

# Characterization of Cu/ZnO Catalysts from a Methanol Plant

By

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(2887)

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CERTIFICATION OF APPROVAL

Characterization of Cu/ZnO Catalysts from a Methanol Plant

By

Wan Norafiza W. Othman

A Project dissertation submitted to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
In partial fulfillment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)

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UNIVERSITY OF MALAYA  
KUALA LUMPUR

### **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(WAN NORAFIZA W. OTHMAN)

## ABSTRACT

The main objectives of this project are to study the physical and chemical properties of fresh and spent catalysts, to identify the type of decays which led to the catalysts deactivation, and to propose the best handling option of the spent catalyst that is economical and environmental friendly, based on the causes of catalyst decay. Samples of fresh and spent Cu/ZnO catalysts were obtained from Petronas Methanol Plant in Labuan. The properties of catalysts studied were the reduction and oxidation profiles, BET surface area, density, morphology, phase changes as well as the chemical contents. Series of experiments were conducted using equipment such as Temperature Programming Desorption, Reduction and Oxidation (TPDRO), Carbon, Hydrogen, Nitrogen, and Sulphur Analyzer (CHNS), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), X-ray Diffraction Unit (XRD), Pycnometer and Fourier Transform Infrared Spectrometer (FTIR).

The BET surface area was  $109.48 \text{ m}^2/\text{g}$  and  $71.15 \text{ m}^2/\text{g}$  for fresh and spent catalysts respectively. The results showed that sulfur and carbon exist in the fresh and spent catalysts. Results of SEM, TPR and TPO analyses showed that the spent catalysts experienced thermal sintering. The spent catalyst cannot be regenerated because of the changes in its physical and chemical properties. The best handling option proposed is disposal and prevention of the catalysts life degradation is preferred because the decayed catalysts cannot be reused.

## **ACKNOWLEDGEMENT**

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# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Twenty years ago, methanol synthesis was carried out at higher pressure (20-40 MPa) and higher temperatures (300-400°C) over ZnO/Cr<sub>2</sub>O<sub>3</sub> catalysts. The fundamental methanol catalyst is ZnO, whereas Chromia acts as a stabilizer. The lowering of synthesis temperature and pressure was made possible by application of copper containing-catalysts with an activity about 100 times higher than the original catalysts [1]. However, methanol is currently produced from CO-rich synthesis gas (CO/CO<sub>2</sub>/H<sub>2</sub>) using a ternary Cu-Zn-Al oxide catalyst at 50-100 bar and 473-523 K. The conventional catalysts (ternary CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst) have been modified to improve the catalytic performance for methanol synthesis from the feeds. The CuO-ZnO catalysts have been widely modified with different metals such as chromium, zirconium, vanadium, cerium, titanium, gallium and palladium [2].

Historically, spent catalysts have been disposed off as landfill in approved dump sites. However, catalysts could be disposed off into landfill only if it could be proven with certainty that the landfill met non-hazardous criteria [3]. Currently, a few technologies have been developed to process the spent catalysts to reduce production cost. Although the spent catalyst can be processed, the nature of the processing depends markedly on the means of deactivation. The level of deactivation has to be determined before any treatment process or disposal can take place. Thus, the characterization of the catalysts plays an important role to the methanol industries, especially in economical aspects.

The three most common causes of catalyst decay are fouling, poisoning or thermal degradation. Fouling involves the deposition of material on catalyst surface which blocks the active sites. As a result, there will be less surface area for the reactions to

occur and leads to the decrease of product yield. One of the examples of impurities that might lead to catalyst fouling is the formation of coke deposition. The coke deposition occurs in the pores and/or on the surface of the catalysts [4].

Poisoning involves strong chemical interaction of a component of the feed or products with active sites on the catalyst surface. Sulfur poisoning of metal is the most widely quoted example, but depending on the catalyst, deactivation may be caused by a wide range of chemicals. The catalyst life might also be degraded by the thermal oversupplied during certain processing activities. Catalyst overheating can often lead to loss of surface area and unwanted chemical reactions. If a high temperature in the absence or presence of a suitable chemical environment arises, the catalyst will rearrange to form the more favorable lower surface area agglomerates, called sintering process [4].

In PETRONAS Methanol Plant (PML) which was commissioned in the middle of 1984, the feedstock to this plant is natural gas, which is 92% for processing and 8% for fuel. The design capacity is 2000 metric tonnes per day and the operating product is the AA grade methanol. The PML uses LURGI Low Pressure Combined Reforming Process (LPCR) for methanol production. The main processing units are;

- Steam Reforming
- Autothermal Reforming
- Methanol Synthesis
- Methanol Purification

[Source: Presentation Slide from Petronas Methanol Labuan]

## 1.2 PROBLEM STATEMENT

### 1.2.1 Problem Identification

Over period of time, the catalysts tend to degrade and the efficiency of reactions reduced due to some factors such as formation of impurities on the surface of catalysts and inside the catalysts' pores. The three most popular catalysts deactivation agents are sulfur, halogens and carbon deposits. These agents can cause decrease in surface tension of the catalyst (based on Gibbs adsorption isotherm rule), less contact area and weaker attraction with the reactants. These agents also can induce changes in surface morphology due to faceting, which results in preferential segregation of one component in a multi-component metal catalyst particle, enhance sintering as a result of adsorbate induced diffusional transport of metal surface components, and modify metal support interactions [1].

Large amount of money was spent to handle the spent catalysts from PML and also for purchasing new catalysts. The catalysts life only ended for 3 years normally, and then had to be disposed. Actually, there are few options in dealing with the spent catalysts. The options could be disposal, regeneration, metal recovery and also utilization of spent catalysts as raw materials to produce other valuable products. However, initial prevention before the poisons or impurities disturb the catalyst performance is preferred. The best method of handling obviously relies on the cause of catalyst decay.

### 1.2.2 Significant of the Project

Some of the catalysts from a reactor can be reused or recovered depending on the degree of deactivation. Tests on the fresh and spent catalysts from the methanol synthesis reactor were conducted to compare the properties of the catalysts. The catalysts were characterized in terms of;

- i. BET surface area
- ii. Metal surface area

- iii. Mean particle diameter
- iv. Dispersion percentage
- v. Oxidation and reduction temperature profiles
- vi. Chemical contents such as carbon, nitrogen, hydrogen and sulfur

Based on the catalysts' characteristics, further studies could be carried out as the catalysts could be modified to enhance its performance for the maximum production yield, to recover some important metal components from the catalysts or to dispose the catalyst as a waste in most economical and safe ways.

### 1.3 OBJECTIVES AND SCOPE OF WORKS

The main objectives of this research project are:

- To study the physical and chemical properties of the fresh and spent catalysts from methanol plant
- To identify the factors that led to catalyst degradation or catalyst damage
- To identify and propose the best handling options based on the characteristics of the spent catalysts

This project involved identification of chemicals on the catalysts' surfaces and inside the catalysts' pores. Based on the physical and chemical properties of fresh and spent catalysts, it gives choices to the methanol industries the best option of handling the spent catalysts based on the economical and environmental aspects. From this project, the level of poisons on the catalysts can be determined.

Characterization of the spent catalyst from methanol plant significantly relates to the spent catalyst handling options. Conventionally, the spent catalysts were disposed as a landfill waste because there were no detailed studies conducted to determine the options either to recover the precious metal content or to convert the spent catalyst to valuable products. This project will give advantage to the methanol industries and also to the

people in societies in general. Just imagine if all the spent catalysts were disposed, there might be no more space for living. The surrounding area might be too hazardous because of the radioactive conditions from the metal waste, and the poisons of the spent catalysts itself.

## CHAPTER 2

### LITERATURE REVIEW AND THEORY

#### 2.1 METHANOL PROCESSING FLOW DESCRIPTION

In PETRONAS Methanol Labuan (PML), the main processing units involved are steam reforming, autothermal reforming, methanol synthesis and methanol purification. The feed to this unit operation is the natural gas. The simplified process flow diagram of this process is shown in Figure 2.1.

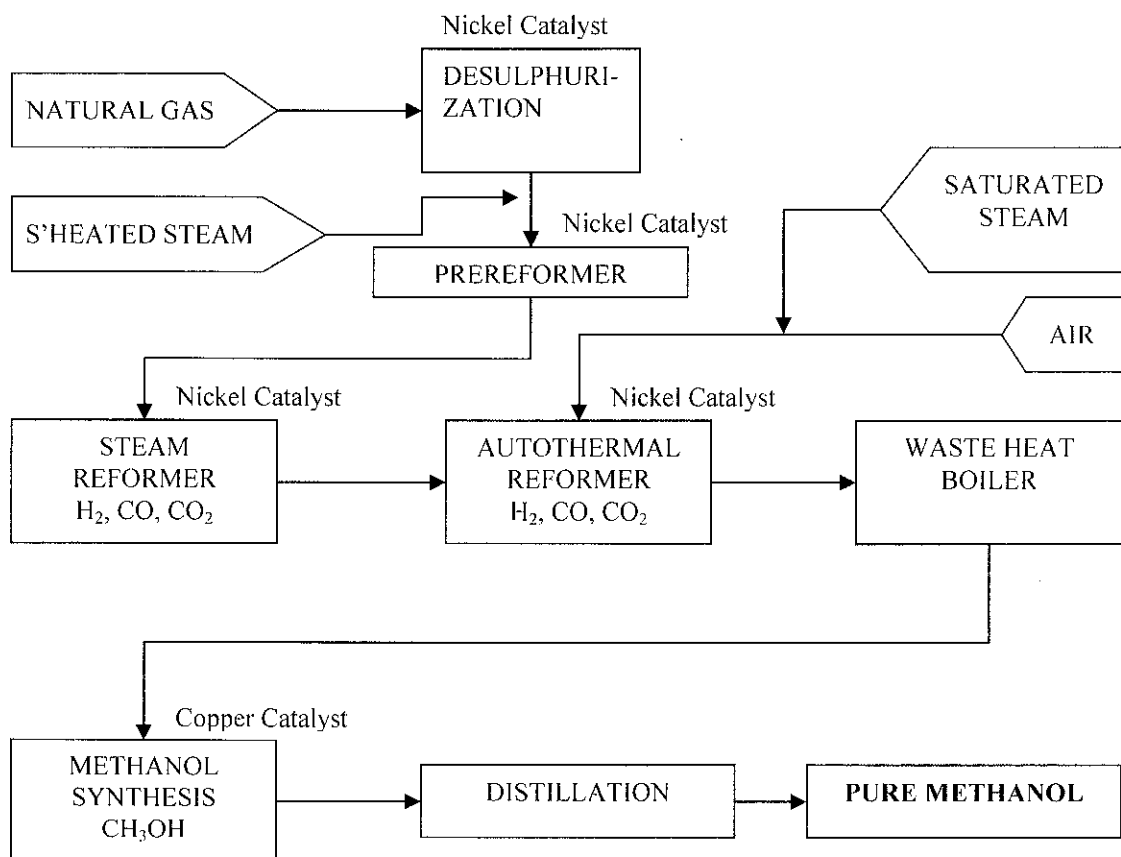
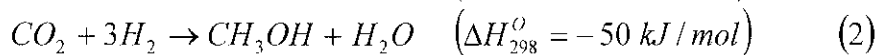
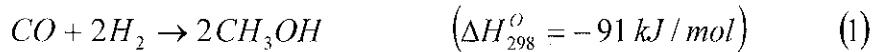


Figure 2.1: The simplified process flow diagram of the LURGI reforming process in Petronas Methanol Plant, Labuan (PML)



Basically, the LURGI (LPCR) process has the desulfurization unit to remove all sulfur in the feed whereby zinc oxide is used as the catalyst. Next, the output of the desulfurization unit will be fed to pre-reformer unit where nickel catalyst supports the prereforming reaction. Nickel is also used in the steam reformer unit and autothermal reformer unit before the product of the unit is fed to methanol synthesis unit to produce methanol and water. The chemical reactions involved in this unit are as follows:



This reaction is slightly exothermic and the equilibrium composition is affected by pressure. Theoretically, for the methanol process, a water-gas shift reaction also takes place [1];



In PML, there are five units processing of reactions which involve catalysts consumption. The catalysts used are zinc oxide for desulfurization, nickel catalysts for pre-reformer, steam reformer and autothermal reformer, and copper catalysts for methanol synthesis. Over the years, PML spent a large amount of money for catalysts disposal and purchase of new catalysts since all the catalysts tend to degrade after certain time of processes.

The main concern here is to look at the copper catalysts, in the methanol synthesis unit. The catalyst used is C79-5-GL, which comprise the Cu/ZnO and alumina. The compositions of this catalyst are listed in the Appendix 2-1.

## 2.2 CATALYSTS FAILURE DUE THE POISONS EXISTENCES

On metal surfaces, the presence of adsorbed species containing sulfur, carbon, and halogens are the most serious causes of catalysts poisoning. The presence of such foreign species on the catalyst surface not only can block reaction sites, but can induce changes in surface morphology due to faceting, which results in preferential segregation of one component in a multi-component metal catalyst particle, enhance sintering as result of adsorbate-induced diffusional transport of metal surface components, and modify metal support interactions [1].

### 2.2.1 Thermodynamics of Adsorption and Segregation

The thermodynamic properties of the surface adlayer interface play an important part in controlling the compositional and structural heterogeneities caused by catalysts poisoning. Equilibrium adsorption (or segregation) is accompanied by a decrease in the total energy of the system. Because of differences in local environment, the bonding of adspecies at the surface can exhibit configuration different from those encountered in the bulk phase. To obtain the relationship between the equilibrium surface density of adspecies and their concentration in the gas phase, it is most useful to employ the Gibbs “dividing surface” rule [1].

The isothermal change in surface tension in the presence of an adsorbate is obtained; where  $\gamma$  is the surface tension and  $\Gamma_i$  is the specific surface area.

$$d\gamma = -RT \Gamma_i d \ln p_i \quad (4)$$

$$\therefore \gamma = \gamma_0 - RT \int \Gamma_i d \ln p_i \quad (5)$$

Based on the Gibbs adsorption isotherm above, a surface adsorbate causes a decrease in the surface tension of a solid (metal) [1].

### **2.2.2 Adsorbate-Induced Surface Modification**

The adsorption of a strongly bonded species may induce complex changes in the structure of a metallic substrate. Therefore, the interplanar spacing normal to the surface may be altered (surface relaxation). Besides, the rearrangement of the atoms in the topmost plane of the crystal may occur (surface reconstruction). Finally, the adsorbate can cause drastic changes in the equilibrium shape of the crystal, which can induce instability of certain monatomic steps (two dimensional faceting) or planes (three dimensional faceting) [1].

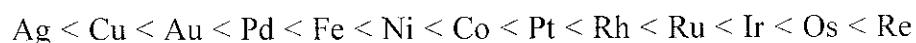
### **2.2.3 Surface Segregation and Interfacial Support**

The mechanical properties of metals can be markedly affected by the presence of impurities which segregate to the grain boundaries. Examination of the transferred interfaces has shown that the segregation impurities are localized in the very narrow region which constitutes the grain boundary. The analogy between surface and grain boundary segregation is further reinforced by the fact that faceting can occur in both cases by segregation of specific impurities [1].

## **2.3 DEACTIVATION MODES**

### **2.3.1 Thermal Sintering**

For metals, the predominant sintering mechanism in the bulk is vacancy diffusion, which suggests a relationship with cohesive energy. Following is the increasing order of stability for metals:



Copper has a relatively low melting point (1083°C) compared with, iron for example (1535°C) and nickel (1455°C). Therefore, copper based catalysts have to be operated at relatively low temperatures, usually not higher than 300°C [5].

New formulations were developed containing  $\text{Cr}_2\text{O}_3$ , and later  $\text{Al}_2\text{O}_3$ , in addition to  $\text{CuO}$  and  $\text{ZnO}$  in the unreduced catalyst. The thermal stability of these catalysts was significantly higher. It is apparent from data shown in Figure 2.2, as well as extensive other results, thermal sintering can be controlled in well-formulated catalysts manufactured under optimal conditions, provided they are operated under well-controlled conditions.

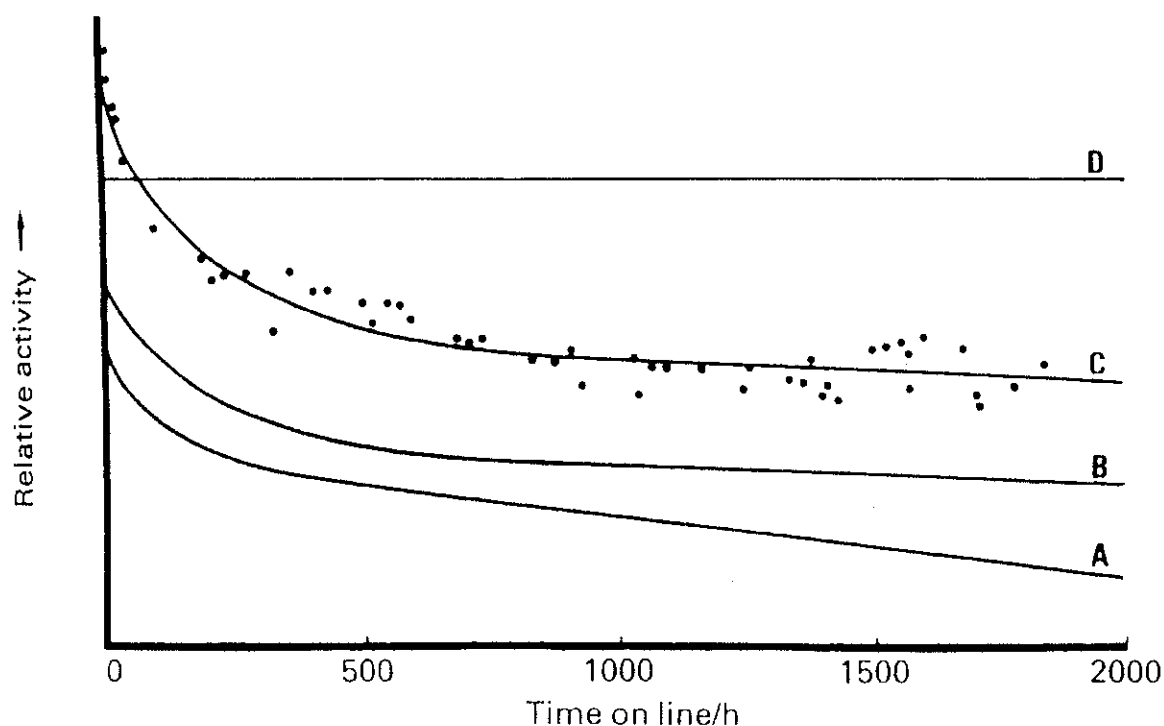


Figure 2.2: Relative activities of typical copper/zinc oxide under poisons free conditions. (A)  $\text{Cr}_2\text{O}_3$ -based catalyst; (B) conventional  $\text{Al}_2\text{O}_3$ -based catalyst; (C) high copper-content  $\text{Al}_2\text{O}_3$ -based catalyst; (D) optimized  $\text{Al}_2\text{O}_3$ -based catalyst. For clarity, experimental points are shown on only one of the curves [5].

### 2.3.2 Carbon Deposition (Coking)

The morphology of the carbon adlayer on metal surfaces plays an important role in catalyst deactivation. In morphological terms, the surface carbons encountered on catalyst surfaces may be divided in the following groups on the basis of varying degrees of metal-carbon or carbon-carbon bonding [1];

- i. Adsorbed carbon atoms bound predominantly to metal sites
- ii. Carbon-atom clusters with a mixture of interlayer carbon-metal bonds and interlayer carbon-carbon bonds
- iii. Amorphous carbon in the form of filaments, whiskers, or fibers characterized by three dimensional arrays
- iv. Crystalline graphite in the form of platelets and fibers
- v. Metal carbides, which in the case of transition metal carbides consist of carbon chains distributed through highly distorted metal lattices, as contrasted to interstitial carbides, in which each carbon occupies an octahedral void in the close-packed metal structure

Unlike reactions involving transition metal catalysts such as those containing iron, nickel or cobalt, or acidic catalysts such as zeolites or sulphated zirconias, Cu catalysts have no strong tendency to catalyze Fischer-Tropsch reactions, or processes involving carbonium ion chemistry. Copper also has a very low activity for breaking C-O bonds or forming C-C bonds and as a result, wax formation is not usually a major problem in CO/H<sub>2</sub> reactions, nor is formation of coke from hydrocarbons. These potential problems are further reduced by the fact that Cu catalysts must be operated at fairly low-temperatures to minimize thermal sintering [5].

### 2.3.3 Sulfur Poisoning

On the basis of geometric consideration, it is apparent that a sulfur atom has an effective blocking radius extending over a number of nearest and next-nearest neighboring metal

atoms. In addition to the occupied hollow site, a sulfur atom may block adjacent sites, depending on the substrate lattice dimension and the surface plane exposed [1].

Operating catalysts at low-temperature thermodynamically favours adsorption of poisons, giving high surface coverage. As a result, copper catalysts are extremely sensitive towards site-blocking poisons, and they are particularly sensitive to even very low levels of poison such as reduced sulphur or phosphorus species. Under normal operating conditions, sulfur is a powerful poison for Cu [5]

### 2.3.4 Chloride Poisoning

The chloride poisoning of Cu catalysts can operate by several parallel mechanisms [5];

- i. Reaction to give adsorbed chlorine atoms that can block or modify catalytic sites
- ii. The low melting point and high surface mobility of Cu(I) chloride (Table 2.1) mean that even extremely small amounts of copper halide are sufficient to provide mobile species that accelerate the sintering of Cu catalysts
- iii. Poisoning of Cu catalysts by reduced sulfur compounds (e.g. H<sub>2</sub>S) is exacerbated by traces of mobile Cu(I) chloride
- iv. Further, ZnO, often present in Cu catalysts, reacts to form Zn halides, which also have low melting points, and causes further poisoning and sintering problems

TABLE 2.1: Melting points of copper, iron and nickel and some of their compounds

	Melting point (°C)			
	Metal	Chloride	Bromide	Sulfide
Copper	1083	430	492	1100
Iron	1535	674	684	1195
Nickel	1455	963	963	790

Consequently, even extremely small amounts of chloride provide the species necessary for a surface migration sintering mechanism of Cu crystallites. Similar processes

involving ZnO take place when chloride is present because zinc chloride species ( $\text{ZnCl}_2$ , mp  $283^\circ\text{C}$ ) also have high surface mobility, and this also contributes to a destructive destabilization of catalytic activity via structural changes that decrease thermal stability.

Figure 2.3 illustrates the decrease in water-gas-shift activity following introduction of a small amount of HCl into the feed gas. Chloride poisoning is particularly difficult problem for water-gas-shift plant operators because it is usually present in process gas in amounts below the normal levels of detection. However, depending on the catalyst concerned, chloride can be retained at the top (inlet region) of the catalyst bed, usually in the form of zinc hydrochlorides, with the result of the overall catalyst charge is partially self-guarding. These species, however, soluble in hot water and it is, therefore, important to avoid conditions that give condensation. Otherwise, condensation will wash chloride further into the bed [5].

It is clear that admission of chloride to process streams involving Cu catalysts should always be kept to an absolute minimum. Strict attention has to be paid to feedstock purity, and traces of chloride have to be removed with an alkali absorbent that has high affinity for HCl during feedstock purification. Similarly, chlorinated solvents should not be used during maintenance operations, and on sites, where gases such as hydrogen are imported, care is necessary to confirm their quality. [5]

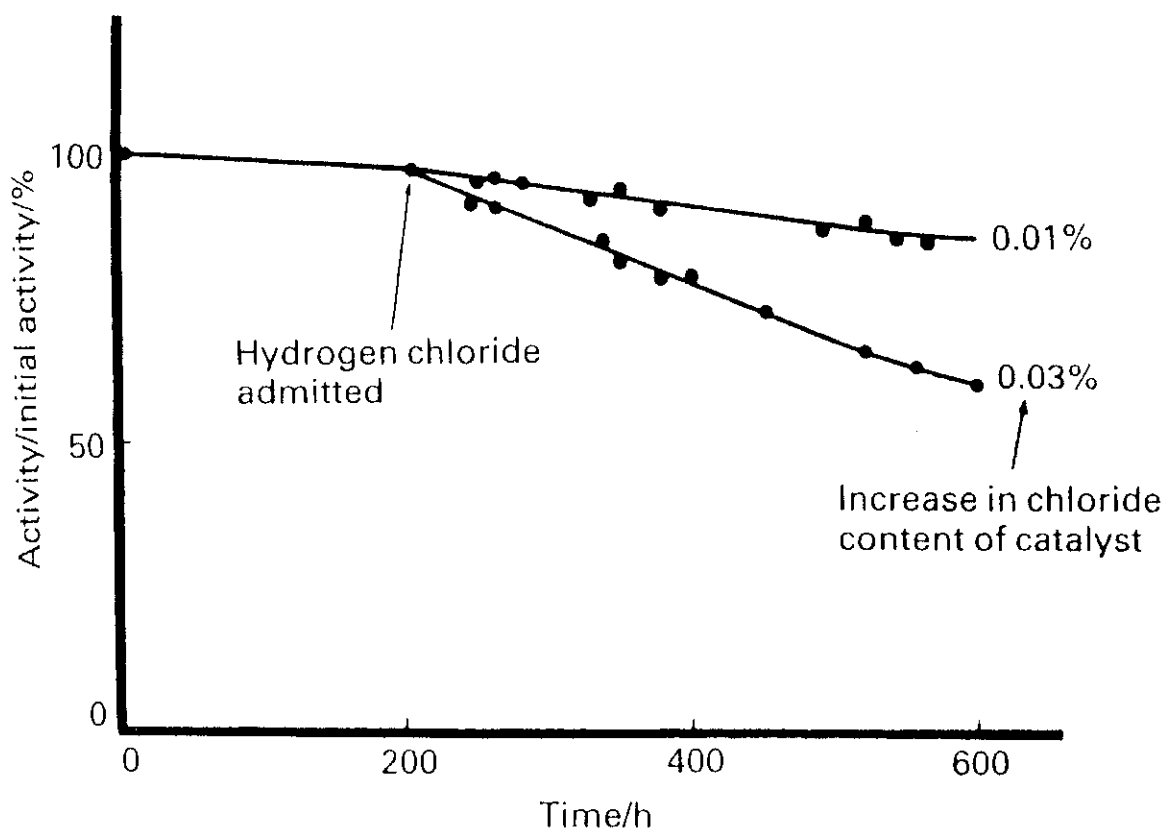


Fig. 2.3: Effect on activity of very small amount of HCl on the water-gas shift activity of a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst

### 2.3.5 Other Poisons

Other poisons for Cu catalysts include arsenic, which might come from some types of CO<sub>2</sub> removal systems in hydrogen or ammonia plants, and trivalent phosphorus, which could originate from boiler water feed treatment, but in practice, these are seldom actually encountered. Silica, transition metals such as iron, cobalt and nickel may also occur as poisons in some processes. [5]

### 2.3.6 Physical Damages

Physical damage is rarely a significant cause of deactivation in Cu catalysts. The main causes of physical damage in other catalytic systems are;

- i. The formation of carbonaceous deposits within the catalyst pore system [5]



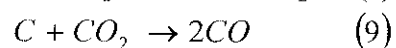
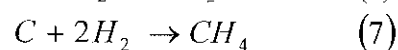
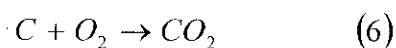
- ii. Catalyst attrition in fluidized or moving bed processes. [5]
- iii. Catalyst attrition due to unloading and loading activity

Copper catalysts, rarely suffer from carbonaceous deposits. None of the main hydrogenation processes using copper catalysts were designed as fluidized or moving bed processes, so this cause of damage is not encountered, but some kinds of plant maloperation can lead to physical damage of any catalyst. For example, inadvertent exposure to hot liquid water can sometimes cause physical breakage of catalyst pellets. Copper catalysts are especially susceptible to careless temperature excursions that lead to excessive sintering of the copper crystallites and irreversible loss of activity. [5]

## 2.4 HANDLING OPTIONS

A few options in dealing with the spent catalyst are catalyst disposal, regeneration, metal recovery and also utilization of spent catalyst as raw materials to produce other valuable products. However, initial prevention before the poisons or impurities disturb the catalyst performance is preferred. The best method of handling must be obviously relying on the cause of catalyst decay.

Various forms of carbonaceous deposits, known collectively as coke, are by far the most common catalyst foulants. All carbonaceous deposits may be removed by gasification as described by the generalized reactions;



For the poisoned catalyst, reactivation is a possible way of catalyst's regeneration. However, it is reusable if only the poisoning processes are reversible. If not, the catalyst

must be discarded [3]. Again, however, prevention is the preferred option, either by using a guard process such as hydrodesulfurization, a guard bed such as zinc oxide or by including additive in the catalyst that will selectively adsorb sulfur, taking example as a popular poison.

Thermal degradation, particularly sintering is very hard to reverse and prevention is better much than after treatment. In general, catalysts undergoing thermal degradation cannot be rejuvenated and replacement is necessary. The most common strategy involves prevention of sintering either by controlling conditions or by stabilizing the catalyst [3].

# CHAPTER 3

## METHODOLOGY

### 3.1 PROJECT METHODOLOGY

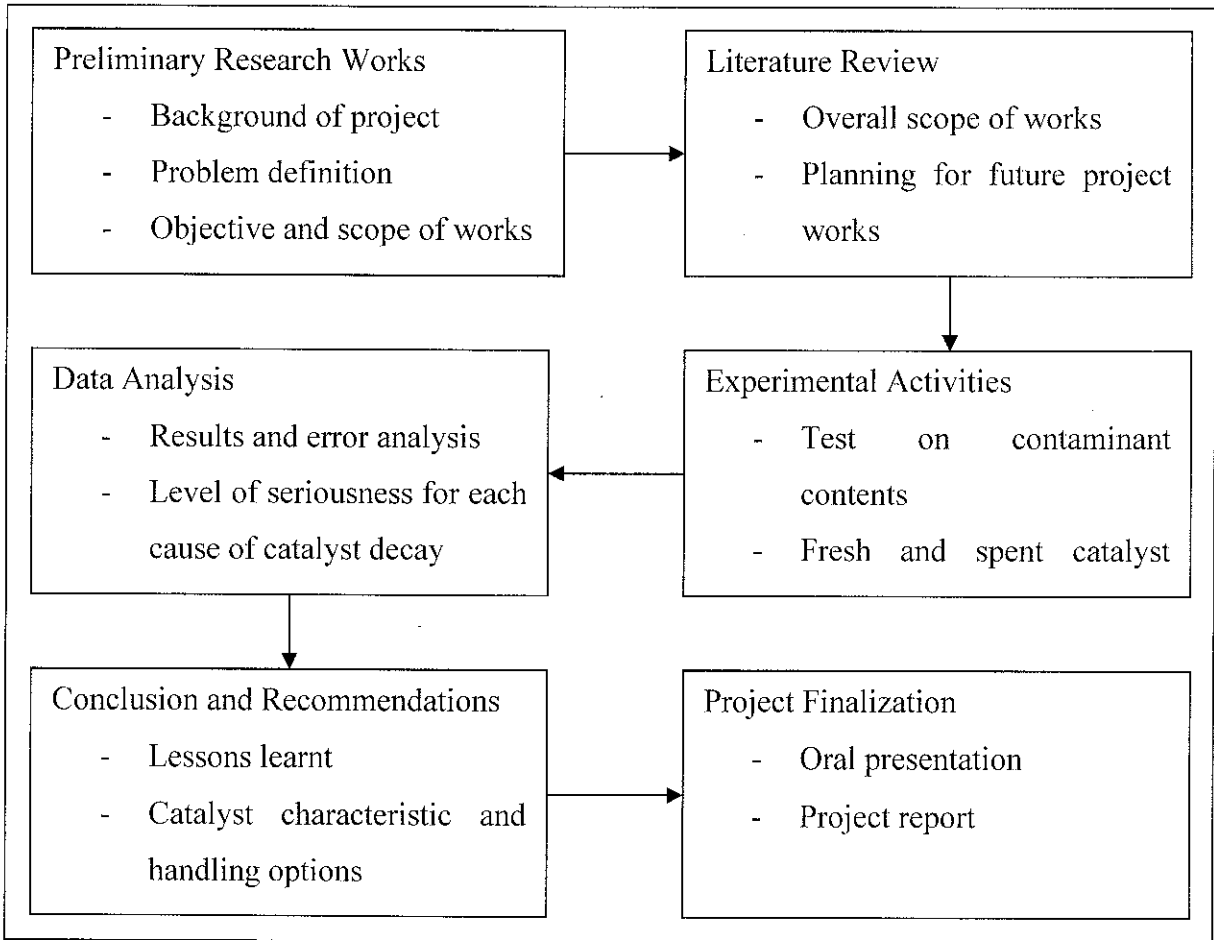


Figure 3.1: Project Methodology

The Gantt Chart of the project is attached in Appendix 3-1.

## 3.2 TOOLS AND EQUIPMENT

To achieve the project objectives, a few series of experiments and analyses were carried out. Followings are the equipment used to characterize the catalysts;

TABLE 3.1: Equipment Involved In Catalysts Characterization

EQUIPMENT	FUNCTION AND CHARACTERIZATION PROPERTIES
1. Temperature - Programming Desorbtion, Reduction and Oxidation (TPDRO)	To determine the desorbtion, reduction and oxidation profiles of the catalyst using temperature programmed equipment, to measure metal surface area, dispersion percentage, mean particle diameter and also to determine BET surface area using N <sub>2</sub> (liquid)
2. Carbon, Hydrogen, Nitrogen, and Sulphur (CHNS) Analyzer	To measure carbon, hydrogen, nitrogen and sulfur contents on the catalysts
3. Scanning Electron Microscope (SEM)	To study surface morphology
4. Energy Dispersion X-ray (EDX)	To measure metal composition of a heterogeneous catalyst (The test was conducted together with SEM)
5. X-ray Diffraction Unit (XRD)	To determine the elemental species
6. Pycnometer	To measure density
7. Fourier Transform Infrared (FTIR)	To observe functional groups in the catalyst

The pictures of equipment used are attached in Appendix 3-2.

### 3.3 TEST PROCEDURES FOR PHYSICAL PROPERTIES DETERMINATION

Experiments were conducted using both the fresh and spent catalyst pellets. The fresh and spent catalysts were obtained from PETRONAS Methanol Plant, Labuan. The catalysts composed by Cu/Zn/Al<sub>2</sub>O<sub>3</sub>.

#### 3.3.1 XRD

The procedures of XRD experiment are as follows;

- 1) All the samples were scanned using Cu K $\alpha$  (nickel-filtered) radiation the range  $10^{\circ} < 2\theta < 75^{\circ}$  in the step mode
- 2) The mean crystallite sizes of CuO and ZnO were determined from the line broadening of the diffraction lines for CuO and ZnO respectively

#### 3.3.2 SEM

The catalyst's morphology was observed using SEM and the procedures are:

- 1) One pellet of fresh and spent catalyst were placed on the stand and labeled
- 2) The samples were coated the gold palladium metal to reduce the oxide effect on catalyst, which block the microscope lenses
- 3) The coated samples were then put on microscope and analyzed at EHT = 25 kV, working distance 10/ 15 mm and Magnification 5000X

#### 3.3.3 Pycnometer

The density of the catalyst was measured by a Pycnometer, using helium gas. The procedures are as the followings:

- 1) catalyst pellets were put in the holder and located in the Pycnometer after the total mass were recorded
- 2) The helium gas was passed through the samples to measure the density, and steps were repeated with spent catalyst sample

## 3.4 TEST PROCEDURES FOR CHEMICAL PROPERTIES DETERMINATION

### 3.4.1 SEM/ EDX

The EDX was conducted together with the SEM analysis. To obtain the metal composition of the catalyst, liquid nitrogen was used. All the metals that were going to be analyzed were chosen from the periodic table in the EDX software and the percentage of the metals were obtained.

### 3.4.2 FTIR

The samples analyzed were prepared in powder form and mixed with KBr. The samples were scanned using FTIR by following settings;

- Range: Start at  $4000\text{ cm}^{-1}$  and end at  $1000\text{cm}^{-1}$
- Scan number: 40
- Resolution: 4
- Angle:  $45^\circ$

The steps for the experiments were;

- 1) The catalysts powder was put in the mortar and grind with the pestle, together with the KBr to dilute the sample
- 2) The grind sample was put in the holder and pressed using Hand Press
- 3) The sample was then analyzed using FTIR equipment and peaks were analyzed

### 3.4.3 CHNS

CHNS analyzer determined the percentage of carbon, hydrogen, nitrogen and sulfur existed in the catalysts. The procedures for CHNS are as follows;

- 1) The fresh and spent catalysts were prepared in powder form, encapsulated in a tin capsule and weighted
- 2) The sample was then dropped into the furnace at the same time, oxygen passed over

- 3) As the sample entered the combustion chamber, oxygen was injected for complete oxidation to occur

#### **3.4.4 TPR**

TPR analysis was conducted to determine the reduction temperatures of fresh and spent catalysts. The metal surface area was also determined from the TPR experiment.

- 1) The samples were treated in a U-shaped reactor at 553 K (1 hr) in a O<sub>2</sub>/He mixture (10 vol%, 60 mL/min)
- 2) The initial temperature was set to be 28°C and stopped at 600°C, and other experiment data were keyed in into the computer
- 3) The TPR experiment was carried for 1 hour

#### **3.4.5 TPO**

TPO analysis was carried out using the oxygen in helium mixture. The TPO was conducted to obtain the profile of oxidation processes for fresh, spent and standard (CuO) sample.

- 1) The samples placed in a U-shaped reactor was first reduced at 553 K (1 hr) in a O<sub>2</sub>/He mixture (10 vol%, 60 mL/min) for 1 hour
- 2) The initial temperature was set at 28°C and final temperature was set at 600°C, other experiment data were keyed in into the computer
- 3) The TPO experiment was conducted for 1 hour

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 PHYSICAL PROPERTIES OF CATALYST

##### 4.1.1 XRD

The results obtained from the XRD tests are attached in Appendix 4-1 and Appendix 4-2. The summary of the results is as follows;

TABLE 4.1: XRD results

SAMPLE	FRESH (2 $\theta$ -scale)	SPENT (2 $\theta$ -scale)	LITERATURE (2 $\theta$ -scale) [6, 7, 8] Fresh and spent)
(1) ZnO	31.8, 35	31.8, 35.5, 37, 56.5	31.8 [6, 7, 8] 35.5, 37, 47.5, 56.5, 63 [6, 8]
(2) CuO	39	39, 63	39 [7, 8] 49.5, 68, 70 [8] 63 [6, 8]
(3) Cu	(not observed)	(not observed)	43 , 50.5 [6],
(4) CuAl <sub>2</sub> O <sub>4</sub>	32	32, 68	32, 58.5 [6]
(5) Cu-Zn	(not observed)	(not observed)	42, 45 [6]
(6) CuAl <sub>2</sub> O <sub>2</sub>	(not observed)	36.5	36.5 [6]

For fresh catalyst, only a few peaks were observed. Peaks for fresh sample occurred at  $2\theta = 12, 15, 17.5, 23.5, 31.8, 32, 35$  and  $39$ . The peaks occurred at scale 30 and below cannot be identified because the interpretations are not included in the literature. The peaks occurred at  $31.8^\circ$  and  $35^\circ$ , indicate the presence ZnO in the catalysts. CuO is indicated by peak occurs at  $2\theta = 39$ . The peak at  $2\theta = 32$  observed for fresh sample indicates the presence of CuAl<sub>2</sub>O<sub>4</sub>.



In the spent catalysts, peaks for ZnO and CuO were observed as sharp signals. There were nine peaks observed at  $2\theta = 31.8, 32, 35.5, 36.5, 37, 39, 56.5, 63$  and  $68$ . The presence of CuO was indicated by peaks at  $39^\circ$  and  $63^\circ$ . ZnO was represented by peaks occurred at  $2\theta = 31.8, 35.5, 37$  and  $56.5$ . For spent catalysts, the existence of  $\text{CuAl}_2\text{O}_4$  was shown by the peaks at  $32^\circ$  and  $68^\circ$ , but it was not observed in fresh sample. There's a peak occurred at  $36.5$  which referred to  $\text{CuAl}_2\text{O}_2$  presence. The XRD peaks for spent catalysts are sharper and narrower compared to those of fresh catalyst. It was evident that industrial conditions produce an increase in the crystal size, due to thermal sintering [6]. No peak was observed due to Cu-Zn alloy formation presence in the fresh and spent catalysts.

#### 4.1.2 SEM

SEM analysis was conducted at 5000X Magnification for both samples, with working distance 10 mm.

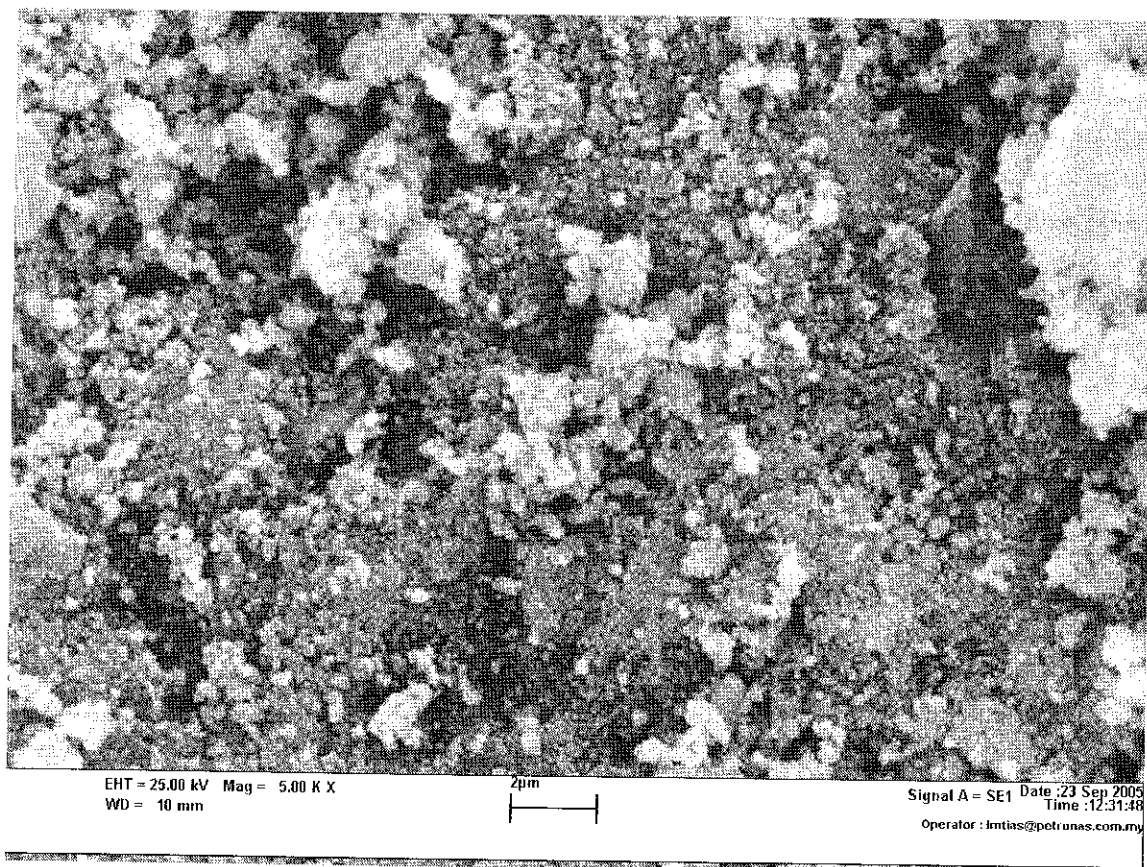


Figure 4.3: Morphology of fresh catalyst, obtained from SEM analysis

Oxide components are represented by the white dots on the fresh catalyst as shown in Figure 4.3. It shows that the metals (Cu/Zn/Al) exist in the oxide form. The particles are very small and have similar sizes as the others.

The result of spent catalyst is represented by Figure 4.4. It can be seen that the white particles (oxides) are less than the fresh catalysts. The particle size appeared larger than that of fresh catalyst, indicating thermal sintering had occurred. Copper has a relatively low melting point (1083°C) and therefore, copper based catalysts have to be operated at relatively low temperatures, usually not higher than 300°C [6].

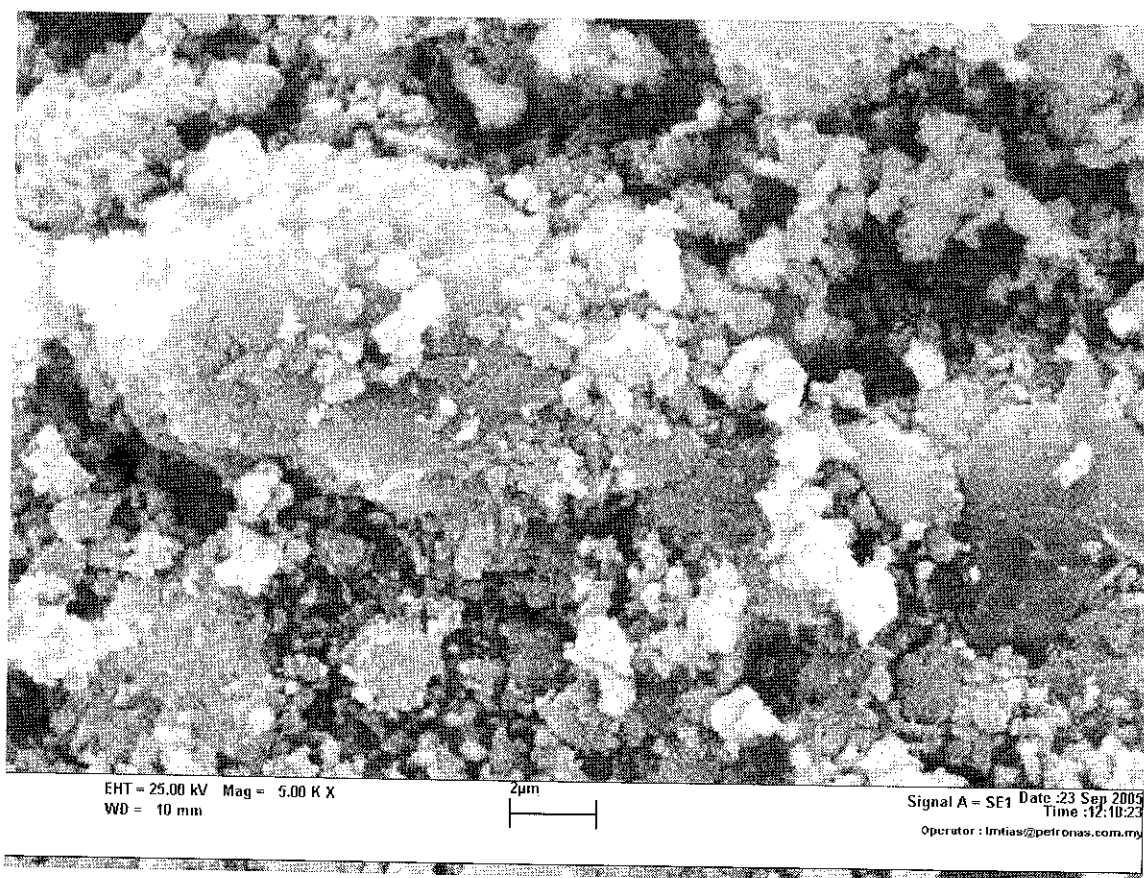


Figure 4.4: Morphology of spent catalyst, obtained from SEM analysis

### 4.1.3 TPR and TPO Analysis (Metal and BET Surface Area)

The complete results of surface area determination are attached in Appendix 4-3 and Appendix 4-4. The summary of the results is as follows;

TABLE 4.2: Surface characterization

PROPERTIES/ SAMPLE	FRESH CATALYST	SPENT CATALYST
BET surface (m <sup>2</sup> /g)	109.48	71.15
Total metal surface (m <sup>2</sup> )	6.70	6.01
Metal surface (m <sup>2</sup> /g)	64.3	41.8
Dispersion degree	11.46	7.45
Total metal (%)	7.22	4.69
Mean particle diameter (nm)	14.38	22.12

From the results obtained, the BET<sup>1</sup> surface area and metal surface area of fresh sample were higher than the spent catalysts. The fresh catalysts also had higher dispersion percentage than the spent catalysts, related by smaller particle size. These results show that the particle diameter of catalysts increased after it had undergone industrial processes. Therefore, the increase in particle size led to a decrease in BET and metal surface area. The catalysts had experienced thermal sintering, as indicated by the increase in particle size.

### 4.1.4 Pycnometer

From the experiment, it was found that density for spent catalyst was slightly higher than the fresh catalyst (See Appendix 4-5 and Appendix 4-6). The mass for both samples was similar, 1.1245 grams for fresh and 1.1222 grams for spent respectively. These were the total mass for 5 pellets of catalysts being used for this experiment. The average solid volume for spent catalysts seemed to be decreased after the catalyst had

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<sup>1</sup> Surface area based on Brunaur, Emmett and Teller (BET) definition. These people derived isotherm for multilayer physical adsorption.

undergone industrial processes, and the difference was quite huge. The catalysts lost about 0.1466 cc of volume after it was used in the methanol processing. The results of this experiment are summarized in Table 4.2.

TABLE 4.3: Summary of Pycnometer results

SAMPLE	MASS (g)	AVERAGE VOLUME OF SOLID (cc)	AVERAGE SKELETAL DENSITY (g/cc)
Fresh	1.1245	0.1983	5.6718
Spent	1.1222	0.0517	21.7039

The results indicate that the volume of the catalysts reduced after it was used in the industry, possibly due to the presence of more void spaces between the catalyst particles. The Pycnometer measured the density by calculating the ratio of mass over solid volume of the material used. All the void spaces (pores volume) was deducted and eliminated in the calculation. Hence, the results showed that there were more void spaces in spent catalysts and caused the skeletal density of spent to be higher than that of fresh catalyst. The increase of skeletal density might be due to catalyst attrition during loading and unloading activities.

## 4.2 CHEMICAL PROPERTIES OF CATALYSTS

### 4.2.1 SEM/ EDX

The quantitative results of metal composition for fresh and spent catalyst are shown in Figure 4.5 and Figure 4.6. The results were analyzed at Magnification 1103 X and the accelerating voltage used was 25 kV. The process time used was 5.

### Quantitative results

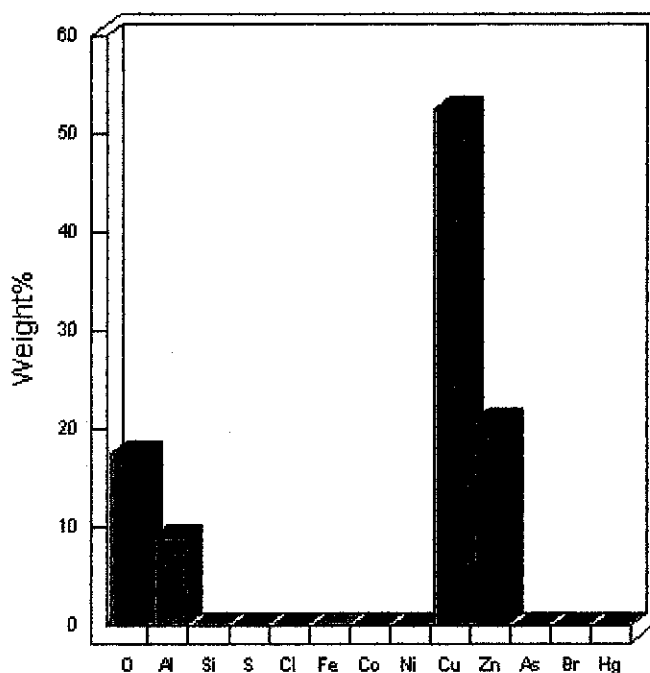


Figure 4.5: Metal composition for fresh catalyst obtained from SEM and EDX analysis

Four metals were observed, which were oxygen, aluminium, copper and zinc. The oxygen had 17.55 wt% and aluminium was 9.03 wt%. The copper and zinc were 52.51wt% and 20.92wt% respectively. No other metal were observed and the complete result is attached in Appendix 4-7.

In Figure 4.6, the analysis at 1103X showed that spent catalyst composed of 4 main components, carbon, oxygen, copper, and zinc (refer Appendix 4-8) for complete result). The carbon content was 10.13 wt% and the atomic percentage was 23.93%. Copper and zinc weight percentage were 31.18 and 30.85 respectively. The oxygen was 27.33 wt% of the overall catalyst. Other metal observed was Fe, 0.5 wt%. At this spot, no aluminum was observed.

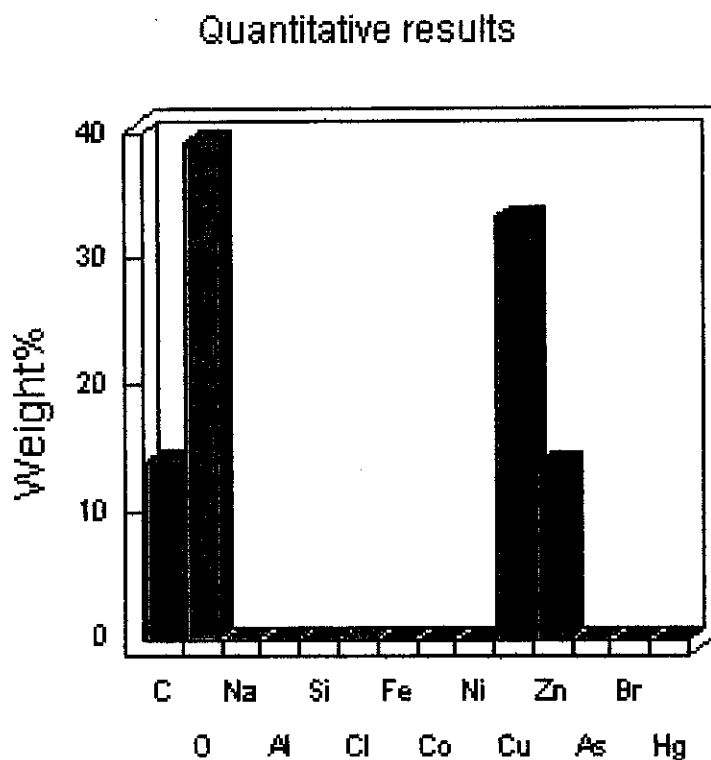


Figure 4.6: Metal composition for spent catalyst obtained from SEM and EDX analysis

By comparing the fresh and spent catalyst, more copper but less zinc were observed in fresh. However, no aluminum was observed in spent catalyst. More oxygen in fresh catalyst indicates that more oxide material at the 1103X spot. It was hard to conclude the exact value of metal compositions in the catalysts sample because only one pellet was used for each test. The EDX only measured the metals those present within the spot range of SEM.

#### 4.2.2 FTIR (Fourier Transform Infrared)

The results of FTIR analysis for fresh and spent catalysts are shown in Appendix 4-9 and Appendix 4-10 respectively. The summary of the results are shown in Table 4.3.

TABLE 4.43: FTIR results

SAMPLE	WAVENUMBER (cm <sup>-1</sup> )	FUNCTIONAL GROUP
Fresh	1020 - 1080	S=O Stretching
	1350 - 1410	Combination C-H stretching
	1470 - 1530	N-H stretching
	1620 - 1700	C-H stretching
	3000 - 3660	O-H Bending
Spent	1590 - 1710	C-H stretching
	3000 - 3660	O-H Bending

The O-H bending for fresh catalyst ranged from 3000-3660 cm<sup>-1</sup> wavelength showing the existence of moisture in the catalyst. The N=H and C=H stretching were also observed at wavelength ranged from 1470-1530 cm<sup>-1</sup> and 1620-1700 cm<sup>-1</sup>. The result also showed the S=O stretching at 1020-1080 cm<sup>-1</sup> indicating the existence of sulfur in the catalyst [8, 9].

Only O-H bending was clearly showed in the spectroscopy analysis for spent catalyst sample. Besides, at 1590-1710 cm<sup>-1</sup> the C-H stretching was noted indicating the existence of hydrogen in the sample [8, 9].

### 4.2.3 CHNS Analysis

The CHNS analysis (see Appendix 4-6) determined the carbon, nitrogen, hydrogen and sulfur of fresh and spent catalysts. The carbon content was 3.4% and 3.7% the spent and fresh samples respectively. The carbon contents for both samples were higher than the amount given by manufacturer. The result also showed that the average sulfur content for fresh sample was 0.017%, which was lower than allowable sulfur content given by manufacturer (0.04%). On the spent catalyst, 0.05% sulfur was obtained from the test indicated that the catalysts might have been poisoned by sulfur [5].

#### 4.2.4 TPR Analysis

The detail TPR results for fresh and spent catalysts are shown in Appendix 4-12. Figure 4.7 shows the TPR curves for standard CuO sample together with the fresh and spent catalyst. The samples were exposed to 5.42% H<sub>2</sub>/He and were heated from 25°C to 600°C. This treatment only caused CuO species to be reduced whereas other components such as Al<sub>2</sub>O<sub>3</sub> and ZnO will not be reduced. The TPR profile for standard CuO sample is symmetrical indicating a homogeneous sample.

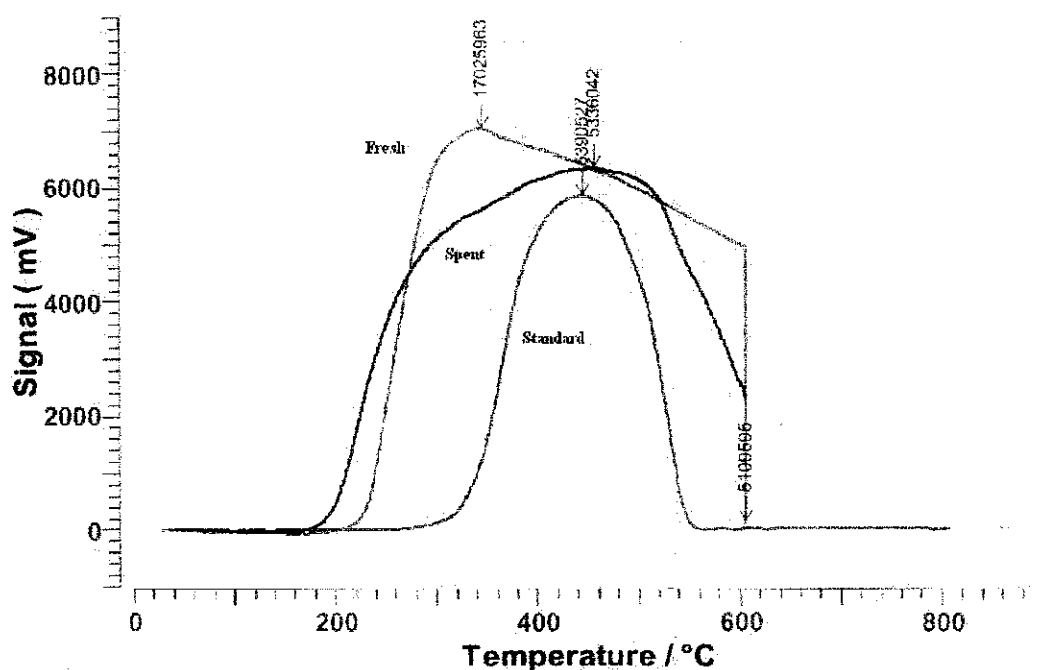


Figure 4.7: TPR patterns for fresh, spent and CuO standard samples

The amount of hydrogen consumed as per attached in the Appendix 4-13 corresponds to reduction of Cu(II) to Cu(0) [5]. For comparison purposes, the reduction of standard CuO was also included, and the three profiles were combined together so that the analysis could be done easily. The area under the curve represented the total amount hydrogen consumption. The summary of TPR results is shown in Table 4.5.



TABLE 4.5: TPR results

SAMPLE	TPR PEAKS ( $^{\circ}\text{C}$ ) (Max. temperature required for complete reduction)
Fresh	344
Spent	456
Standard	445

For the fresh sample, a peak observed at  $344^{\circ}\text{C}$ , with hydrogen consumption of  $8473.4387\mu\text{mol/g}$ . However, a shoulder was observed at the higher temperature indicates strong interaction between CuO and ZnO. Large amount of hydrogen consumed for reduction indicating that more oxides component in the fresh catalysts. The peak for spent catalyst was broader than spent and standard CuO sample.

For fresh catalyst, the reduction property of Cu(II) to Cu(0) was distinguishable because Cu(II) were highly concentrated [5]. This could be due to;

- A broadening of the peaks in presence of high amount of Cu (II)
- The large heat released that increased the temperature of the sample speeding up the second reduction step

Highly dispersed CuO gave TPR signals at lower temperature than bulk CuO [5]. Therefore, from the results it showed that the fresh catalysts having high dispersion percentage and hence gave lower reduction temperature than bulk CuO.

The TPR profile for spent showed a reduction peak which occurred at  $456^{\circ}\text{C}$ . The peak of spent catalysts showed the reduction step of Cu(II) to Cu(0). Compared to the fresh catalyst, higher temperature was required to complete the reduction process of spent catalyst, indicating larger CuO particles [8]. Therefore, it could be concluded that the spent catalysts deactivated due to thermal sintering which caused the particles sizes to larger and this conclusion was supported by BET surface area and SEM result.

## 4.2.5 TPO Analysis

Figure 4.8 shows the TPO profiles for standard CuO, fresh and spent catalysts. The TPO process was carried out after the reduction process. Thus, it was assumed that no oxides components were not present in the samples before TPO analysis. The oxidation process was carried for 1 hr in 5% O<sub>2</sub>/He and stopped at 600°C. (See Appendix 4-14 and Appendix 4-15 for complete results of TPO)

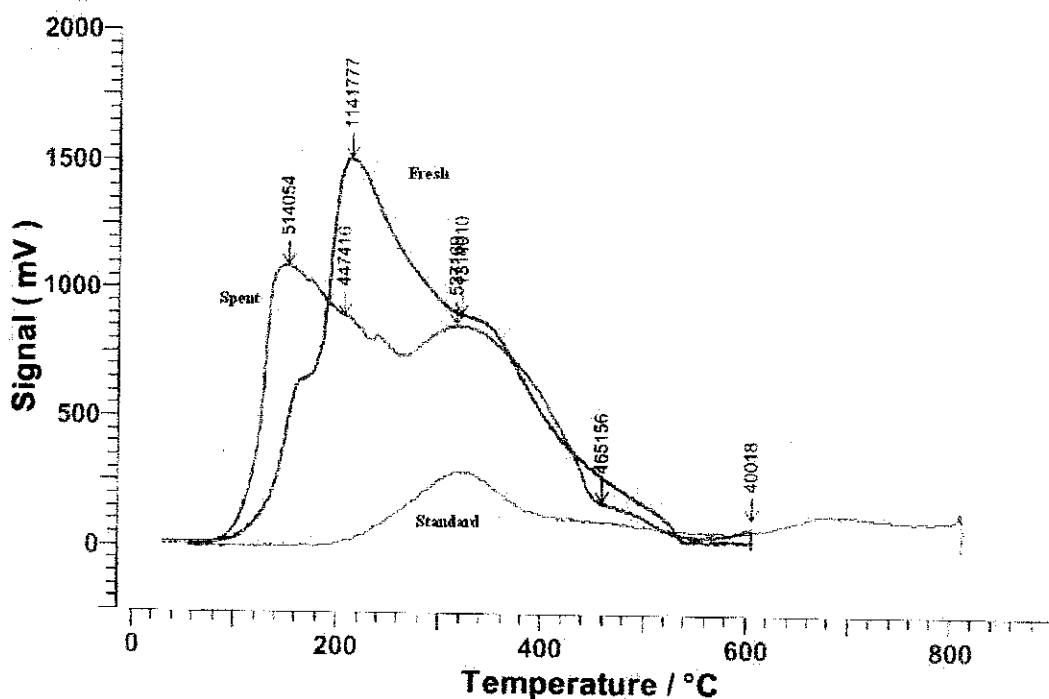


Figure 4.8: TPO patterns for fresh, spent and CuO standard samples

The results of TPO analysis is summarized in Table 4.4

TABLE 4.6: TPO results

SAMPLE	TPO PEAKS (°C) (Max. temperature required for complete oxidation)
Fresh	213, 320
Spent	185, 316
Standard	320

From the TPO plot, profile for spent samples was quite complex and contained three or four peaks. However, for fresh samples, 1 clear peak and a shoulder was observed; and for standard there was one peak observed. For CuO standard, the peak occurred at 320°C indicating the oxidation of Cu(0) to Cu(II).

The oxidation process for fresh sample started at higher temperature (205°C), about 10°C higher than start up point for spent catalyst's oxidation process. For fresh sample, the first peak occurred at 213°C indicating the oxidation of Cu(0) to Cu(I) and the high temperature peak (320°C) was assigned to oxidation of Cu(I) to Cu(II) [5]. An intermediate peak, which was observed for the fresh catalysts was believed to span the transformation of Cu(0) in a hard oxidized state to Cu(I), and Cu(I) is an easily oxidized state to Cu(II) [8]. From literature, it is suggested that the hard oxidized state consists of crystalline Cu, while the easily oxidized state corresponds to amorphous Copper [8].

For spent catalysts, the oxidation profile started at around 185°C and ended at 600°C. A shoulder observed for spent catalyst's curve which occurred at higher temperature than the maximum peak temperature. The peak occurred at 185°C was due to the oxidation of Cu(0) to Cu(I), and the shoulder at 316°C corresponded to the oxidation of Cu(I) to Cu(II). The temperature profiles obtained showed that the spent catalyst was easily oxidized than the fresh sample because the temperature gap for oxidation of Cu(0)→Cu(I)→Cu(II) was small. Therefore, it could be concluded that the amorphous Cu exist in the spent sample, might be due to thermal sintering during processing [1, 4, 8].

#### **4.2.6 TPR and TPO**

From the TPR and TPO profiles, it could be seen that the oxidation stages for fresh and spent catalysts were clearly shown by two peaks. The first peak represents the oxidation of Cu(0) to Cu(I) and the second peak represents the oxidation of Cu(I) to Cu(II). However, the reduction processes for both fresh and spent catalyst were only shown by a single peak. From literatures, the reduction and oxidation stages from TPR and TPO

profiles are supposed to be represented by two peaks respectively. In summary, the results for TPR and TPO is shown in Table 4.5

TABLE 4.5: Summary of TPR and TPO results

SAMPLE	TPR PEAKS (°C)	TPO PEAKS (°C)
Fresh	344	213, 320
Sample	456	151, 206, 316, 459
Standard	445	320

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION

The physical and chemical properties of the fresh and the spent catalysts samples were analyzed using several equipment such as SEM, XRD, EDX, CHNS, TPDRO, Pycnometer, and FTIR. The fresh and spent catalysts are characterized based on metals surface area, density, catalysts structure, functional group, impurities content, metal dispersion and also temperature programmed profiles, TPR and TPO. The results indicated that the catalysts were degraded due to sulfur, which poisoned the catalysts. However, the major factor which caused the catalysts decay is thermal sintering, as supported the SEM, TPR and TPO analyses. The results showed that the BET surface area, metal surface area and dispersion degree for the spent catalysts were decreasing after experienced industrial processes. Besides, the mean particle diameter was increasing as showed by TPR results and approved by SEM image. Thus, the regeneration activity is not appropriate for the spent catalysts and disposal is the best option of handling the aged catalysts from methanol plant. Therefore, the initial prevention is required to avoid the thermal sintering, by controlling the operating temperature or by stabilizing the catalyst.

#### 5.2 RECOMMENDATIONS FOR FUTURE WORKS

Further works need to be performed on this project. Some of the recommendations are;

- i. Use other characterization technique such as AAS (Atomic Absorption Spectrometry) to determine the metal compositions present in the catalysts
- ii. Repeat the SEM and EDX analysis to see the exact components in the catalysts
- iii. Test for catalysts regeneration activity using TPDRO

- iv. Check for catalyst' pores distribution using mercury porosimeter and other appropriate equipment
- v. Find the equipment that can test large number of catalysts because the equipment used in this project only consider a few pellets of catalysts, which is not representative for the whole catalysts in real industry environment.
- vi. Research on production of a more valuable product from the spent Cu/ZnO catalyst

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## CATALYST COMPOSITION

<b>Composition</b>	<b>Weight (%)</b>
CuO	63 ± 2
Zinc Oxide, ZnO	25 ± 2
Aluminum Oxide, Al <sub>2</sub> O <sub>3</sub>	12 ± 2
Sodium, Na	Max 0.7
Iron, Fe	Max 0.02
Nickel, Ni	Max 0.01
Sulfur, S	Max 0.04
Carbon, C	Max 0.01

[Source: Petronas Methanol Labuan]

APPENDIX 3-1

GANTT CHART

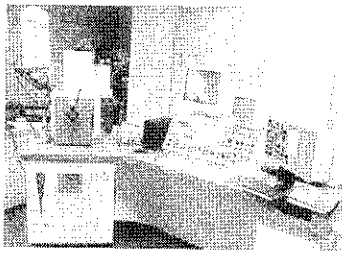
No.	ACTIVITIES	WEEK NO.																	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1.	Preliminary Research																		
	- Objectives																		
	- Problem Statement																		
	- Scope of works																		
2.	Research works																		
	- Information gathering																		
	- Literature Review																		
	- Theory																		
	- Methods/ Tools																		
3.	Project Proposal report																		
4.	Project Works																		
	- Laboratory Work																		
	- Data Analysis																		
	- Discussion																		
	- Conclusion																		
5.	Progress report																		
6.	Dissertation draft																		
8.	Dissertation final draft																		
9.	Oral Presentation																		

EQUIPMENT USED

(A) Physical properties characterization

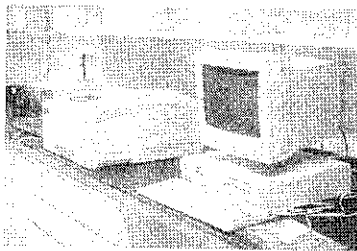


Pycnometer

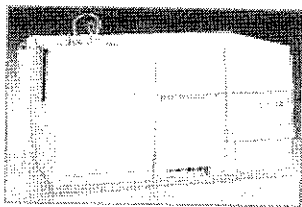


SEM

(B) Chemical properties characterization



FTIR



TPDRO

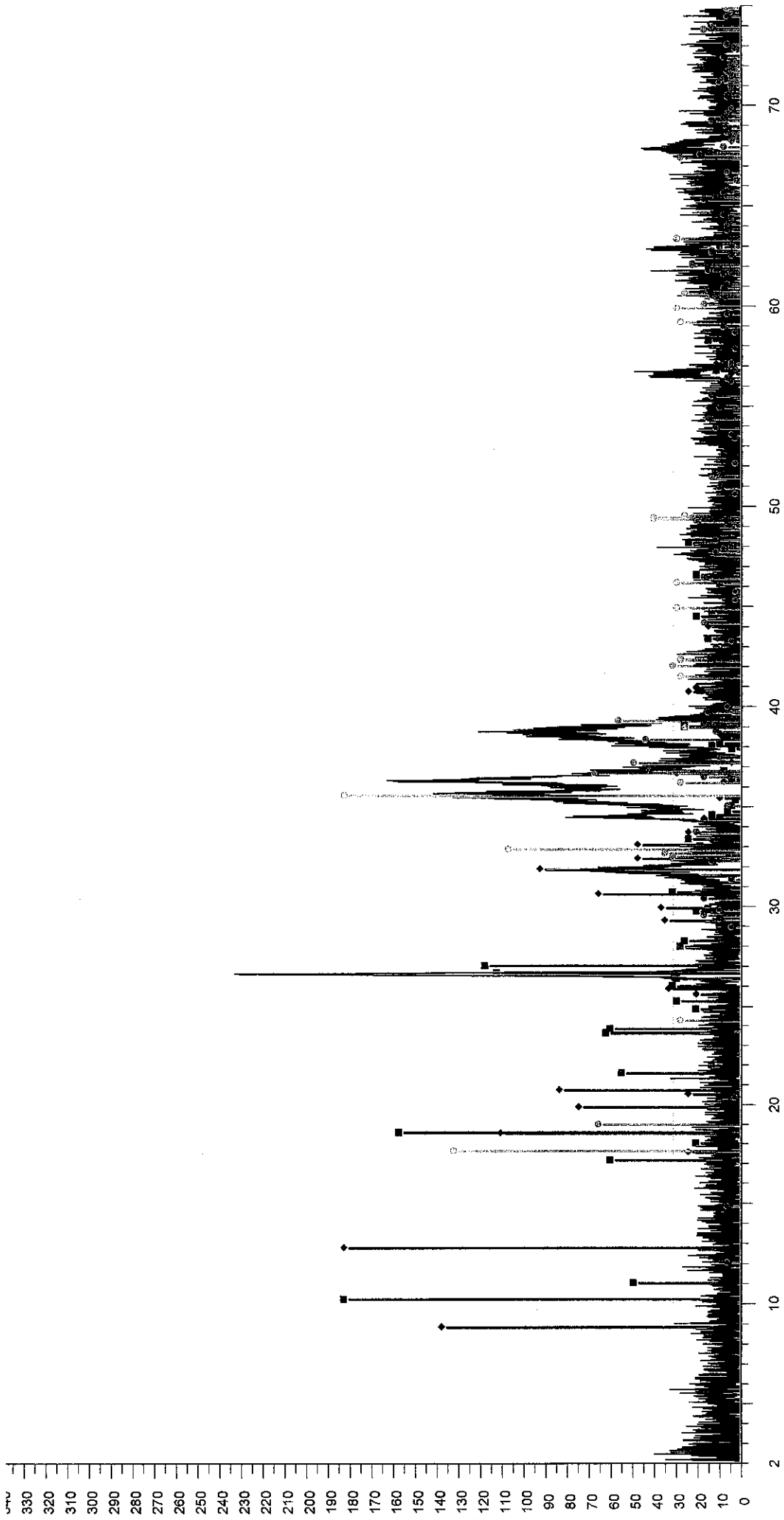


2-Theta - Scale

X C79-5-GL Fresh - File: C79-5-GL Fresh.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 75.000 ° - Step: 0.010 ° - Step time: 1. s - Temp.: 27 °C (Room) - Time Started: 21 s - 2-Theta: 2.000 ° - Theta: 1.000 °  
 Operations: Background 1.000,1.000 | Import

■ 75-1163 (C) - Malachite - Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 9.48000 - b 12.03000 - c 3.21000 - alpha 90.000 - beta 98.000 - gamma 90.000 - Primitive - P21/a (14) - 4 - 362.

◆ 75-1243 (C) - Cobalt Carbonyl Carbide Sulfide - Co<sub>6</sub>(C<sub>2</sub>)(CO)<sub>14</sub>S - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Orthorhombic - a 18.61800 - b 13.52800 - c 9.15100 - alpha 90.000 - beta 90.000 - gamma 90.000 - Pr



C79-5-GL Spent - File: C79-5-GL Spent.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 75.000 ° - Step: 0.010 ° - Step time: 1. s - Temp.: 27 °C (Room) - Time Started: 15 s - 2-Theta: 2.000 ° - Theta: 1.000 °  
 Operations: Background 1.000, 1.000 | Import  
86-1759 (C) - Copper Iron Borate Oxide -  $\text{Cu}_2\text{Fe}(\text{BO}_3)_2$  - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 3.10800 - b 12.00260 - c 9.45900 - alpha 90.000 - beta 96.660 - gamma 90.000 - Primitive - P21  
71-2375 (C) - Ransomite -  $\text{CuFe}_2(\text{SO}_4)(\text{H}_2\text{O})_6$  - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 4.81100 - b 16.21700 - c 10.40300 - alpha 90.000 - beta 93.020 - gamma 90.000 - Primitive - P21/c (14) -  
36-0400 (\*) - Arthurite -  $\text{Cu}_2\text{Fe}_2(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$  - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 10.16030 - b 9.61860 - c 5.57770 - alpha 90.000 - beta 92.117 - gamma 90.000 - Primitive - P21/

## Standard Data Report

### Sample Nr.: 363

Path: D:\Data 2\Fiza\BET CuO\_ZnO in Al2O3 Fresh 261005.110

Operator: Asnizam

Temperature: 26°C

Atmospheric Pressure: 1000hPa

### Sample

Sample Name: PML

Sample Description: CuO/ZnO:AL2O3 Fresh

Sample Weight: 0.1655 g

Preparation:

Sample-Code: 0

Customer-Code: 0

Support: Al2O3

Metals: 1

63% Copper Oxide

### Pre-treatment

Pre-treatment: Pre CuO/ZnO Al2O3 Fresh

Info:

Instrument: TPDRO1100 MS with Ser.Nr.20022897 on Right Oven

Date/Time: 10/25/2005 at 4:17:17 PM finished 6:39:47 PM

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Flowing Nitrogen	20	Off			5
Nitrogen	20	Off	10	120	120
Off					
Off					
Off					

Pre-treatment with Oven Off

### TPD/R/O

Sample Name: BET CuO/ZnO Al2O3 Fresh

Info:

Instrument: TPDRO1100 MS with Ser.Nr.20022897 on Left Oven

Date/Time: 10/26/2005 at 1:29:03 PM finished 1:45:15 PM

Start when Ready: (a) Nitrogen

Stop when End: (a) Nitrogen

Flow rate: 1 s

Flow rate: 10

Response: Positive

Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Nitrogen 30.1% in Helium		20	Off	0	030

### Results

Nitrogen adsorbed: 907.78055  $\mu\text{mol/g}$ 

Geometric factor: 1

Amount of metal reacted: 907.78055  $\mu\text{mol/g}$  (sample)Total metal surface: 6.704  $\text{m}^2$ Metal surface: 40.509  $\text{m}^2/\text{g}$  (sample)Metal surface: 64.3  $\text{m}^2/\text{g}$  (metal)Metal surface: 109.483  $\text{m}^2/\text{g}$ 

Dispersion degree: 11.461 %

Average particle diameter: 14.378 nm (spheres)

Total Metal: 7.220 %

Specific surface area: 91.48124 (m<sup>2</sup>/g)  
Molecular area: 16.0 (Å<sup>2</sup>)

## Baseline

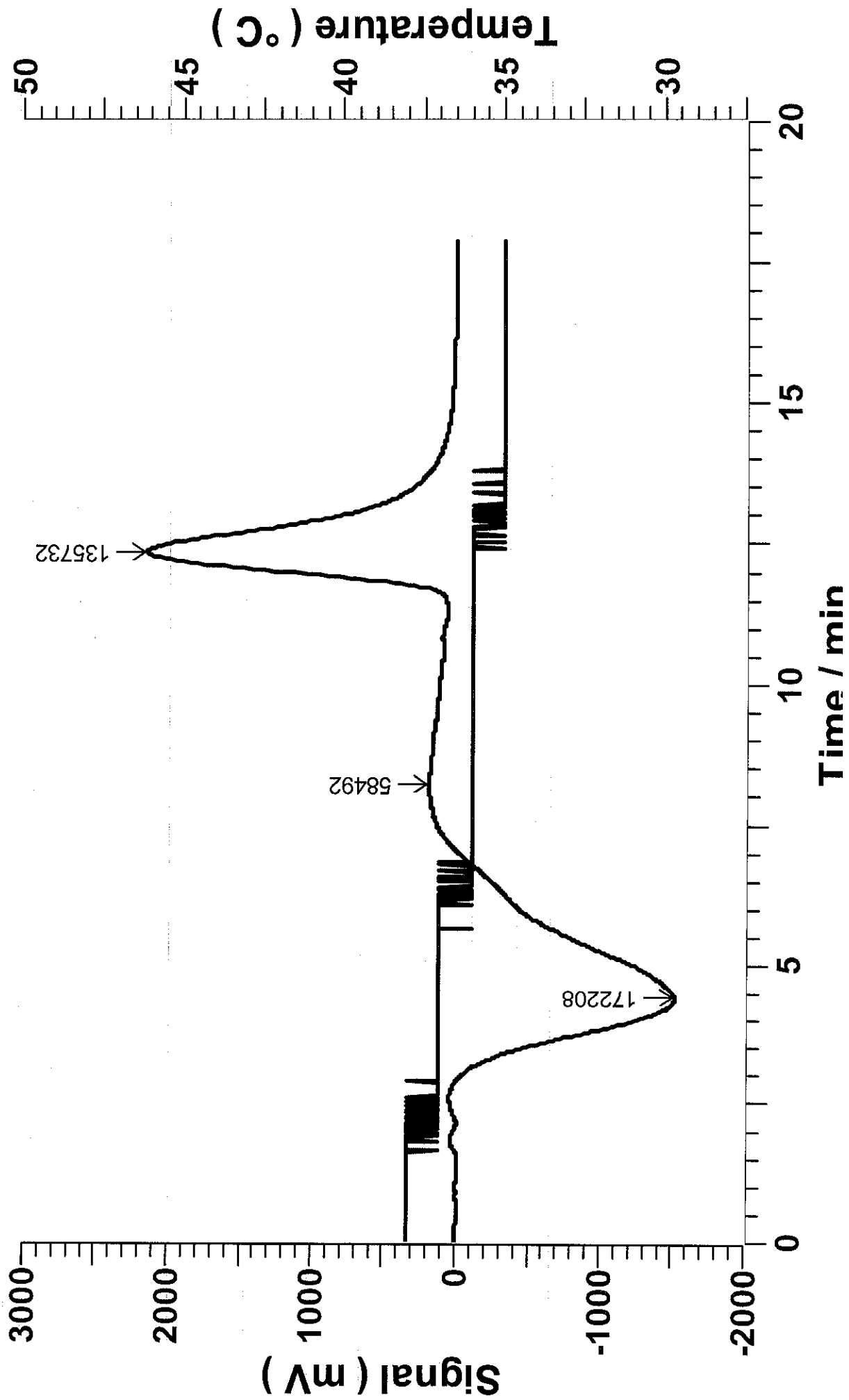
0.0167 min 2.69572 mV. Stop at 16.0333 min 12.25789 mV

## Calibration

Calibration Factor: 3.673958 \*10e-7 mmol/mVs

## Peaks

Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[μmol/g]	[%]
5.000	6.8500	4.7833	43	180375.61	400.41841	44.11
14.170	15.6830	12.6170	40	228550.32	507.36214	55.89





## Standard Data Report

### Sample No.: 365

Path: \Data 2\Fiza\BET CuO\_ZnO in Al2O3 Spent 261005.110

Instrument:

Operator: Asnizam

Temperature: 26°C

Atmospheric Pressure: 1000hPa

### Sample

Operator: PML

Sample: CuOZnO in Al2O3 Spent

Weight: 0.2282 g

Location:

Sample-Code: 0

Customer-Code: 0

Support: Al2O3

Metals: 1

63% Copper Oxide

### Pretreatment

Pretreatment: not defined or external pretreatment

Instrument: with Ser.Nr. on

Status: finished

Info:

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Off	0	Off			0

With Gas: Off

Flow: Off

Start at T: Off

Ramp: Off

Stop at T: Off

### D/R/O

Sample Name: BET CuO/ZnO Al2O3 Spent

Instrument: TPDRO1100 MS with Ser.Nr.20022897 on Left Oven

Date: 10/26/2005 at 2:05:15 PM finished 2:23:16 PM

Start when Ready: (a) Nitrogen

Stop when End: (a) Nitrogen

Flow rate: 1 s

Pulse rate: 10

Polarity: Positive

Info:

Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Nitrogen 30.1% in Helium	20	Off	Off	0	060

### Results

Amount of gas adsorbed: 589.94650  $\mu\text{mol/g}$ 

Stoichiometric factor: 1

Amount of metal reacted: 589.94650  $\mu\text{mol/g}$  (sample)Total metal surface: 6.008  $\text{m}^2$ Metal surface: 26.326  $\text{m}^2/\text{g}$  (sample)Metal surface: 41.8  $\text{m}^2/\text{g}$  (metal)Metal surface: 71.151  $\text{m}^2/\text{g}$ 

Dispersion degree: 7.448 %

Average particle diameter: 22.124 nm (spheres)

Total Metal: 4.692 %

## Baseline

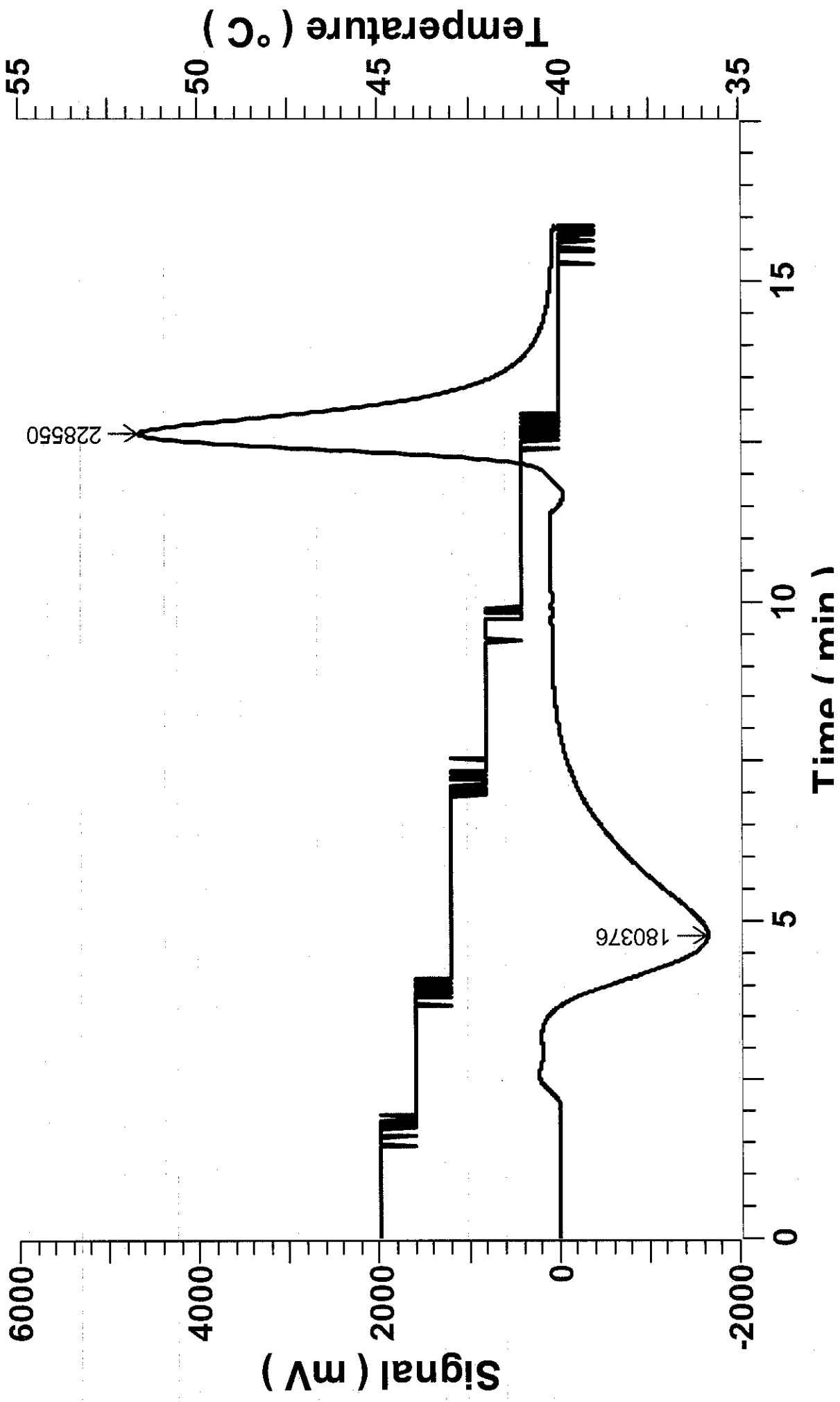
0.0167 min 5.95093 mV. Stop at 17.8500 min -16.53036 mV

## Calibration

Calibration Factor: 3.673958 \*10e-7 mmol/mVs

## Peaks

Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[μmol/g]	[%]
8.167	8.0333	4.4167	37	172208.16	277.25049	47.00
6500	11.1833	8.2000	36	58492.11	94.17072	15.96
5500	15.6000	12.3333	36	135732.28	218.52529	37.04



QUANTACHROME CORPORATION  
 Ultrapychnometer 1000 Version 2.2  
 Analysis Report

## Sample &amp; User Parameters

Sample ID: C79-5-6L-FRESH  
 Weight: 1.1245 grams  
 Analysis Temperature: 32.4 degC  
  
 Date: 10-24-05  
 Time: 15:39:33  
 User ID: 111136

## Analysis Parameters

Cell Size: Small  
 V added - Small: 12.5122 cc  
 V cell: 21.0687 cc  
 Target Pressure: 19.0 psi  
 Equilibrium Time: Auto  
 Pulse Purge: 20 Pulses  
 Maximum Runs: 10  
 Number of Runs Averaged: 3

## Results

Deviation Requested: 0.005 %	Deviation Achieved: +/- 0.44'
Average Volume: 0.1983 cc	Std. Dev. : 0.0021 cc
Average Density: 5.6718 g/cc	Std. Dev. : 0.0608 g/cc
Coefficient of Variation: 1.0730 %	

## Tabular Data

RUN	VOLUME (cc)	DENSITY (g/cc)
1	0.1919	5.8592
2	0.1834	6.1305
3	0.1791	6.2794
4	0.1843	6.1026
5	0.1863	6.0360
6	0.1924	5.8450
7	0.1955	5.7531
8	0.1957	5.7455
9	0.1981	5.6751
10	0.2009	5.5966

QUANTACHROME CORPORATION  
 Ultrapycnometer 1000 Version 2.2  
 Analysis Report

## Sample &amp; User Parameters

Sample ID: C79-5-6L-SPENT  
 Weight: 1.1222 grams  
 Analysis Temperature: 32.3 degC  
  
 Date: 10-24-05  
 Time: 16:13:58  
 User ID: 111136

## Analysis Parameters

Cell Size: Small  
 V added - Small: 12.5122 cc  
 V cell: 21.0687 cc  
 Target Pressure: 19.0 psi  
 Equilibrium Time: Auto  
 Pulse Purge: 20 Pulses  
 Maximum Runs: 10  
 Number of Runs Averaged: 3

## Results

Deviation Requested: 0.005 %	Deviation Achieved: +/- 2.102
Average Volume: 0.0517 cc	Std. Dev. : 0.0023 cc
Average Density: 21.7039 g/cc	Std. Dev. : 0.9434 g/cc
Coefficient of Variation: 4.4718 %	

## Tabular Data

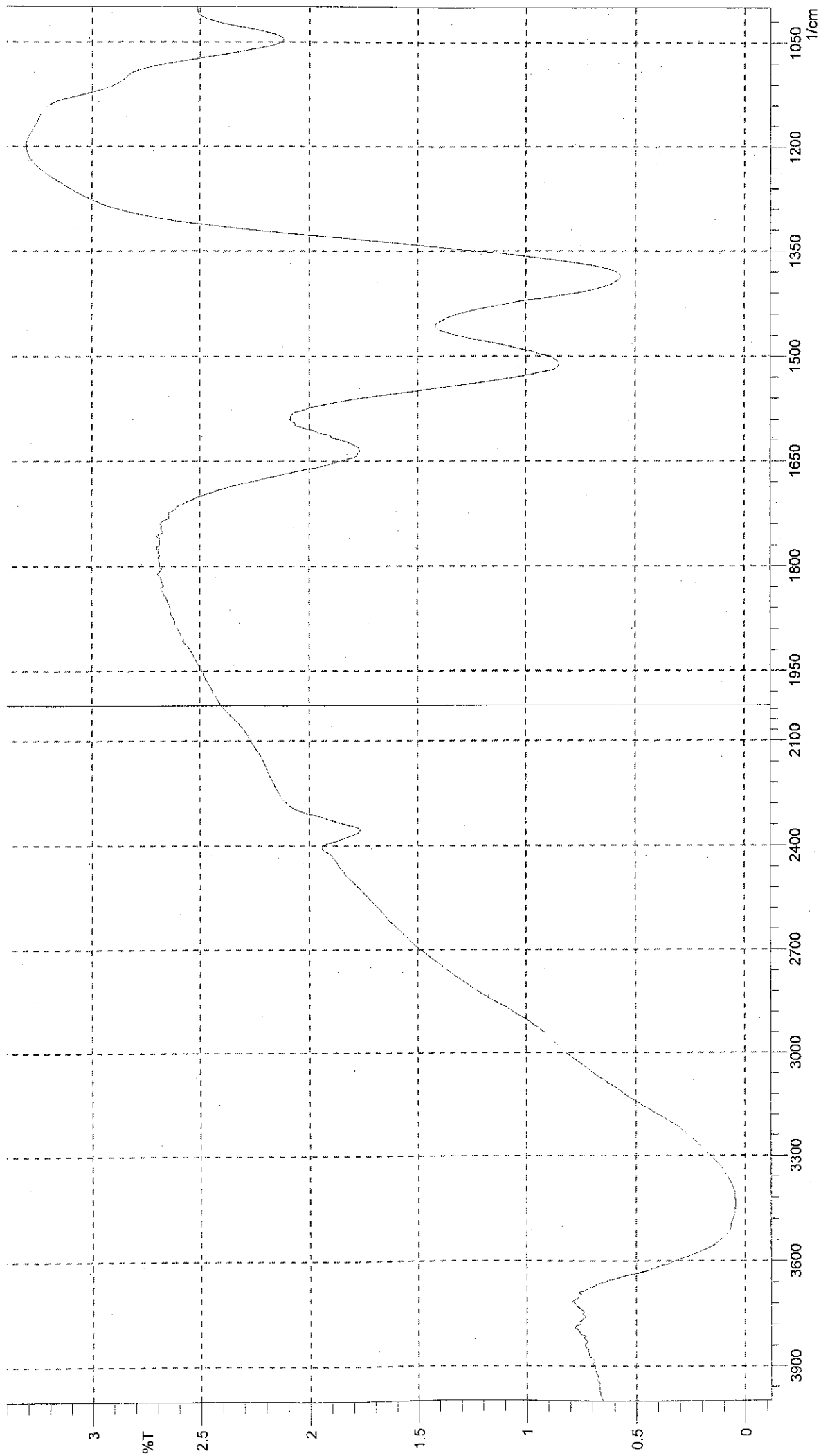
RUN	VOLUME (cc)	DENSITY (g/cc)
1	0.0541	20.7460
2	0.0497	22.5995
3	0.0474	23.6944
4	0.0441	25.4358
5	0.0412	27.2652
6	0.0423	26.5504
7	0.0491	22.8710
8	0.0499	22.5044
9	0.0550	20.4163
10	0.0503	22.3175

## SEM/ EDX result for fresh

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corn.		Sigma	
C K	0.00	0.2626	0.00	0.00	0.00
O K	34.84	0.8581	17.55	1.50	42.55
Al K	6.05	0.2898	9.03	2.99	12.98
Si K	0.00	0.3544	0.00	0.00	0.00
S K	0.00	0.5738	0.00	0.00	0.00
Cl K	0.00	0.5877	0.00	0.00	0.00
Fe K	0.00	1.1483	0.00	0.00	0.00
Co K	0.00	1.2307	0.00	0.00	0.00
Ni K	0.00	1.0921	0.00	0.00	0.00
Cu K	114.54	0.9427	52.51	2.16	32.06
Zn K	45.79	0.9460	20.92	1.29	12.42
As K	0.00	0.7841	0.00	0.00	0.00
Br K	0.00	0.9477	0.00	0.00	0.00
Hg M	0.00	0.6164	0.00	0.00	0.00
Totals			100.00		

## SEM/ EDX result for spent

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	7.90	0.3175	10.13	3.73	23.93
O K	52.75	0.7857	27.33	1.84	48.49
Na K	0.00	0.2702	0.00	0.00	0.00
Al K	0.00	0.3008	0.00	0.00	0.00
Si K	0.00	0.4051	0.00	0.00	0.00
S K	0.00	0.6283	0.00	0.00	0.00
Cl K	0.00	0.6288	0.00	0.00	0.00
Fe K	1.36	1.1015	0.50	0.24	0.26
Co K	0.00	1.1729	0.00	0.00	0.00
Ni K	0.00	1.1230	0.00	0.00	0.00
Cu K	69.34	0.9054	31.18	1.69	13.93
Zn K	68.74	0.9070	30.85	1.73	13.40
As K	0.00	0.7595	0.00	0.00	0.00
Br K	0.00	0.9122	0.00	0.00	0.00
Totals			100.00		



Date/Time; 02/26/2003 03:23:53 AM

User; Organic chemistry

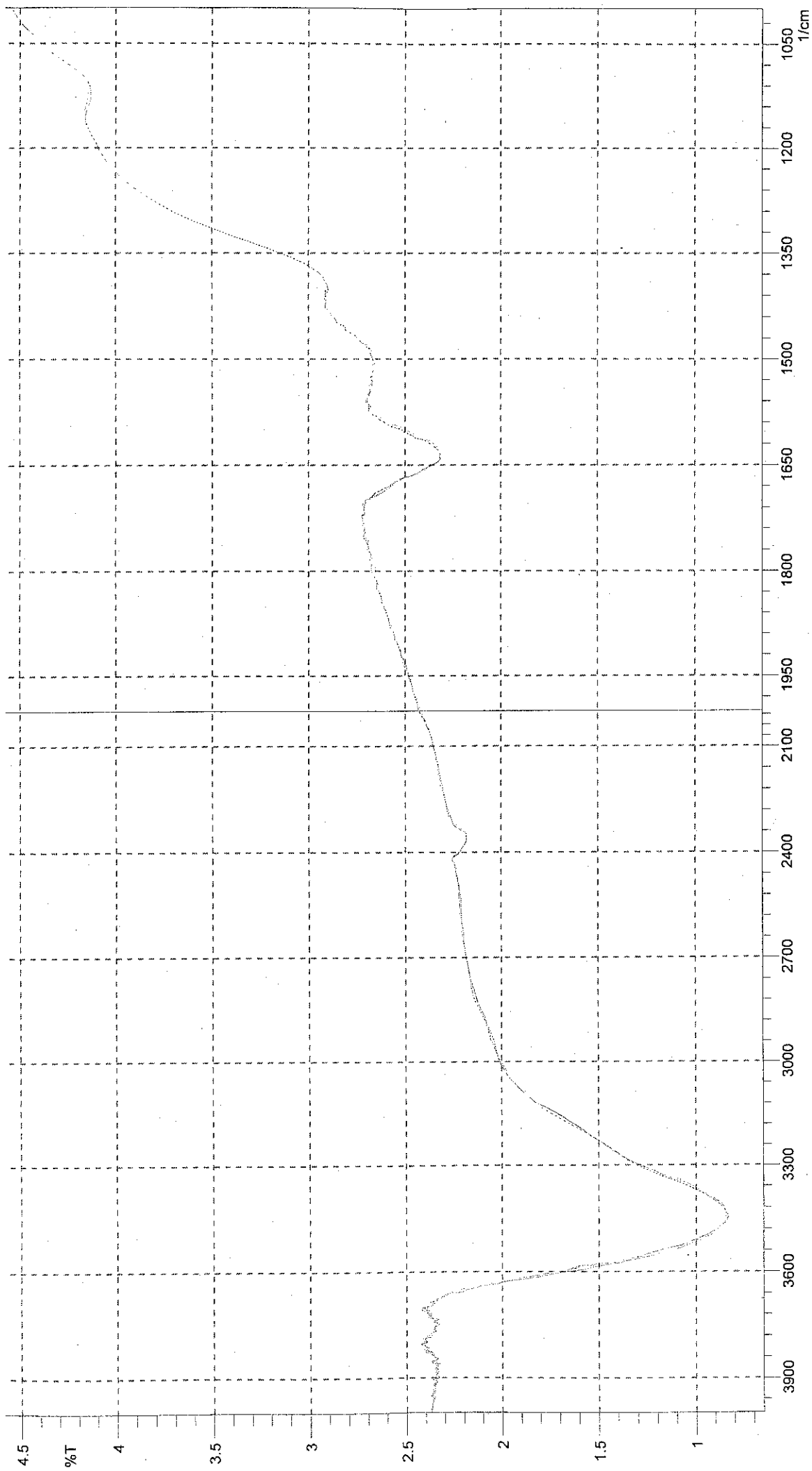
No. of Scans;

Resolution;

Apodization;

Comment;





Date/Time; 02/26/2003 04:15:33 AM  
User; Organic chemistry

No. of Scans;  
Resolution;  
Apodization;

Comment;

## CHNS RESULTS

TEST	SAMPLE NO.	FRESH				SPENT			
		C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)
FIRST	1	3.874	1.504	0.135	0.126	2.908	0.444	0.016	-0.199
	2	3.828	1.525	0.138	0.041	3.051	0.446	0.034	0.252
	3	3.228	1.322	0.122	-0.069	3.408	0.419	0.029	-0.012
SECOND	1	3.931	1.561	0.145	0.010	4.162	0.618	0.028	0.146
	2	3.535	1.268	-0.088	0.020	3.218	0.490	0.010	0.205
	3	3.607	1.443	0.147	0.015	3.373	0.467	0.028	0.205
THIRD	1	3.880	1.628	0.139	-0.004	3.015	0.463	0.032	-0.170
	2	3.718	1.624	0.156	0.004	3.507	0.445	0.034	-0.022
	3	3.786	1.572	0.144	0.010	3.569	0.436	0.022	0.049
<b>AVERAGE</b>		<b>3.710</b>	<b>1.494</b>	<b>0.115</b>	<b>0.017</b>	<b>3.357</b>	<b>0.470</b>	<b>0.026</b>	<b>0.050</b>
<b>STD. DEVIATION</b>		<b>0.210</b>	<b>0.120</b>	<b>0.072</b>	<b>0.048</b>	<b>0.357</b>	<b>0.056</b>	<b>0.008</b>	<b>0.156</b>
<b>STD. DEVIATION (OVERALL)</b>		<b>1.515</b>				<b>1.416</b>			

## Standard Data Report

### Run Nr.: 360

Path: \Data 2\Fiza\TPR CuO\_ZnO in Al2O3 Fresh 251005.110

Operator: Asnizam  
Temperature: 26°C

Atmospheric Pressure: 1000hPa

### Sample

Operator: PML  
CuO/ZnO AL2O3 Fresh  
Weight: 0.2587 gSample-Code: 0  
Customer-Code: 0  
Support: Al2O3  
Metals: 1  
63% Copper Oxide

### Pretreatment

Pretreatment: not defined or external pretreatment  
Instrument: with Ser.Nr. on  
Status: at finished

Info:

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
ing	0	Off			0

Off  
Off  
Off  
Off

retreatment with Oven Off

### TPD/R/O

Instrument Name: TPR CuO/ZnO Fresh  
 Instrument: TPDRO1100 MS with Ser.Nr.20022897 on Right Oven  
 Date: 10/25/2005 at 10:51:47 AM finished 12:19:21 PM  
 Start when Ready: (a) Nitrogen  
 Stop when End: (a) Nitrogen  
 Rate: 1 s  
 10  
 Result: Positive

Info:

Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
gen 5.42% in Nitrogen		20	Off	10	600 30

### Results

Total gas adsorbed: 8473.43870  $\mu\text{mol/g}$   
 Geometric factor: 1  
 Total metal reacted: 8473.43870  $\mu\text{mol/g}$  (sample)  
 Total metal surface: 97.819  $\text{m}^2$   
 Metal surface: 378.119  $\text{m}^2/\text{g}$  (sample)  
 600.2  $\text{m}^2/\text{g}$  (metal)  
 1021.943  $\text{m}^2/\text{g}$   
 Dispersion degree: 106.981 %  
 Particle diameter: 1.540 nm (spheres)  
 Total Metal: 67.398 %

## Baseline

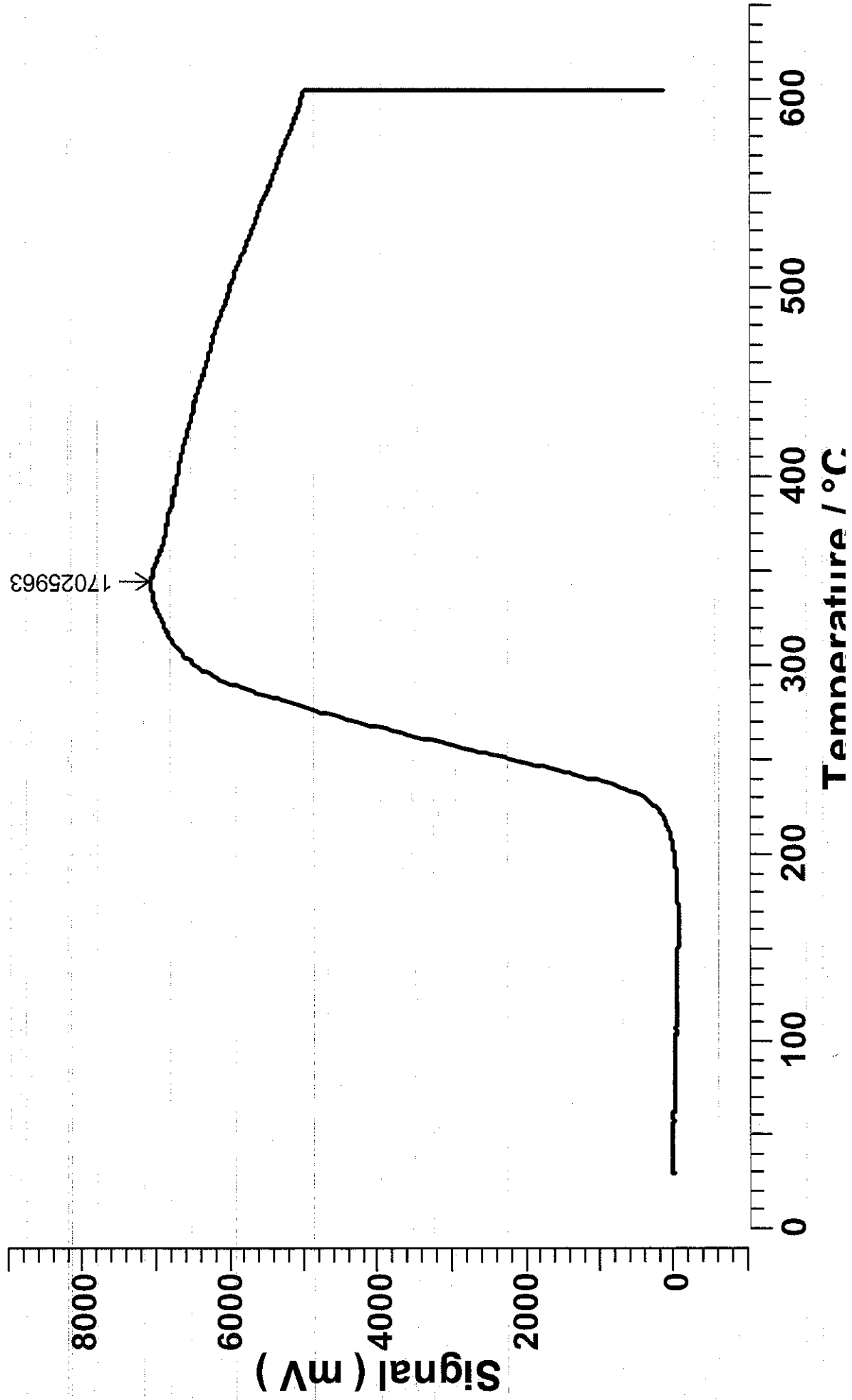
0.0167 min -18.61572 mV. Stop at 87.4167 min 542.24650 mV

## Calibration

Calibration Factor: 1.287492 \*10e-7 mmol/mVs

## Peaks

Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[ $\mu\text{mol/g}$ ]	[%]
0.3167	87.0667	31.6000	344	17025963.33	8473.43870	100.00



## Standard Data Report

### Run Nr.: 361

Path: \Data 2\Fiza\TPR CuO\_ZnO in Al2O3 Spent 251005.110

Mount:   
 Operator: Asnizam   
 Temperature: 26°C

Atmospheric Pressure: 1000hPa

### Sample

Sample Name: PML   
 Sample: CuO/ZnO AL2O3 Spent   
 Weight: 0.1543 g

Sample-Code: 0   
 Customer-Code: 0   
 Support: Al2O3   
 Metals: 1   
 63% Copper Oxide

Location:

### Pretreatment

Pretreatment: not defined or external pretreatment   
 Instrument: with Ser.Nr. on   
 Status: at finished

Info:

Condition	With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Initial	Off	0	Off			0
1	Off					
2	Off					
3	Off					

Pretreatment with Oven Off

### TPD/R/O

Sample Name: TPR CuO/ZnO Spent   
 Instrument: TPDRO1100 MS with Ser.Nr.20022897 on Left Oven   
 Date: 10/25/2005 at 1:25:19 PM finished 2:52:19 PM

Info:

Start when Ready: (a) Nitrogen   
 Stop when End: (a) Nitrogen   
 Flow rate: 1 s   
 10   
 Polarity: Positive

Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Argon 5.42% in Nitrogen		20	Off	10	600 30

### Results

Volume of gas adsorbed: 8715.92374 µmol/g   
 Geometric factor: 1   
 Volume of metal reacted: 8715.92374 µmol/g (sample)   
 Total metal surface: 60.013 m²   
 Metal surface: 388.940 m²/g (sample)   
 617.4 m²/g (metal)   
 1051.188 m²/g   
 Dispersion degree: 110.042 %   
 Particle diameter: 1.497 nm (spheres)   
 Total Metal: 69.326 %

# Baseline

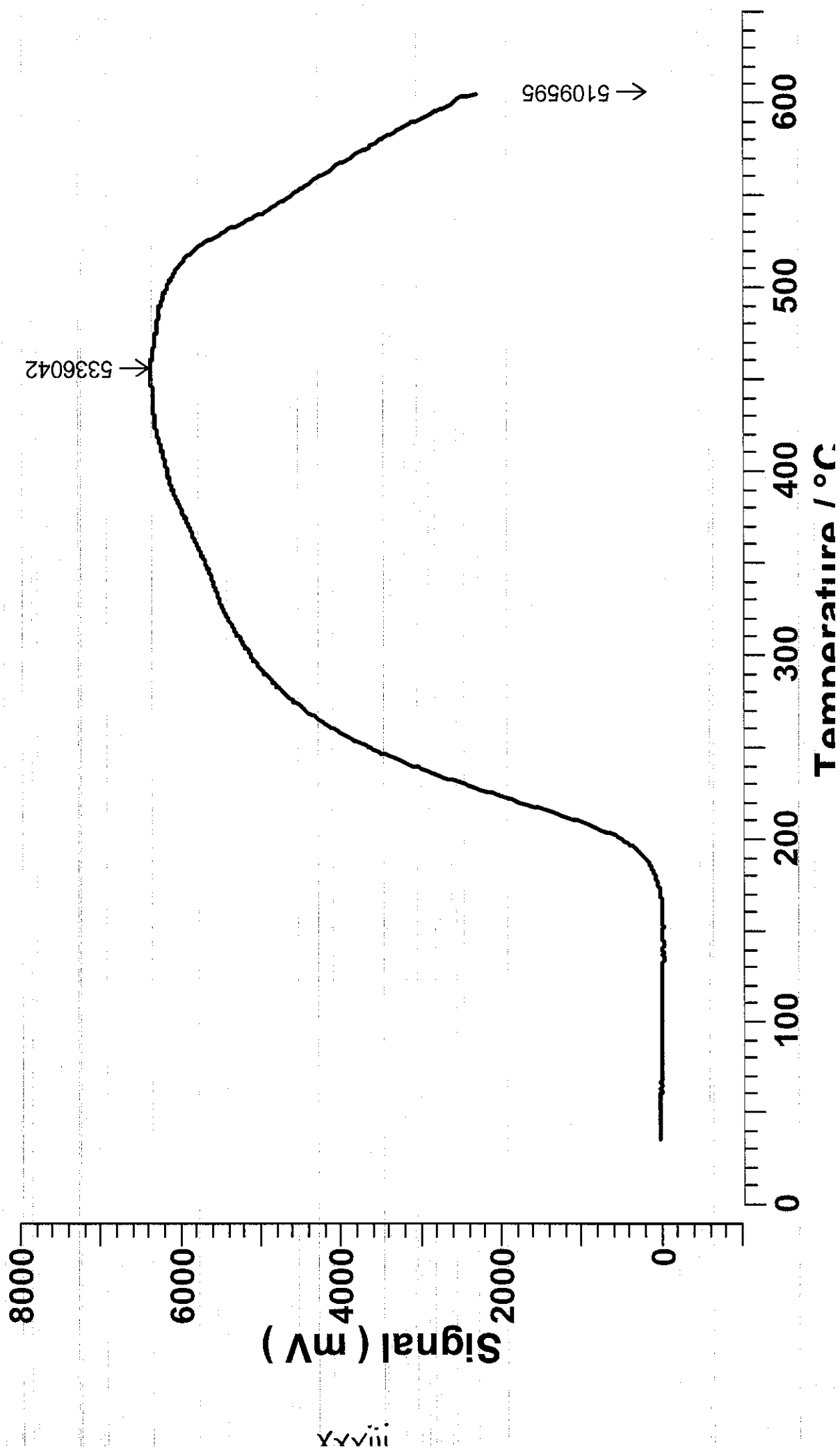
0.0167 min -11.03719 mV. Stop at 86.8167 min 280.96517 mV

# Integration

Integration Factor: 1.287492 \*10e-7 mmol/mVs

# Peaks

Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[μmol/g]	[%]
0.9833	75.6667	42.3500	456	5336042.08	4452.43660	51.08
1.6833	81.9667	75.8500	606	5109594.70	4263.48710	48.92





## Standard Data Report

### 7 Nr.:364

Data 2\Fiza\TPO CuO\_ZnO in Al2O3 Fresh 261005.110

Operator: Asnizam  
Temperature 26°C

Atmospheric Pressure 1000hPa

### Sample

Sample: PML  
CuOZnO in Al2O3 Fresh  
Weight: 0.1726 g

Sample-Code: 0  
Customer-Code: 0  
Support: Al2O3  
Metals: 1  
63% Copper Oxide

### Treatment

Program: not defined or external pretreatment  
Start: 10/26/2005 at 10:33:12 AM finished 12:00:42 PM

Info:

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
ing	0	Off			0
Off					
Off					
Off					
Off					

retreatment with Oven Off

### TPD/R/O

Sample Name: TPO CuO/ZnO Fresh  
Program: TPDRO1100 MS with Ser.Nr.20022897 on Left Oven  
Start: 10/26/2005 at 10:33:12 AM finished 12:00:42 PM  
Start when Ready: (b) Helium  
Start when End: (b) Helium  
Rate: 1 s  
Flow: 10  
Pressure: Negative

Info:

Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
in 5.3% in Helium	20	Off	10	600	30

### Results

Adsorbed gas: 6954.02151 µmol/g  
Geometric factor: 1  
Amount of metal reacted: 6954.02151 µmol/g (sample)  
Total metal surface: 53.561 m²  
Metal surface: 310.316 m²/g (sample)  
492.6 m²/g (metal)  
838.693 m²/g  
Dispersion degree: 87.797 %  
particle diameter: 1.877 nm (spheres)  
Total Metal: 55.312 %

## Baseline

0.0167 min -6.61214 mV. Stop at 87.3333 min -17.44588 mV

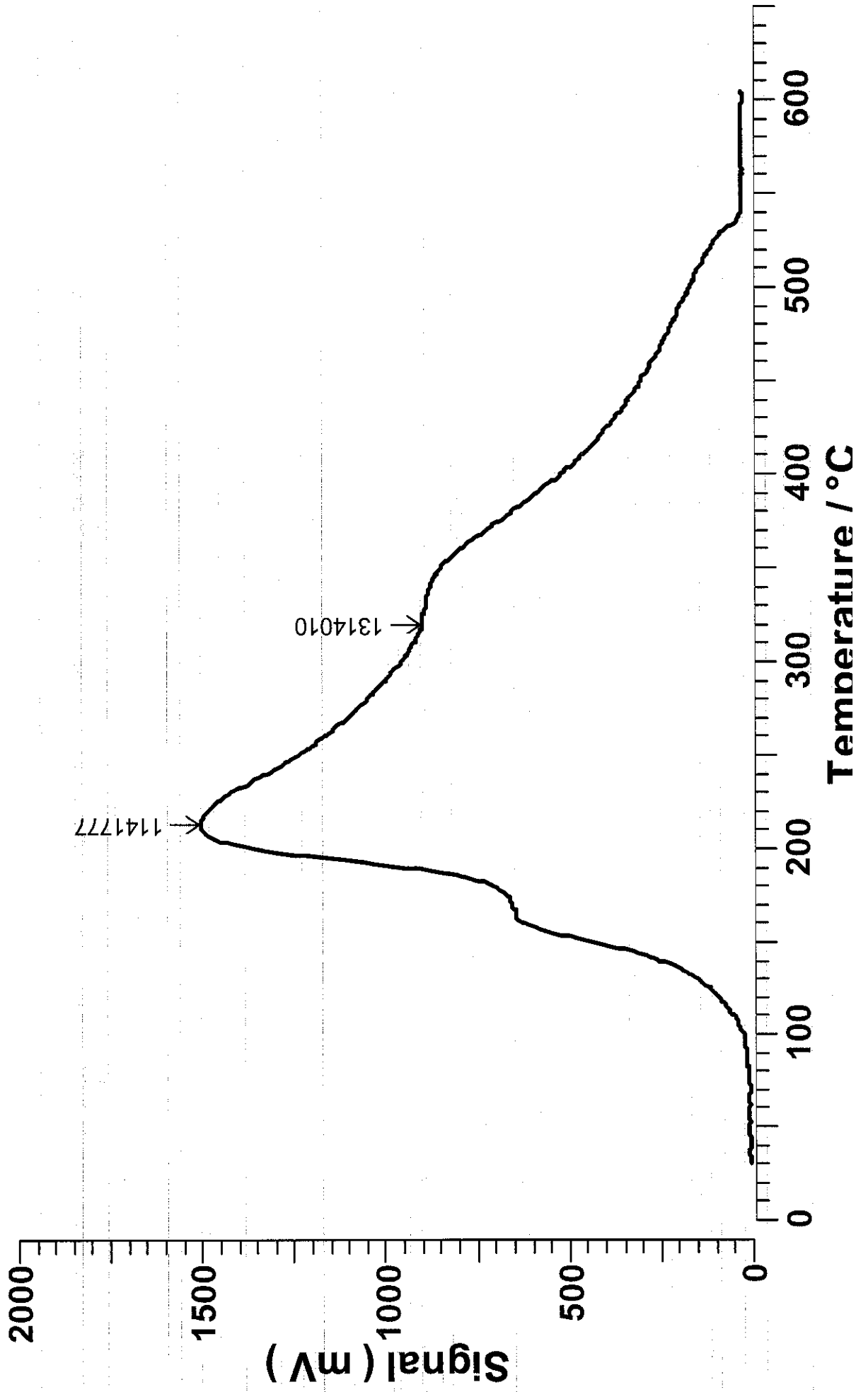
## Integration

Integration Factor: 4.887493 \*10e-7 mmol/mVs

## Peaks

Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[μmol/g]	[%]
9.000	28.9667	18.2000	213	1141776.69	3233.15520	46.49
31.5500	51.4500	28.9833	320	1314010.02	3720.86630	53.51

11/18/84 4:11 PM PLOT OF DSC SIGNAL (mV) VS TEMPERATURE (°C)



## Standard Data Report

### 1 Nr.:362

Data 2\Fiza\TPO CuO\_ZnO in Al2O3 Spent 251005.110

1t:

r: Asnizam

Temperature 26°C

Atmospheric Pressure 1000hPa

### Sample

r: PML

CuO/ZnO AL2O3 Spent

.1543 g

ion:

Sample-Code: 0

Customer-Code: 0

Support: Al2O3

Metals: 1

63% Copper Oxide

### treatment

not defined or external pretreatment

treatment: with Ser.Nr. on

at finished

Info:

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
ng	0	Off			0
Off					
Off					
Off					
Off					

retreatment with Oven Off

### D/R/O

Name: TPO CuO/ZnO Spent

treatment: TPDRO1100 MS with Ser.Nr.20022897 on Left Oven

10/25/2005 at 3:56:44 PM finished 5:21:32 PM

t when Ready: (a) Nitrogen

t when End: (a) Nitrogen

rate: 1 s

10

: Negative

Info:

Gas	Flow [ccm/min]	Start at T [°C]	Ramp °C/min	Stop at T [°C]	Hold for [min]
n 5.3% in Helium	20	Off	10	600	30

### Results

t gas adsorbed: 6347.12989 µmol/g

ometric factor: 1

t of metal reacted: 6347.12989 µmol/g (sample)

otal metal surface: 43.703 m²

Metal surface: 283.235 m²/g (sample)

449.6 m²/g (metal)

765.499 m²/g

Dispersion degree: 80.135 %

particle diameter: 2.056 nm (spheres)

Total Metal: 50.485 %

## Baseline

0.0167 min -0.40690 mV. Stop at 84.6333 min -31.22966 mV

## Calibration

Calibration Factor: 4.887493 \*10e-7 mmol/mVs

## Peaks

Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[μmol/g]	[%]
167	14.7667	9.2333	151	514053.57	1628.27830	25.65
6833	20.2667	14.7833	206	447415.79	1417.20140	22.33
6167	40.3667	25.9833	316	537169.43	1701.49840	26.81
9833	46.5833	40.4500	459	465155.65	1473.39280	23.21
2167	71.0000	56.4167	606	40018.30	126.75904	2.00

