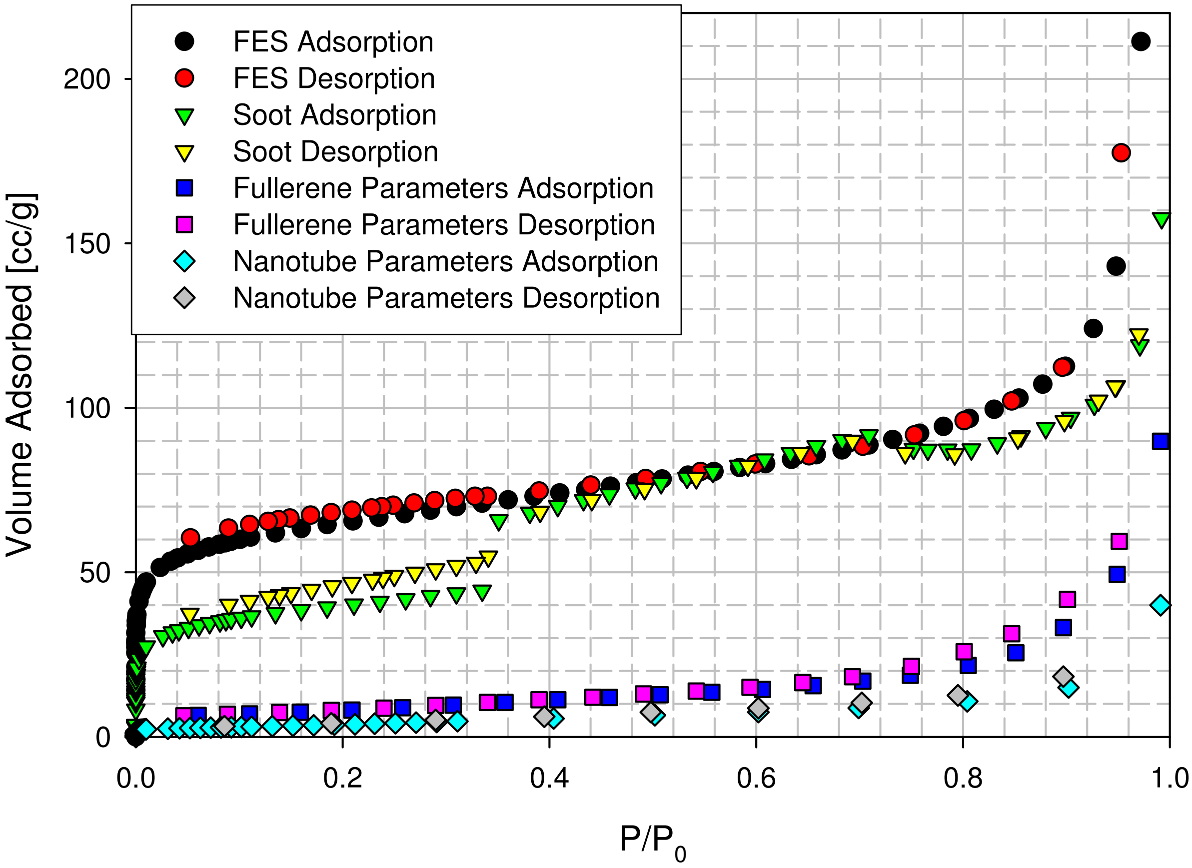


Figure 5.3.: Nitrogen adsorption/desorption isotherms at 77 K for FES, soot and
two cathodic deposits produced under fullerene and nanotube conditions

As seen in isotherm data, all four adsorption/desorption isotherms can be classified somewhere between type II and type IV isotherms due to BDDT classification. In all the isotherms the rounded knee indicates the approximate location of monolayer formation. Low slope region in the middle of the isotherm indicates the formation of few multilayers. These behaviours were also seen in our samples. Small hysteresises occurring on the isotherms of all samples. Generally for the isotherms, very fast filling of micropores is observed below $P/P_0 < 0.1$ region and mesopore filling up to $P/P_0 = 0.96$ after that a sharp increase is observed. Soot has the largest amount gas adsorbed in physisorption isotherms after FES. This indicates while fullerenes moving, large void places remained in the media that have slightly increased surface area. For cathodic deposits produced under nanotube and fullerene conditions, which is assumed to be having multilayer nanotubes, on the other hand shows very little adsorption in comparison to FES and soot. This may be a result of nanotubes with too many layers, e.g. 50 layers therefore leaving very small gaps for $N_2$ to adsorb, or having no pores at all [29]. Surface areas show a descending order from FES to deposit produced under nanotube conditions. Cathode with FES having the largest surface area of 240 $m^2/g$ and deposit produced under nanotube conditions 14.6 $m^2/g$ (see table 5.3.). Due to the enlargement of pores by extraction, difference between the isotherms of FES and soot can be observed at $P/Po > 0.7$ region. The volume adsorbed by FES is about 40% higher than the gas volume adsorbed by soot. While the volume adsorbed by soot is 155 cc/g, this value increased to 210 cc/g for FES sample. Same kind of shift can be seen at the micropore region at $P/Po < 0.3$ and two isotherms are almost equal at mesopore region ($0.3 < P/Po < 0.7$).

It is also notable that deformed shape of the soot isotherm may tend condensation of some nitrogen between the particles. Micropore information can be interpreted by Horwath Kowazoe (assuming slit sahep pore geometry) and Saito Foley (assuming a cylinder pore geometry) plots. Result are 5 $A^0$ for FES, 5 $A^0$ for soot, 6 $A^0$ for cathodic deposit produced under nanotube conditions and 2.2 $A^0$ for cathodic deposit produced under fullerene conditions respectively for Horwath Kowazoe method and 10 $A^0$ for FES, 10 $A^0$ for soot, 12 $A^0$ for cathodic deposit produced under nanotube conditions and 5 $A^0$ for cathodic deposit produced under fullerene conditions respectively for Saito Foley method. It may be said that all the samples might have micropore sizes ranging from 5 to 12 $A^0$.

Figure 5.4. and figure 5.5. give the results of Horwath Kowazoe and Saito Foley methods used to find micropore distribution data. Although all samples have nearly same sized micropores, samples have different amounts of micropores in them. From these graphs it is seen that FES has the largest amount of micropores followed by soot as expected. It is notable here that cathodic deposit produced under nanotube conditions has a very small amount of micropores and cathodic deposit produced under fullerene conditions do not show occurance of micropores. Active carbons have mainly slit-like micropores within the structure, which is similar to FES and soot in active site structure. Defining these pores as having slit shape geometry would be inaccurate because the structure of these samples are not exactly known. Therefore we included both slit and cylindrical pore shape geometries with pore structure closer to slit. Therefore it can be concluded if FES, soot, two cathodic deposits produced under fullerene and nanotube conditions have slit shape pores, it would be in range of 5 $A^0$ and in case of cylindrical pore assumption the range would be 10 $A^0$ in diameter. Thus the samples have micropores having average pore diameter ranging 5 – 10 $A^0$ depending on the micropore geometry. For nanotube parameters obtained deposit, the range is between 6 – 10 $A^0$ which indicates that it has pores, and have

small pore volume. But in the plots that fullerene parameters obtained cathodic deposit have no distinct peaks for the methods which also indicate that either it has smaller pores outside HK and SF method calculation range or no pores at all due to multilayer nanotube formation with layers up to 50 [29].

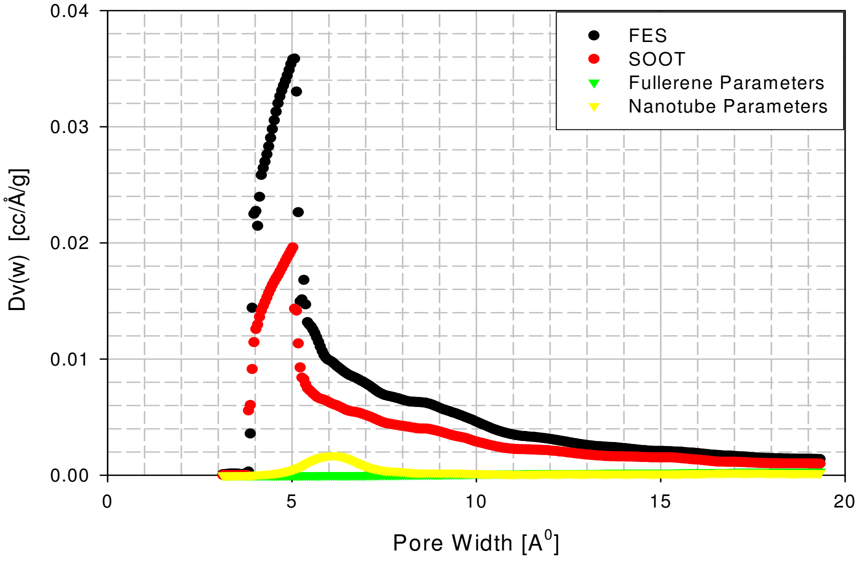


Figure 5.4.: Pore size distribution for FES, soot and two cathodic deposits produced under fullerene and nanotube conditions

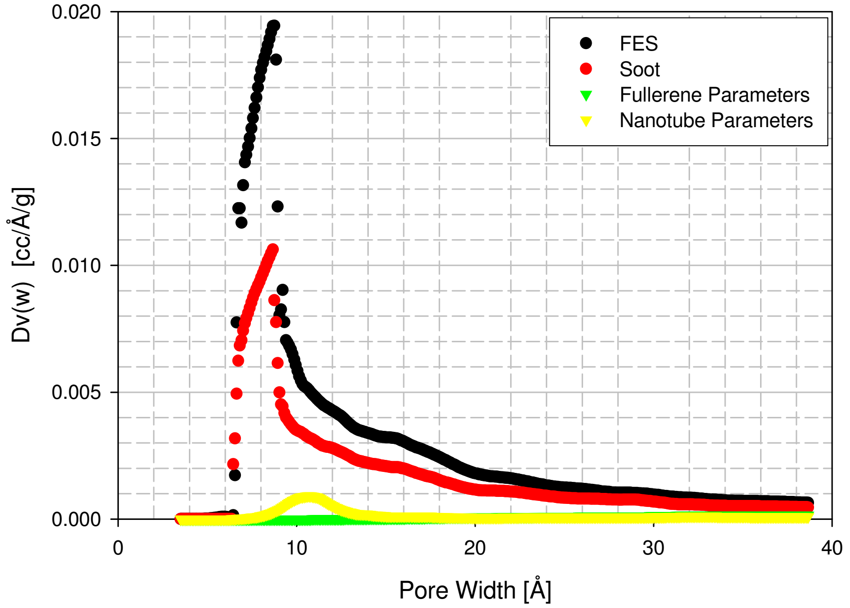


Figure 5.5.: Pore size distribution from Saito Foley method, cylindrical shaped pore assumption for FES, soot and two cathodic deposits produced under fullerene and nanotube conditions

In order to get more information about the pore size distribution, micropore volume and surface area calculations, V – t plot of samples is drawn (Figure 5.6.). V – t plots for FES and soot samples have two distinct similar segments indicating micropores on the other hand, these linear segments cannot be seen in other two samples. Extrapolation of these segments to ordinate gives the micropore volume of the sample.

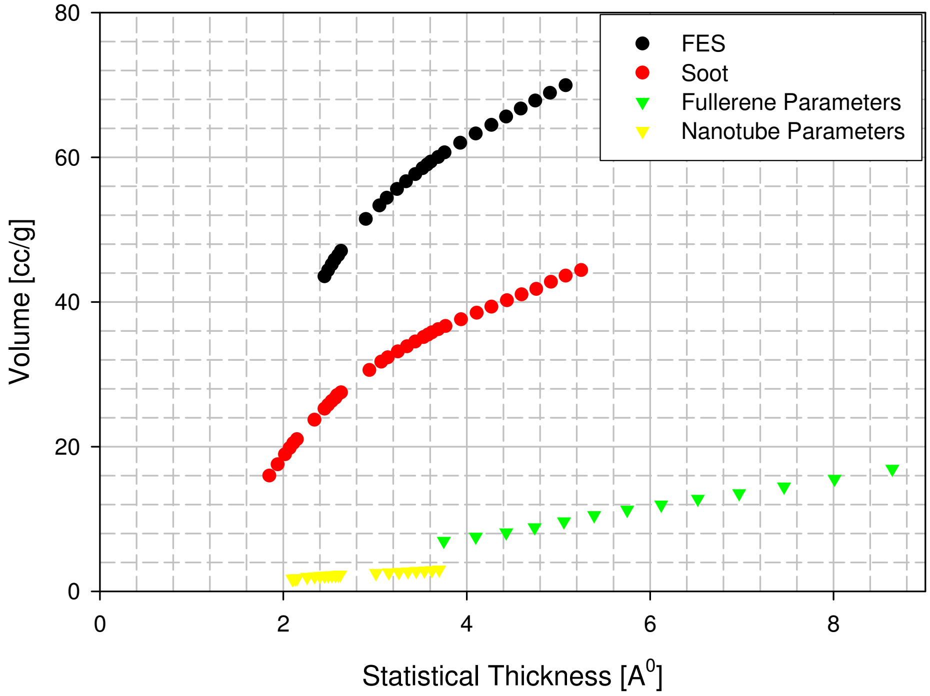


Figure 5.6.: the variation of gas volume adsorbed vs. the statistical thickness of adsorbate.

The V-t plots used to have a second idea about the surface areas of the samples and they are in agreement with the surface areas obtained from BET method (240 from BET and 239 from V-t plot for FES, 180 vs. 163 for soot, 29.7 vs. 30.94 for cathodic deposit produced under fullerene conditions and 14.6 vs. 16.9 for cathodic deposit produced under nanotube conditions). Micropore volumes are calculated also from these plots for samples (table 5.3.). Very small micropore volumes are obtained for cathodic deposits here this also indicates that these deposits have small amount of pores on the surface that $N_2$ can adsorbed.

## 5.3. CHEMICAL ADSORPTION RESULTS

### 5.3.1. HYDROGEN ADSORPTION

Hydrogen adsorption experiments were done for FES and Norit CN1 active carbon sample for comparison of the results.

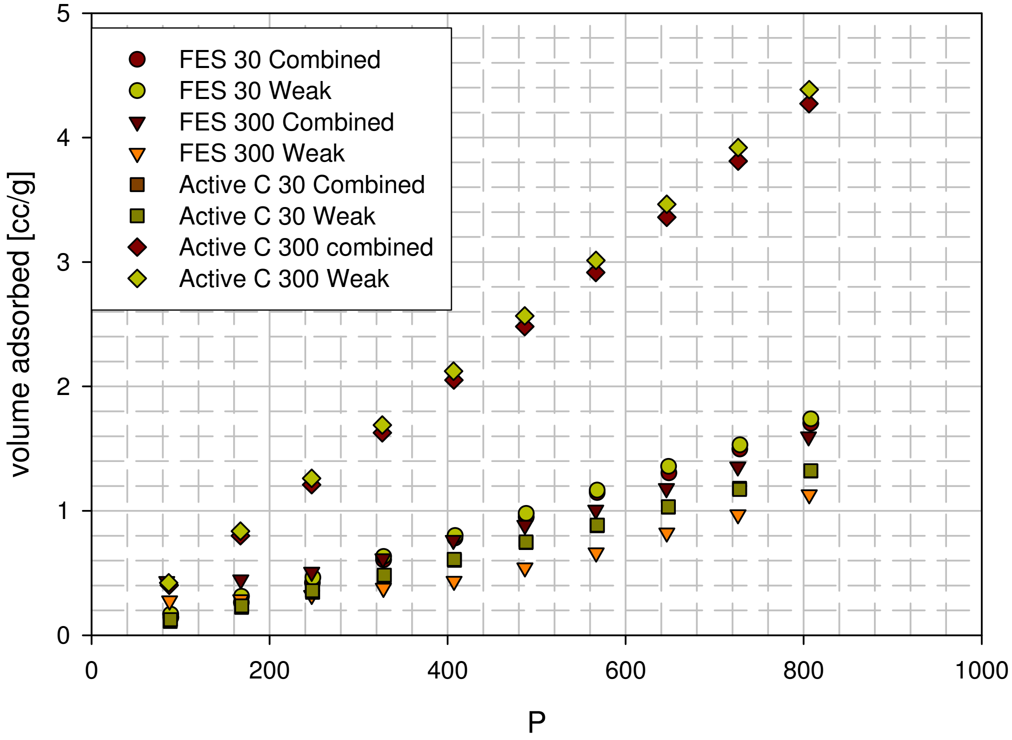


Figure 5.10.: $H_2$ chemisorption data comparing FES and a commercial active carbon at 303 and 573 K

As seen in figure 5.10. Hydrogen chemisorption on FES and active carbon sample at room temperature, chemically and physically adsorbed hydrogen amounts are a bit higher in FES sample but at $300^0$ C, adsorption on FES decreases while adsorption on the active carbon increases.

Linearity of the data points in figure 5.3.1.1. confirms the possibility of adsorption at high pressures without any indication of surface saturation. And at elevated temperatures, hydrogen adsorbs on the surface and may only be desorbed at elevated temperatures above $350^0$ C [27]. This may explain why the hydrogen adsorption at $300^0$ C is linear and adsorbed amount. But even in this case, active surface area for FES is higher than the active carbon sample's as the slope of the FES isotherm is higher.

Active metal areas have not been computed for $H_2$ chemisorption data because the reason these data taken were not to bind hydrogen on the surface irreversibly but to find how much of the gas can be adsorbed and desorbed on the surface for storage applications.

### 5.3.2. AMMONIA ADSORPTION

Ammonia adsorption on FES, soot, cathodic deposit produced under fullerene conditions, cathodic deposit produced under nanotube conditions were conducted and compared with Norit CN1 active carbon sample at 303 K and 503 K respectively.

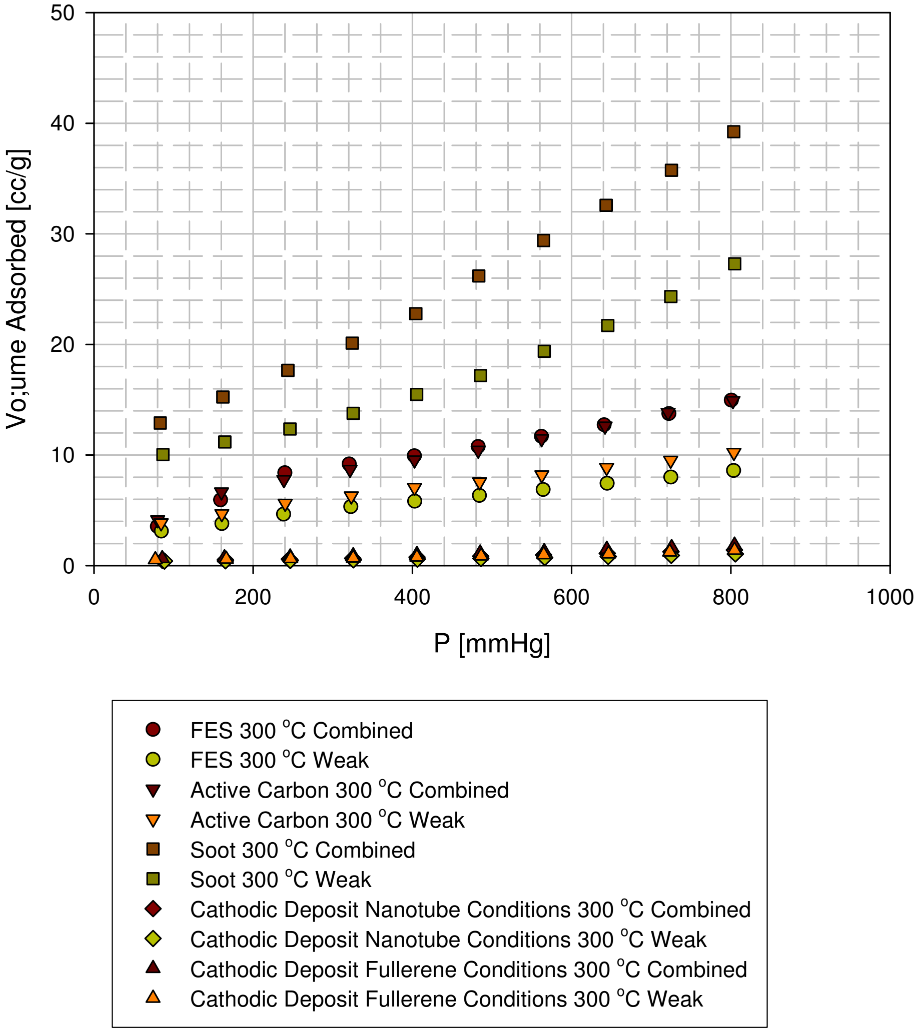


Figure 5.11.: $NH_3$ chemisorption data comparing FES, Soot and a commercial active carbon at 303 K

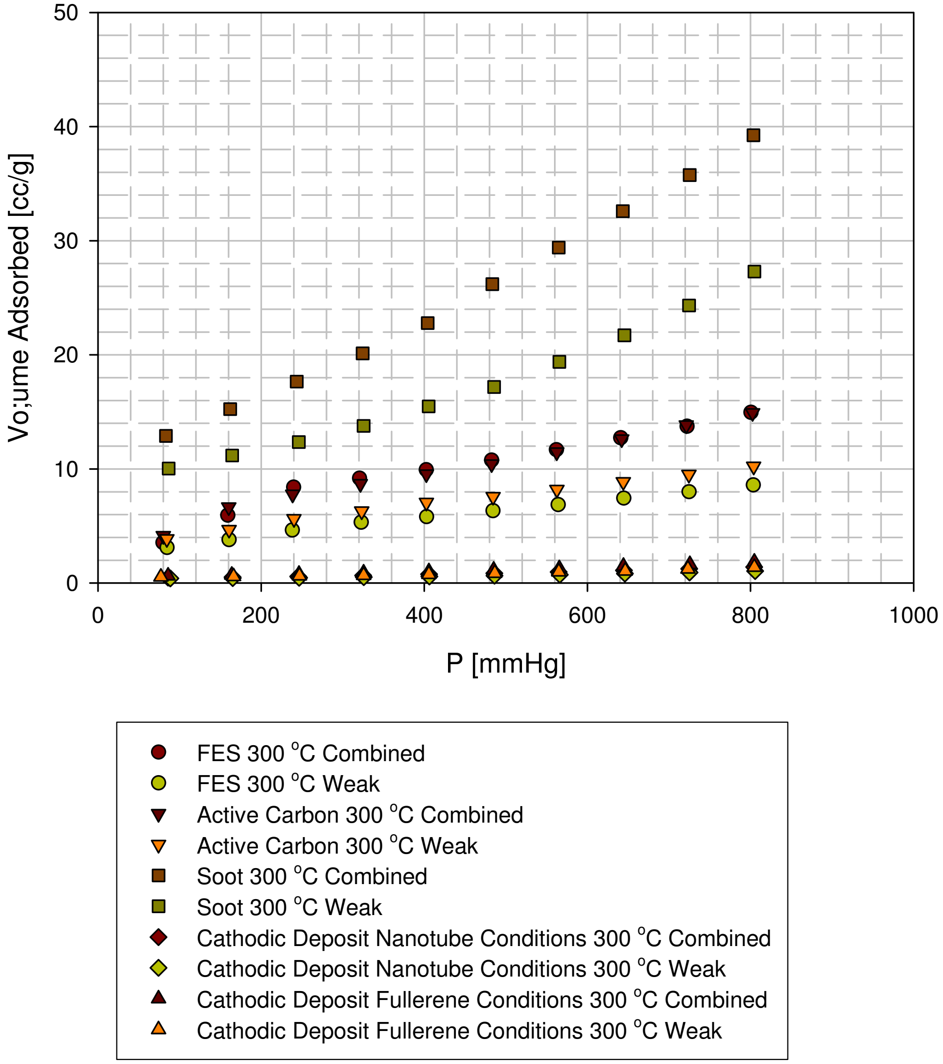


Figure 5.12.: $NH_3$ chemisorption data comparing FES, Soot and a commercial active carbon at 503 K

Figures 5.1.1. and 5.1.2. show ammonia adsorption data in comparison by means of adsorption order with the $H_2$ chemisorption data. Although adsorbed amount on active carbon is larger than the FES sample, active monolayer capacity for FES is higher. 32 $m^2/g$ on active carbon and 39 $m^2/g$ on FES due to higher slopes of monolayer uptake also active metal areas for cathodic deposit produced under fullerene conditions is 0.51 $m^2/g$ at 303 K and 0.194 $m^2/g$ at 503 K and cathodic deposit produced under nanotube conditions is 0.481 $m^2/g$ at 303 K and 0.468 $m^2/g$ at 503 K respectively. Soot sample has the highest active area with 49.6 $m^2/g$, even better than the active carbon. This is expected as fullerene particles in the soot fraction are highly active.

Also expected, there has been a sharp decrease in the adsorbed amount and active surface areas at $300^0$ C. Total amount adsorbed in this temperature has fallen even weak adsorption amount at $30^0$ C. While adsorption amounts are almost equal for active carbon and soot at $30^0$ C, adsorption amount for soot is distinctively higher than other samples at $300^0$ C

## 5.4. ELEMENTAL ANALYSIS AND He PYCNOMETER EXPERIMENTS

Table 5.1.: Elemental analysis of material subject to this study. (numbers are weight%)

| | **%C** | **%H** | **%N** | **%O** |
|---|---|---|---|---|
| **FES** | 88.24 | 0.58 | 0.18 | 11 |
| **Soot** | 85.48 | 1.05 | 0 | 13.47 |
| **Spectroscopic graphite** | 98.96 | 0.04 | 0 | 1 |
| **Commercial graphite** | 93.6 | 0.25 | 0.51 | 5.64 |

Data were taken from C, H, N analyzer. Oxygen amount is calculated from the difference. It is notable that oxygen amount are quite high for the FES and soot samples and carbon amount decreases up to 8%. And increase in oxygen cannot be explained with excess air or water because stoichiometries do not match. There is either a miscalculation or samples had impurities upon analysis.

Table 5.2.: He pycnometer data for void volume for FES and soot fractions

| | **Volume** | **Mass** | **density** |
|---|---|---|---|
| **Soot** | 0,0709 $cm^3$ | 0,0885 g | 1,248 $g/cm^3$ |
| **FES** | 0,2983 $cm^3$ | 0,5077 g | 1,7 $g/cm^3$ |

These data give information about the solid density of the samples. As soot density is around active carbon densities (which is amorphous carbon like the contents of the large proportion of soot), an increase in the FES density can be observed. This may be a result of the agglomeration of particles during extraction.

## 5.5. ACID SITE ANALYSIS

In order to have a rough idea about the active sites on FES and soot samples, acid-base titration have been made using $H_2SO_4$ and NaOH (see appendix F). 780 meg/100 g FES and 1800 meg/100 g soot have been found. It is a promising result in comparison to Al-layered clay samples that have only 47 meg/100 g of sample.

Table 5.3.: Results Table for Physisorption and Chemisorption Experiments

| | **FES** | **Soot** | **$C_{60}$ Cathode** | **Nanotube Cathode** | **Active Carbon** |
|---|---|---|---|---|---|
| **Surface Area (BET) [m2/g]** | 240 | 180 | 29.7 | 14.6 | - |
| **V-t method surface area [m2/g]** | 239 | 163 | 30.94 | 16.9 | - |
| **Micropore Volume [cc/g]** | 0.045 | 0.034 | $2.38*10^{-3}$ | $1.19*10^{-3}$ | - |
| **Micropore +Mesopore volume [cc/g]** | 0.279 | 0.256 | 0.093 | 0.048 | - |
| **Void Volume [cc/g]** | 0.58 | 0.801 | - | - | - |
| **Pore dimension [nm]** | 5 -10 | 5 - 10 | - | 6 - 11 | - |
| **Active Metal Area from $NH_3$ at $30^0$ C Adsorption [$m^2$/g]** | 39.2 | 54.6 | 0.51 | 0.481 | 32.5 |
| **Active Metal Area from $NH_3$ at $300^0$ C Adsorption [$m^2$/g]** | 6.35 | 14.65 | 0.194 | 0.468 | 6.59 |

# CHAPTER 6

# CONCLUSIONS

1. Physisorption data of the given samples indicate that they are somewhere between type II and type IV which is expected because these materials are not pure but mixtures of carbon structures which may vary from amorphous carbon to graphite. Horwath - Kowazoe and Saito - Foley method findings, show that materials studied have both slit and cylindrical pores.

2. Both hydrogen and ammonia chemisorption data give promising results in comparison with the active carbon, meaning these material or just FES can be used instead of active carbon in some applications. Acid site analysis results are also in the same range with active carbon properties.

# CHAPTER 7

# RECOMMENDATIONS

A $CO_2$ adsorption data can give more detailed information for these structures as $CO_2$ can adsorb on smaller pores and one advantage is these isotherms are obtained in much higher temperatures like 273 K instead of 77 K.

Pyridine adsorption data can be used in order to have a more detailed idea of active acid sites on the surface of samples.

Hydrogen uptake of FES can be enhanced by activating additional sites on the surface by pretreatment with suitable gases.

Gases such as oxygen, carbon dioxide, nitrogen and methane can be used for chemisorption to understand more adsorption characteristics for the samples. But again, the surface may be pretreated to increase the adsorption capacity.

$NO_x$ adsorption analysis can be made as this kind of material is known to be able to adsorb high amounts of gases with similar structures.

# REFERENCES

[1] Koichi Nagata, Eiji Dejima, Yasuharu Kikuchi, Masahiko Hashiguchi Kilogram-scale [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) Chemistry Letters Vol. 34 (2005) , No. 2 p.178.

[2] Lisa Wray and Versacor, Process Comparison Table, (www.nano-c.com), http://www.nano-c.com/process_comparison_table.asp, August 2005

[3] R. Malhotra, A.S. Hirschon, D.F. McMillen, W.L. Bell, Catalytic Properties of Fullerene Materials, Energy Fuels 7, 685 (1993)

[5] C. Smart, B. Elbridge, W. Reuter, W.R. Creasy, Extraction of Giant Fullerene Molecules and Their Subsequent Solution in Low Boiling Point Solvents, Chemical Physics Letters v188 n3,4 p171 (1992)

[6] S.A.M. Silva, J. Perez, R. M. Toressi, E. A. Ticianelli, Surface and Electrochemical Investigations of a Fullerene Soot, Electrochemica Acta v44 p3565 (1999 )

[7] W. Kratschmer et al, Solid C(60) : A New Form of Carbon, Nature, 347, p354, (1990)

[8] H. Kroto et al, C60 : Buckminsterfullerene, Nature, V318, p162, (1985)

[9] S, Iijima, Helical Microtubules of Graphitic Carbon, Nature V354, p56, (1991)

[10] T. W. Ebessen et al, Science of Fullerenes and Carbon Nanotubes, Science, Nature 358, 220 (1992)

[11] Yiming Li, Woong Kim, Yuegang Zhang, Marco Rolandi, Dunwei Wang and Hongjie Dai, Growth of Single Walled Carbon Nanotubes From Discrete Catalytic Nanoparticles of Various Sized, J. Phys. Chem., 105(#46), 11424-11431, (2001).

[12] Quantichrome instruments Autosorb 1-C surface analyzer user`s manual

[13] Howard Fairbrother, derivation of the BET isotherm, Johns Hopkins University Department of Chemistry (chemistry.jhu.edu), http://www.jhu.-edu/~chem/fairbr/derive.html (2005)

[14] S. J. Gregg, K. S. W. Sing, Adsorption, Surface Area and Porosity, Academic Press London (1982)

[15] Duong D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, (1998)

[16] Thomas W. Ebessen, Carbon Nanotubes, CRC Press Inc., New Jersey (1997)

[17] Lowell D. Lamb and Donald R. Hufmann, Fullerene Production, J. Phys. Chem solids vol 54 no 12 1635-1643 (1993)

[18] N.N. Below, K.D. Nadezhdin, N.G. Shirina, G.A. Charneava, N.S. Kamusheva, The Structure of Fullerene Soot Particles, J. Aerosol Sci. vol 26 suppl 1 5665-5666 (1995)

[19] P.Scharff, New Carbon Materials for Research and Technology, Carbon, vol 36 no 5-6 481-486 (1998)

[20] Minato Egashira , Hisao Koura , Yozo Korai , Isao Mochida , John C. Crelling, Carbon Framework Structures Produced in the Fullerene Related Materials, Carbon 38 615–621(2000)

[21] Dendritics inc., mysterious allotropes of carbon, (Dendritics.com), http://dendritics.com/scales/c-allotropes.asp, August 2005

[22] R. Mäder, consulting and training for Mathematica, (www.mathconsult.ch), August 2005

[23] M. Taner, types of nanotubes, NIST center for neotron research (ncnr.nist.gov), www.ncnr.nist.gov/staff/taner/nanotube/types.html, August 2005.

[24] 7th wave inc., nanotubes and buckyballs, Nanotechnology Now (http://www.nanotech-now.com/), www.nanotech-now.com/nanotube-buckyball-sites.htm, August 2005

[25] M. Khalfaoui, S. Knani, M.A. Hachica and A. Ben Lamine, New Theoretical Expressions for the Five Adsorption Type Isotherms Classified by BET Based on Statistical Physics Treatment, J. of Coll. Interf. Sci., 263 350-356 (2003)

[26] Grigoriy Aranovich and Marc Donohue, Analysis of Adsorption Isotherms: Lattice Theory Predictions, Classification of Isotherms for Gas–Solid Equilibria, and Similarities in Gas and Liquid Adsorption Behavior, J. of Coll. and Interface Sci. 200, 273–290 (1998)

[27] A. Züttel, Ch. Nützenadel, P. Sudan, Ph. Mauron, Ch. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaffa, T. Kiyobayashib, Hydrogen Sorption by Carbon Nanotubes and Other Carbon Nanostructures, J. of alloys and Compounds, accepted copy 1-7 (2001)

[28] S. Lowell and Joan E. Shields, Powder Surface Area and Porosity, Chapman and Hall, London (1991)

[29] A. Peigney , Ch. Laurent, E. Flahaut, R.R. Bacsa, A. Rousset, Specific surface area of carbon nanotubes and bundles of carbon nanotubes, Carbon 39 507–514 (2001)

[30] R. Shimshi, a. Khong, R.J. Cross and M. Saunders, Tetrahedron, 52 5143 (1996)

[31] E. G. Gillan, C. Yeretzian, K. S. Min, M. M. Alvarez, J. Phys. Chem, 96. 6869 (1992)

[32] Roger Taylor, Lecture Notes on Fullerene Chemistry, Imperial College Press, London (1999)

# APPENDIX A

## SEPERATION EQUIPMENT

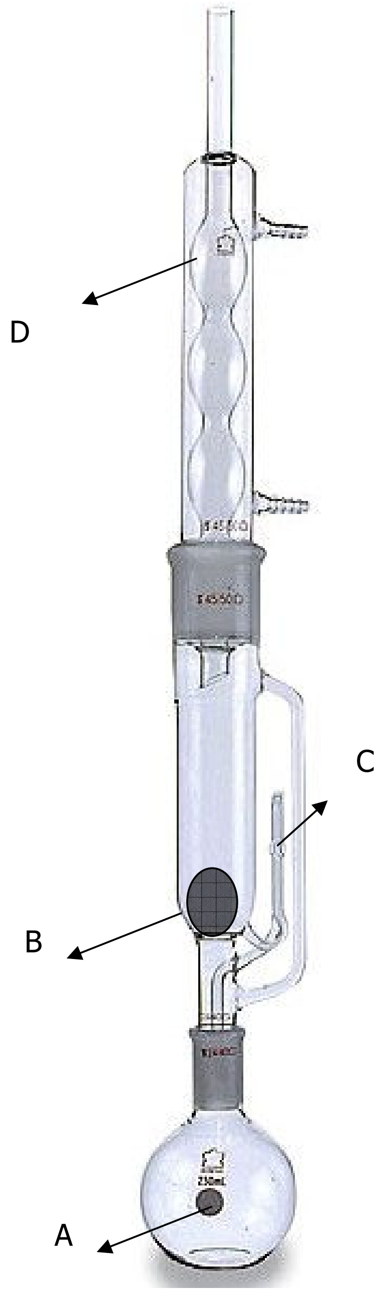


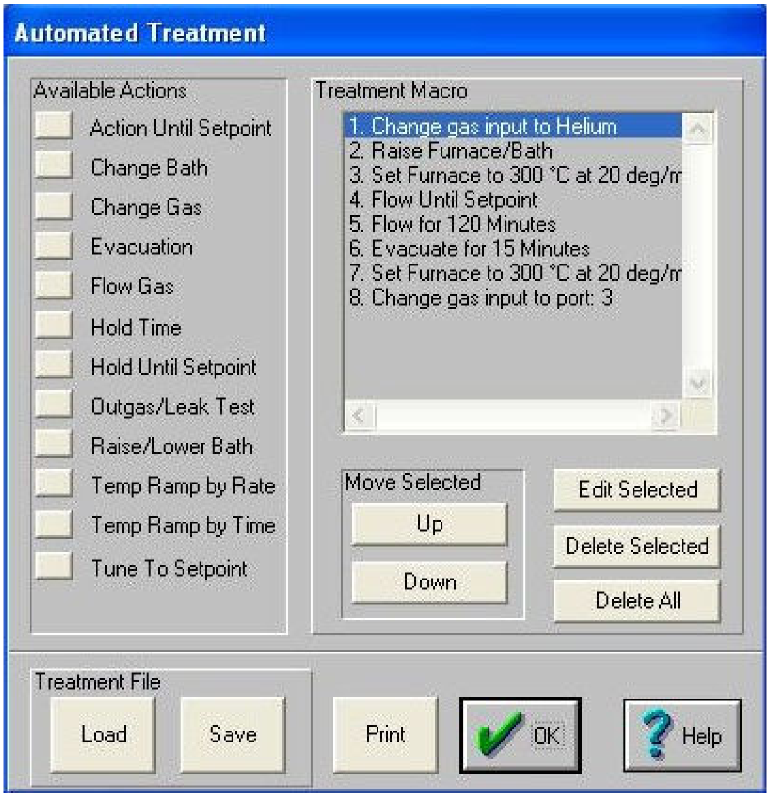
Figure A1: Soxhlet extraction equipment

In order to separate the contents of the soot, fullerene formations have to be extracted as much as possible, this is mainly done by chemical extraction methods with various organic solvents. Toluene is used mainly for the extraction of $C_{60}$ and $C_{70}$ from soot but this solvent is unsufficient for dissolving higher fullerenes. Some more complex structured organic solvents and processes like hydrothermal treatment were found to be efficient for extraction of higher fullerenes. But these higher fullerenes forms only 1% wt of the formed soot product, therefore are neglected in this study.

Soot is extracted using soxhlet equipment that allows fresh solvent to extract over and over again until no soluble component remains. Setup can be seen on the left. Solvent (toluene) is placed in A and then heated, bolining solvent fills in compartment B washing the sample. Comtaminated solvent fills back in A after some time by the syphon C. solvent loss is prevented by water cooler D.

# APPENDIX B

## TREATMENT MACRO FOR CHEMISORPTION EXPERIMENTS



1. Change gas input to Helium
2. Raise Furnace/Bath
3. Set Furnace to 300 °C at 20 deg/m
4. Flow Until Setpoint
5. Flow for 120 Minutes
6. Evacuate for 15 Minutes
7. Set Furnace to 300 °C at 20 deg/m
8. Change gas input to port: 3

Note: Port 3 is the port where the chemisorbed gas was attached.

# APPENDIX C

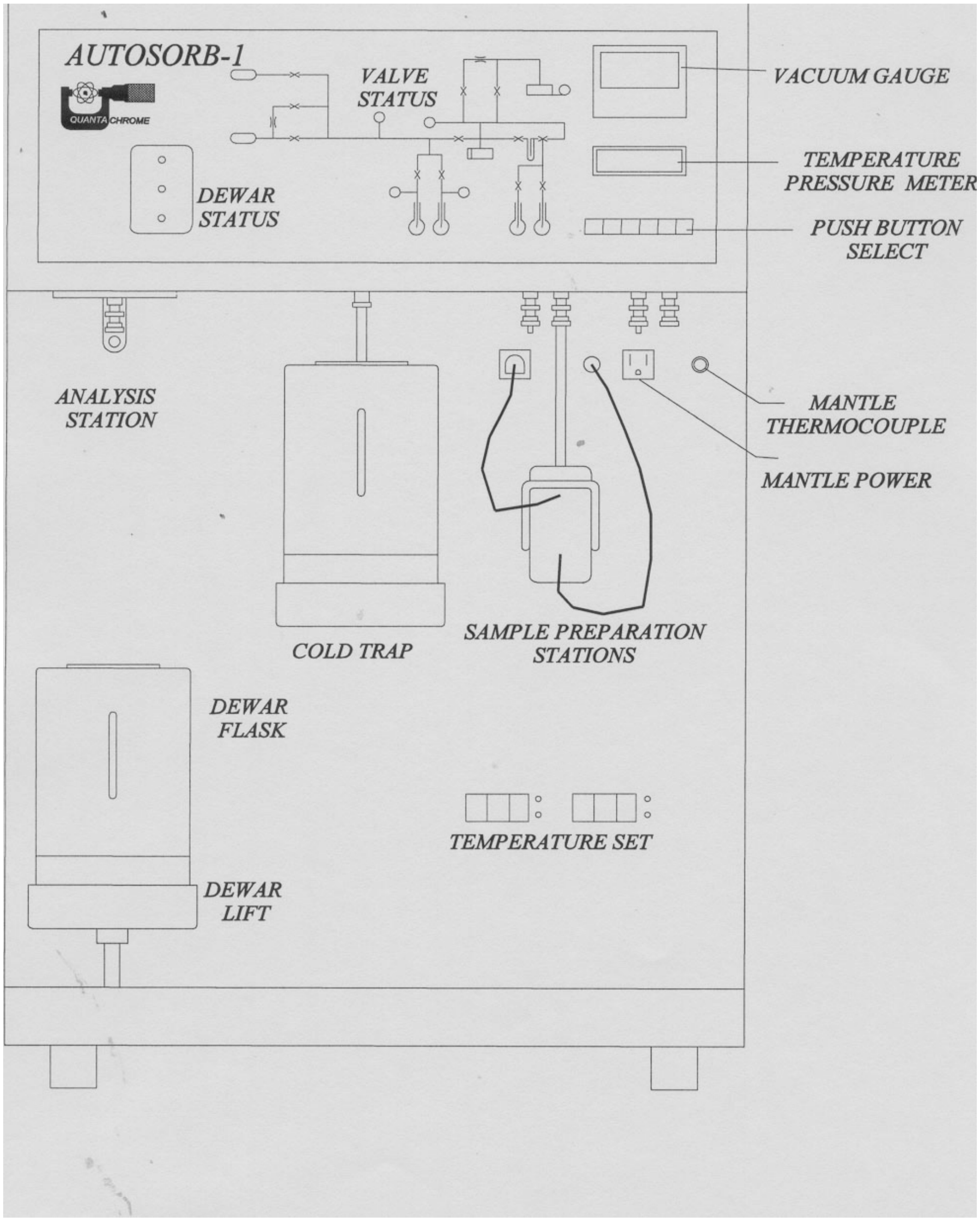
## CONTROL PROGRAM

```
DIM yon(4)
OPEN "o", #1, "data.dat"
CLS
dort = 0
hata = 0
n = 0
yon(1) = 9: yon(2) = 12: yon(3) = 6: yon(4) = 3

INPUT "set degeri:", set
REM PRINT #1, "okunan ortalama degerler"
420 last = dort
GOSUB 550
hata = set - dort
IF dort > 330 GOTO 800
REM bekle = .135
REM IF hata <= set THEN bekle = 40 / (ABS(hata) + 1) + .015
bekle = 40 / (ABS(hata) + 1) + .015
IF hata < 0 THEN GOTO 700
IF hata > 50 THEN GOTO 600
GOTO 420

REM ileri
600 IF (n = 4) THEN n = 0
n = n + 1
OUT &H378, yon(n): SOUND 37, bekle: GOTO 420

REM geri
700 IF (n = 1 OR n = 0) THEN n = 5
n = n - 1
OUT &H378, yon(n): SOUND 50, bekle: GOTO 420

800 FOR k = 0 TO 100
IF (n = 1 OR n = 0) THEN n = 5
n = n - 1
OUT &H378, yon(n): SOUND 500, .135
NEXT k
GOTO 420
```

```
550
REM kk = kk + 1
ch = 13
port = 632
OUT port + 3, 0
OUT port + 0, ch
FOR I = 1 TO 5: A = INP(port + 4): NEXT I
FOR I = 1 TO 9: A = INP(port + 5): NEXT I
B = INP(port + 2)
C = INP(port + 1)
dort = (B / 16 - INT(B / 16)) * 16 * 256 + C
LOCATE 10, 10: PRINT " CHANNEL="; ch, "DATA="; dort
REM IF (kk = 5) THEN
REM t = t + 1
REM PRINT #1, USING " #####.## "; dort; t:
REM kk = 0
PRINT USING "okunan ortalama deger : #####.## "; dort
PRINT USING "set degeri ile farki  : #####.## "; hata
REM END IF
RETURN
```

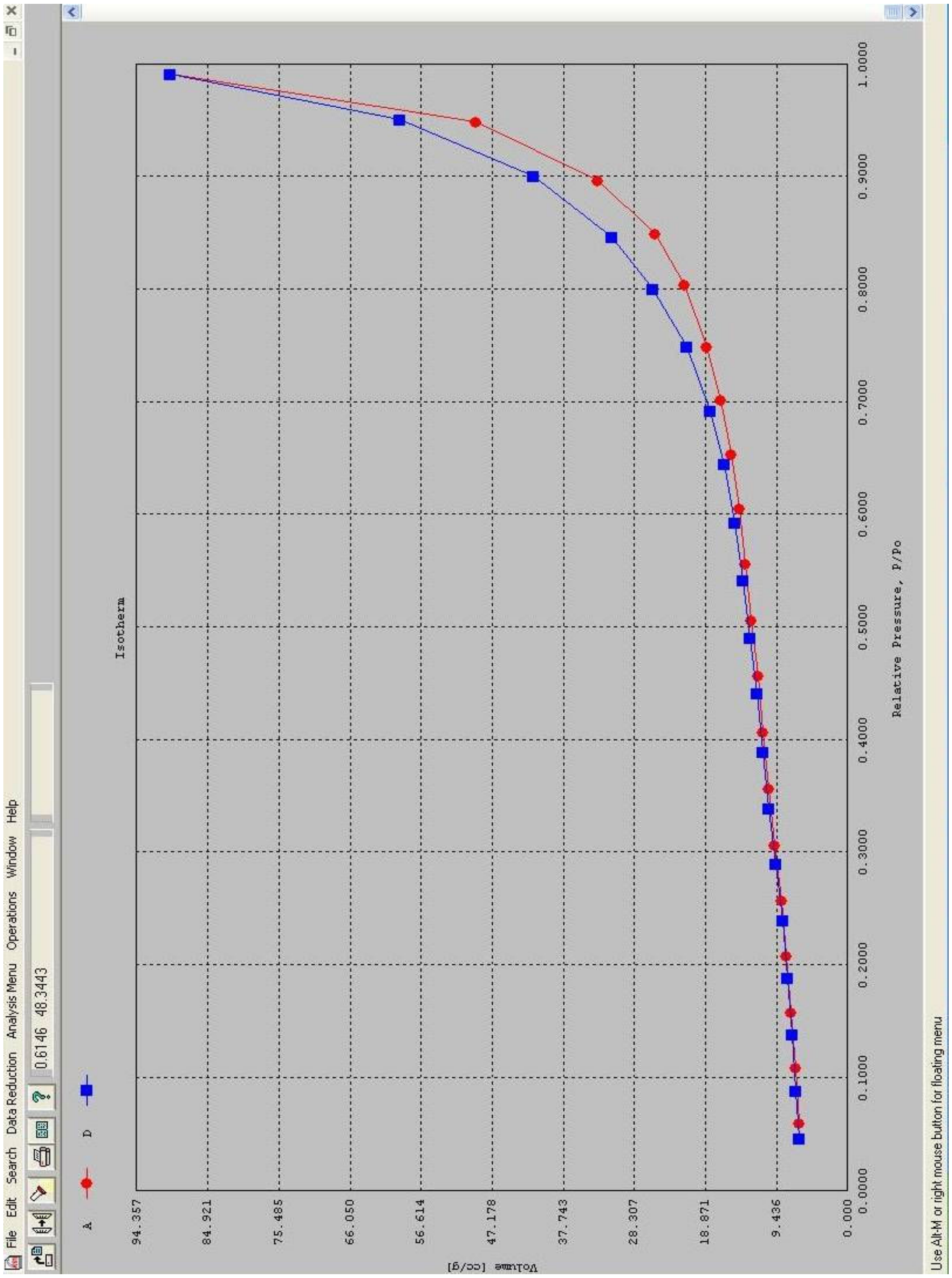
# APPENDIX D

## SIMPLIFIED SCHEME OF THE AUTOSORB 1-C SURFACE ANALYZER, FRONT VIEW



# APPENDIX E

# AN OVERVIEW OF AN ISOTHERM



# APPENDIX F

# THEORETICAL INFORMATION

## A. Physical Adsorption:

When a gas is applied on a given solid medium, adsorption and desorption occurs depending on the surface properties of the solid. Number of moles gas adsorbed is a function of P, T, gas and solid. When T is fixed for a specific gas and solid pair, this is called an adsorption isotherm expression. Left hand of the expression can be expressed as volume of gas instead of moles of gas.

$$n = f\ (P, T, \text{gas}, \text{solid})$$

$$\left.\begin{array}{l} n = f\ (P)_{\text{T. gas. Solid}} \\ \text{or} \\ n = f\ (P/P0)_{\text{T. gas. Solid}} \end{array}\right\} \text{adsorption isotherm expressions}$$

Generally these 5 isotherms are obtained if amount of adsorbed gas is plotted versus relative pressure. This classification is known as the BDDT classification which was first introduced by Brunauer and coworkers.
B point here shows where the monolayer coverage (capacity) of solid surface ends. Isotherms are almost linear to point B (small pressure region), where Henry's Law is applicable.

Hysteresises can be seen in some of the isotherms indicating different pathways for adsorption and desorption of gas molecules from the surface. Information about the pore structure can be obtained from these Hysteresises

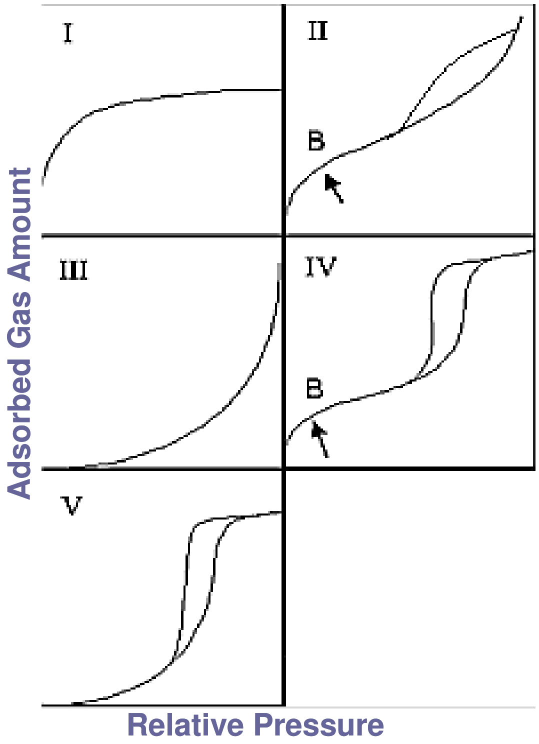


Figure F1: Five main isotherms for physical adsorption [14]

Type I: Steep region for low $P/P_0$ shows very strong adsorption in micropores. Plateau formation can be seen as a result of filled pores or in mayn cases non-porous material

Type II: Knee formation indicates the approximate location for monolayer coverage. Increase of slope in the middle region shows the formation of first multilayers. Meaning of a non-hysteresis isotherm is that the adsorption/desorption occurs on non-porous surface.

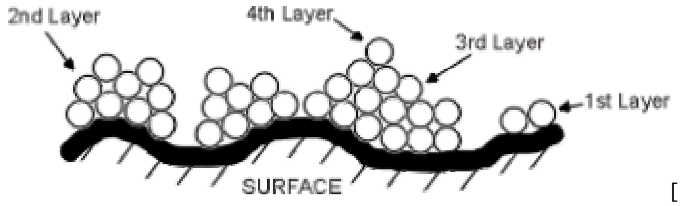
Type III: Isotherm without the knee shows extremely low interaction between adsorbent and adsorbate. BET is not applicable for Type III isotherms.

Type IV: Steep region especially $P/P_0 < 0.4$ region indicates presence of small micropores. Knee formation here again indicates the approximate location for monolayer coverage. Slope of the isotherm in the middle region indicates formation of multilayers. Hysteresises in these type of isotherms indicates cappillary condensation into meso and macropores.

Type V: lack of a knee shows extremely low adsorbate/adsorbent interaction therefore BET is not applicable.

## Measurement of Surface Area:

The principal method of measuring total surface area of porous structures is adsorption of a particular molecular species from a gas or liquid onto a surface. If the conditions under which a complete adsorbed layer, averaging one molecule thick, can be established and the area covered by molecule is known, then the quantity of adsorbed material gives directly the total surface area of the sample.



[13]

Figure F2: Adsorption layers on a solid surface

The most useful measurements are by adsorption of a gas or vapor of sufficiently small molecular dimensions that goes down to pores with diameters a few tenths of a nanometer.

Surface area is calculated from:

$$S_g = \left[ \frac{V_m N_0}{V} \right] \alpha$$

**V:** Volume of gas at STP conditions $V_m$ (22400 $cm^3$/mole)
**$V_m$:** Volume of one monomolecular layer of gas
$\alpha$ **:** Projected area of one adsorbed gas molecule.

$V_m$ value can be calculated from various expressions such as BET, Langmuir and BJH. $V_m$ can be expresssed as $C_m$, monolayer concentration, $n_m$ mole of gas forming the monolayer etc…

**Derived Adsorption Isotherms:**

Pure component adsorption equilibrium is described from fundamental point of view by many scientists. Simplest one is Langmuir isotherm which was derived from kinetic approach. Below, a list and short explanations of generally encountered isotherms are given, note that they are listed chronogically therefore they are from simplest to more complex. [14] [15]

**Langmuir Isotherm (1918):**

Describes the process of adsorption onto a flat surface from a kinetic point of view. It is a theoretical equation that includes simplifying assumptions:

- Surface is homogenous.
- Molecules are adsorbed onto definite sites (no mobile adsorption).
- Each site can accommodate only one molecule or atom.

Fraction of the surface occupied is given below where b is an empirical constant.

$$\theta = \frac{bP}{1 + bP} \qquad \theta = \frac{C_{\mu}}{C_{\mu s}}$$

But practical solids, due to their complex pore and surface structure, rarely conform completely to these assumptions.

Many semi-empirical approaches have been proposed and the resulting adsorption equations are used with success in describing equilibrium data.

**Freundlich Isotherm:**

One of the earliest (1932) empirical equations used to describe equilibrium data. Very popularly used in the description of organics from aqueous streams onto activated carbon. It is also applicable to gas phase systems with a limited pressure range as the equation does not behave according to Henry law at low pressures and does not have a finite limit at high pressures.

$$C\mu = KP^{1/n}$$

K & n are temperature dependant constants

**Sips (Langmuir-Freundlich) Isotherm:**

Sips (1948) proposed an equation similar to Freundlich equation but with a finite limit at high pressures.

$$C_{\mu} = C_{\mu s}\frac{(bP)^{1/n}}{1+(bP)^{1/n}} \qquad \theta = \frac{C_{\mu}}{C_{\mu s}}$$

The equation is similar to Langmuir equation with an additional parameter n. when n is 1; we obtain the Langmuir equation for ideal surfaces. Parameter n here can be regarded as a factor for system heterogeneity. b is a temperature dependant constant. This equation sometimes regarded as the Langmuir – Freundlich equation because it is the combination of these two equations.

**Toth Isotherm:**

One of the empirical equations that is popularly used and satisfying the low and high pressure limits is the Toth equation.

$$C_\mu = C_{\mu s} \frac{bP}{\left[1+(bP)^t\right]^{1/t}}$$

Here t is a parameter which is usually less than unity. Parameters b and t are specific for adsorbate-adsorbent pairs. When t=1, Toth equation also reduces to Langmuir equation. We can also be saying that parameter t characterizes system heterogeneity.

**Keller, Staudt & Toth Isotherm:**

Very similar to Toth's equation with differences:

1. $\gamma$ is a function of pressure instead of a constant in the case of Toth.
2. $\gamma_m$ is a constant depending on species.

$$C_\mu = C_{\mu s} \gamma_m \frac{bP}{\left[1+(bP)^\gamma\right]^{1/\gamma}}$$

**Dubinin-Radushkevich Isotherm**

Freundlich, Toth, Sips, Keller et. al. equations are applicable to supercritical as well as sub critical vapors. This equation is developed originally for sub critical vapors in microporous solids where the adsorption process follows a pore filling mechanism.

$$\ln(V) = \ln(V_0) - BA^2 \qquad A = R_g T \ln\left(\frac{P_0}{P}\right)$$

**Brunauer Emmett Teller (BET) Equation**

BET treatment is based on a kinetic model of the adsorption process put forward by Langmuir, in which the surface of the solid was regarded as an array of adsorption sites.

Langmuir referred to a possibility that the evaporation-condensation mechanism could also apply to second and higher molecular layers, but the equation he derived for the isotherm was complex and was not used extensively. By adopting the Langmuir mechanism but introducing number of simplifying assumptions, Brunauer, Emmett and Teller in 1938 were able to arrive at their well known equation for multilayer adsorption, which has found widespread use ever since.

$$\frac{P}{V\left(P_0 - P\right)} = \frac{1}{V_m c} + \frac{c-1}{V_m c}\frac{P}{P_0}$$

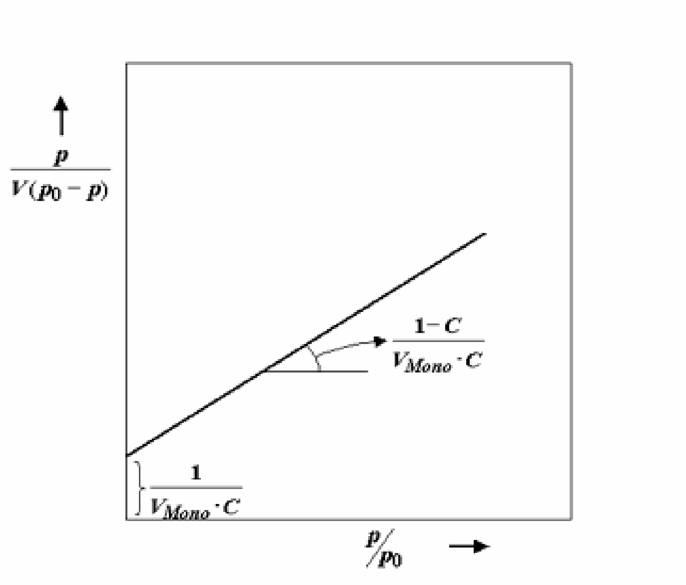


Figure F3: Finding of monolayer coverage and BET constant, c from slope and intersection

From the slope and intercept Vm (or Nm) can be calculated. If we multiply Vm with the projected area of adsorbed atom, surface area can be calculated.

Other gases that can be used for adsorption methods:

Carbon dioxide

- $CO_2$ is a linear molecule which can penetrate smaller pores and can be used at quite high temperatures (273 K)
- $CO_2$ is sensitive to surface polarity of solids; it can be suitable for the study of the polarity of the surfaces in systems where chemisorption methods are not used. And also for BET.
- $CO_2$ adsorption is very fast in comparison with $N_2$ adsorption
- Unfortunately not as common as $N_2$ due to sensitivity

Argon

- Advantage to analyze such narrow micropores by using argon *at liquid argon temperature (87.3 K).*
- Argon fills these micropores (0.5 – 1nm) at much higher relative pressures (i.e., at relative pressures 10-5 to 10-3) compared to nitrogen.
- Argon sorption at 77 K is limited to pore diameters under 12 nm.

### Micro and Mesopore Size Determination by Gas Sorption

Gas sorption methods can give information about pore structure, pore volume, pore structure and shape of pores in addition to surface area of the sample.

Table F1: Mechanism of physisorption and calculation methods that can be used for different relative pressure ranges

| P/Po range | Mechanism | Calculation model |
|---|---|---|
| **$1x10^{-7}$ to 0.02** | micropore filling | *HK, SF (see section 3.3.4.1.)* |
| **0.05 to 0.3** | monolayer complete | *BET, Langmuir* |
| **> 0.1** | multilayer formation | *t-plot(de-Boer,Halsey), (see section 3.3.4.3.)* |
| **> 0.35** | capillary condensation | *BJH (see section 3.3.4.2.)* |
| **0.1 to 0.5** | capillary filling | *BJH* |

Pore shapes are determined from the shape of the adsorption – desorption hysteresis (ink bottle, flat, cone etc…)

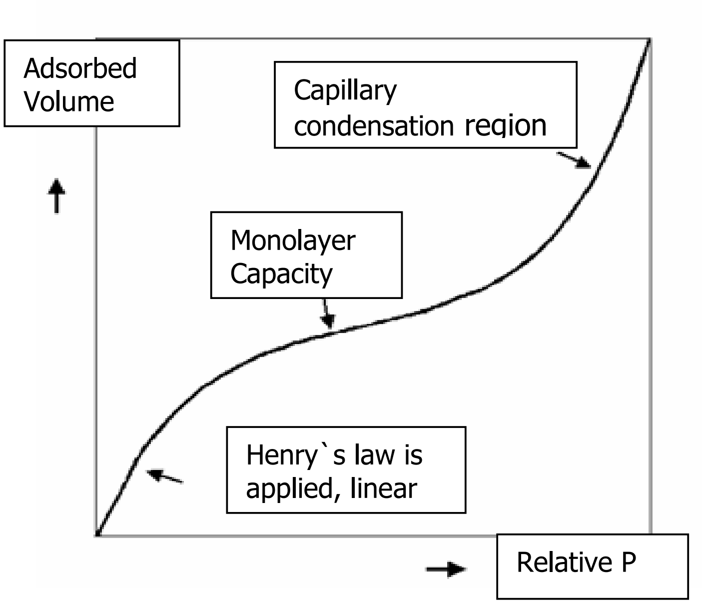


Figure F4: Regions in physisorption

Micropore (Greek *micro* = small): 0 nm - 2 nm diameter

Mesopore (Greek *meso* = middle): 2nm - 50 nm diameter

Macropore (Greek *macro* = large): >50 nm diameter

Pore volume distribution is determined by a material that can totally wet the surface of the sample.

- Hg Porosimetry method is generally used where Hg forced to enter capillaries by pressure. This method is not applicable for micropores, but can be used for meso and macropore region.

- Adsorption - desorption isotherms extended to condensation region. These analysises can be done in micro – mesopore region.

In mercury porosimetry method, mercury is forced to enter capillaries by pressure or for surfaces that can be damaged by mercury, some gases can be used to probe the surface.

**HK and SF Methods for Micropores:**

**Horwath-Kowazoe Method**

Direct mathematical relationship between relative pressure (P/Po) and pore size. Relationship calculated from modified Young-Laplace equation, and takes into account parameters such as magnetic susceptibility. Based on slit-shape pore geometry (e.g. activated carbons). Calculation restricted to micropore region (≤ 2nm width).

Equation relates gas pressure in terms of width of the slit shape pore (2d) therefore by measuring the adsorption isotherm as a function of the reduced pressure we can calculate the amount adsorbed from the second equation. N and A parameters in the equation are calculated constants for the species. [15]

$$R_g T \ln\left(\frac{P}{P_0}\right) = K \frac{N_1 A_1 + N_2 A_2}{\sigma^4 \left[2d - (\sigma_1 + \sigma_2)\right]} \left[ \frac{\sigma^{10}}{9\left(\frac{\sigma_1+\sigma_2}{2}\right)^9} - \frac{\sigma^4}{3\left(\frac{\sigma_1+\sigma_2}{2}\right)^3} - \frac{\sigma^{10}}{9\left(2d - \frac{\sigma_1+\sigma_2}{2}\right)^9} + \frac{\sigma^4}{3\left(2d - \frac{\sigma_1+\sigma_2}{2}\right)^3} \right]$$

$$C_\mu = C_{\mu s} f\left( {}^{P}\!/_{P_0} \right)$$

### Saito-Foley Method

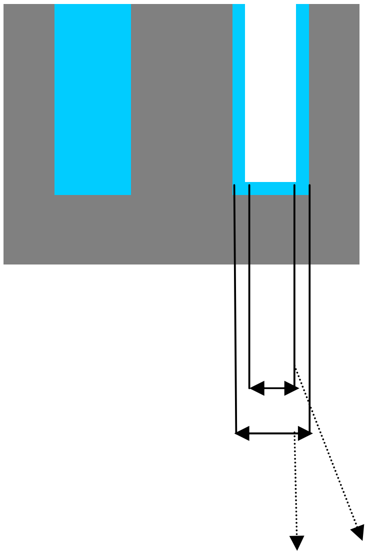
Similar mathematics to HK method, but based on cylindrical pore geometry (e.g. zeolites). Calculation restricted to micropore region (≤ 2 nm diameter). Here again N, A, α, β are calculated constants for the species. [15]

$$R_g T \ln\left(\frac{P}{P_0}\right) = \frac{3\pi N_o}{4}\frac{N_1A_1+N_2A_2}{\sigma^4_{12}}\left[\frac{21}{32}\left(\frac{\sigma_{12}}{R}\right)^{10}\sum_{k=0}^{\infty}\frac{\alpha_k}{(2k+1)}\left(1-\frac{\sigma_{12}}{R}\right)^{2k} - \left(\frac{\sigma_{12}}{R}\right)^{4}\sum_{k=0}^{\infty}\frac{\beta_k}{(2k+1)}\left(1-\frac{\sigma_{12}}{R}\right)^{2k}\right]$$

$$C_\mu = C_{\mu s} f\left({}^{P}\!/_{P_0}\right)$$

### BJH Method for Mesopores:

Known also as the modified Kelvin equation. Kelvin equation predicts pressure at which adsorptive will spontaneously condense (and evaporate) in a cylindrical pore of a given size.  Condensation occurs in pores that already have some multilayer on the walls.  Therefore, the pore size is calculated from the Kelvin equation and the selected statistical thickness (t-curve) equation. [15]



Note:  Kelvin Equation

$$r_k(A) = \frac{4.15}{\log(P/P_0)}$$

$$\Longrightarrow \quad r_p = r_k + t$$

BJH Equation:
$r_p$ = actual radius of the pore
$r_k$ = Kelvin radius of the pore
t = thickness of the adsorbed film

Figure F5: Layer approximation for BJH equation

### t-plot and $\alpha_s$ Method:

These methods use a mathematical representation of multi-layer adsorption.  The thickness, t, of an adsorbate layer increases with increasing pressure.  The t-*curve* so produced is very similar in appearance to a type II isotherm. It is actually a test of deviation from the standard isotherm. estimated statistical thickness of adsorbed layer (in meso- and macropores) can be calculated from Halsey / Frenkel-Halsey-Hill (FHH) if the pores are assumed cylindrical or De Boer equations if the pores are assumed slit-shaped.

## t-Plot Method

The procedure of using t-plot:

1. A reference non-porous material with similar surface characteristics is chosen to obtain the information on the statistical film thickness as a function of the reduced pressure ($P/P_0$). The t values for difference reference adsorbents as a function of the reduced pressure are available in the literature. But as the t-*curve* so produced is very similar in appearance to a type II isotherm, reference data can be chosen as a general type II.

2. The equilibrium data of the amount adsorbed versus the reduced pressure are plotted as the amount adsorbed versus the statistical thickness by using the data of non porous material in step 1

3. from the plot of step 2, there are usually two distinct linear regions (A and B) and two straight lines can be drawn from these two regions. The slope of the first linear line passing through the origin can be used to calculate the total surface area. While the slope of the second straight line is used to calculate the external surface area. The intercept of the latter gives the volume of micropores (C).

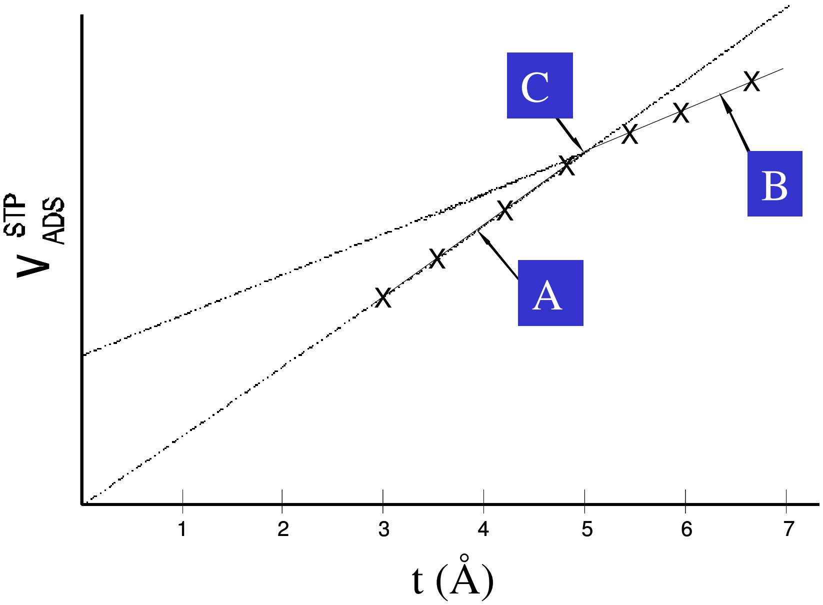


Figure F6: Reading of surface area from slope A and micropore volume from intersection of B in V-t method [12]

### $a_s$ Method

$a_s$ method was introduced by K.S.W. Sing [15]. In some respects it is very similar to the de Boer's t-plot method, because it compares your adsorption data with a standard isotherm of adsorption on some non-porous solid. It is also assumed, that the adsorption in a certain region may be described by a straight line in which a y-intercept describes a saturated adsorption isotherm on micropores (i.e. maximum adsorption in micropores), whereas the slope is related to the adsorption on a non-microporous part. However, in contrast to the t-plot method, the standard isotherm in $a_s$-plot is usually some experimental isotherm on a non-porous adsorbent selected specifically for its chemical and structural similarity to the adsorbent in question.

Another positive side of $a_s$ method is its universality. It may be used in determination of mesopore volume, mesopore surface area, macropore volume and area etc. - it depends only on the data range available (in fact t-plot could be used in a similar manner as well). However, it also helps if pore size distribution has well defined peaks.

### B. Chemical Adsorption

Chemisorption is a process where a molecule attaches to the surface through a formation of a chemical bond, unlike physisorption where attachment of molecule happens through physical bonds. This kind of bonding often found to occur at temperatures far above the critical temperature of the adsorbate. Chemisorption is therefore used primarily to evaluate quantitatively the number of surface active sites which are likely to promote (catalyze) chemical reactions. However, further physical adsorption on top of the chemisorbed layer and diffusion of the chemisorbed species into the bulk solid should not be missed for the fact that

chemisorbed material can be only one layer in depth

Chemisorption is usually associated with a high activation energy, which means that adsorbate molecules attracted to a surface must go through an energy barrier before they become strongly bonded to the surface. Because the formation of a chemical bond takes place between an adsorbate molecule and a localized, or specific, site on the surface of the adsorbent, the number of active sites on catalysts can be determined simply by measuring the quantity of chemisorbed gas. Obtained adsorption isoterms are the same explained as before.

# APPENDIX G

# DETAILED INSTRUCTIONS FOR AUTOSORB 1-C

## OPERATION

## A. INITIAL SETUP

The AUTOSORB requires a minimum amount of setup before powering the system on for the first time. The system requires the following:

The AUTOSORB-1 requires a 120V/60Hz - 15 amp power line. See Section VII-E of the AUTOSORB manual for conversion to 220 volts and setup of the uninterruptable power supply (UPS) option.

Set the vacuum gauge setpoints. The vacuum gauge has two red setpoints, the upper one should be set to about 200 millitorr and the lower one should be set slightly higher than the best vacuum the system can achieve when pumping on the manifold. This should be set for about 20 millitorr initially, then readjusted once the system is operating.

### 1. SAMPLE STATION CONFIGURATION

In order to use the AUTOSORB-1-C for chemisorption studies, the sample station must have the following configuration:

a. The thermistor (used to detect the level of coolant bath in physisorption) must be removed from its station.

b. The $P_0$ cell must be removed and its station must be sealed using the stainless steel dowel supplied.

c. When switching from physisorption to chemisorption, be sure to remove any O-rings that may remain in the sample cell station. Use only the O-rings and ferrules required by the chemisorption cell.

### 2. CONNECTING THE GAS LINES

All gas lines are connected to the gas input manifold on the rear panel of the AUTOSORB. The ports are labeled *Helium, 1 Adsorbate and 2 through 4*. Only Helium should be connected to the helium input port. Nitrogen, or any other gas used for physisorption is to be connected to port 1. All other gasses used for sample treatment and/or chemisorption are to be connected to ports 2, 3 and 4. Stainless steel tubing with quick connect fittings is supplied for connecting gas tanks to the instrument.

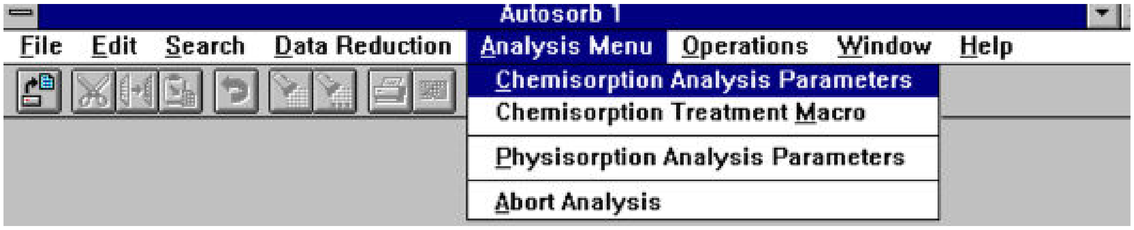
## C. STARTING THE CHEMISORB PROGRAM

See the AUTOSORB-1 manual for program installation and startup instructions.

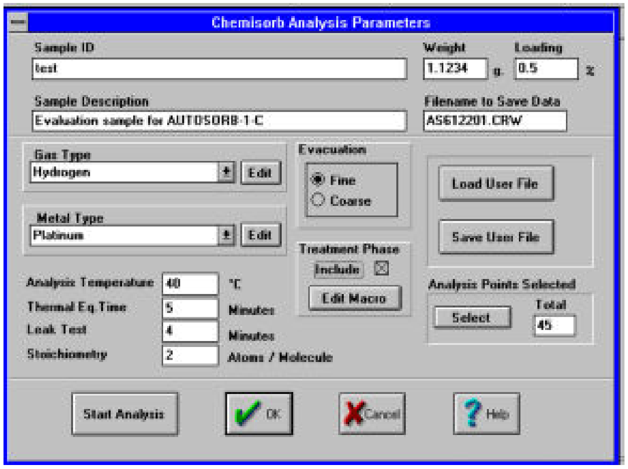
D. ANALYSIS

1. INITIALIZATION Select [ANALYSIS MENU] from the menu bar and then click on [CHEMISORPTION ANALYSIS PARAMETERS] on the drop down menu.

-



This brings up the dialog box that defines all the operational parameters used to analyze a sample.



Chemisorb Analysis Parameters

Sample ID: test

Weight: 1.1234 g.

Loading: 0.5 %

Sample Description: Evaluation sample for AUTOSORB-1-C

Filename to Save Data: AS612201.CRW

Gas Type: Hydrogen

Metal Type: Platinum

Evacuation: ● Fine ○ Coarse

Treatment Phase: Include ☒

Analysis Temperature: 40 °C

Thermal Eq.Time: 5 Minutes

Leak Test: 4 Minutes

Stoichiometry: 2 Atoms / Molecule

Analysis Points Selected: Total 45

Place the cursor in the desired field and click the left button of the mouse to move from field to field.

SAMPLE ID - Enter a sample identification of up to 50 characters.

WEIGHT - Enter the sample weight or leave the default weight of 1.0000 gram (the weight may be altered later during data reduction).

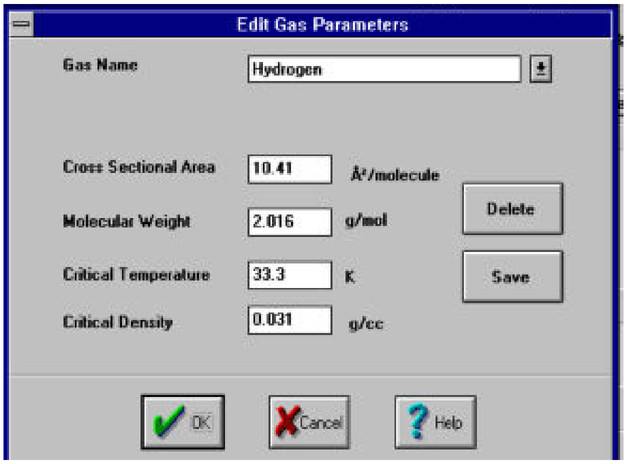
LOADING - Enter the active metal content in the sample on a percent weight basis.

SAMPLE DESCRIPTION - Any brief description (up to 50 characters) may be entered.

### GAS TYPE

Click on the down arrow 9 to bring up a list of gas types:
Move the cursor to the desired gas and press the left mouse button to select it. The gas name and all pertinent gas parameters will be loaded.

EDIT GAS PARAMETERS - To edit, delete or add a new gas to the gas table, place the cursor on [EDIT] and press the left mouse button. The Edit Gas Parameters dialog box will be displayed.



Edit Gas Parameters

Gas Name: Hydrogen

Cross Sectional Area: 10.41 Å²/molecule

Molecular Weight: 2.016 g/mol

Critical Temperature: 33.3 K

Critical Density: 0.031 g/cc

Select the gas to be edited by clicking on the down arrow, 9, and highlighting the desired gas. Move the cursor to the parameter(s) to be changed. When all the parameters are acceptable, click on [SAVE].

To delete a gas from the table, click on the down arrow, 9, select the gas to be deleted, move to the [DELETE] button and press the left mouse button. <u>CAUTION</u> If a user=s file has been defined with a gas that has been deleted, an error message will appear when that file is called for initialization.

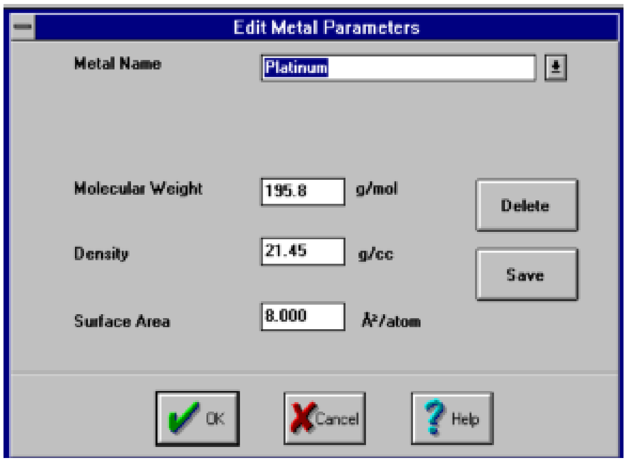
If a new gas is being added to the gas table, select any gas and replace it with name of the new gas. Move the cursor to the Cross Sectional Area box and enter the correct value. Then repeat for Molecular Weight, Critical Temperature and Critical Density. Several examples of gas parameters are listed in Appendix 2. When all the parameters are acceptable, click on [SAVE].

When all the necessary changes have been made, move the cursor to [OK] in the Gas Parameters box and click the left mouse button.

METAL TYPE

Click on the down arrow 9 to bring up a list of metal types. Move the cursor to the desired metal type and press the left mouse button to select it. The metal name and all pertinent metal parameters will be loaded.

EDIT METAL PARAMETERS - To edit, delete or add a new metal to the gas table, place the cursor on [EDIT] and press the left mouse button. The Edit Metal Parameters dialog box will be displayed.



Metal Name: Platinum

Molecular Weight: 195.8 g/mol

Density: 21.45 g/cc

Surface Area: 8.000 Å²/atom

Select the metal to be edited by clicking on the down arrow, 9, and highlighting the desired metal. Move the cursor to the parameter(s) to be changed. When all the parameters are acceptable, click on [SAVE].

To delete a metal from the table, click on the down arrow, 9, select the metal to be deleted, move to the [DELETE] button and press the left mouse button.

CAUTION If a user=s file has been defined with a metal that has been deleted, an error message will appear when that file is called for initialization.

If a new metal is being added to the gas table, select any metal and replace it with name of the new metal. Move the cursor to the Molecular Weight box and enter the correct value. Then repeat for Density and Surface Area. Several examples of metal parameters are listed in Appendix 2. When all the parameters are acceptable, click on [SAVE].

When all the necessary changes have been made, click on [OK] in the Edit Metal Parameters box. To return to the Metal Parameters dialog box without making any changes, click on [Cancel].

ANALYSIS TEMP - The temperature of the analysis (EC) can be entered by the user or the previous value used may be left in.

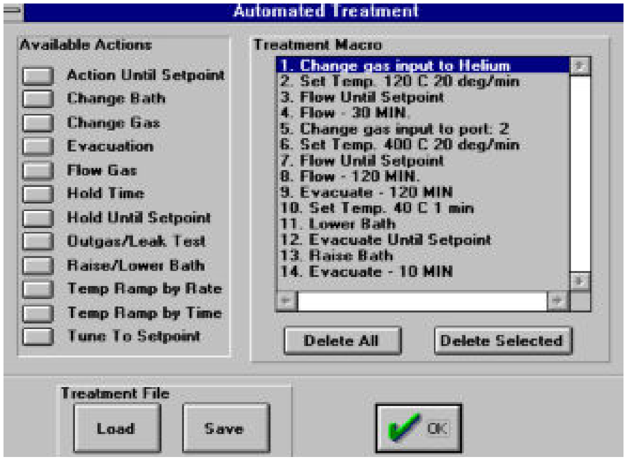
THERMAL EQ. TIME - Thermal equilibration time is the period of time allowed for the attainment of a constant sample temperature once the thermal bath is raised immediately preceding the analysis. Enter 0 for ambient temperature analyses, and up to 99 minutes for chemisorption runs at elevated temperatures. Higher temperatures may require longer thermal equilibration times.

LEAK TEST - Specify the duration of the leak test preceding the analysis (from 0 to 30 minutes).

STOICHIOMETRY - Enter the number 'S' of active metal atoms covered by each adsorbate molecule. A list of typical 'S' values can be found in Appendix 3.

EVACUATION - Select fine to evacuate slowly if the sample is a fine powder that might elutriate if the system is evacuated rapidly. Select coarse to evacuate quickly when analyzing pellets or heavy granular samples.

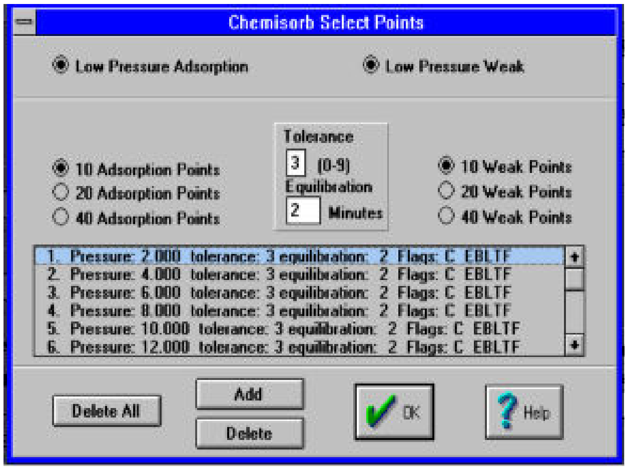
TREATMENT PHASE - allows the user to load and execute a pre-defined treatment program for sample preparation. The only limit to the number of treatment programs is the available disk space.



1. Change gas input to Helium
2. Set Temp. 120 C 20 deg/min
3. Flow Until Setpoint
4. Flow - 30 MIN.
5. Change gas input to port: 2
6. Set Temp. 400 C 20 deg/min
7. Flow Until Setpoint
8. Flow - 120 MIN.
9. Evacuate - 120 MIN
10. Set Temp. 40 C 1 min
11. Lower Bath
12. Evacuate Until Setpoint
13. Raise Bath
14. Evacuate - 10 MIN

See section 3 for a complete description of the AUTO-TREATMENT function, the available commands, their functions and how to build, save and use a treatment macro.

ANALYSIS POINTS SELECTED -Clicking on [SELECT] with the left mouse brings up the CHEMISORB SELECT POINTS Dialog Box.



● Low Pressure Adsorption
● Low Pressure Weak

● 10 Adsorption Points
○ 20 Adsorption Points
○ 40 Adsorption Points

Tolerance 3 (0-9)
Equilibration 2 Minutes

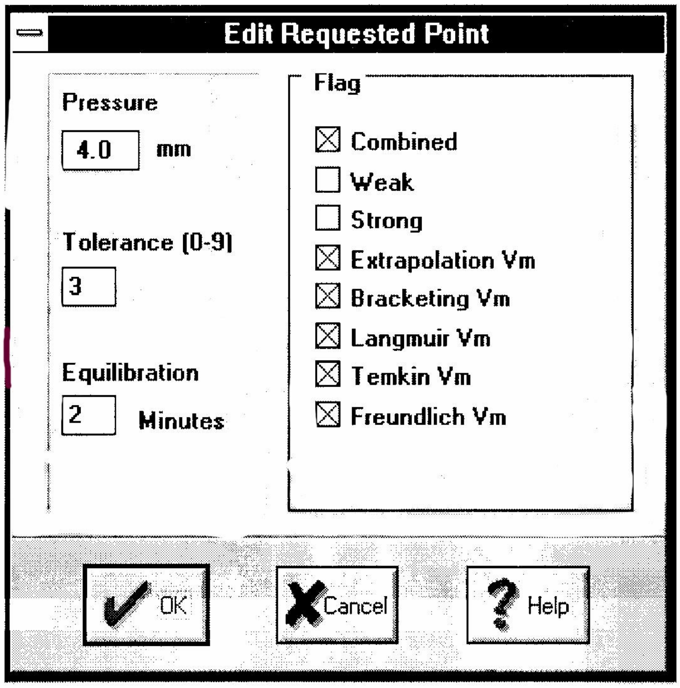
● 10 Weak Points
○ 20 Weak Points
○ 40 Weak Points

1. Pressure: 2.000 tolerance: 3 equilibration: 2 Flags: C EBLTF
2. Pressure: 4.000 tolerance: 3 equilibration: 2 Flags: C EBLTF
3. Pressure: 6.000 tolerance: 3 equilibration: 2 Flags: C EBLTF
4. Pressure: 8.000 tolerance: 3 equilibration: 2 Flags: C EBLTF
5. Pressure: 10.000 tolerance: 3 equilibration: 2 Flags: C EBLTF
6. Pressure: 12.000 tolerance: 3 equilibration: 2 Flags: C EBLTF

TOLERANCE - Select a tolerance from 0 to 9. A tolerance value of 0 insures the tightest match between the pressures selected and the pressures achieved, while a tolerance of 9 results in a faster analysis with a looser pressure tolerance. A tolerance of 4 is a good general tolerance. See Appendix 1 for further details.

EQUILIBRATION TIME - Select an equilibration time between 1 minute and 99 minutes. A value of 2 minutes is ideal in most cases. See Appendix 1 for further details.

As points are selected they will be added to the Point List table which displays up to six points at a time. All of the points can be viewed by scrolling through the list of points using the scroll bar. A point can be edited by placing the cursor on the selected point and double clicking the left mouse button. This will bring up the EDIT REQUESTED POINT dialog box.



Edit Requested Point

Pressure
4.0 mm

Tolerance (0-9)
3

Equilibration
2 Minutes

Flag
☒ Combined
☐ Weak
☐ Strong
☒ Extrapolation Vm
☒ Bracketing Vm
☒ Langmuir Vm
☒ Temkin Vm
☒ Freundlich Vm

Within this dialog box all the parameters of a specific point can be changed. For Pressure, Tolerance and Equilibration Time enter the desired values. To set a flag, use the up and down arrows to move the highlight bar to the desired flag. Click the left mouse button to toggle a flag on or off. A flag is on when an ς or a Tappears in the brackets next to its name.

When all of the parameters are acceptable, move to the [OK] box and click the left mouse button. To return to the Select Points dialog box without saving the changes, move to the [CANCEL] box and click the left mouse button.

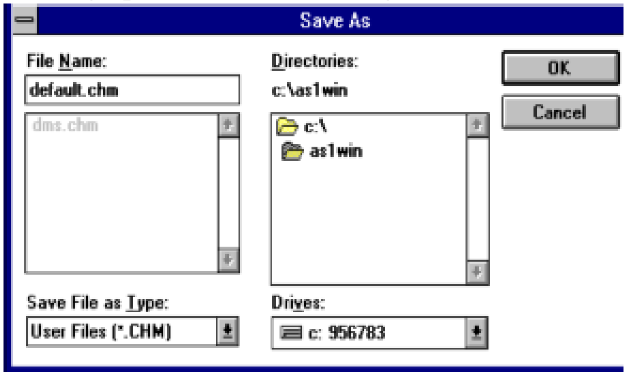
Individual points can be added to the list by moving to the [ADD] box and pressing the left mouse button. The EDIT REQUESTED POINT dialog box will again be displayed but the new point will be added to the table instead of replacing an existing point, as is done in editing.

To delete a point, place the highlight bar on the point, move to the [DELETE] box and click the left mouse button. To remove all the points, click on [DELETE ALL].

When all the desired points have been selected, move to the [OK] box and click the left mouse button to return to the Sample Parameter dialog box. The total number of points requested will be displayed in the Number of Points Selected field.

To start the analysis, move to the [START ANALYSIS] box and click the left mouse button.

2. SAVE USER FILE - To save the parameters in a User file for later analyses, move to the [SAVE USER FILE] box and click the left mouse button. This will bring up the "Save As" dialog box.



File Name: default.chm

dms.chm

Directories: c:\as1win

c:\
as1win

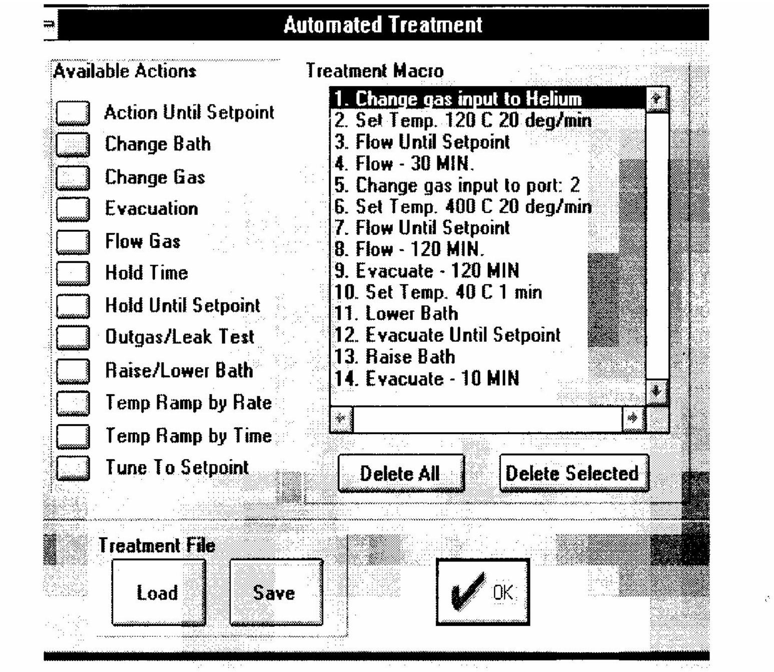
Save File as Type: User Files (*.CHM)

Drives: c: 956783

The name of the user file to be saved is entered into the File Name field. The computer will append the extension CHM to the name of the file. If the new parameters are to replace those of an older file, the highlight bar can be moved to the name of the older file, at which time the selected file will appear in the File Name field. Clicking on [OK] will save the file with the new parameters.

To exit the Save User File box without saving the parameters, move to the [CANCEL] button and press the left mouse button.

3. CHEMISORPTION TREATMENT MACRO- Selecting CHEMISORPTION TREATMENT MACRO from the Analysis Menu drop down menu or EDIT MACRO from the Chemisorb Analysis Parameters dialog box brings up the AUTOMATED TREATMENT dialog box which allows the user to select, create or modify macros for the automated treatment of samples prior to the start of the analysis.

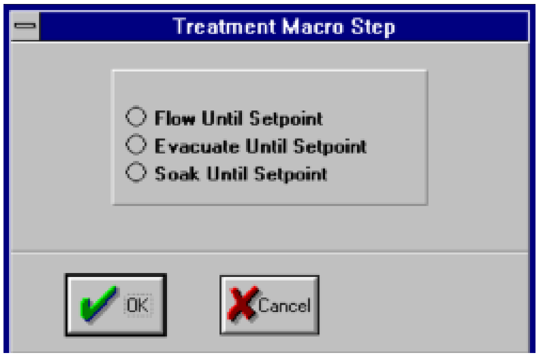


1. Change gas input to Helium
2. Set Temp. 120 C 20 deg/min
3. Flow Until Setpoint
4. Flow - 30 MIN.
5. Change gas input to port: 2
6. Set Temp. 400 C 20 deg/min
7. Flow Until Setpoint
8. Flow - 120 MIN.
9. Evacuate - 120 MIN
10. Set Temp. 40 C 1 min
11. Lower Bath
12. Evacuate Until Setpoint
13. Raise Bath
14. Evacuate - 10 MIN

The left side of the dialog box shows a list of all of the available actions that can be used to create the macro. To select one of the available actions, click the left mouse button on the desired action. For many of the actions, a dialog box will appear allowing the user to enter the desired parameters. When the parameters have been entered, click on [OK] and the action will be added to the MACRO list on the right side of the dialog box **.**

The following is a description of each of the available actions:

a. ACTION UNTIL SETPOINT

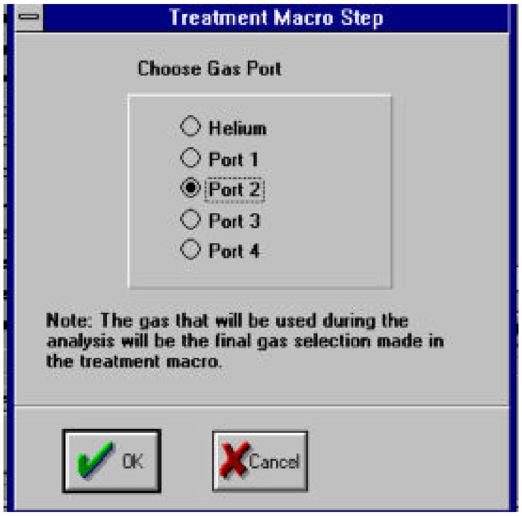


This action is used in conjunction with the TEMPERATURE RAMP actions. The desired action will continue until the requested temperature is reached regardless of the time it takes to reach the desired temperature. If flow is selected, the appropriate gas should be chosen in advance using the CHOOSE GAS action. If soak is selected, the sample cell will be isolated until the desired temperature is reached. A TEMPERATURE RAMP action must be inserted into the macro before this action can be used.

b. CHANGE BATH

This option lowers the bath support platform to allow the operator to change the bath or switch to the furnace. The platform is then raised when <C> is pressed. <X> can be pressed to continue without raising the bath again.

c. CHOOSE GAS



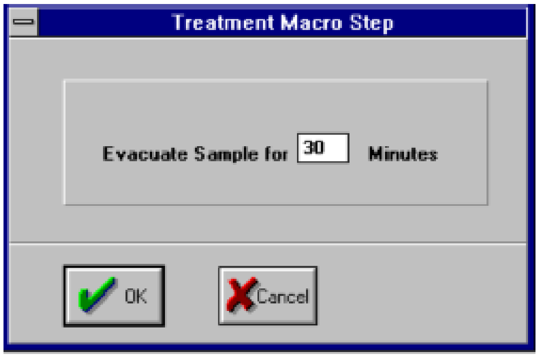
Choose Gas Port

○ Helium
○ Port 1
● Port 2
○ Port 3
○ Port 4

Note: The gas that will be used during the analysis will be the final gas selection made in the treatment macro.

This action allows the user to switch from one gas input port to any other port. In order to insure the safety of the operator and the instrument, the following procedure is performed: The cell and lines are evacuated. They are then purged with helium, re-evacuated and purged with the new gas.

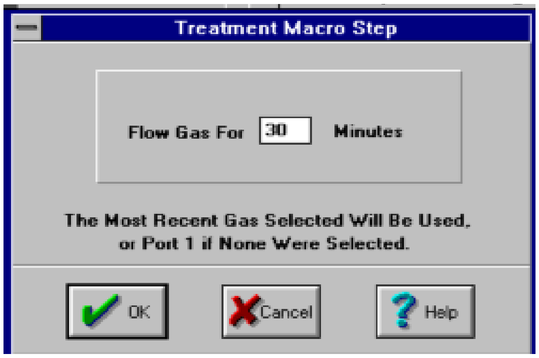
d. EVACUATION



Evacuate Sample for 30 Minutes

This action allows the user to evacuate the sample cell and maintain the vacuum for a given amount of time. When executed, the fine vacuum valve is opened until the system reaches 35 mm of mercury. Then the coarse vacuum valve is opened and the timing begins.

e. FLOW GAS


Treatment Macro Step

Flow Gas For 30 Minutes

The Most Recent Gas Selected Will Be Used,
or Port 1 if None Were Selected.

This action allows the user to specify how long the selected gas will flow. The gas must be selected using the CHOOSE GAS action prior to the use of this action.

f. HOLD TIME


Treatment Macro Step

Hold For 30 Minutes

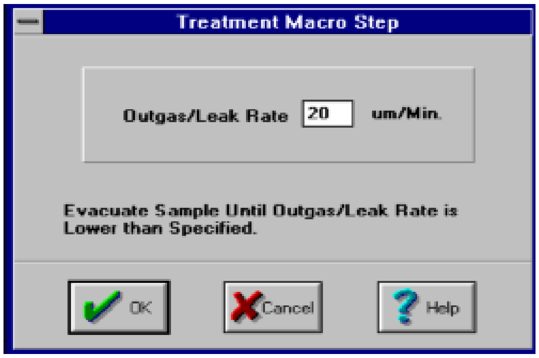
Close Sample Cell and Wait.

This action closes off the sample cell and prevents ANY further action for the specified length of time.

g. HOLD UNTIL SETPOINT

This action closes off the sample cell and prevents any further action until the specified temperature has been reached. It is used in conjunction with one of the TEMP RAMP actions, which must be selected prior to selecting HOLD UNTIL SETPOINT.

### h. OUTGAS/LEAK TEST


Treatment Macro Step

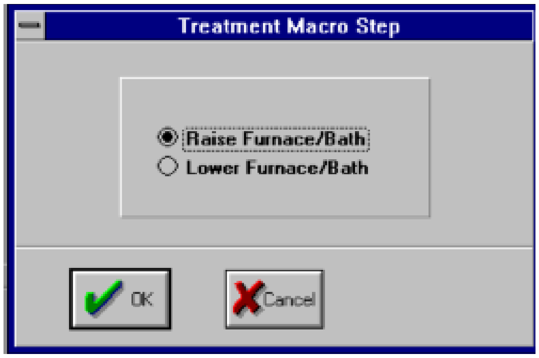
Outgas/Leak Rate 20 um/Min.

Evacuate Sample Until Outgas/Leak Rate is Lower than Specified.

This action will evacuate the sample cell and check for an increase in pressure for one minute. If the pressure increase is less than the acceptable rate, the next step will be started. If the acceptable rate is exceeded, the cell will again be evacuated for about one minute and the outgas rate will be tested again. This will continue until the outgas rate is equal to or less than the specified rate.

The operator can bypass or discontinue the test by pressing <Y>.

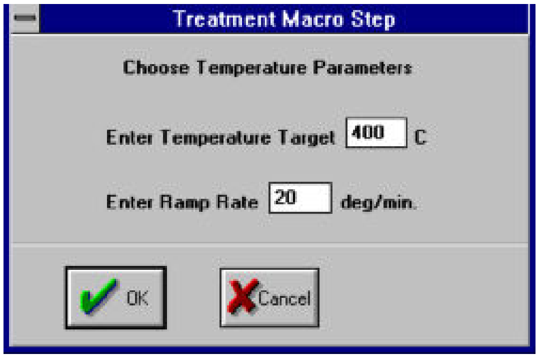
### I. RAISE/LOWER BATH


Treatment Macro Step

● Raise Furnace/Bath
○ Lower Furnace/Bath

This action moves the bath/furnace up or down as instructed.

j. TEMP RAMP BY RATE



Treatment Macro Step

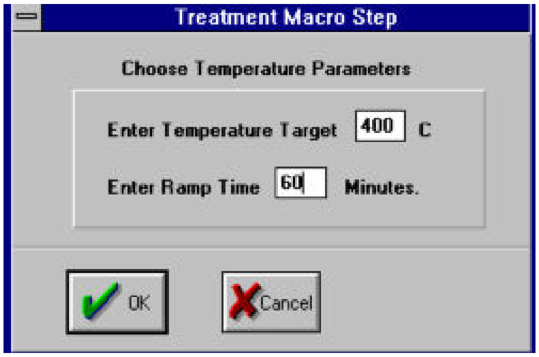
Choose Temperature Parameters

Enter Temperature Target 400 C

Enter Ramp Rate 20 deg/min.

This action causes the furnace to be raised and the temperature controller to change the furnace temperature to the selected target at the desired rate in degrees Celsius per minute. Changing from a higher to a lower temperature (cooling) may proceed at a slower rate than requested since the controller cannot exceed the heat dissipation rate of the furnace.

k. TEMP. RAMP BY TIME



Treatment Macro Step

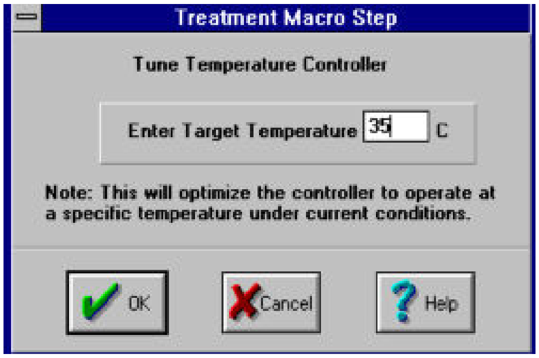
Choose Temperature Parameters

Enter Temperature Target 400 C

Enter Ramp Time 60 Minutes.

This action causes the furnace to be raised and the temperature controller to change the furnace temperature to the selected target in the specified time. Changing from a higher to a lower temperature (cooling) may require a longer time than requested since the controller cannot exceed the heat dissipation rate of the furnace.

## I. TUNE TO SETPOINT



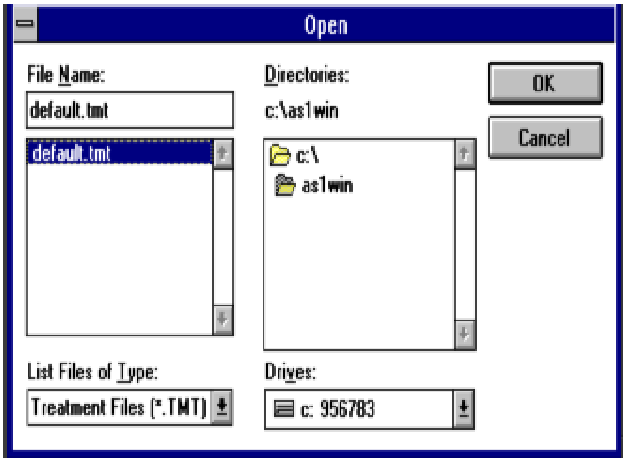
Tune Temperature Controller

Enter Target Temperature 35 C

Note: This will optimize the controller to operate at a specific temperature under current conditions.

This action causes the furnace to be raised and allows the controller and furnace to be calibrated to the specified temperature under the existing environmental and operating conditions. It is not recommended for use at temperatures less than 10EC above ambient.

<u>LOAD</u> Allows a previously save treatment macro to be loaded for editing or for use with a sample.



File Name: default.tmt

Directories: c:\as1win

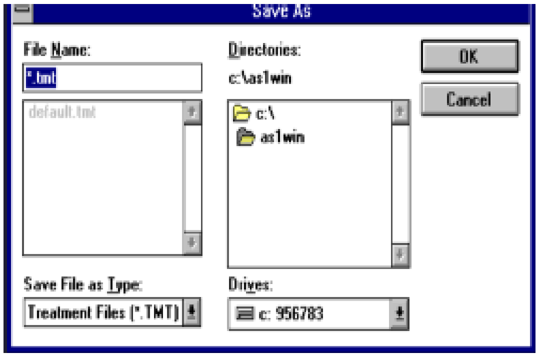
List Files of Type: Treatment Files (*.TMT)

Drives: c: 956783

Click on the desired treatment macro file and then click on [OK] to load it.

<u>SAVE</u>

To save the macro for future use, click on [SAVE] with the left mouse button. This will bring up the SAVE AS dialog box.

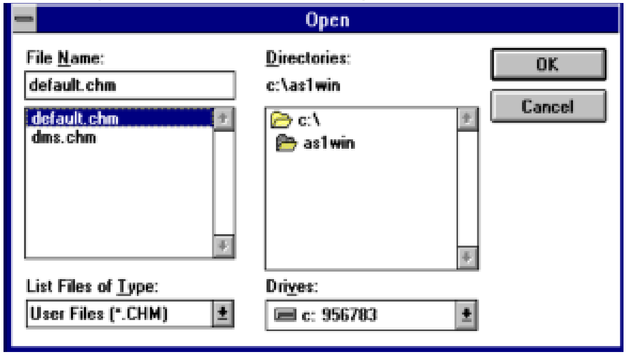


File Name: *.tmt
default.tmt
Directories: c:\as1win
c:\
as1win
Save File as Type: Treatment Files (*.TMT)
Drives: c: 956783

The name of the macro file to be saved is entered into the Name field. The computer will append the extension TMT to the name of the file. If the new parameters are to replace those of an older file, the highlight bar can be moved to the name of the older file, at which time the selected file will appear in the Name field. Clicking the left mouse button will save the file with the new parameters.

To exit the Save Treatment File box without saving the parameters, move to the [Cancel] button and press <ENTER> or <ESC>.

3. RETRIEVE USER FILE - To start an analysis using a previously saved user file, select Open User File... from the Initialization menu. This will bring up the Open dialog box.



File Name: default.chm
default.chm
dms.chm
Directories: c:\as1win
c:\
as1win
List Files of Type: User Files (*.CHM)
Drives: c: 956703

Select a user file by moving the highlight bar to the desired name and clicking the left mouse button. Then move the cursor to [OK] and click the left mouse button again. The sample parameters will appear with all of the previously saved information filled in. This information may be edited as described above or accepted without change.

FILE NAME TO SAVE DATA

A default filename will appear in this field. File names assigned by the computer have the following format.

AS -- represents AUTOSORB

6 -- represents 1996, 7 for 1997 and so on
1 -- represents 1 (the first month); 1-9 represent the first nine months, A-C represent months 10-12
02 -- represents the second day of the month
01 -- represents the first analysis to be started; this number is automatically incremented.

If a different filename is desired, any valid DOS filename can be used. The filename must be no more than 8 characters long (not including the extension), and it can use numbers and characters only. Spaces may not be included in the file name.

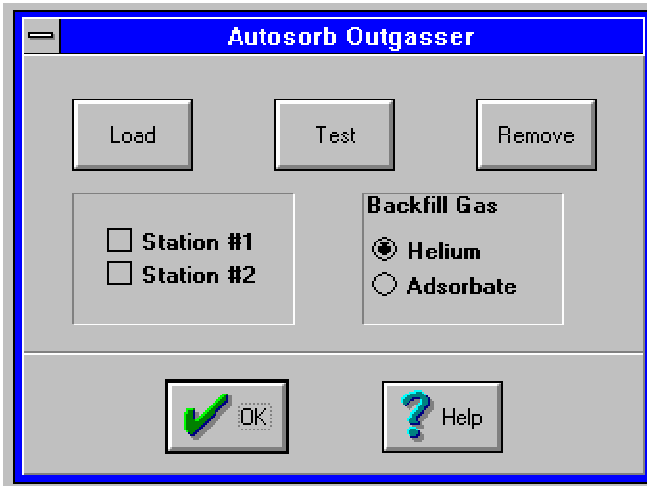
**CAUTION:** If a filename is entered that has already been used, the data in the old file will be overwritten and cannot be recovered.

START ANALYSIS - Start the analysis by moving to [START ANALYSIS] and clicking the left mouse button.

## E. OPERATIONS

### 1. OUTGASSER

Sample outgassing is performed on the two dedicated outgassing stations on the front of the AUTOSORB-1. The outgas menu can be accessed from the Operations menu and presents the following available options:



Stations are selected by moving to the station field and pressing the left mouse button for each desired station. A mark will appear in the box next to the station number when it is selected. A station must be selected before an operation is selected. If the chemisorption cell is used in the outgassing station, the Ultra-Torr end cap must be placed on the narrow arm of the cell in order to seal it.

LOAD - Click on load to load one or two samples into the outgassing stations. To heat a sample during outgassing, set the desired temperature (EC) on the digital temperature control below the station, plug the mantle power and thermocouple connectors into the jacks, place the mantle over the sample cell, slide a clamp over the mantle and turn on the heater enable switch.

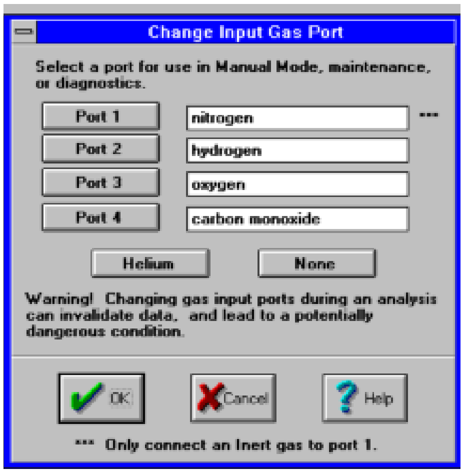
TEST - Click on [Test] to select the test mode. A rapid rise on the vacuum gauge indicates that at least one of the samples being tested is poorly outgassed. A steady reading indicates that outgassing is complete. The system will stay in the test mode for five minutes or until ESC is pressed. If no station is in use, an error message will appear.

REMOVE - Click on [Remove] to begin removal of samples from the outgassing stations. The heaters will turn off and the cells will be back-filled with helium. In the case where a high temperature is used for outgassing, it is recommended to manually turn off the heater several minutes before starting the REMOVE sequence to give the sample cells and heating mantles time to cool. If no station is in use, an error message will appear.

When a sample cell is removed from the outgas station, it is backfilled with the selected gas, either helium or the adsorbate connected to port 1. Select which gas is to be used by clicking on the radio button next to your choice.
Because the outgassing station and the analysis system share common resources, frequent use of the outgassing options while an analysis is running will increase analysis time.

## 2. CHANGE INPUT PORT

The port selected for the gas input can be selected using this operation. It is usually used for diagnostics or setting the flow rates.



Select a port for use in Manual Mode, maintenance, or diagnostics.

Port 1: nitrogen ***
Port 2: hydrogen
Port 3: oxygen
Port 4: carbon monoxide

Warning! Changing gas input ports during an analysis can invalidate data, and lead to a potentially dangerous condition.

*** Only connect an Inert gas to port 1.

When a new input port is selected, the input lines and manifold are first evacuated, then purged with helium, re-evacuated and then purged with the new gas. The labels next to the selection bars are for user identification of the gas connected to each port. They are text boxes only and may be filled in or left empty as desired. If they are filled in, the text will remain until changed or deleted.

## 3. <u>CALIBRATION</u>

Since all the results obtained on the AUTOSORB are based on the volume of the manifold, it is a good practice to calibrate regularly. The manifold cannot be calibrated while a sample is being analyzed or outgassed.

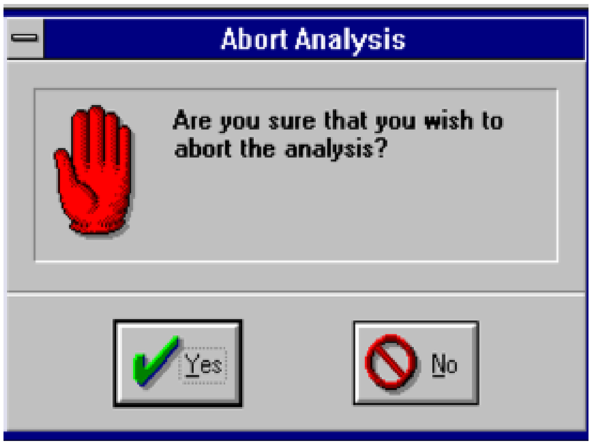
Select INSTRUMENT CALIBRATION from the drop down menu. Confirm that you do want to recalibrate the manifold. When prompted, enter the volume of the calibration sphere. Be sure the empty sleeve is in the calibration chamber, fully seat the cover and press any key. When prompted, place the calibration sphere and sleeve into the chamber and again press any key. The system will complete the calibration and display the following:

```
CALCULATED MANIFOLD VOLUME = XX.XX   OLD MANIFOLD
VOLUME = XX.XX

          1. USE OLD VALUE
          2. USE NEW VALUE
          3. ENTER NEW VALUE

          PRESS SELECTION (1-3)
```

The choice of selection 1 results in the retention of the previous calibration value; selection 2 accepts the value just acquired and a different volume can be entered by choosing 3. This entry is useful for averaging several calibration values.

4. ABORT

Selecting ABORT from the Analysis drop down menu is used to abort the sample run. This selection must be confirmed, thus preventing accidental aborts.



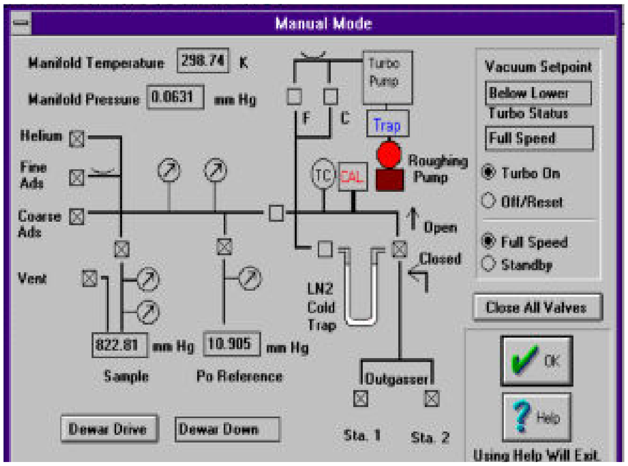
Are you sure that you wish to abort the analysis?

Select [Yes] to confirm or [No] to cancel.

5. MANUAL MODE

Selecting Manual Mode from the Operations menu allows entry into the manual mode which gives complete manual control of the system's valves and Dewar flask and the ability to display the system temperature and pressures. Entry into the manual mode while an analysis is in progress is not recommended, since this mode stops automatic processing and can allow a system overpressurization.

When the manual mode is selected the state of each valve (9-open, :-closed) and the direction of the liquid nitrogen bath (up, down) are displayed. A typical display of the manual mode is shown below:


Manual Mode

Manifold Temperature 298.74 K

Manifold Pressure 0.0631 mm Hg

822.81 mm Hg Sample

10.905 mm Hg Po Reference

Vacuum Setpoint: Below Lower

Turbo Status: Full Speed

● Turbo On
○ Off/Reset

● Full Speed
○ Standby

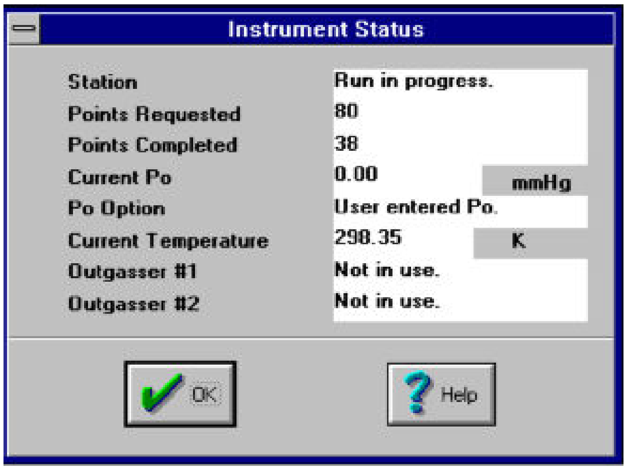
Note: The outgasser vent is a three way valve that directs the gas flow through the cold trap during normal operation ⁚. During loading, unloading or testing of the outgas stations, the gas flow is directed around the cold trap 9.

The pressure of the station and the manifold is given in mm of mercury and the temperature in Kelvin. The state of any valve or the direction of the liquid nitrogen Dewar flask may be manually altered by moving the cursor to the desired position, then pressing the left mouse button. All the valves can be closed at once by selecting [CLOSE ALL VALVES].

To exit from the manual mode, move to the [OK] button and press the left mouse button. All valves and the Dewar flask will be restored to their original status.

## 6. <u>INSTRUMENT STATUS (F8)</u>

Pressing <F8> or selecting [INSTRUMENT STATUS] from the OPERATIONS drop down menu will produce a system status report. The status of the sample and outgassing stations, the progress of the analysis, the current $P_0$ in mm Hg and the current manifold temperature (K) are displayed.



| | |
|---|---|
| Station | Run in progress. |
| Points Requested | 80 |
| Points Completed | 38 |
| Current Po | 0.00 mmHg |
| Po Option | User entered Po. |
| Current Temperature | 298.35 K |
| Outgasser #1 | Not in use. |
| Outgasser #2 | Not in use. |

Click the left mouse button on [OK] to close the Instrument Status display.

7. <u>UPLOAD DATA</u> (F9)

Pressing F9 or selecting [UPLOAD DATA] from the operations drop down menu will cause the computer to read the data currently stored in the AUTOSORB Into the file designated to save that data. A graph of the combined isotherm will be displayed. Any desired data reduction can be performed if the data for the function has been acquired.

## I. SAMPLE PREPARATION AND CELL SELECTION

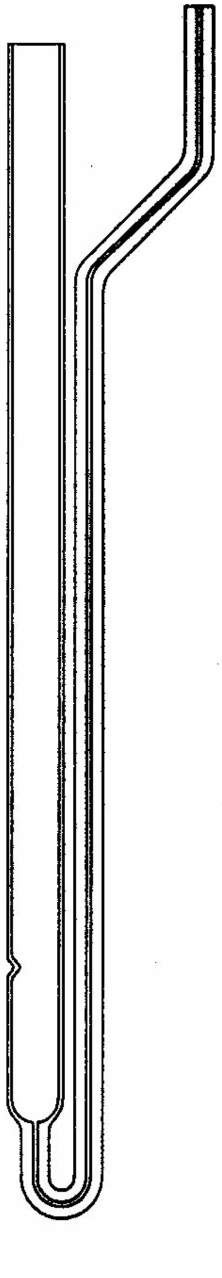
Exact details for sample preparation and cell selection will vary with sample characteristics. Some basic guidelines are given below.

### 1. SAMPLE WEIGHT

Since the quantity of gas adsorbed determines the length of the analysis, larger amounts of sample result in longer analyses times. Even though smaller sample amounts will not affect the accuracy of the results, about 1 g of sample should be adequate in most cases.

## 2. SAMPLE CELL

The cell used with the AUTOSORB-1-C for chemisorption is shown below:



Quartz chemisorption sample cell for use at temperatures up to 1000E C (Part No. 74067)

Quartz insert for chemisorption sample cell (not shown) (Part No. 74068)

## J. SHUTTING DOWN THE AUTOSORB

It is recommended that the AUTOSORB-1-C be left on at all times if it is to be used on a regular basis. However, if the instrument will not be used for a prolonged time, the following procedure should be used to shut it down.

### 1. SHORT TERM SHUT-DOWN

a. Insert a sample cell or stainless steel dowel in the sample station, $P_0$ station and each outgassing station.

b. Turn off the electronics and the vacuum pump.

### 2. LONG TERM SHUT-DOWN

Follow steps a and b above. In addition, disconnect the gas input lines from the instrument.

NOTE: If, when restarting the AUTOSORB after a shut-down, the system shows over-pressurization and will not initialize, remove the sample cell or stainless steel dowel from the sample station to allow the excess pressure to dissipate.