

**CHARACTERIZATION OF E-WASTE : RARE  
EARTH ELEMENT IDENTIFICATION**

**MUHAMAD ARIFF SHAZLAN BIN ROSLAN**

**BACHELOR OF CHEMICAL ENGINEERING (PURE)  
UNIVERSITI MALAYSIA PAHANG**

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# **CHARACTERIZATION OF E-WASTE : RARE EARTH ELEMENT IDENTIFICATION**

**MUHAMAD ARIFF SHAZLAN BIN ROSLAN**

Thesis submitted in partial fulfilment of the requirements  
for the award of the degree of  
Bachelor of Chemical Engineering (Pure)

**Faculty of Chemical & Natural Resources Engineering  
UNIVERSITI MALAYSIA PAHANG**

JANUARY 2015

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## **SUPERVISOR'S DECLARATION**

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Pure).

Signature :  
Name of main supervisor : DR. ANWARUDDIN HISYAM  
Position : SENIOR LECTURER  
Date : 21 JANUARY 2015

## **STUDENT'S DECLARATION**

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :  
Name : MUHAMAD ARIFF SHAZLAN BIN ROSLAN  
ID Number : KA11175  
Date : 21 JANUARY 2015

## *Dedication*

In The Name of Allah, Most Gracious, Most Merciful

Love special dedicated to...

Special inspiring and special encouraging of my lovely parent: Roslan Bin Hashim

and Siti Aishah Binti Selamat;

My siblings,

and

also my truly best friends,

Those who has influenced my life on the right course

Thank you so much

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Not to be left, my almost thought for my beloved mum and dad, Roslan Hashim and Siti Aishah Selamat, and my family members who have been firing up my spirit.

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## ABSTRACT

Rare Earth Element (REE) or rare earth metal is one of a set of seventeen chemical elements in the periodic table. Rare earth elements are widely used in many consumer electronics products such as smartphones, LED monitors, powerful magnets in electric drive motors and etc. This research describes the study of the coating powder leaching from computer monitor scraps to obtain liquor which can be treated by hydrometallurgical techniques to extract the metals. Television (TV) tubes and computer monitors exist as coating powder that contain some rare earth elements (REEs). The recovery of the REEs from electronics scraps is very important in lieu of the economic and concerns. Leaching is a method of separation between solid and liquid. To separate the components, acid solvents such as nitric acid, hydrochloric acid, and sulphuric acid can be used. The results of this study pointed out the technical viability of the recovery of the metals. The coating powder used in this study was obtained by manually scraping the inner surfaces of computer monitor. Sulphuric ( $H_2SO_4$ ), nitric acid ( $HNO_3$ ) and hydrochloric (HCl) acids will be used in the leaching experiments. All solutions are analytical grade reagents and diluted with distilled water. The extract sample will be characterized by X-ray diffractometer. From the X-ray diffractometer, the data shows that LCD contain large value of indium. The conclusion that can be made from this study is for leaching process to extract rare earth elements, hydrochloric acid is the best solvent that can be used. Besides, in order to make sure the leaching process is effective, higher molarity of acid solvent is needed.

*Key words: Environmental, Hydrometallurgy, Leaching process, Rare earth element, X-ray diffraction*



## ABSTRAK

Logam nadir bumi adalah salah satu daripada satu set tujuh belas unsur-unsur kimia dalam jadual berkala. Unsur nadir bumi banyak digunakan dalam banyak produk elektronik pengguna seperti telefon pintar, membawa monitor, magnet berkuasa di motor pemacu elektrik dan lain-lain. Kertas kerja ini menerangkan kajian tentang larut lesap serbuk salutan dari komputer monitor terbangun untuk mendapatkan cecair yang boleh dirawat dengan teknik hidrometalurgi untuk mengekstrak logam. Televisyen (TV) tiub dan monitor komputer wujud dalam serbuk salutan yang mengandungi beberapa unsur-unsur nadir bumi. Pemulihan unsur nadir bumi dari sisa elektronik adalah sangat penting dalam sektor ekonomi. Larut lesap adalah kaedah pemisahan antara pepejal dan cecair. Untuk memisahkan komponen, pelarut asid seperti asid nitrik, asid hidroklorik, dan asid sulfurik boleh digunakan. Hasil kajian ini menunjukkan daya maju teknikal dalam pemulihan logam. Serbuk salutan yang digunakan dalam kajian ini diperolehi secara manual dengan mengikis permukaan dalaman komputer monitor. Sulfurik ( $H_2SO_4$ ), asid nitrik ( $HNO_3$ ) dan hidroklorik asid ( $HCl$ ) akan digunakan dalam eksperimen larut lesap. Semua larutan adalah gred reagen yang saintifik dan akan dicairkan dengan air suling. Sampel ekstrak akan dianalisa menggunakan X-ray diffractometer. Dari data yang diperolehi dari diffractometer X-ray, ia menunjukkan bahawa LCD mengandungi jumlah indium yang sangat tinggi. Kesimpulan yang boleh dibuat daripada kajian ini adalah, untuk proses larut lesap untuk mengeluarkan unsur-unsur nadir bumi, asid hidroklorik adalah pelarut terbaik yang boleh digunakan. Selain itu, bagi memastikan proses larut lesap adalah berkesan, kepekatan asid pelarut yang tinggi diperlukan.

Kata kunci: Alam Sekitar, Hidrometalurgi, Proses Larut Lesap, Unsur Nadir Bumi, Pembelauan Sinar-X

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## LIST OF ABBREVIATIONS

<i>t</i>	<i>time(s)</i>
<i>D</i>	<i>diffusivity(<math>m^2 s^{-1}</math>)</i>
<i>X</i>	<i>distance of diffusion(m)</i>
<i>C</i>	concentration of the solute
$\theta$	<i>angles of incidence</i>
<i>d</i>	<i>distance between atomic layers in a crystal</i>
$\lambda$	<i>wavelength of the incident X-ray beam</i>
<i>n</i>	<i>integer</i>

## **LIST OF ABBREVIATIONS**

NIB	Neodymium Iron Boron
REE	Rare Earth Elements
REM	Rare Earth Magnet
REO	Rare Earth Oxide
XRD	X-Ray Diffraction

# 1 INTRODUCTION

## 1.1 Background

Rare Earth Element (REE) or rare earth metal is one group of 17 chemical elements in the periodic table, particularly the lanthanides series, scandium and yttrium (Connelly, 2005). Scandium and yttrium are also considered as rare earth elements because they are always found in the same ore deposits as the lanthanides and exhibit similar chemical properties. The 17 REEs are found in all REE deposits but their distribution and concentrations vary. They are referred to as 'rare' because it is not common to find them in commercially viable concentrations. Significantly it is difficult to identify the physical and chemical properties as well as characteristics of the rare earth elements due to their near similarity (Gupta, C.K, & Krishnamurthy, 2005)

Rare Earth Elements																					
by Geology.com																					
H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt													
			Lanthanides																		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
			Actinides																		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Table 1 Rare Earth Element In Periodic Table

There are two categories of rare earth element which are light rare earth and heavy rare earth

Light Rare Earths	Heavy Rare Earths
<ul style="list-style-type: none"> <li>• Lanthanum (La)</li> <li>• Cerium (Ce)</li> <li>• Praseodymium (Pr)</li> <li>• Neodymium (Nd)</li> <li>• Samarium (Sm)</li> </ul>	<ul style="list-style-type: none"> <li>• Europium (Eu)</li> <li>• Gadolinium (Gd)</li> <li>• Terbium (Tb)</li> <li>• Dysprosium (Dy)</li> <li>• Holmium (Ho)</li> <li>• Erbium (Er)</li> <li>• Thulium (Tm)</li> <li>• Ytterbium (Yb)</li> <li>• Lutetium (Lu)</li> <li>• Yttrium (Y)</li> </ul>

*Table 2 Types of Rare Earths*

## ***1.2 Motivation and statement of problem***

Rare earth element are used in many electronics products and gadgets such as smartphones, led monitor, powerful magnets in electric drive motors and etc. Eventhough rare earth element (REEs) is present in relatively large amount in the earth's crust, REEs rarely come in concentrated forms,hence infeasible to mine. According to (Castor & Hendrick, 2003), China is the main supplier for rare earth element (REEs) globally. For the Chinese, their mining areas concentrated in Bayan Obo, Weishan and Mouniping. In 2003, China have supplied 90000 metric tonnes of rare earth element represents world's rare earth production for about 97% (Gowing & Matt, 2011).As rare earth element is widely used in high technology application, there are concerns that in coming years,the demand of these rare earth elements is more than what the Chinese can supply (York, Geoffrey, & Bouw, 2011). Furthermore,there are also indications that China had will decrease the rare earth export. (Hollins, 2010). By 2015, it has been predicted that China will not export rare earth elements anymore. This situation has caused an increase of interest among big companies from all over the world in production and recycling of rare earth elements.

Leaching is the extraction process involving solid and liquid. In leaching process, liquid will act as diluents while solid will be a composite solid whereby the separation posed a high degree of difficulty. According to (Perry's), leaching comprised of two types



namely is percolation (filtration) and disperse solid into liquid. The mechanism that present in leaching is between simple physical solutions by chemical reaction. Leaching rate can be affected by solvent concentration, reaction temperature, reaction time, liquid to solid ratio, and also stirring speed during mixing between solvent and rare earth. In leaching, transport process will occur between solvent and the surface of element. Leaching mechanism of rare earth is ion exchange between positive-ion in solution and the surface of rare earth material

Solvent selection criteria includes among others high saturation limit and selectivity for the extraction of the solute, must be able to produce high quality extracted product, low viscosity, low flammability and toxicity, low surface tension and low density. Most of the solvent used in leaching is acidic such as sulfuric acid and hydrochloric acid (Martins T. S., 2005). However, sulfuric acid will release sulfur dioxide ( $\text{SO}_2$ ) and hydrogen fluoric (HF) which are difficult to be recycled and environmentally unfriendly. To mitigate this, other more benign chemical such as ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , HCL- $\text{AlCl}_3$  and  $\text{NH}_4\text{NO}_3$  may be used

### ***1.3 Objectives***

The objectives of this research are:

To study the characterization of the coating powder leaching from e-scrap aiming at obtaining liquor which can be treated through metallurgical techniques to purify the metals. The parameters investigated will be leaching agent, acid/sample ratio, time of acid leaching, solids percentage and temperature of leaching.

#### ***1.4 Scope of this research***

The following are the scope of this research:

In this leaching process, the rare earth elements from electronic waste will be used which is liquid crystal display (LCD) while the solvent (acid solution) used is such as hydrochloric (HCl), nitric acid (HNO<sub>3</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The rare earth elements will be leach with the acid solvents for three steps leaching. The acid is used to extract rare earth metal from the LCD. The leaching is conducted by mixing the meshing LCD and the solvent. The method used for data analysis is x-ray diffraction (XRD). In the XRD, the rare earth metal will be analyze in solid phase. From the data collected, determination of the concentration of the rare earth metal that loss through the leaching process is obtain. The time duration for this research is about 3 weeks until the optimum of the rare earth meal is extracted from the liquid crystal display (LCD).

#### ***1.5 Main contribution of this work***

Nowadays rare earth materials are used in many more products than is generally understood. Their uses are almost too numerous to list, but the major uses include ultra strong magnets for electric motors, advanced batteries, and phosphors for fluorescent lighting and display panels. Solid state laser systems, phosphors used in fluorescent lighting and plasma flat panel displays, optical fiber communications, and satellite communications all rely on rare earth materials.

Ultra strong (neodymium-iron-boron) magnets were discovered in the 1980s. More than twice as strong as previously known magnets, this touched off a revolution in miniaturizing electronic devices. Rare earth magnets lie at the heart of many of the consumer electronic products that have become so familiar in recent years, including: cell phones, laptop computers, small hard drives, and many personal electronic devices. Rare earth element are quite important to efforts to produce clean energy, especially LCD where large amounts of rare earth metals are used in the display panel.

Therefore, the recycling of the rare earth element is really worthwhile since there are really in highly demands.

## ***1.6 Organisation of this thesis***

The structure of the remainder of the thesis is outlined as follow:

Chapter 2 provides a description of the applications and general features rare earth elements. A general description on the characteristics of rare earth element, as well as the uses of rare earth elements. This chapter also provides a brief discussion of the advanced experimental techniques available for recycling and also leaching process of the rare earth elements, mentioning their applications. A summary of the previous experimental work on recovery of rare earth element is also presented. A brief discussion on the scale-up methods is also provided..

Chapter 3 gives a review method and procedure of the experiment.

Chapter 4 gives the expected result and discussion of the experiment.

Chapter 7 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work

## **2 LITERATURE REVIEW**

### ***2.1 Overview***

The most important reason in increasing of interest in recycling rare earth metals or elements is the highly demand of rare earth element in the electronic industries. In 2012, China had produced about 85 percent and consumed 70 percent of world's rare earth element, and reported in a that it will reduce production. Japan has no rare earth metal production capacity, it only consumed 15 percent of the global yearly production mainly by importing from China.

It is worth noting that it is not the rarity of rare earth metals that is the challenge, but rather finding it in commercially viable ore concentrations. (LeBlanc, 2013) A large rare earth ore concentration has been found on the ocean floor that may be 20 to 30 times as large as that of China, but the extraction cost would be really high,

So, countries which consume rare earth minerals need to depend on China. By recycling, countries can help meet their demand of rare earth minerals. The recycling of rare earth metals can make metal prices down. Other important reason for recycling rare earth elements is the high possibility of serious environmental damage related to the mining and refining of rare earth metals. Beside the risk of radioactive tailings, rare earth minerals refining need the use of toxic acids (LeBlanc, 2013)

The recycling rates for rare earth metals is about 1 percent, only a very little of what could be reused. Most of the applications that uses rare earth elements is such as computer hard drives, cell phones, fluorescent lighting, REE can be recovered and reused, eventhough plenty of e-waste material must be recycled to generate a small amount of rare earth metals. For example, 300 tons of circuit boards can produce only 150 grams of rare earth metals through a smelting process.

In future, technologies for successful rare earth metal recycling continue to developed, while some product manufacturers had decided to eliminate their use of these materials. At the same time, there is also interest in product design to support recycling - allowing for more cost effective recycling. (LeBlanc, 2013)

### 2.1.1 Rare Earth Elements

The rare earth element (REEs) are group of 17 elements consist of lanthanides, scandium and yttrium. Among the REEs, promethium (Pm) is the most rare, however some of the REEs are not really rare and occur spread in a many types of forms (Greenwood, N.M, & Earnshaw) (Tyler, 2004).The infinite applications of the REEs are based on their particular properties, for the most is their spectroscopic and magnetic properties (Martins, S, Isolani, & Celso, 2005). REEs have been mainly used in agriculture, electronics, superconductors, nuclear medicine, automobile industry, special inks – which is used in radar invisible airplanes, X-ray screens, high intensity mercury vapour light bulbs, neutron scintillators, charged-particle detectors and optical memory reading systems (Maestro, 1995) (Sanchez, 2001). Rare earth elements has very specific and versatile metallurgical, chemical, catalytic, electrical, magnetic and optical properties (Geology.com). Table 3 shows the summary of unique properties of Rare Earth Elements.

<b>Chemical</b>	Has unique electron configuration
<b>Catalytic</b>	Oxygen storage and release
<b>Electrical</b>	High conductivity
<b>Magnetic</b>	High magnetic anisotropy and large magnetic moment
<b>Optical</b>	Fluorescence, high refractive index
<b>Metallurgical</b>	Efficient hydrogen storage in rare earth alloys

*Table 3 Unique Properties of Rare Earth Elements*

Table 4 shows the types of Rare Earth Element with their unique properties

<b>REE</b>	<b>Catalytic</b>	<b>Magnetic</b>	<b>Electrical</b>	<b>Chemical</b>	<b>Optical</b>
<b>Lanthanum (La)</b>	<b>X</b>		<b>X</b>	<b>X</b>	<b>X</b>
<b>Cerium (Ce)</b>	<b>X</b>		<b>X</b>	<b>X</b>	<b>X</b>
<b>Praseodymium (Pr)</b>		<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>
<b>Neodymium (Nd)</b>	<b>X</b>	<b>X</b>	<b>X</b>		<b>X</b>
<b>Samarium (Sm)</b>		<b>X</b>			
<b>Europium (Eu)</b>					<b>X</b>
<b>Gadolinium (Gd)</b>		<b>X</b>			<b>X</b>
<b>Terbium (Tb)</b>		<b>X</b>			<b>X</b>
<b>Dysprosium (Dy)</b>		<b>X</b>			<b>X</b>
<b>Erbium (Er)</b>					<b>X</b>
<b>Yttrium (Y)</b>					<b>X</b>

*Table 4 Types of Rare Earth Element with Their Unique Properties*

The technological development of the last 10 years in the differing sectors of the electronic industry has stimulated the replacement of out-of-date gadgets. As a result, there is an increasing number of disposal of out-of-date computers and other electronic equipments into landfill sites all over the world.

## 2.1.2 Rare Earth Applications

Every types of Rare Earth Element(REEs) have their own application and uses (Ernst & Young, 2011)

<b>REE</b>	<b>Uses</b>
<b>Scandium</b>	Metal alloys for the aerospace industry
<b>Yttrium</b>	Ceramics; metal alloys; lasers; fuel efficiency; microwave communication for satellite industries; color televisions; computer monitors; temperature sensors. Used in targeting and weapon systems and communication devices.
<b>Lanthanum</b>	Batteries; catalysts for petroleum refining; electric car batteries; high-tech digital cameras; video cameras; laptop batteries; X-ray films; lasers. Used in communication devices.
<b>Cerium</b>	Catalysts; polishing; metal alloys; lens polishes (for glass, television faceplates, mirrors, optical glass, silicon microprocessors, and disk drives).
<b>Praseodymium</b>	Improved magnet corrosion resistance; pigment; searchlights; airport signal lenses; photographic filters.
<b>Neodymium</b>	High-power magnets for laptops, lasers, fluid-fracking catalysts. Used in guidance and control systems, electric motors, and communication devices.
<b>Promethium</b>	Beta radiation source, fluid-fracking catalysts
<b>Samarium</b>	High-temperature magnets, reactor control rods. Used in guidance and control systems and electric motors.

<b>Europium</b>	Liquid crystal displays (LCDs), fluorescent lighting, glass additives. Used in targeting and weapon systems and communication devices.
<b>Gadolinium</b>	Magnetic resonance imaging contrast agent, glass additives.
<b>Terbium</b>	Phosphors for lighting and display. Used in guidance and control systems, targeting and weapon systems, and electric motors..
<b>Dysprosium</b>	High-power magnets, lasers. Used guidance and control systems and electric motors.
<b>Holmium</b>	Highest power magnets known.
<b>Erbium</b>	Lasers, glass colorant
<b>Thulium</b>	High-power magnets
<b>Ytterbium</b>	Fiber-optic technology, solar panels, alloys (stainless steel), lasers, radiation source for portable X-ray units
<b>Lutetium</b>	X-ray phosphors

*Table 5 Types of Rare Earth Element and Its Uses*

Rare Earth Element also have their own specific application which widely used in electronic product (Fogler & Tim, 2011).

<b>Application</b>	<b>Description</b>
Permanent Magnets	They are in high demand due to their strength, heat resistance and ability to maintain their magnetism over very long periods of time. Magnets made from rare earth elements, such as neodymium, praseodymium, and dysprosium are the strongest known permanent magnets.



Rechargeable Batteries	Rechargeable batteries (NiMH ) made from lanthanum, cerium, neodymium and praseodymium (combined with nickel, cobalt, manganese and/or aluminum) are used in car batteries in hybrid electric vehicles, electronic devices and power tools
Auto Catalysts	Lanthanum and Cerium are used in the manufacture of catalytic converters which convert the pollutants in engine exhaust to non-toxic compounds
Fluid Cracking Catalysts	Fluid cracking catalysts, which contain lanthanum and cerium, are used in the refining of crude oil.
Polishing Powders	Cerium Oxide polishing powder is one of the best polishing materials. It is used for polishing glass, lenses, CRTs, jewels, silicon chips, TV screens and monitors.
Glass Additives	Cerium reduces transmission of UV light and Lanthanum increases the glass reflective index for digital camera lenses.
Phosphors	Europium, terbium and yttrium are REEs used extensively in the electronics industry to manufacture LCDs and colour TVs. Used as phosphors they enable colour changes as electrical currents are transmitted through them.

*Table 6 Rare Earth Application*

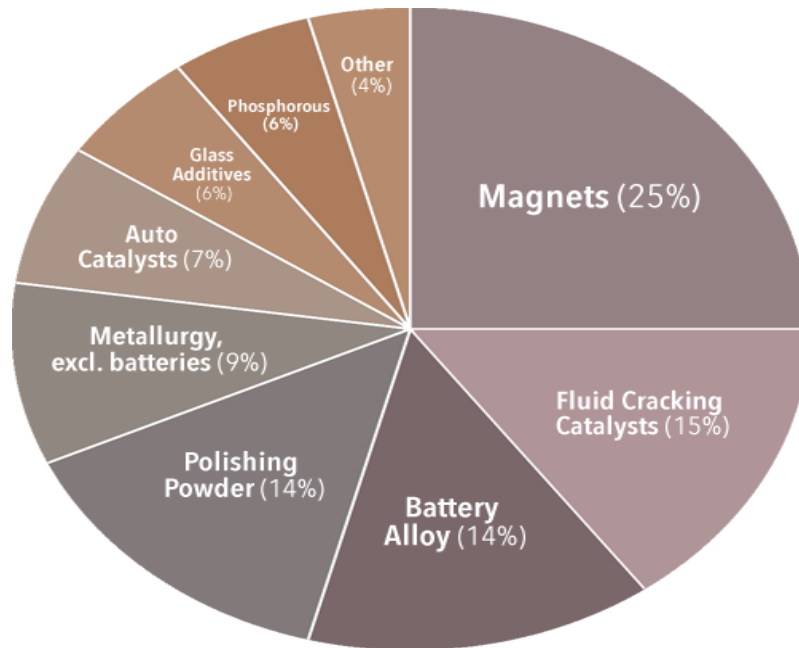


Figure 1 Rare Earth Element Product Usage by Industry

### 2.1.3 Liquid Crystal Display (LCD)

A liquid-crystal display (LCD) is a flat panel display, electronic visual display, or video display that uses the light modulating properties of liquid crystals. Liquid crystals do not emit light directly (Arpaci-Dusseau, RemziH, & C, 2014). Liquid crystal Display (LCD) is divided into two components which is cold cathode fluorescent lamps and light emitting diodes. They are used in the LCD panel as the backlight unit. In the structure of LCD, LCD glass (panel), various optical films, and backlight are arranged in laminar structure. The differences can be seen in the production of LCD of television and LCD of computer monitor where the location of lamp behind the screen is different. For the LCD TV the lamp are arranged in a row in the back of the module while in monitor lamp it is placed at each long edges of the module behind the panel and “light guide” is used to redirect the lightning towards the panel. ITO is the component of rare earth element that located in the LCD panel. In figure 2 below, the structure of the key components in a panel and LCD was put in between two glass panels is shown. The recovery of the REEs from the electronics scraps (e-scrap) and other metals is very important due to economic and environmental issues (Kingsnorth & J., 2010).

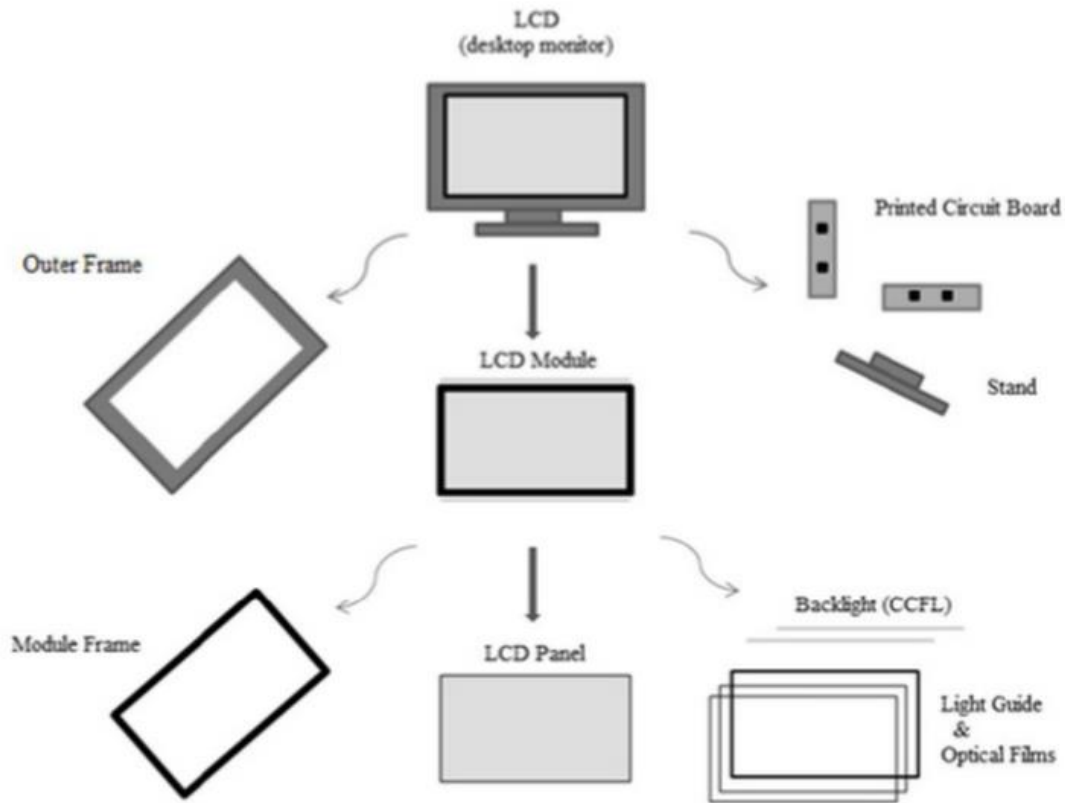
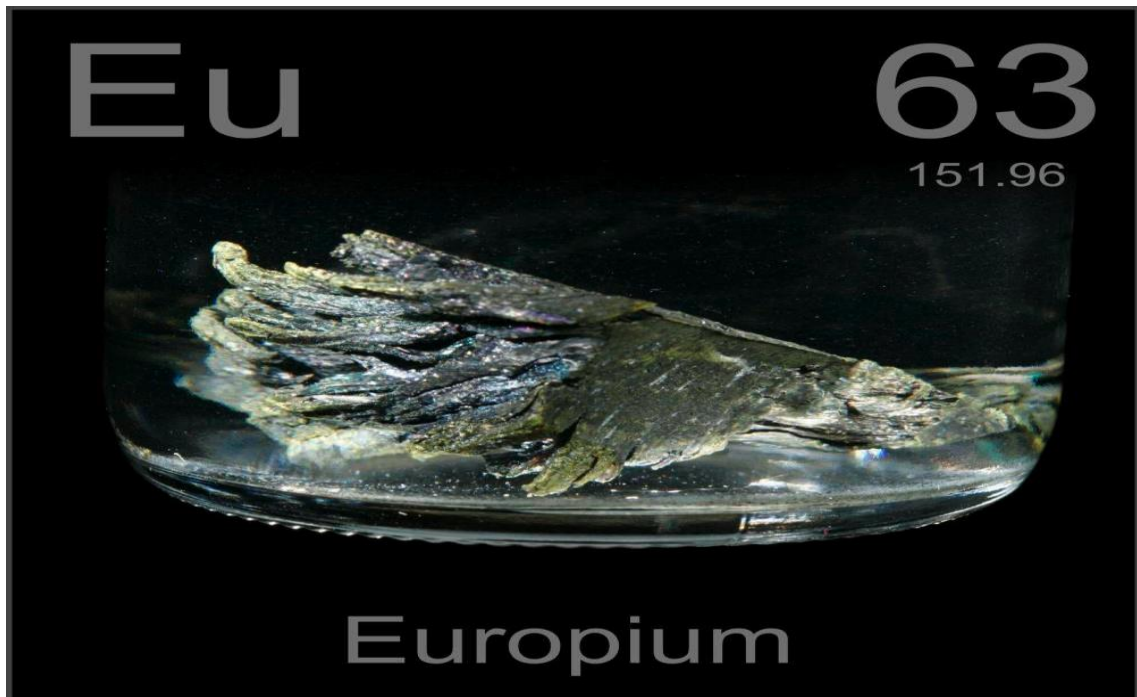


Figure 2 Component of LCD and Its General Structure

### 2.1.4 Europium

Eventhough Europium is one of the most important light rare earth elements (USGS definition) which is more abundant than the heavy rare earths, it is been classified as one of the most expensive rare earth elements and also has been categorized as one of the critical rare earths (Buchert & e.V., 2011). Shortages have been predicted with a high degree of probability (Schüler & Buchert, 2011). Because of high prices of europium and terbium, lighting and display systems represent one of the most economic rare earth applications (Buchert, Manhart, Bleher, & Pingel, 2012). Europium is usually used in phosphors, for example materials which can emit light when exposed to a light or electron source (Schüler & Buchert, 2011). It is different with the element phosphorus whose light emitting properties are down to a different phenomenon (Schüler & Buchert, 2011). To get phosphor materials, salt-like host lattices (matrices) are dotted with metal ions (e.g.  $\text{Eu}^{2+}$  or  $\text{Eu}^{3+}$ ), which are act as activators of the dopants (Schüler & Buchert, 2011). Europium can produce a red or blue light depending on the

oxidation state (Schüler & Buchert, 2011). By combining the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  in the phosphor application, it can yield a white light that is been used in compact fluorescent bulbs (Stewart, 2014). Europium is one of the most common rare earth that widely used as an activator in phosphors, followed by terbium, but it should be alert that the rare earths used in the phosphor matrices such as yttrium are more important in terms of absolute quantities used (Buchert, Manhart, Bleher, & Pingel, 2012). Activators are used in low concentrations of phosphor material (Schüler & Buchert, 2011). Even though Europium and other rare earths such as terbium, samarium, erbium, thulium, cerium and dysprosium are used in very small amount, their role in the respective application is important and there is a lack of suitable substitutes in the short term (Schüler & Buchert, 2011). Rare earths are used in most energy efficient lighting technologies, including compact fluorescent light bulbs (energy saving light bulbs), fluorescent tubes, LEDs, EL foils, plasma displays and LCD displays. This rare earths use to helps achieve good color qualities and higher energy efficiencies (Schüler & Buchert, 2011)



*Figure 3 Europium*

### ***2.1.5 Recovery Of Rare Earth Element***

(Morais, 2001) had stated that the recovery of europium from computer LCD uses sulphuric acid as the leaching agent. In this study, the Eu and Y solubilisation is 90 wt% and 95 wt.% respectively when conducted at 90°C, 2 hour of leaching, acid/sample ratio of 1000 kg/t and 40% solids. At 70°C, 1500 kg/t acid/sample ratio, 2 hour of leaching, and 40% solids, the solubilisation of both metals was 80wt%.

(Rabah, 2008) had stated that the recovery of europium from computer LCD will use a mixture of sulphuric/nitric acids as the leaching agent. At critical conditions for example autoclave digestion, at 125°C, 4 hour and 5 MPa using a mixture of sulphuric/nitric acids, the Eu and Y solubilisation is 92.8 wt% and 96.4 wt% respectively.

### ***2.1.6 Separation Of Rare Earth Element***

The separation of REE is very difficult due to its chemical properties. However, the REEs can be very easily replaced for one another making refinement to pure metal difficult (British Geological Survey, 2010). Hence, the separation of REE into two stages which are Extraction of Rare Earth Oxides (REO) from Monazite or xenotime and Purification of Rare Earth Oxides (REO)

Monazite is known as a reddish-brown phosphate mineral that contain REEs. There are four different type of monazite, which is monazite-Ce (Ce, La, Pr, Nd, Th, Y)PO<sub>4</sub>, monazite-La (La, Ce, Nd, Pr)PO<sub>4</sub>, monazite-Nd (Nd, La, Ce, Pr)PO<sub>4</sub> and monazite-Sm (Sm, Gd, Ce, Th)PO<sub>4</sub>. In the other hand, xenotime is rare earth phosphate mineral. The major component of xenotime is yttrium orthophosphate (YPO<sub>4</sub>). It will forms a solid solution series with chernovite-(Y) (YAsO<sub>4</sub>) and may have trace impurities of arsenic, silicon dioxide and calcium. Monazite will be obtain from the milling process which is a process where valuable mineral material in the ore is separated from impurities. (Kidela Capital Group, 2011)

### ***2.1.7 Extraction Of Rare Earth Elements***

There are two chemical process route in extraction of REEs that can be performed. The two route are Acid Treatment and Caustic Soda Method. According to (British Geological Survey, 2011), extraction of REEs from monazite and xenotime will involves dissolution of the minerals in hot concentrated alkaline(caustic soda method) or acidic solutions (acid treatment).

### ***2.1.8 Leaching***

Leaching is the extraction between solid and liquid. In leaching process, liquid act as a diluents where as the solid usually was a composite solid where there is quite hard to separate the composite matter. Actually, rare earth element is one type of composite element. Leaching is a liquid-solid operation. The two phases are in intimate contact, the solute(s) can diffuse from the solid to the liquid phase, which causes a separation of the components originally in the solid. Solid–liquid extraction uses a solvent to remove a soluble fraction from an insoluble, permeable solid. (J.E.Cacace and G. Mazza, 2003)

Leaching process can be divided into two types. First is percolation which also known as filtration and second is disperse solid into liquid (Perry's). In leaching process, the mechanism that involved is between simple physical solutions by chemical reaction. Leaching rate can be changing by many factor which are solvent concentration, reaction temperature, reaction time, liquid to solid ratio, and also stirring speed during mixing between solvent and rare earth (Li, 2012)

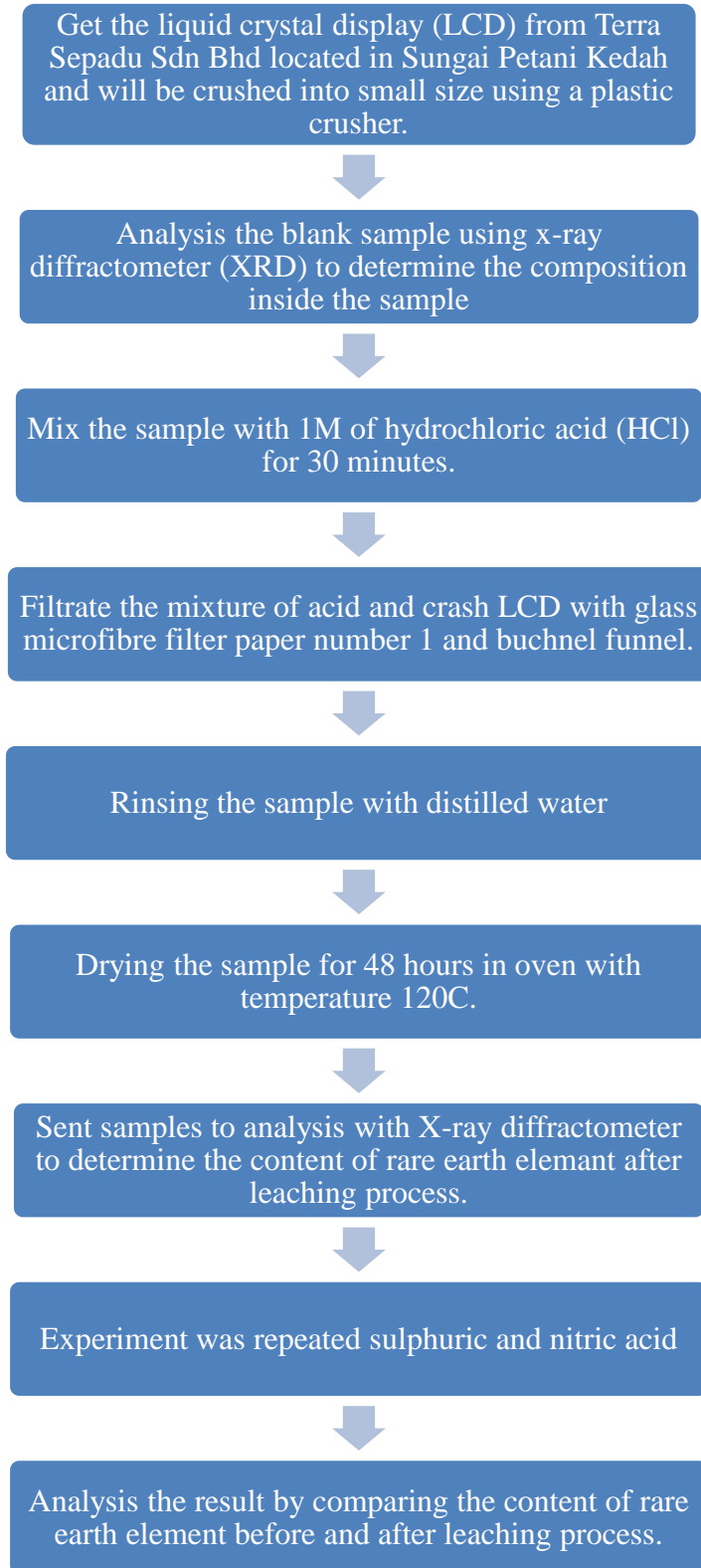
The increasing of the extraction temperature increased the rate of extraction and reduced the extraction time by increasing the diffusivity (J.E.Cacace and G. Mazza, 2003). Other than that, based on (J.E.Cacace and G. Mazza, 2003), the rate of extraction increases with a larger concentration gradient. It can also be improved by increasing the diffusion coefficient or reducing the particle size.

Smaller particle size reduces the diffusion distance of the solute within the solid and increases the concentration gradient, which increase the extraction rate. Since the path of solute to reach the surface is shorter, extraction time is reduced.

In leaching actually, transport process was occurred between solvent and the surface of element. Leaching mechanism of rare earth is ion exchange between positive-ion in solution and the surface of rare earth material (Yang & Zhang, 2012). In order to increase the surface contact between the mixture, the technique involve is by increasing the mixture concentration, increasing the temperature and also increasing the mechanical stirring to make sure the colliding between two mixture will occur rapidly. Solvent criteria that is used as leaching diluents is the solvent must have higher saturation limit and selectivity for the solute to be extracted. Second is the solvent able to produce quality extracted product, low viscosity, low flammability and toxicity, low surface tension and low density. The solvent that is commonly used in leaching of rare earth element must be acidic such as sulfuric acid and hydrochloric acid.

### 3 MATERIALS AND METHODS

#### 3.1 Overview



*Figure 4 Experiment Procedure*



### 3.1.1 Chemicals

Chemicals used is hydrochloric acid (HCl) with 90 % purity, nitric acid (HNO<sub>3</sub>) with 63 % purity and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) with 97 % purity will be diluted in different concentration such as 1.0 mol/L, 3.0 mol/L and 5.0 mol/L. The entire chemicals were obtained from Sigma-Aldrich Malaysia. Ratio used in leaching process for solvent to solid is in weight ratio.

$$\text{Molarity of acid (M)} = \text{purity (\%)} / \text{specific gravity molecular weight of acid}$$

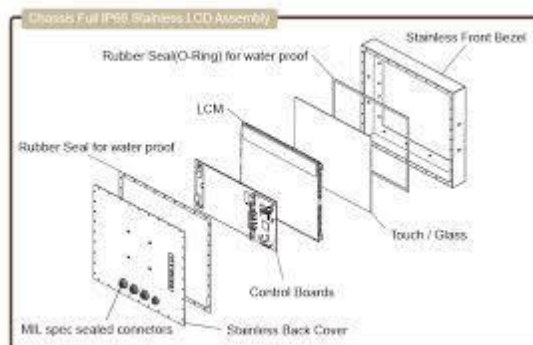
*Equation 1: Determination of Molarity of acid*

### 3.1.2 Rare earth element (REE)

The LCD screen containing rare earth element is collected from unwanted waste of electronic device from Terra Sepadu Sdn Bhd located in Sungai Petani Kedah and is crushed into small size using a plastic crusher. When LCD screen is completely grind into small size, the sample is mix with the acid solvent and filtrate by filter paper before dry the sample in oven. After that, it will be sent to be analyze the contain of rare earth metal by using x-ray diffraction (XRD) equipment to know the real contain of rare earth metal in sample.. This process is repeated for three times leaching. Then when finish dry in oven, the sample must be analyze using XRD to determine the rare earth metal that loss during leaching process. The component of LCD that must be crash is LCM.

$$\text{Number or rare earth loss in the experiment} = \text{Number of rare earth metal before leaching process start} - \text{Number of rare earth after leaching process}$$

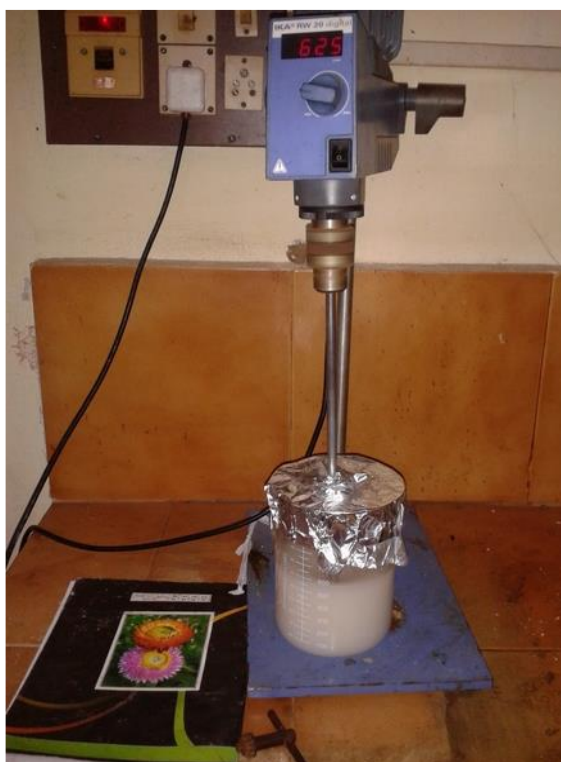
*Equation 2: To determine the number of rare earth loss in the experiment*



*Figure 5 Minor Part in LCD Screen*

### **3.1.3 Leaching process**

Weight ratio for the solvent to solid is 1:5. Solid of rare earth element must be mixed with 25 mL chemicals in a 100 mL beaker. For mechanical stirring equipment used was mechanical stirrer and it will be stirred for 30 minutes.



*Figure 6 Mechanical Stirrer*

### **3.1.4 Filtration of solution**

The solution that formed by rare earth element and solvent will be filtered using micro fibre filter paper and dried in the oven for 120°C for 48 hours.

### **3.1.5 Analysis of product**

The analysis equipment that is used is X-ray diffraction. There are few reasons why choosing X-ray diffraction as the analysis equipment. The benefit of using XRD is the short term analysis can ensure the chemical compositions to be determined in seconds depending on mass of sample. Besides, it is easy to use because it is a modern instruments that run under computer control, which is also provide with effective software to handle measurement set-up and results calculation. In addition, XRD required only minimal preparation because of the penetration of X-rays in the mid-Z X-ray region beyond the surface, and while it does incorporate any contamination on the surface as it is generally not an issue if some soil remains in the flake scars. The analyzed volume is relatively very large compared to any surface contamination. The most important thing that need to be concerned is sample will not be destructed and the neutrality of the sample is guaranteed. This is not the case with most metals, where chemical weathering can radically change the composition at the surface and yield erroneous results. The electronic chipboard that is dried will be collected in small amount around 5 mg before it will be analyze using XRD in central lab. The data collected by this equipment will be analyze to know the number of element metal present in each sample.

### **3.2 *X-Ray Diffractometer (XRD)***

An x-ray diffractometer help to explain or clarify a sample of material with x-rays of known wavelength, moving the sample and detector in order to measure the intensity of the diffracted radiation as a function of beam and sample orientation. From the resulting intensity versus angle plot much can be conclude about the structure of the material. (Wiley, 2004)

X-Ray diffraction (XRD) is a powerful technique used to characterize crystalline materials. The crystals that make up a crystalline material have unique dimensions that are characteristic of a material. Using an x-ray diffractometer, and Bragg's law the crystallography of a material can be determined. Conversely, unknown materials can be identified using XRD and standards that have been previously determined (Ying, 2010)

## **Bragg's Law**

$$n\lambda = 2d \sin \theta$$

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta,  $\theta$ ). The variable  $d$  is the distance between atomic layers in a crystal, and the variable lambda  $\lambda$  is the wavelength of the incident X-ray beam;  $n$  is an integer (McQuarrie & A, 1997). This observation is an example of X-ray wave interference (Roentgenstrahlinterferenzen), commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries (W., Ashcroft, & Mermin, 1976)

### 3.2.1 Types of X-Ray Diffractometer (XRD)



*Figure 7 ADX-2500 X-ray Diffraction Instrument*



*Figure 8 ADX-2700 X-ray Diffraction Instrument*

## 4 RESULT AND DISCUSSION

This section is where the discussion of the results obtained from the experiments will be done. The graph shows the comparison between the results of XRD, the best solvent that can be used in the leaching process and last but not least the best solvent concentration that can be used.

### 4.1 RELEVANT OF LCD CRUSHING

X-ray diffractometer (XRD) is an equipment that is used to identify the crystalline material and it is widely used by geologist in the geological field. The main uses of this equipment are for mineral identification, quantitative mineral fractions, quantitative clay fractions and by inference clay volume and clay or silt ratio. In order to made an analysis of minerals or substance using XRD, the materials should be crushed into small particles or powder form. This is important because to make sure large statistical variations may be expected from the samples. For bulk powder analysis, it just need 1g of samples. X-Ray diffraction analysis will shows final result include printed spectra, digital spectra images, and spreadsheets of tabular data.



*Figure 9 LCD Screen Powder After Crushed by Plastic Crusher*

## 4.2 EFFECTS OF SOLVENT

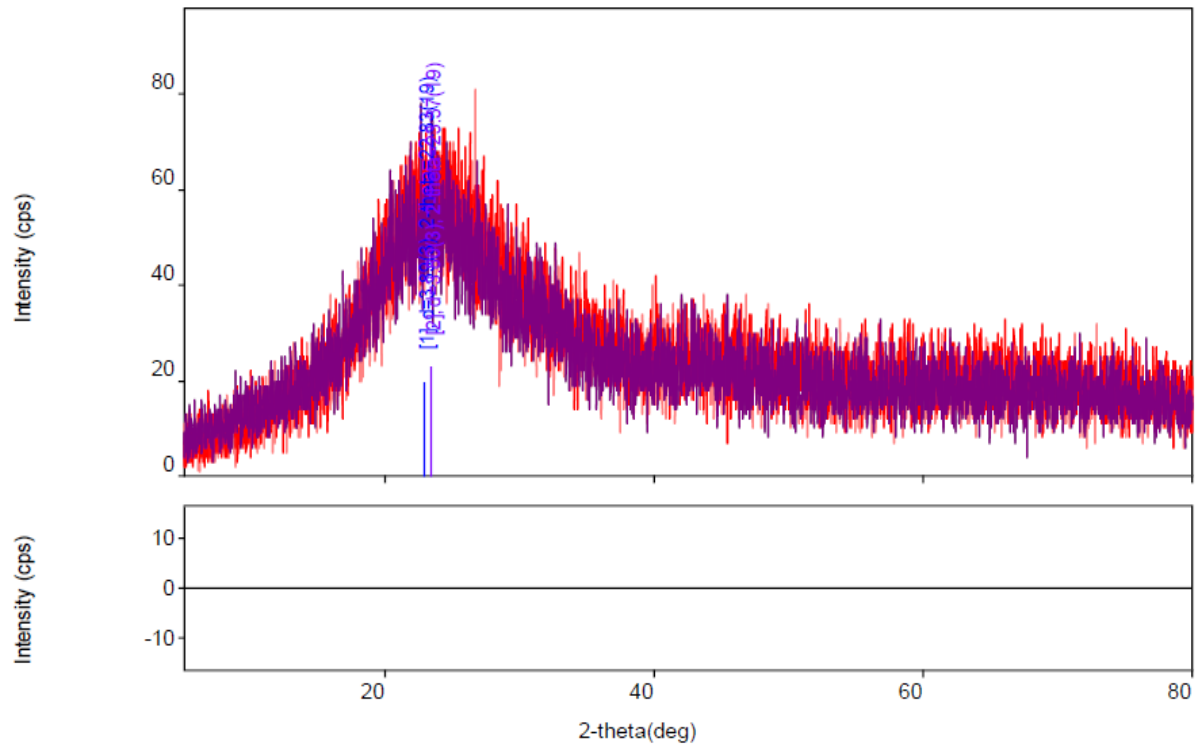


Figure 10 : XRD analysis to compare 1M concentration of acid

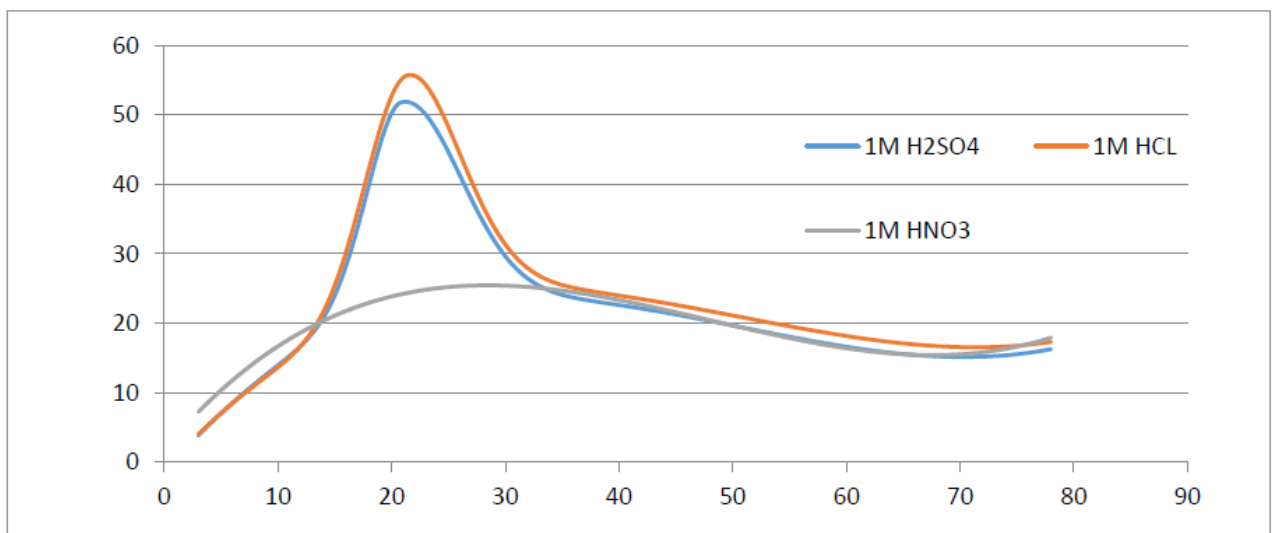


Figure 11: Intensity vs peak number in XRD with 1M concentration

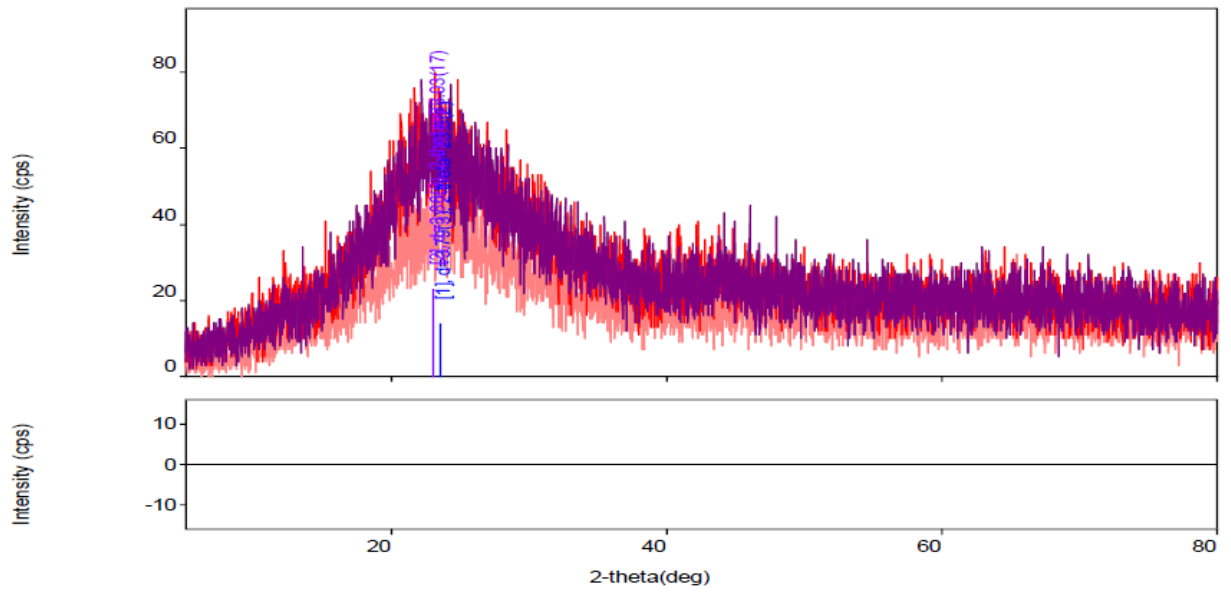


Figure 12 : XRD analysis to compare 3M concentration of acids

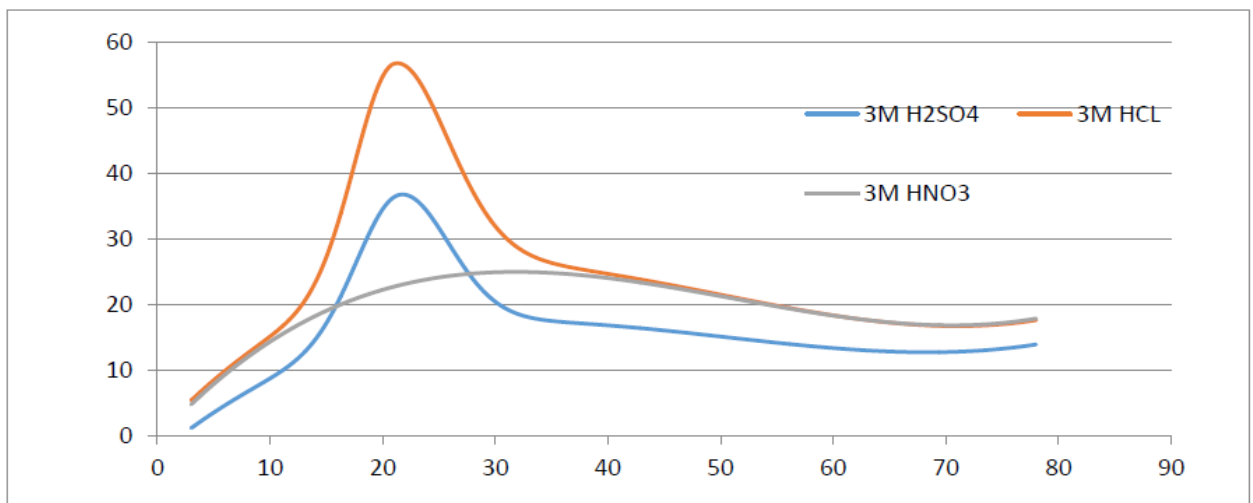


Figure 13: Intensity vs peak number in XRD with 3M concentration



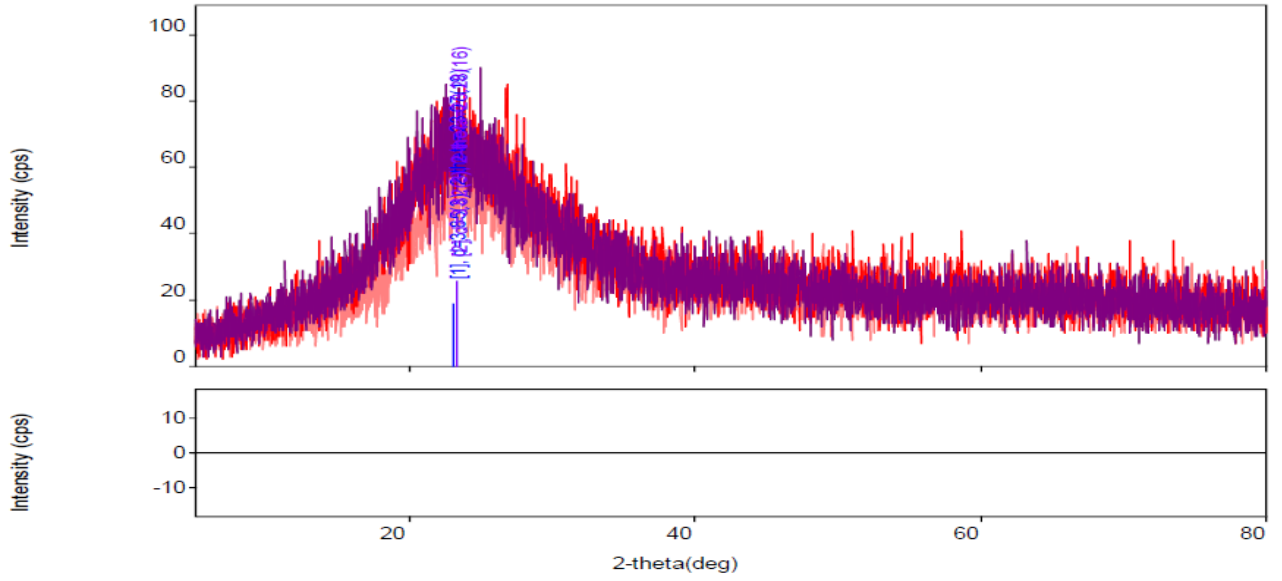


Figure 14: XRD analysis to compare 5M concentration of acids

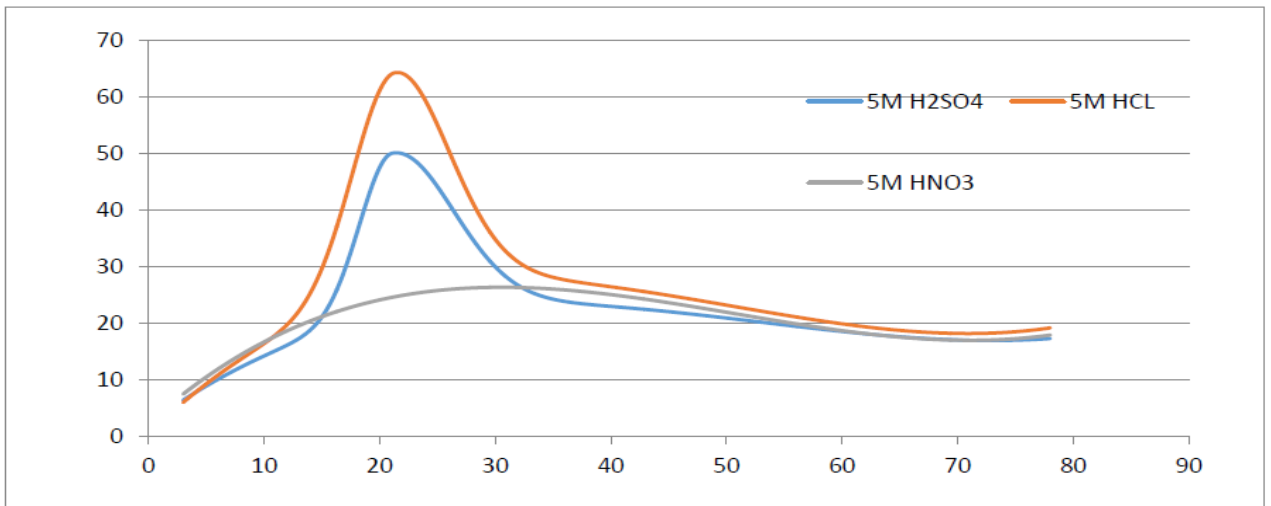


Figure 15: Intensity vs peak number in XRD with 5M concentration

Figure 10, 12 and 14 shows the XRD analysis result for different type of solvent used in leaching process for the extraction of the rare earth element. Figure 11, 13 and 15 is the graph that we obtained using the microsoft excel. After analyses and study the result, the conclusion that can be made is the best solvent for the extraction of rare earth elements is hydrochloric acids. Other solvents used in the leaching process is sulphuric acid and nitric acid. The reason why hydrochloric acid can extract more element from LCD screen compared to sulphuric acid is due to the volume of the solvent.

The mass of LCD screen used in this research is 5 g while for the volume of acid is depending on the weight ratio of acid and the weight of the mesh LCD. The ratio used is 1:20. In order to get volume of solvent,

$$\text{volume of acid (ml)} = \frac{\text{weight of acid (g)}}{\text{density of acid (g/ml)}}$$

Since the volume of solvent is inversely proportional to the density of solvent, it can be said that the higher the density, the less volume of acid used in the leaching process.

Ratio	Weight Of Mesh LCD (g)	Volume of HNO <sub>3</sub> (ml)	Volume of H <sub>2</sub> SO <sub>4</sub> (ml)	Volume of HCl (ml)
1:20	5	66.23	54.4	67.12

*Table 7 Volume of Different Solvents*

From the table above, it is justified that the higher the volume acid used, the higher the amount of rare earth metal can be extracted.

Young's law had stated when the surface contact between solid and liquid is higher, the contact angle between solid and liquid will be lower. After this leaching process, it shows that hydrochloric acid has higher surface contact with the mesh LCD compared to nitric acid and sulphuric acid. So, it can be said that when the surface contact between the solvent and solid is higher, the reaction of the solvent will be more efficient in order to extract high amount of rare earth element..

### 4.3 EFFECTS OF MOLARITY

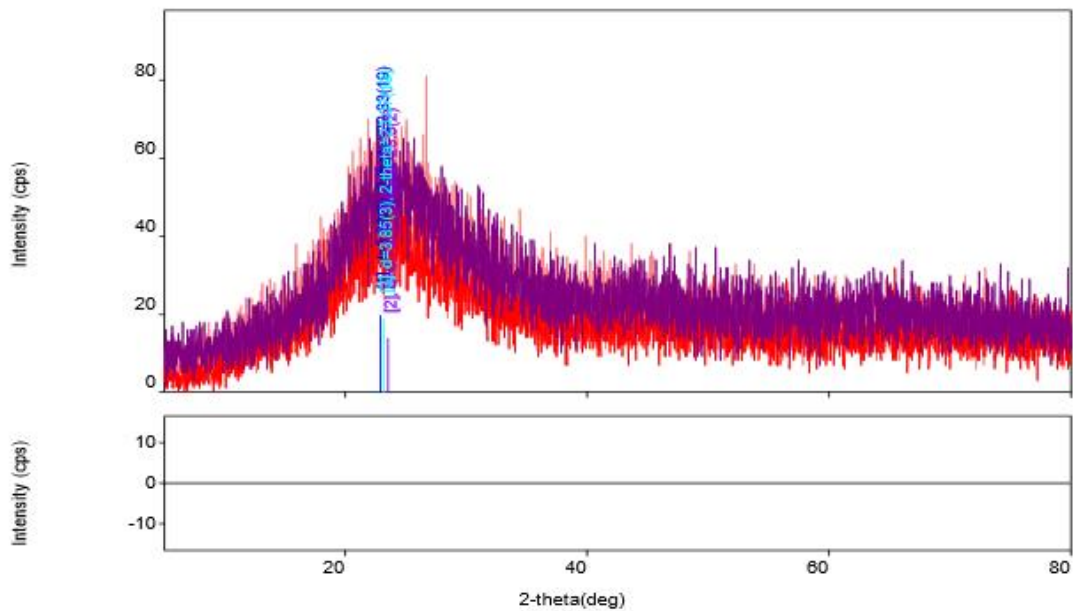


Figure 16 : XRD analysis to compare sulphuric in different concentration

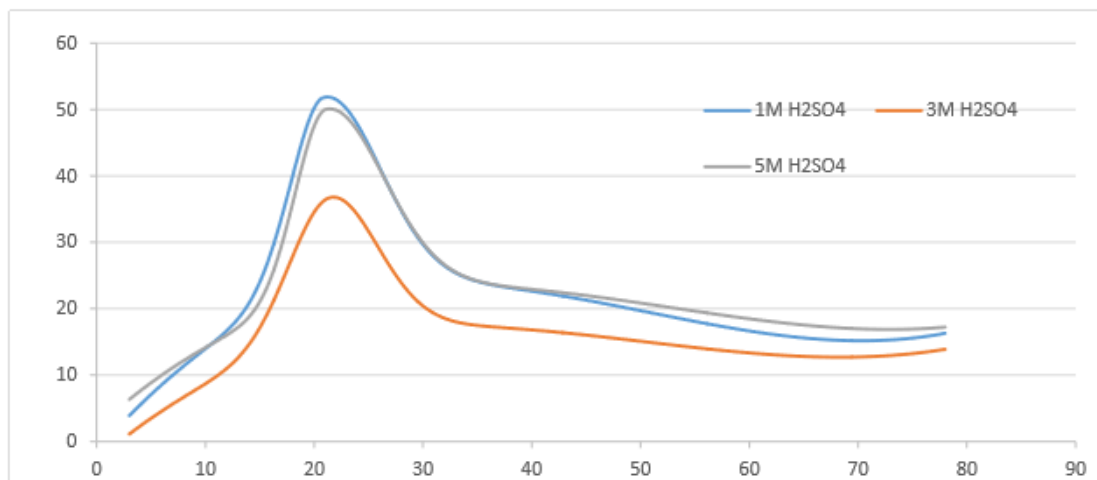


Figure 17 : Intensity vs peak number in XRD of sulphuric acid with different concentration

As we can see from figure 17, concentration of 1M of sulphuric acid can be said as the best condition for leaching process. Sulphuric acid is one of the most strong acid, which have two number of cationic proton also known as diprotic acid. But unfortunately it cannot be the best solvent in leaching process. Basically in reaction process theory, diprotic acid had no ability to lose the second proton which cause the reaction between the surface of acid and the mesh LCD to be low since the acid had a difficulties to remove the proton.

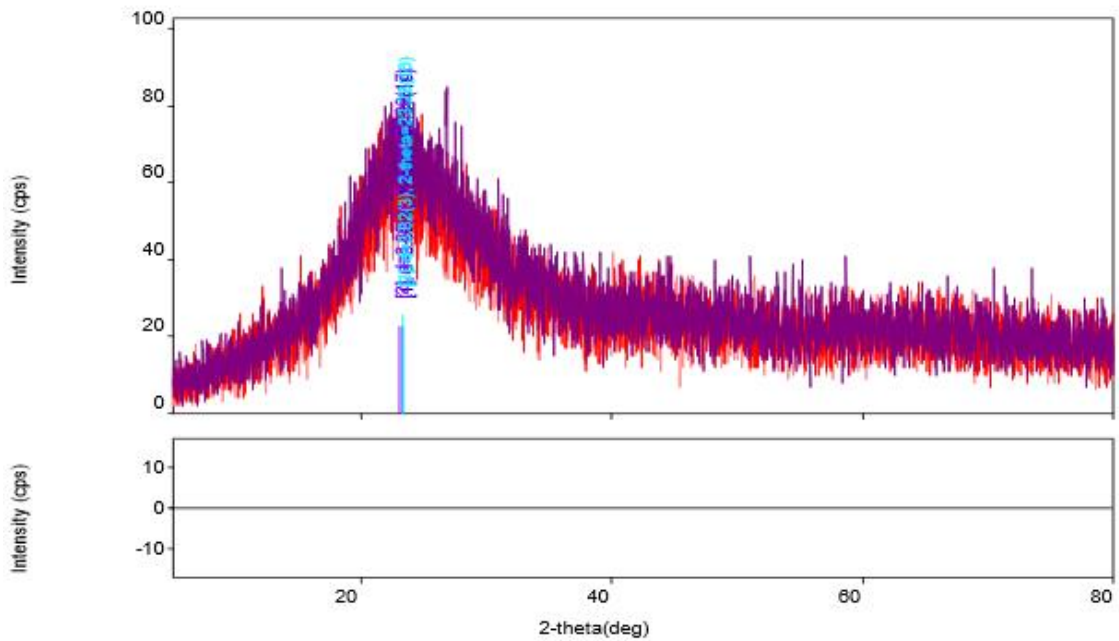


Figure 18 : XRD analysis to compare hydrochloric acid in different concentration

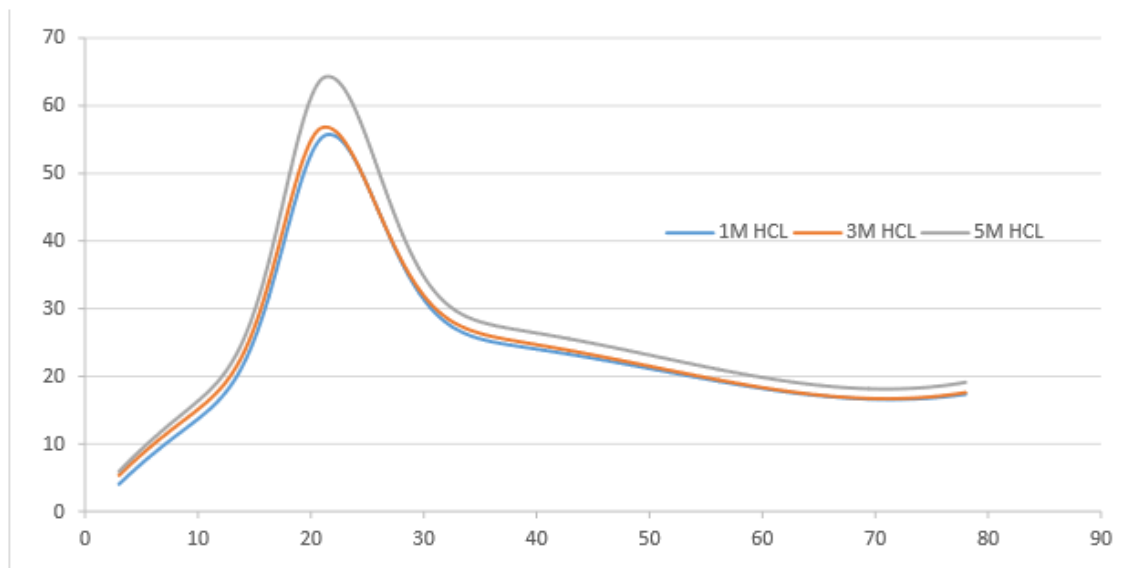


Figure 19 : Intensity vs peak number in XRD of hydrochloric with different concentration

As can be seen in figure 19, we can see the number of molarity increases as the number of intensity increases. From there, we can said that the intensity is directly proportional to the molarity of acid. In theory of reaction, chlorine is an element that can reacts rigorously with metal. So, when the concentration increase, the quantity of rare earth element extracted also increase.

From figure 20 and 21, what we can see is leaching process with the nitric acid give a poor result. Nitric acid is a monoprotic and non-organic acid which is same as hydrochloric acid. Therefore, it also cannot be the good solvent in leaching because acid dissociation constant,  $K_a$ , for the nitric acid is lower than hydrochloric acid ( $\text{HNO}_3$  : 28 and  $\text{HCl}$  :  $1 \times 10^{28}$ ). Nitric acid used is in liquid form and already dilute with water to obtain the desired molarity. When the dissociation constant is low, this means that the reaction between the solid LCD with acid also low. So, only small amount of rare earth element can be extracted.

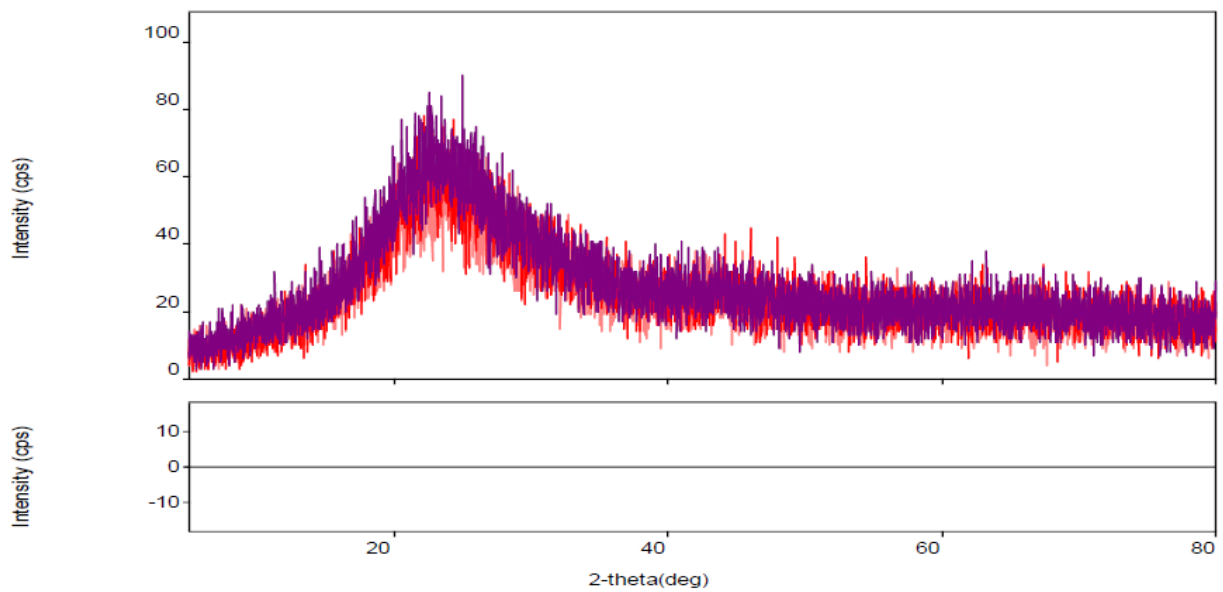


Figure 20 : XRD analysis to compare nitric acid in different concentration

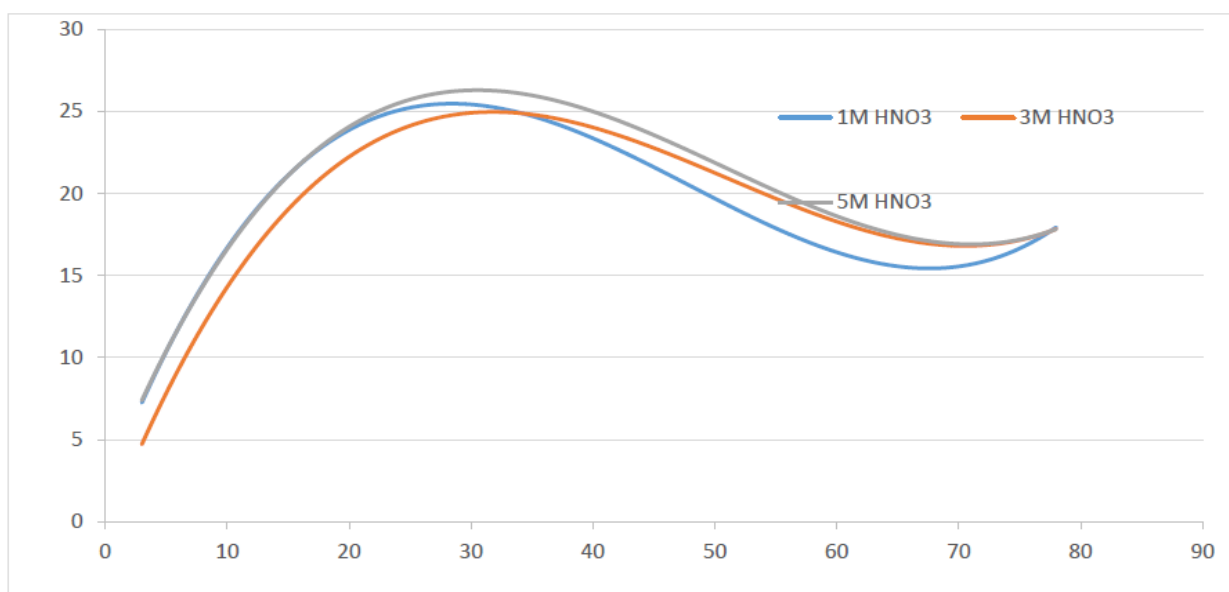


Figure 21 : Intensity vs peak number in XRD of nitric acid with different concentration

#### **4.4 INDIUM**

After the research, XRD analysis had shown that the element that present in the LCD screen monitor is indium instead of europium. Indium is a chemical element with symbol In and have an atomic number of 49. Indium is a rare earth element that is rare in Earth's crust. It is one of very important element in industrial processes especially electronics industry. Indium is very soft, malleable and easily fusible. The melting point of Indium is 429.7485 K (156.5985 °C) which is higher than sodium, but lower than lithium or tin. Based on the physical and its position in the periodic table, Indium can be classified as heavy metal and it is not toxic hazard. Indium is relatively have same chemical properties with gallium and thallium.

Most indium is used to produce indium tin oxide (ITO). It is an important part of touch screens, flatscreen TVs and solar panels (Emsley, 2014). ITO is used to conducts electricity, it bonds strongly to glass and it is transparent. Indium oxide ( $\text{In}_2\text{O}_3$ ) and indium tin oxide (ITO) are used as a transparent conductive coating which is applied to glass substrates in the making of electroluminescent panels (Azonano, 2007) Besides, indium nitride, indium phosphide (Bachmann, 1995) and indium nitride (Bhuiyan, Hashimoto, & Yamamoto, 2003) are semiconductors which is used in transistors and microchips. Indium is also used in the synthesis of the semiconductor copper indium gallium selenide (CIGS), which is used to manufacture the thin film solar cells (Powalla & Dimmler, 2000). In addition, indium also used in light-emitting diodes (LEDs) and laser diodes based on compound semiconductors such as InGaN (Schubert, 2003). Then, indium metal can be used to give a mirror finish to windows of tall buildings, It also can be a protective film on welders' goggles. Formula 1 racing cars also used it to coat ball bearings because it has low friction

## **CONCLUSION**

Based on the result of effect of solvent, it can be said that the higher the volume of solvent used in the leaching process, the higher the amount of rare earth element extracted. From the result, it can be concluded that hydrochloric acid (HCl) is the best solvent for the leaching process in extraction of rare earth element.

Next, in the result of effect of molarity, it can be said that, the higher the molarity used, the higher the amount of rare earth element can be extracted. Therefore, it can be concluded that to ensure the effectiveness of leaching process, high molarity of acid is needed.

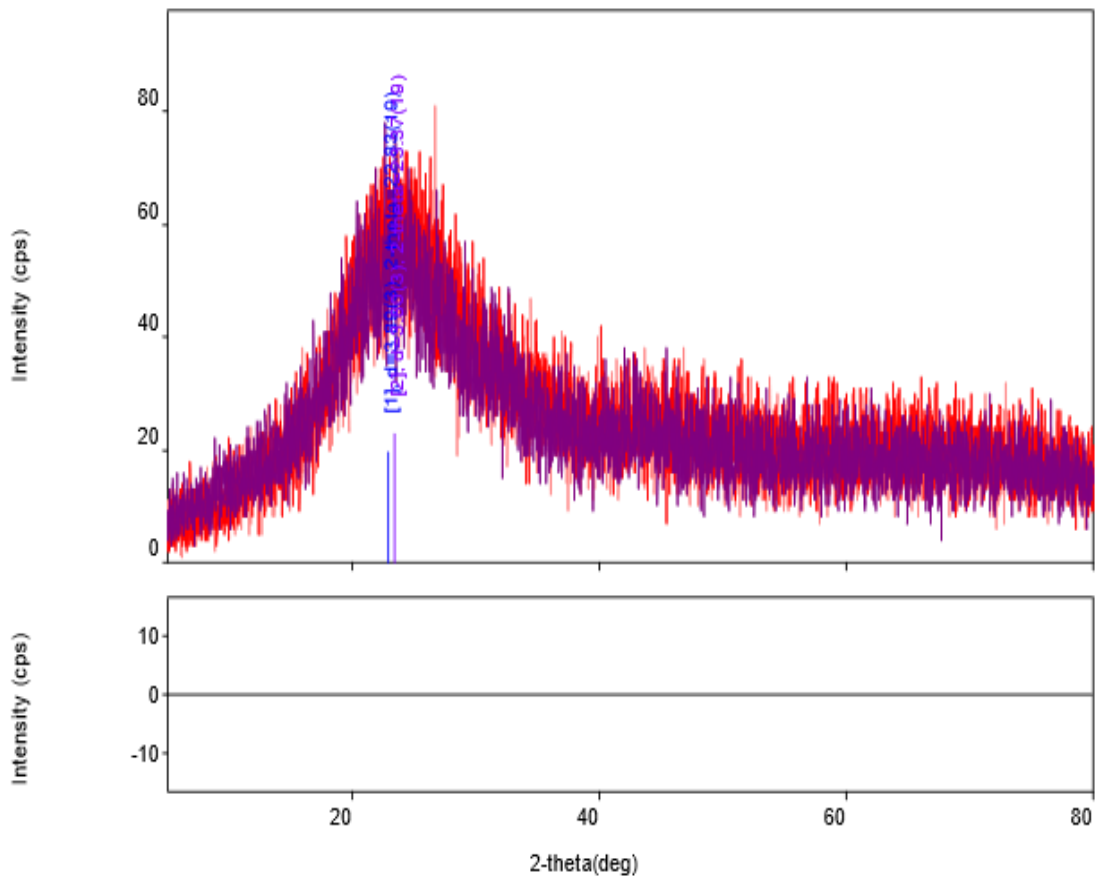
Besides, the dried powder after the leaching process which contain Indium, can be recycled back and used in the electronic industries which is the major user of Indium.

## 5 APPENDIX

XRD Analysis

File Name : C 1M H2SO4 1-20.raw

### Measurement profile



### Measurement conditions

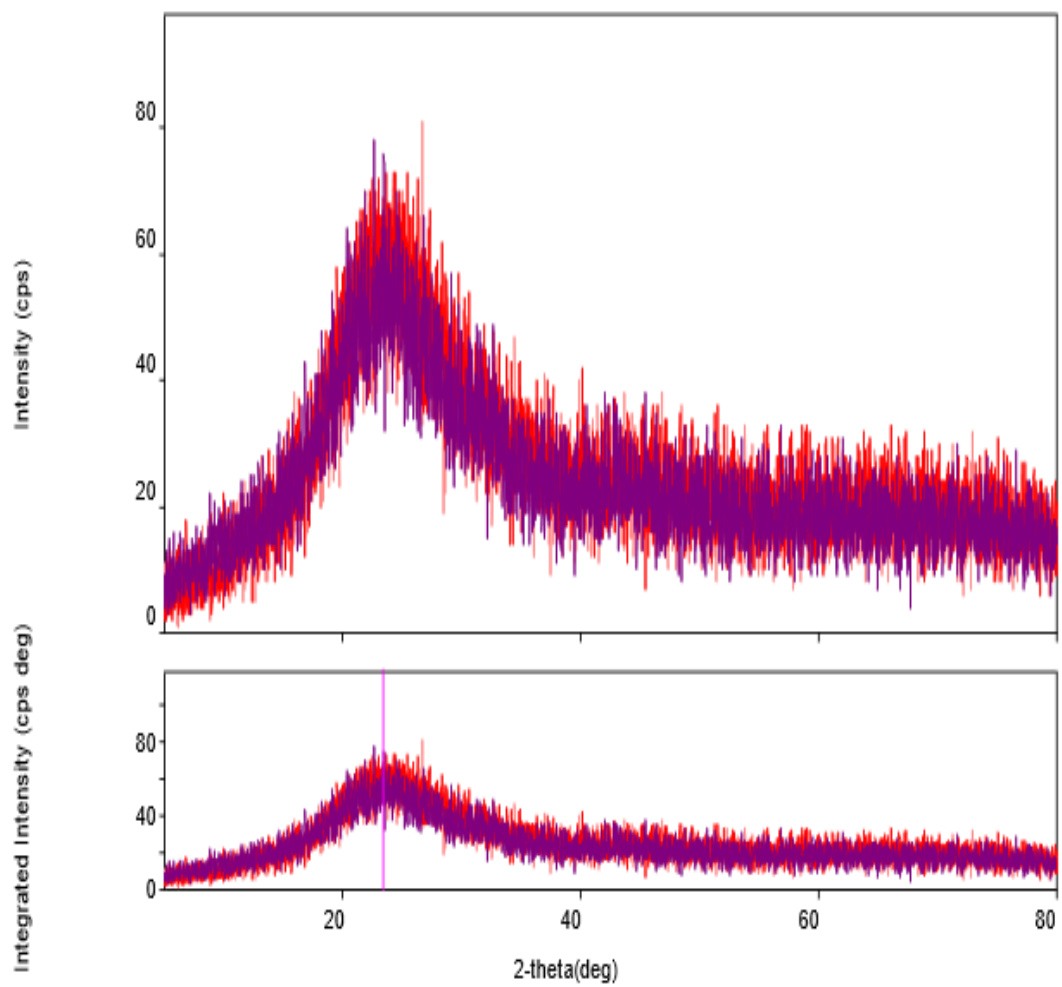
XG	Cu/30 kV/15 mA	Duration time / Scan speed
Goniometer		Step / Sampling step
Attachment	-	Measurement axis
K-beta filter	-	Scan range
Incident monochromator	-	Incident slit
Receiving monochromator	-	Vertical divergence slit
Counter	-	Receiving slit #1
		Receiving slit #2



## Qualitative analysis results

Phase name	Formula	Figure of merit
------------	---------	-----------------

Phase name	Formula	Space group
------------	---------	-------------

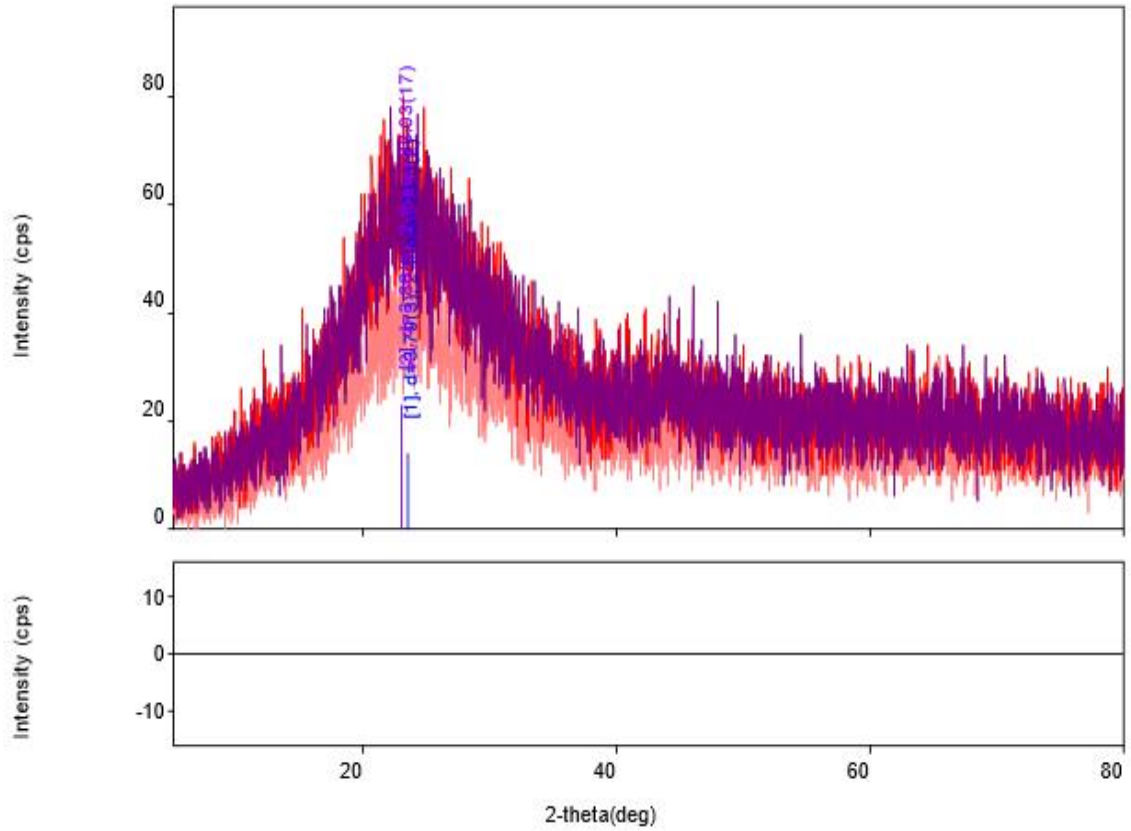


## Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps#deg)	FWHM(deg)	Size
22.83(19)	3.89(3)	20(4)	217(4)	9.69(17)	8.7
23.37(19)	3.80(3)	23(5)	251(5)	9.92(17)	8.5

XRD Analysis  
 File Name : C 3M H2SO4 1-20.raw

**Measurement profile**



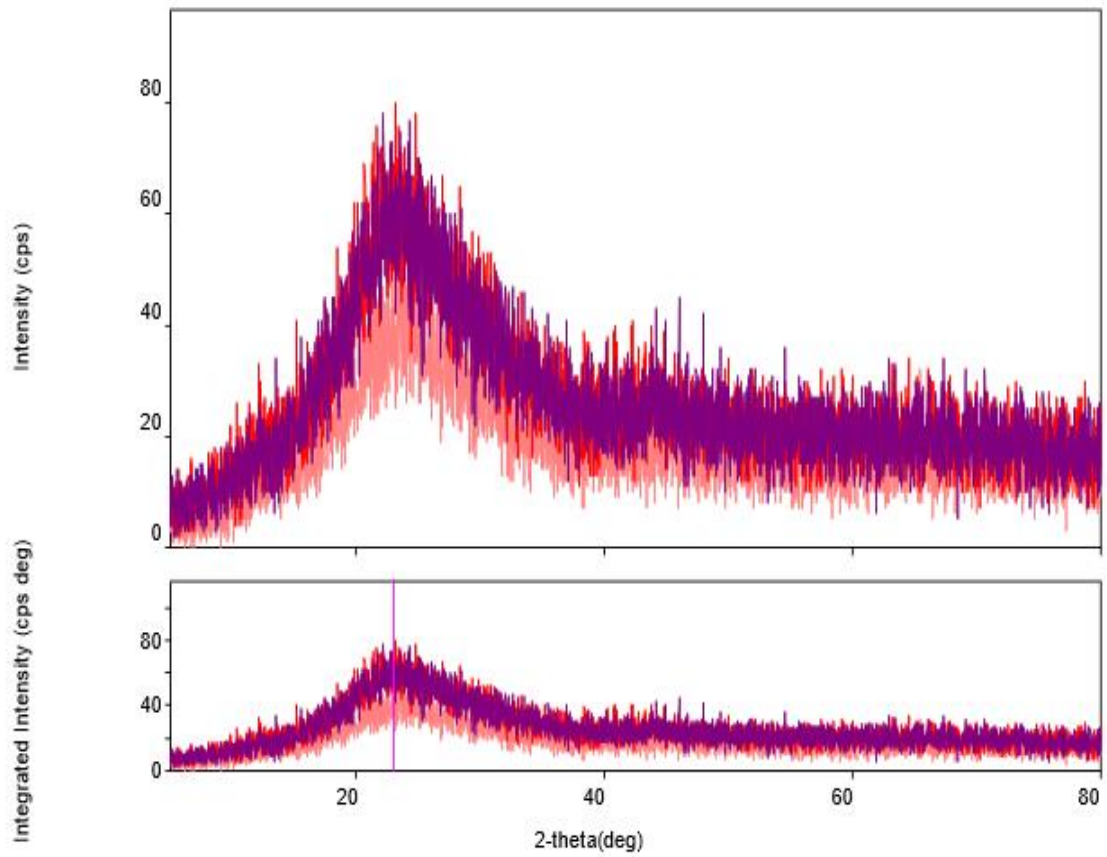
**Measurement conditions**

XG	Cu/30 kV/15 mA	Duration time / Scan speed
Goniometer		Step / Sampling step
Attachment	-	Measurement axis
K-beta filter	-	Scan range
Incident monochromator	-	Incident slit
Receiving monochromator	-	Vertical divergence slit
Counter	-	Receiving slit #1
		Receiving slit #2

## Qualitative analysis results

Phase name	Formula	Figure of merit

Phase name	Formula	Space group

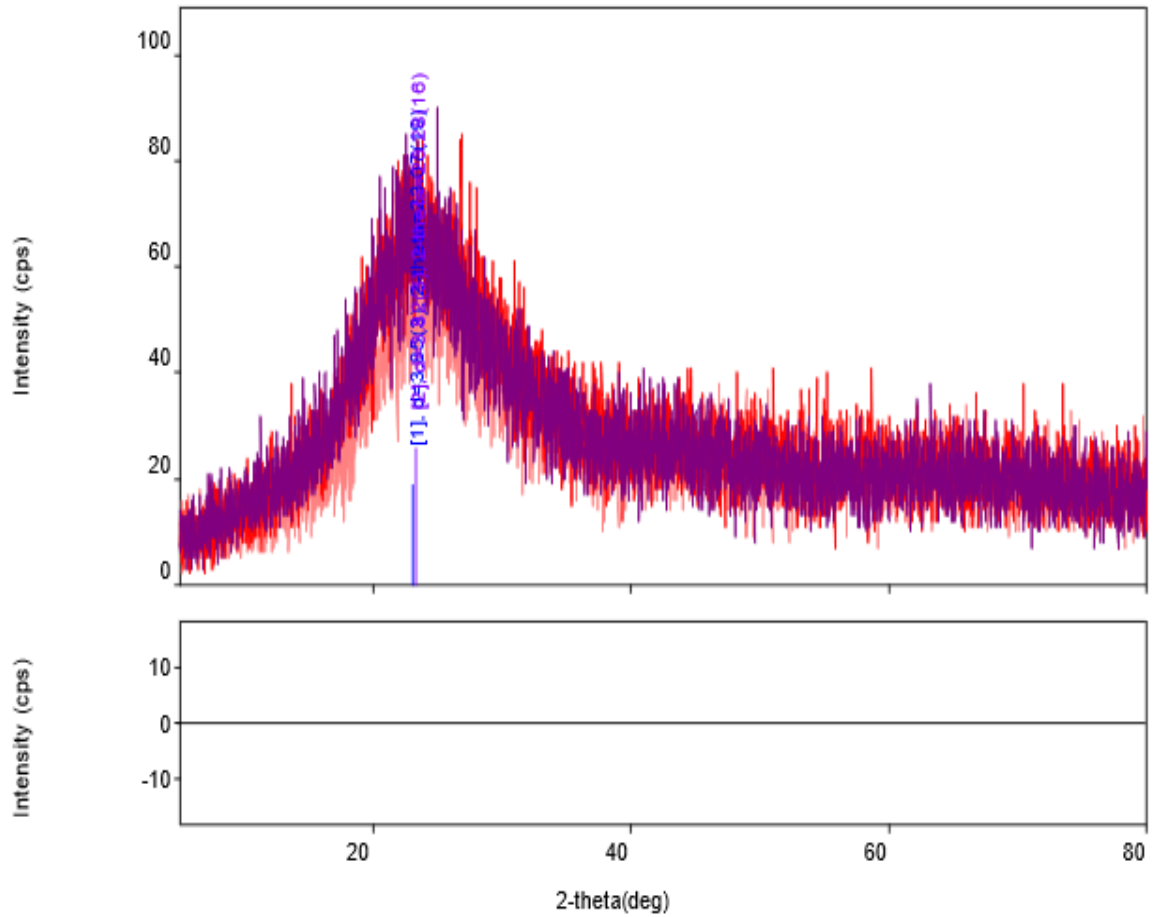


## Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps#deg)	FWHM(deg)	Size
23.5(2)	3.79(3)	14(4)	155(3)	9.62(19)	8.8
23.03(17)	3.86(3)	23(5)	253(4)	9.86(15)	8.5

XRD Analysis  
 File Name : C 5M H2SO4 1-20.raw

**Measurement profile**



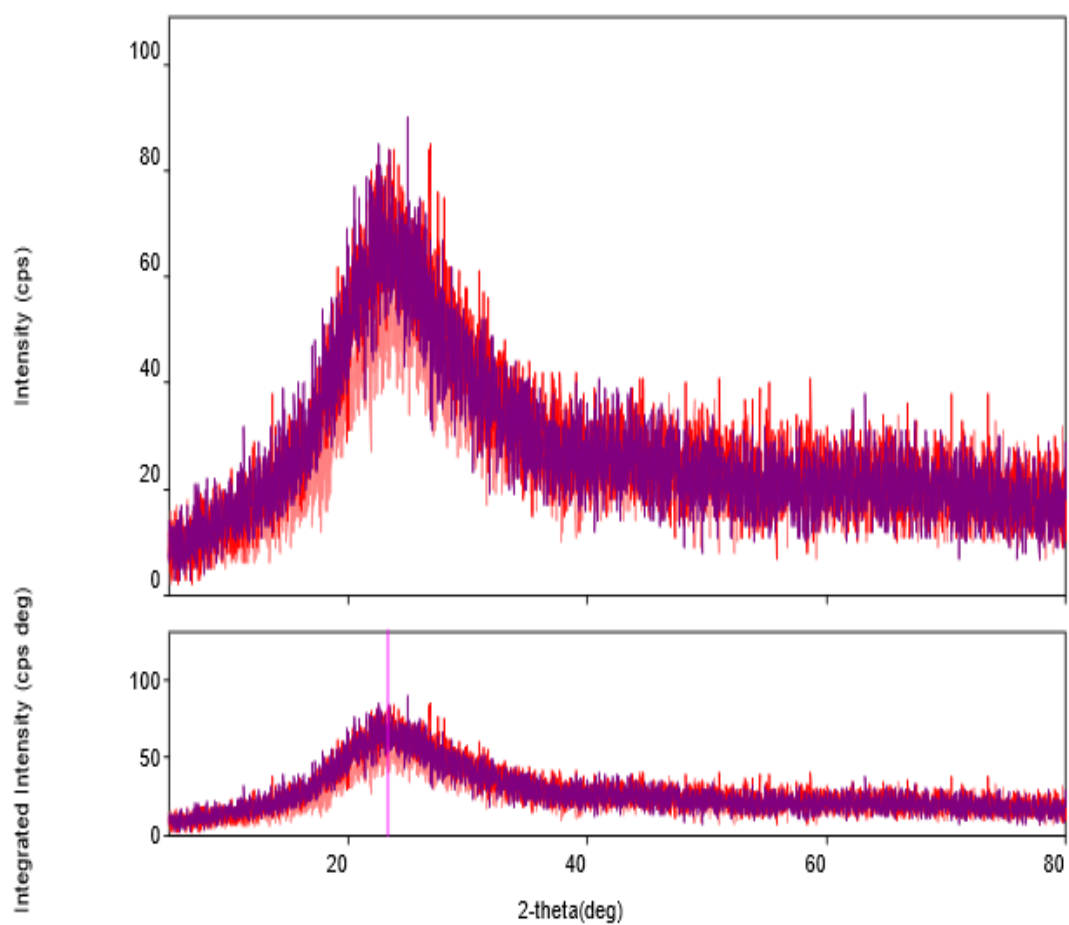
**Measurement conditions**

XG	Cu/30 kV/15 mA	Duration time / Scan speed
Goniometer		Step / Sampling step
Attachment	-	Measurement axis
K-beta filter	-	Scan range
Incident monochromator	-	Incident slit
Receiving monochromator	-	Vertical divergence slit
Counter	-	Receiving slit #1
		Receiving slit #2

## Qualitative analysis results

Phase name	Formula	Figure of merit
------------	---------	-----------------

Phase name	Formula	Space group
------------	---------	-------------



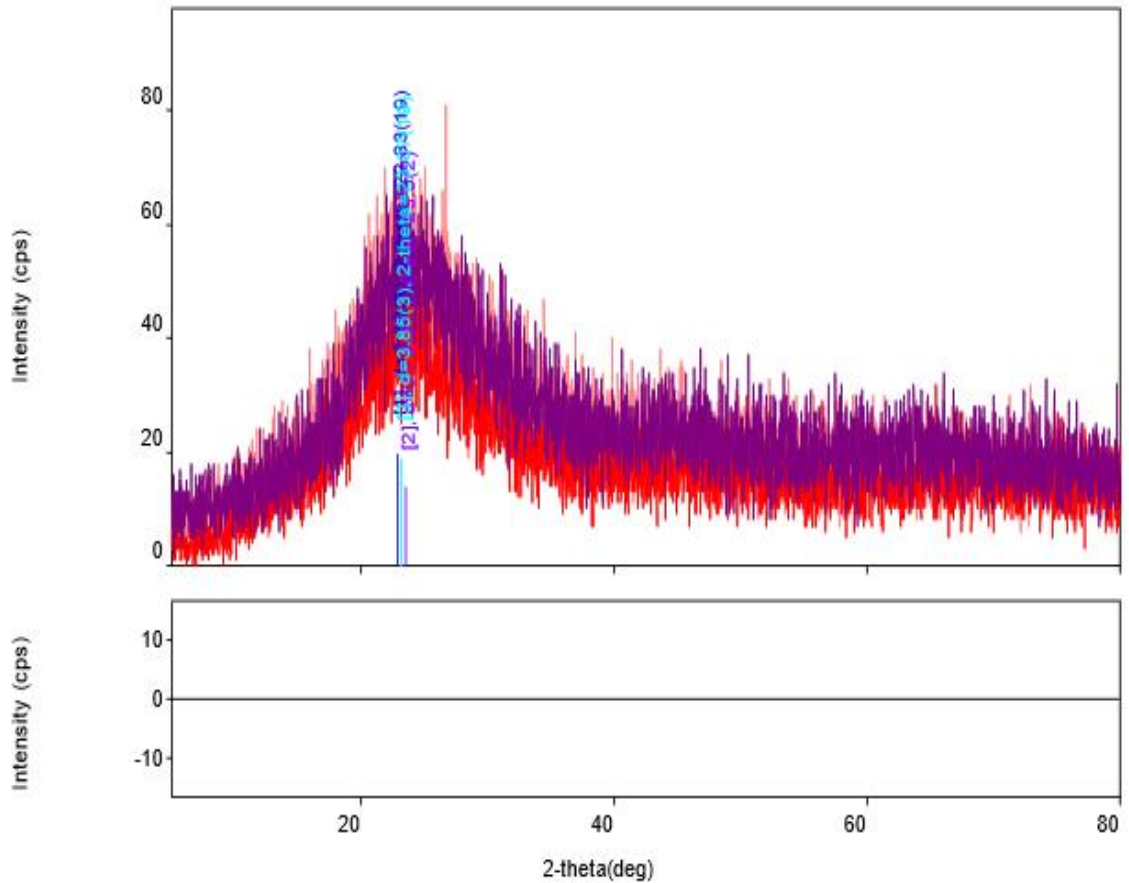
## Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps#deg)	FWHM(deg)	Size
23.07(19)	3.85(3)	19(4)	200(5)	9.49(18)	8.9
23.28(16)	3.82(3)	26(5)	286(4)	9.83(14)	8.6



XRD Analysis  
 File Name : C 1M H2SO4 1-20.raw

**Measurement profile**



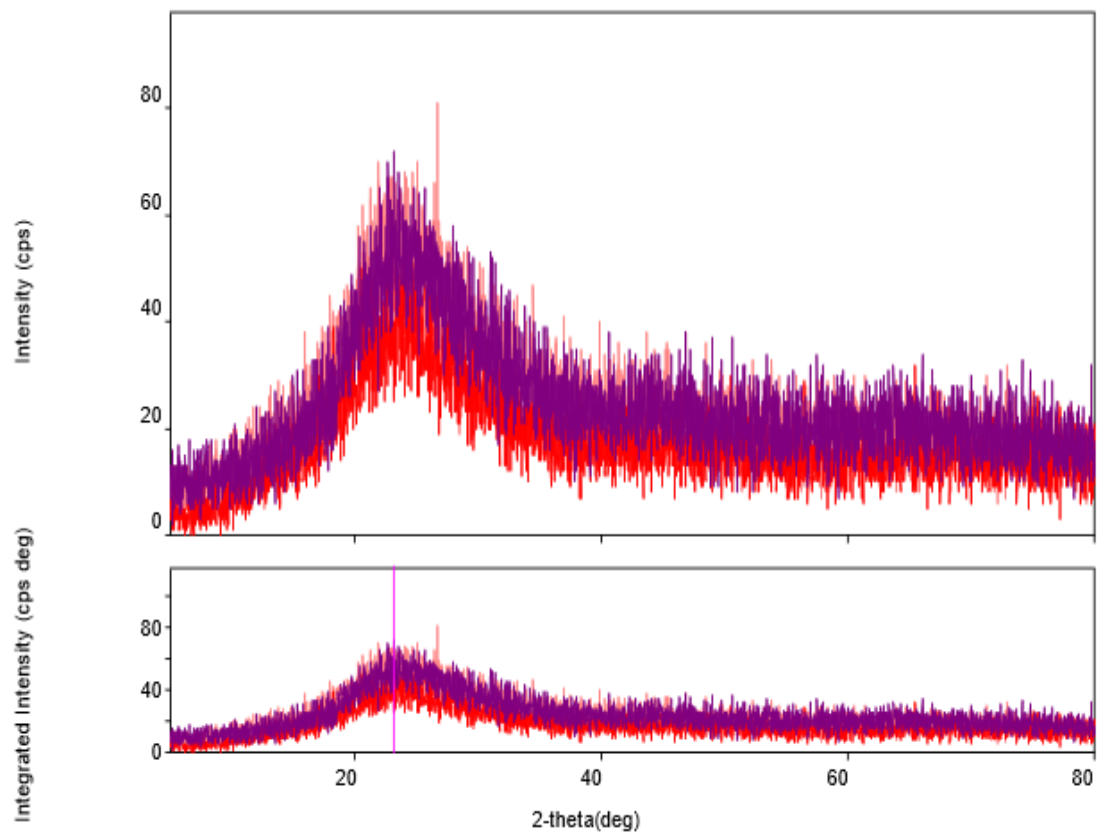
**Measurement conditions**

XG	Cu/30 kV/15 mA	Duration time / Scan speed
Goniometer		Step / Sampling step
Attachment	-	Measurement axis
K-beta filter	-	Scan range
Incident monochromator	-	Incident slit
Receiving monochromator	-	Vertical divergence slit
Counter	-	Receiving slit #1
		Receiving slit #2

## Qualitative analysis results

Phase name	Formula	Figure of merit
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Phase name	Formula	Space group
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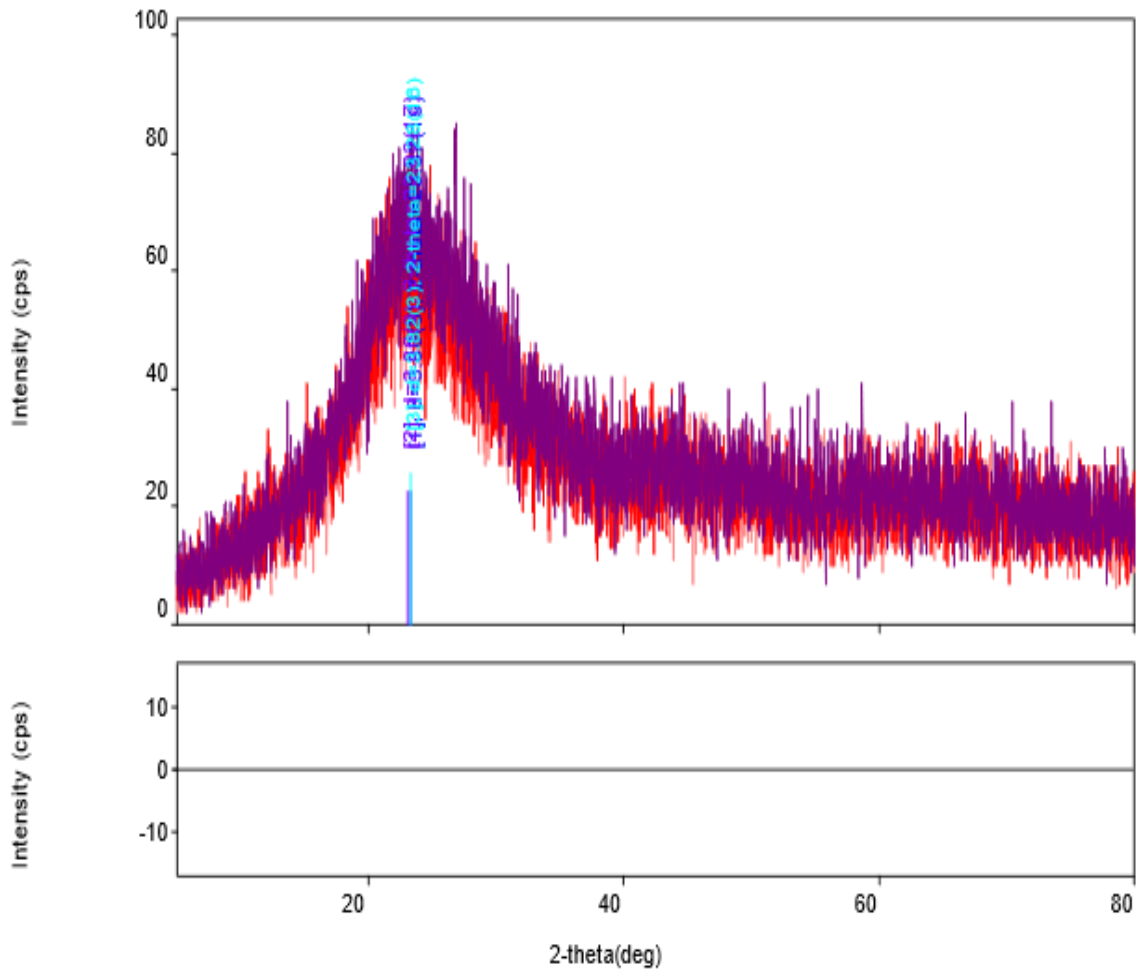


## Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps#deg)	FWHM(deg)	Size
22.83(19)	3.89(3)	20(4)	217(4)	9.69(17)	8.7
23.5(2)	3.79(3)	14(4)	155(3)	9.62(19)	8.8
23.07(19)	3.85(3)	19(4)	200(5)	9.49(18)	8.9

XRD Analysis  
 File Name : C 1M HCl 1-20.raw

**Measurement profile**



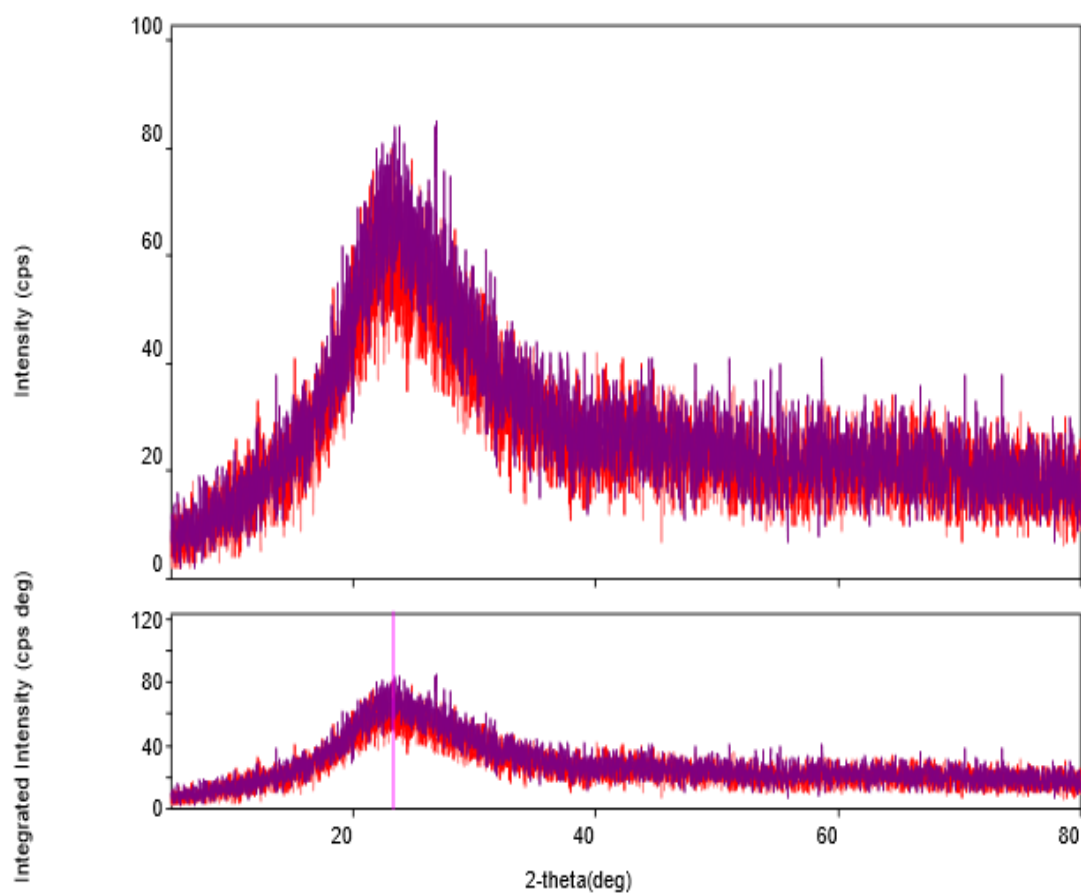
**Measurement conditions**

XG	Cu/30 kV/15 mA	Duration time / Scan speed
Goniometer		Step / Sampling step
Attachment	-	Measurement axis
K-beta filter	-	Scan range
Incident monochromator	-	Incident slit
Receiving monochromator	-	Vertical divergence slit
Counter	-	Receiving slit #1
		Receiving slit #2

## Qualitative analysis results

Phase name	Formula	Figure of merit
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Phase name	Formula	Space group
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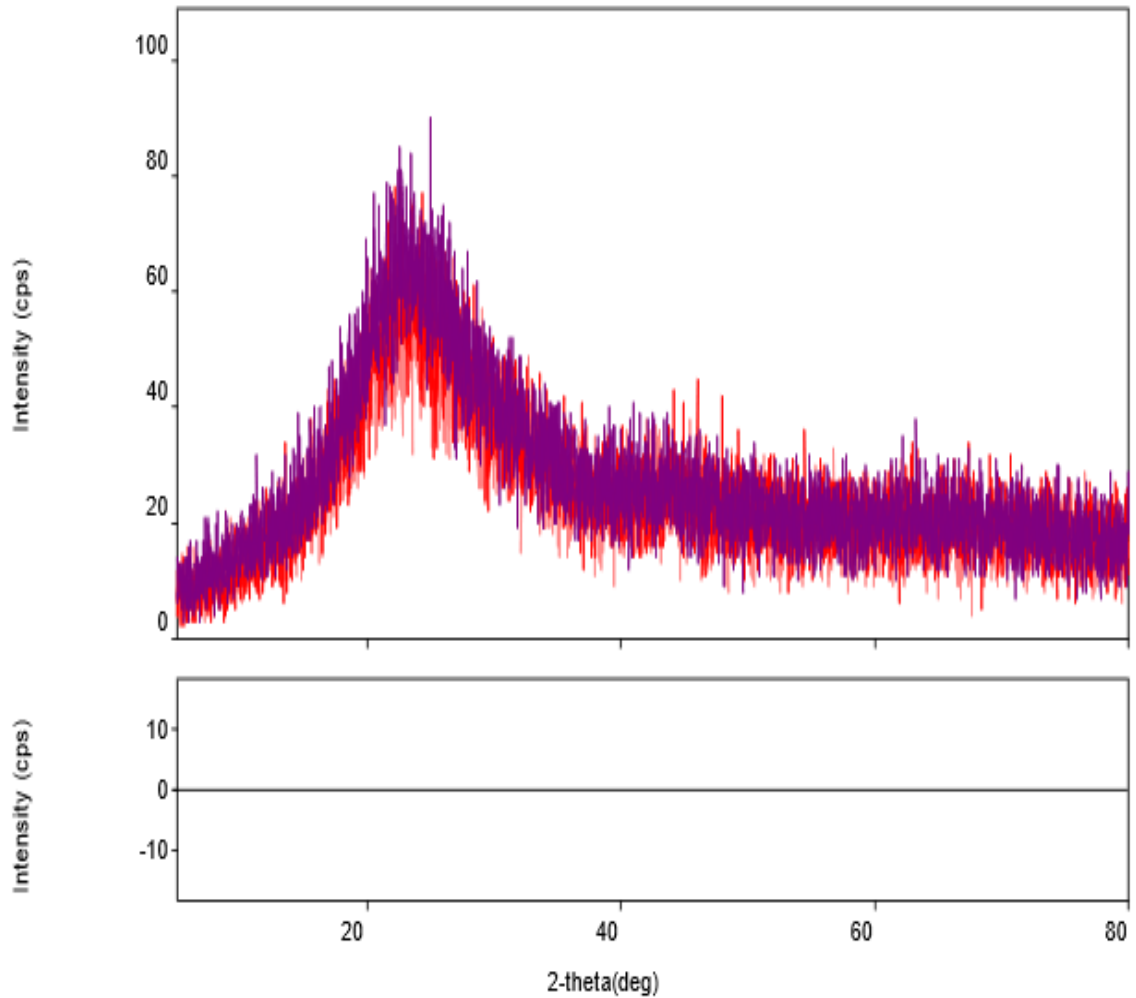


## Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps*deg)	FWHM(deg)	Siz
23.37(19)	3.80(3)	23(5)	251(5)	9.92(17)	8.5
23.03(17)	3.86(3)	23(5)	253(4)	9.86(15)	8.5
23.28(16)	3.82(3)	26(5)	286(4)	9.83(14)	8.6

XRD Analysis  
 File Name : C 1M HNO3 1-20.raw

**Measurement profile**

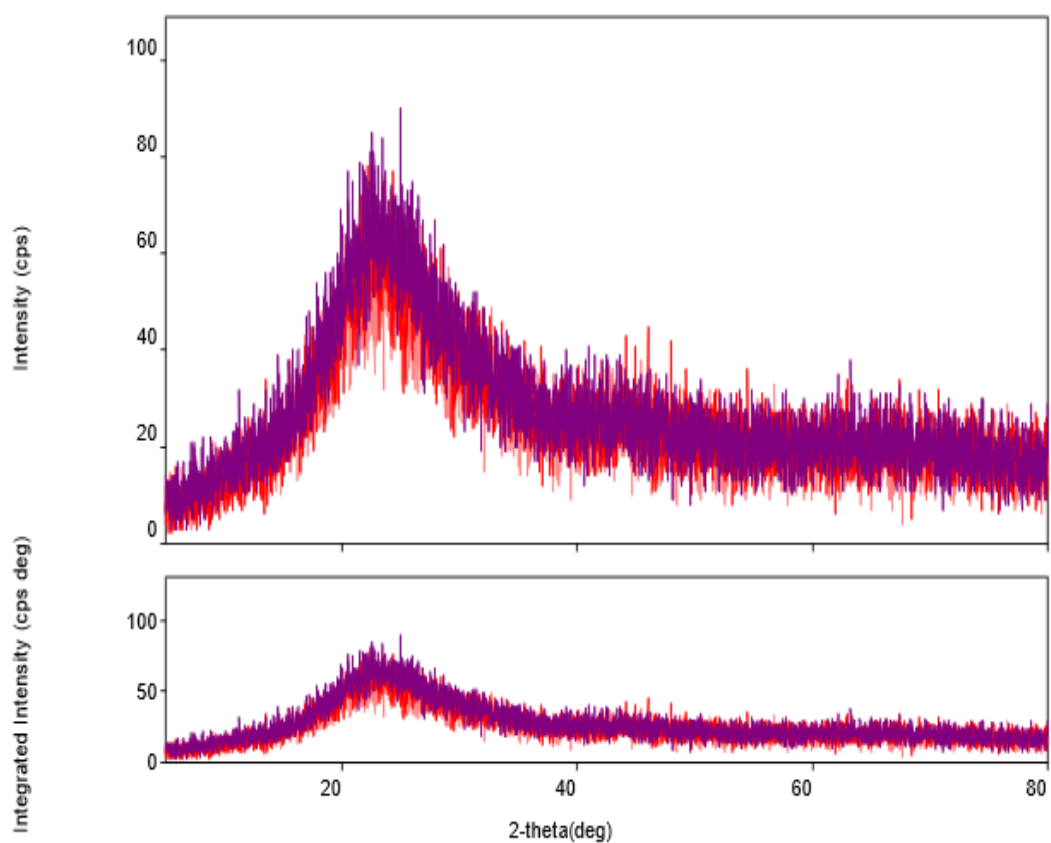


**Measurement conditions**

XG	Cu/30 kV/15 mA	Duration time / Scan speed
Goniometer		Step / Sampling step
Attachment	-	Measurement axis
K-beta filter	-	Scan range
Incident monochromator	-	Incident slit
Receiving monochromator	-	Vertical divergence slit
Counter	-	Receiving slit #1
		Receiving slit #2

## Qualitative analysis results

Phase name	Formula	Figure of merit
Phase name	Formula	Space group



## Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps*deg)	FWHM(deg)	Siz



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