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การสกัดโลหะมีค่าจากเครื่องฟอกไอเสียเชิงเร่งปฏิกิริยา

**EXTRACTION FOR THE RECOVERY OF
PRECIOUS METALS FROM CATALYTIC CONVERTERS**



ปริญญาบัตรนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรบัณฑิต
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สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
ปีการศึกษา 2549

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า
ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

**EXTRACTION FOR THE RECOVERY OF
PRECIOUS METALS FROM CATALYTIC CONVERTERS**



**A REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR
THE DEGREE OF BACHELOR OF ENGINEERING
IN CHEMICAL ENGINEERING
FACULTY OF ENGINEERING
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG**

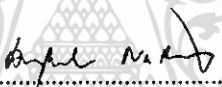
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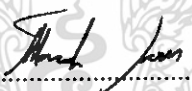
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Report Title Extraction for the Recovery of Precious Metals from Catalytic Converters
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ปริญญานิพนธ์เรื่อง การสกัดโลหะมีค่าจากเครื่องฟอกไอเสียเชิงเร่งปฏิกิริยา
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บทคัดย่อ

ปัจจุบันเครื่องฟอกไอเสียเชิงเร่งปฏิกิริยาเป็นอุปกรณ์สำคัญที่ใช้ในการกำจัดไอเสียซึ่งเกิดจากการเผาไหม้ไม่สมบูรณ์ของน้ำมันเชื้อเพลิงภายในเครื่องยนต์ ภายในเครื่องฟอกไอเสียเชิงเร่งปฏิกิริยามีส่วนประกอบของโลหะกลุ่มแพลทินัม ได้แก่ แพลทินัม โรเดียม และ/หรือ พาลาเดียม ซึ่งเป็นโลหะหายาก มีราคาแพง ดังนั้นจึงควรสกัดแยกโลหะมีค่าเหล่านี้ออกจากเครื่องฟอกอากาศเชิงเร่งปฏิกิริยาที่หมดอายุการใช้งานแล้วก่อนนำไปฝังกลบ

ในงานวิจัยนี้ได้ศึกษาการสกัดแยกโลหะแพลทินัมและโรเดียมจากกัน โดยพิจารณาตัวแปรที่มีอิทธิพลต่อการสกัด ได้แก่ ความเข้มข้นกรดไฮโดรคลอริก ชนิดของตัวทำละลายอินทรีย์ และความเข้มข้นของสารสกัด (ไดรอกทิลเอมีน) พบว่าแพลทินัมสามารถสกัดออกจากสารละลายกรดได้ง่ายกว่าโรเดียม ที่ความเข้มข้นของสารสกัดร้อยละ 2.5 โดยน้ำหนัก สามารถสกัดแพลทินัมได้ถึงร้อยละ 97.53 ส่วนโรเดียมนั้นยังคงอยู่ในสารละลายกรดไฮโดรคลอริก ชนิดของตัวทำละลายอินทรีย์มีผลค่อนข้างน้อยต่อประสิทธิภาพการสกัด ความเข้มข้นที่สูงของกรดไฮโดรคลอริกมีผลทำให้ประสิทธิภาพการสกัดโลหะทั้งสองชนิดลดลง สารละลายที่สกัดได้เมื่อนำมาสัมผัสกับกรดไนตริกความเข้มข้น 4 โมลาร์ด้วยสัดส่วนปริมาตรเป็น 1 ต่อ 2 สามารถแยกแพลทินัมออกได้ถึง 90.81%

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่าจะกรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

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Report for Bachelor Degree of Engineering (Chemical Engineering)

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ABSTRACT

Nowadays, a catalytic converter is a standard device that eliminates exhaust gas from fuel combustion in automobiles. In each catalytic converter, there are the platinum group metals on the washcoat layer such as platinum, rhodium and/or palladium. Therefore, the recovery of these metals from the spent catalytic converter should be applied before dumping them into landfills.

The separation of platinum and rhodium dissolved in hydrochloric acid solution was studied. The variables were hydrochloric acid concentration, type of organic solvent, and active component (trioctylamine) concentration. It was found that platinum was extracted more easily than rhodium. Using 2.5 wt% TOA, 97.53% of platinum was transferred into the organic phase while virtually all rhodium was left in the aqueous phase. Type of organic solvent on the extraction performance was found negligible. Higher hydrochloric acid concentration lowered the extraction efficiency for both metals. The stripping of platinum from the organic phase using 4.0 M nitric acid with the volume ratio of 1 : 2 recovered 90.81% of platinum.

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CHAPTER 1

Introduction

1.1 Statement and significance of the problems

In the early 80's, incomplete combustion sparked the awareness of air pollution from automobiles. Concerns over environmental problems such as smog and acid rain propelled many scientific researches in the field of catalysis and catalytic reaction engineering in order to reduce the toxic gases. As a result, "catalytic converter" was invented and was found to be very efficient in cleaning up the unburned hydrocarbon, nitrogen oxides, and carbon monoxide. However, the operating window in terms of the air-to-fuel ratio is very narrow, which made it impractical. As the computer technology quickly developed, a mini-computer became a standard equipment that controls the air-to-fuel ratio for the catalytic converter to function efficiently in most automobiles nowadays.

As the world's population keeps rising, especially in major cities, the demand for transportation also increases. The auto industry then needs more catalytic converters to be installed in each unit. Like other catalysts, catalytic converters have limited service time. The efficiency in reducing the toxic gases decreases with time. It is suggested that the catalytic converter be changed every five years or every 80,000 kilometers of driving distance [3]. This has prompted another environmental issue as the waste materials (deactivated catalytic converters) accumulate. In each catalytic converter unit, there are some precious metals coated on the ceramic support. These are platinum group metals such as platinum, rhodium, and palladium. Therefore, prior to disposing them into landfills, it is wise to recover as much metals as possible. It is estimated that billions of Baht worth of precious metals are used in automobiles in Thailand.

In the attempt to recover the precious metals from the deactivated catalytic converters, many processes have been employed such as thermal process, leaching, solvent extraction, etc. Thailand, however, has yet to develop a practical means for recovering these metals. Therefore, to prepare for such waste materials as a result of more stringent air regulations in the near future, this work will demonstrate the technique of solvent extraction using ubiquitous local organic compounds, which also supports the principle of sustainable economy.

1.2 Goal and objectives

- 1.2.1 Study the influence of operating conditions such as time, pH and concentration of active component on the extraction efficiency
- 1.2.2 Demonstrate the effects of various organic solvents and volume ratio of stripping agents to organic phase on the metal extraction efficiency

1.3 Scope of the study

To accomplish these objectives, series of laboratory-scale experiments were performed by using TOA (tri-octyl amine) as an active component in the concentration range of 0.01-10 wt% for metal extraction. Stock solutions of platinum (IV) 80 ppm and rhodium (III) 40 ppm in hydrochloric acid are used to simulate the result of metal leaching by hydrochloric acid from the actual catalytic converter. Organic solvents are soyabean oil, sunflower oil, palm oil and toluene. The stripping agent is 4 M nitric acid by varying volume as equal- volume and twofold of organic phase. The metal extraction efficiency was determined by means of the atomic absorption spectrometer.

1.4 Process of the study

- 1.4.1 Study preliminary theory and literature review
- 1.4.2 Design experiment and apparatus
- 1.4.3 Explore the effect of operating conditions, various organic solvents and stripping agents on the metal extraction efficiency
- 1.4.4 Analyze data and draw conclusion

1.5 Benefit of the study

Primary data and potentials of local vegetable oils as an organic solvent for further development of solvent extraction process for the recovery of platinum and rhodium from spent catalytic converters.

CHAPTER 2

Literature Review

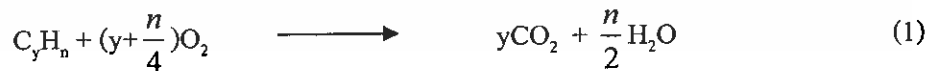
2.1 Catalytic converter

Energy liberated during the combustion of gasoline in the spark-ignited internal combustion engine powers the modern automobiles. The fuel and air mixture is injected into the combustion chamber where it is compressed by a piston and ignited with a spark plug; the derived energy forces the piston down in a power stroke. Thus, heat energy generated by combustion is converted to mechanical energy and translated to the shaft which drives the vehicle. The combustion process generates large quantities of CO_2 and H_2O ; however, significant amounts of carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO_x) are also produced. HCs and CO are generated in the internal combustion engine due to the inefficiencies of the combustion process. NO_x , mainly in the form of NO, results from the high temperature reaction between N_2 and O_2 . The quantity of each pollutant varies considerably with the air-to-fuel ratio.

In 1993, Legislation enforced to install catalytic converters in order to decrease exhaust gas from combustion engine in an automobile. Consequently, pollutant quantity in the atmosphere and public road area begins to decrease [4].

Catalytic converter is an automobile component found in the exhaust system. It oxidizes carbon monoxide and hydrocarbons, using platinum and/or palladium while rhodium reducing nitrogen oxides to create nitrogen. This greatly reduces toxic tailpipe emissions and reduces smog. The basic operation of the catalyst is to perform the following reactions in the exhaust of the automobile.

Oxidation of CO and HC to CO_2 and H_2O :



Reduction of NO/NO_2 to N_2 :



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The catalyst bed is usually in the form of either honeycombed ceramic or ceramic beads covered in the catalyst. They have been used for passenger vehicles from the onset of automotive emission control. The amount of PGMs used in catalytic converters depends on the engine size, configuration and the legislative environment in which the vehicle is operating. The amount of PGMs used in catalytic converters average is four to five grams of PGMs in the converter.

1. The beaded catalyst

The most traditional way was to use a spherical particulate γ -Al₂O₃ particles, anywhere from 1/8 to 1/4 inch in diameter, into which the stabilizers and active catalytic components (i.e., precious metals) would be incorporated, these “beads” would be mounted in a spring-loaded reactor bed downstream, just before the muffler. Figure 2.1 shows the catalyst beads. Since the engine exhaust gas was deficient in oxygen, air was added to the exhaust using an air pump. The rationale was simple catalysts had been made of these types of supports for many years, and manufacturing facilities to mass produce them were already in place. One major concern was the attrition resistance of the γ -Al₂O₃ particles, since they would experience many mechanical stresses during the lifetime of the converter.

The beads are manufactured with the stabilizers incorporated into the structure. The precious metal salts are impregnated into the beads and, using proprietary methods, fixed in particular locations to ensure adequate performance and durability for 50,000 miles. They are then dried, typically at 120°C, and calcined to about 500°C to their finished state. The finished catalyst usually had about 0.05 wt% of precious metal with a Pt-to-Pd weight ratio of 2.5 to 1. After 1979, the need for NO_x reduction required the introduction of small amounts of Rh into the second-generation catalysts.

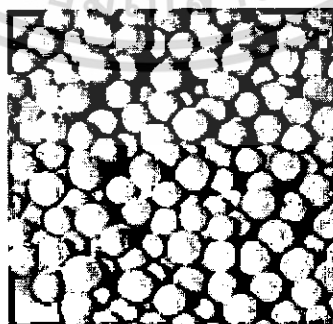


Figure 2.1 Catalyst bead. Source: http://www.intellishare-env.com/catalyst_modules.html

2. The honeycomb catalyst

An alternative approach for supporting the catalytic components was that of a ceramic honeycomb monolith with parallel. Open channels. Some PTX converters had operational life of 10,000 hours. This background experience showed that the monolithic support was a viable material for automotive applications. The precious metal γ -Al₂O₃ catalyst was washcoated or deposited onto the walls of the honeycomb channels as illustrated in figure 2.2. One major advantage would be low pressure drop, since the honeycomb structure had a very high open frontal area (about 70 percent) and parallel channels. Furthermore, given their monolithic structure, they could be oriented in a number of ways to fit in the exhaust manifold. Also, the monoliths were available in different cell densities or cells per square inch (cpsi).

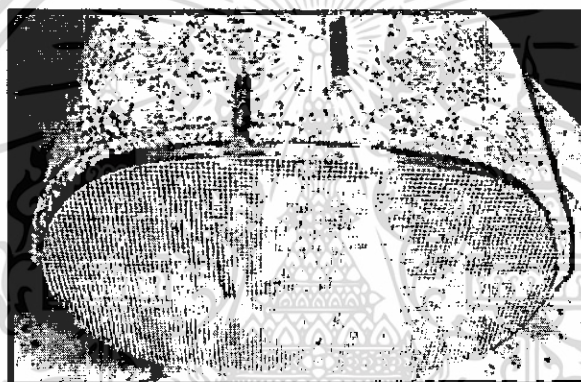


Figure 2.2 Ceramic honeycomb catalyst structures.

Source: auto.howstuffworks.com/catalytic-converter2.htm

The ceramic companies continued to modify the materials and structures to provide sufficient strength and crack resistance under thermal shock conditions experienced during rapid accelerations and decelerations. The thermal shock condition was eventually satisfied by mechanical design coupled with the use of a low thermal expansion ceramic material called cordierite (synthetic cordierite has a composition approximating 2MgO, 5SiO₂, and 2Al₂O₃). The first honeycomb catalysts to be used in auto exhaust had 300 cells per square inch, wall thicknesses of about 0.012 inches, and open frontal area of about 63 percent. These dimensions were finalized, based on mechanical specifications and activity performance requirements to ensure a high degree of contact between the reactants and the catalyst washcoat (high mass transfer) and the lowest possible light off temperature. Later developments in extrusion technology resulted in 400 cpsi honeycomb with a wall thickness of 0.006 inches and open frontal

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

are of 71 percent. This increased the geometric surface area for the mass transfer controlled reactions. The catalytic coating could be deposited onto the walls of the honeycomb to produce adherent “washcoats”. The washcoat thickness could be kept to a minimum to decrease pore diffusional effects while allowing sufficient thickness for anticipated aging due to deposition of contaminants. The washcoat is about 20 and 60 microns on the walls and corners (fillets), respectively. Typically, the catalyst contains about 0.1-0.15 percent precious metals. For the oxidation catalysts of the first generation, the weight ratio of Pt to Pd was 2.5 to 1, whereas the second generation contained a weight ratio of 5 Pt to 1 Rh.

The honeycomb catalyst is mounted in a steel container with a resilient matting material wrapped around it to ensure vibration resistance and retention.



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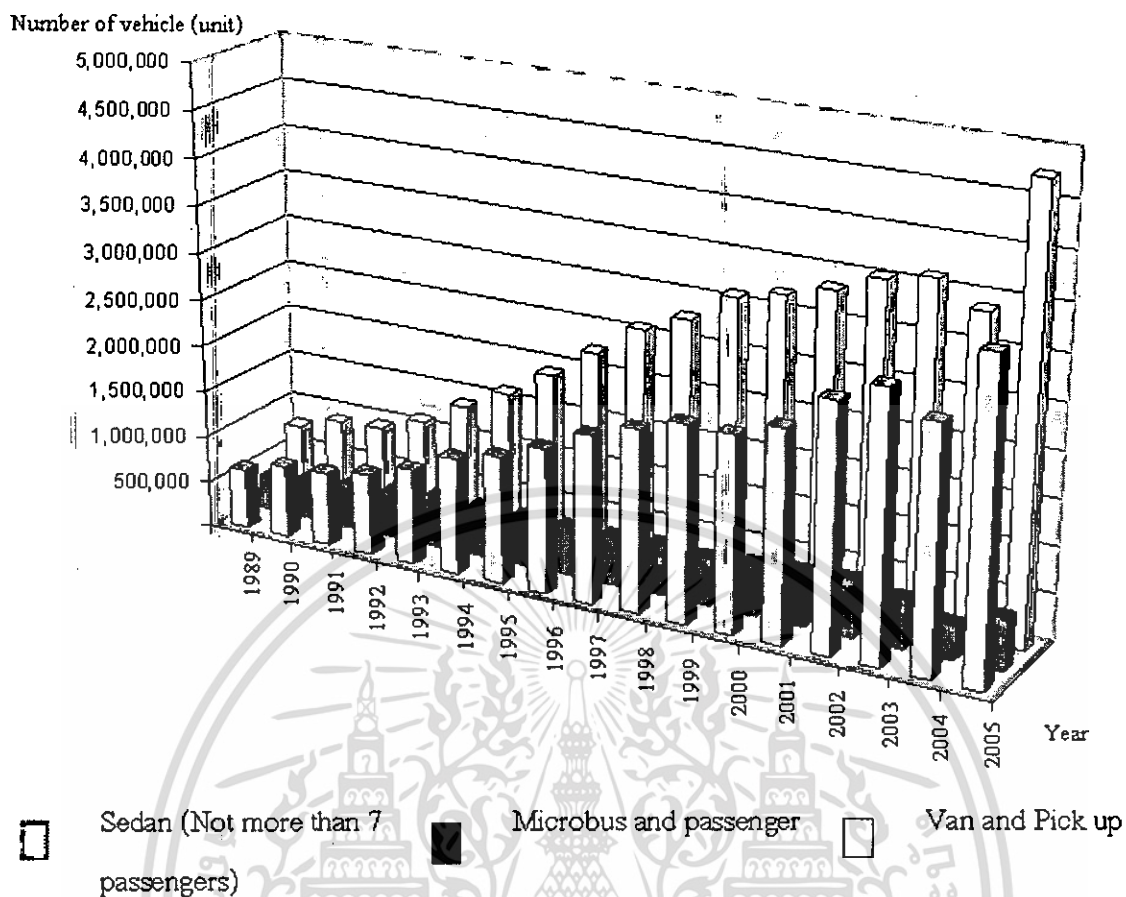


Figure 2.3 Number of vehicle registered in Thailand as of December 1989-2005. [3]

The number of vehicles in Thailand has increased substantially as shown in fig 2.3. It was observed that the number of sedan (not more than 7 passengers) registered at the department of land transportation in 2000 have 2,111,136 units; each with a catalytic converter installed. When these cars are well over the useful lifetime, there are about two million units of spent catalytic converter. Each catalytic converter consists of precious metals in average of four to five grams. Therefore, eight to ten tons of precious metals are in the waste materials. If the recovery of these metals is effective, it will greatly help reduce the environmental impact from the mining industry.

2.2 Precious metals in catalytic converter

Platinum characteristics

Platinum appears silvery-white when pure and firm. It is hard and extremely dense. (Platinum is nearly twice as dense as lead and 11% more dense than gold). It has a high melting point, high temperature stability and corrosion resistance. It is a good oxidation catalyst, conductive and oxidation resistant.

All these properties have been exploited for industrial applications. Jewellery represents about 40% of overall platinum used. While the amount of platinum used for catalytic converters to control exhaust emissions is around 37%, with the remaining approximately 23% being used in other industrial applications.

Platinum ore is found in Canada, South Africa, Russia, and the United States. South Africa is the largest producer of platinum. It is an extremely rare metal, occurring as only 5 ppb in the Earth's crust. World supply of platinum is around 6m troy ounces¹ per year. The price of platinum changes along with its availability, but it normally costs slightly less than twice the price of gold. As shown in figure 2.4, the price of platinum has tripled during the last decade.

This metal is insoluble in hydrochloric and nitric acid but does dissolve in the mixture known as aqua regia to form chloroplatinic acid (H_2PtCl_6).

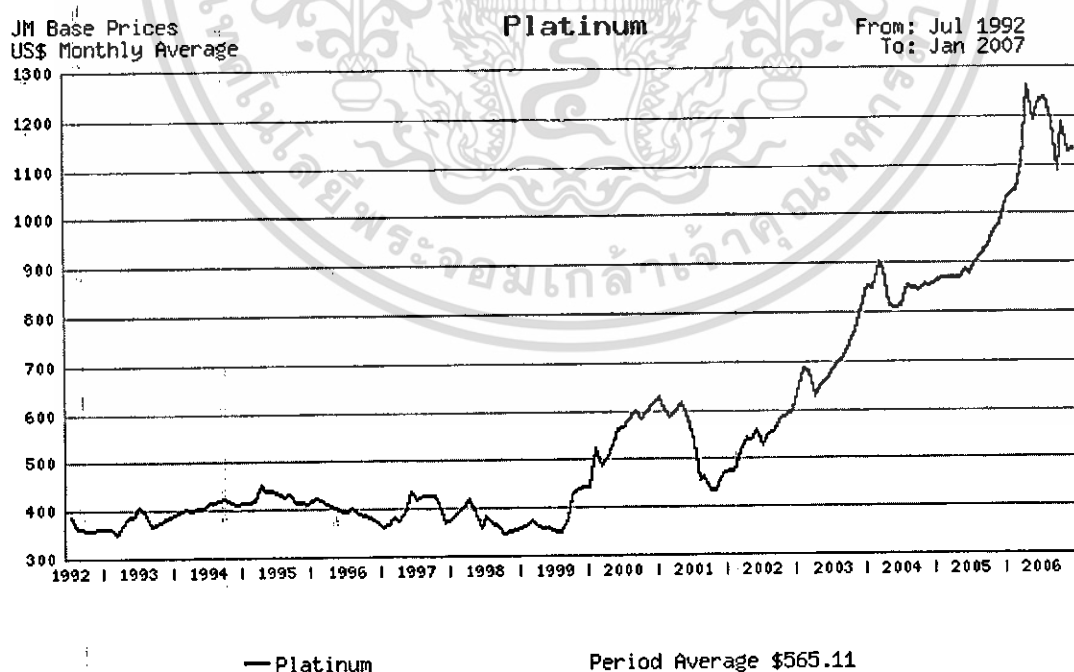


Figure 2.4 Price of platinum from July, 1992 to January, 2007 [8]

¹ A troy ounce, the only currently used unit of the system, one troy ounce is exactly 31.1034768 g. The troy ounce is the only ounce used in the pricing of precious metals, such as gold, platinum, and silver

Rhodium characteristics

Rhodium has a cool-gray colour. It is durable metal that has a high reflectance. Rhodium has both a higher melting point and lower density than platinum. It is known to be extremely hard and corrosion resistant.

All these properties have been exploited for industrial applications. As catalysts, especially in the organic chemicals industry. Rhodium-platinum gauzes are used in the production of nitric acid. In vehicle exhaust emission control, catalysts containing rhodium to catalyst the reduction of nitrogen oxides to nitrogen.

Principal sources of rhodium are located in South Africa, North and South America. The annual world production of this element is only about 20 tons and there are very few rhodium minerals. As of 2006, rhodium cost approximately six times as much as gold, by weight.

It is not attacked by acids and only dissolves in aqua regia to form rhodium trichloride (RhCl_3)

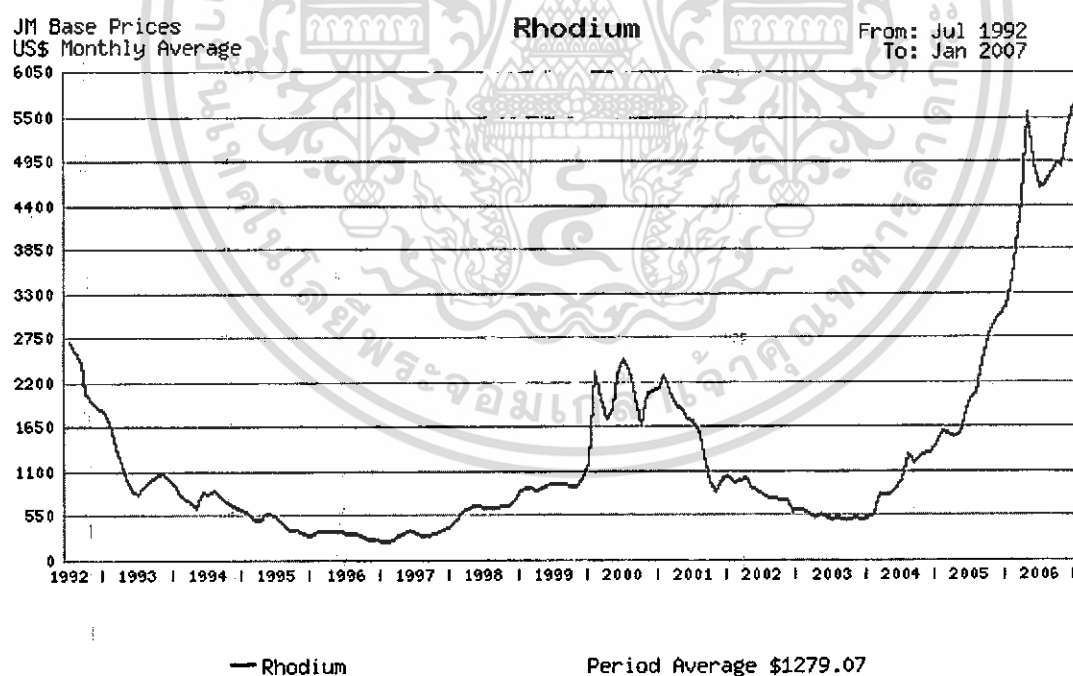


Figure 2.5 Price of rhodium from July, 1992 to January, 2007 [8]

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Palladium characteristics

Palladium is a soft silver-white metal that resembles platinum. It is the least dense and has the lowest melting point of the platinum group metals. It is soft and ductile when annealed and greatly increases its strength and hardness when it is cold-worked.

All these properties have been exploited for industrial applications. The largest use of palladium today is in catalytic converters. Also, this metal can be alloyed with gold to produce white gold. Moreover, palladium is used as electrodes in multi-layer ceramic capacitors and it is also used as Palladium-Hydrogen electrode in electrochemical studies.

Palladium ore is found in South Africa and Russia. Russia is the largest producer of palladium. It is an extremely rare metal.

Palladium is chemically attacked by sulfuric, nitric acid and hydrochloric acid in which it dissolves slowly. This metal also does not react with oxygen at normal temperatures. Palladium heated to 800 °C produce layer of palladium (II)-oxide (PdO).

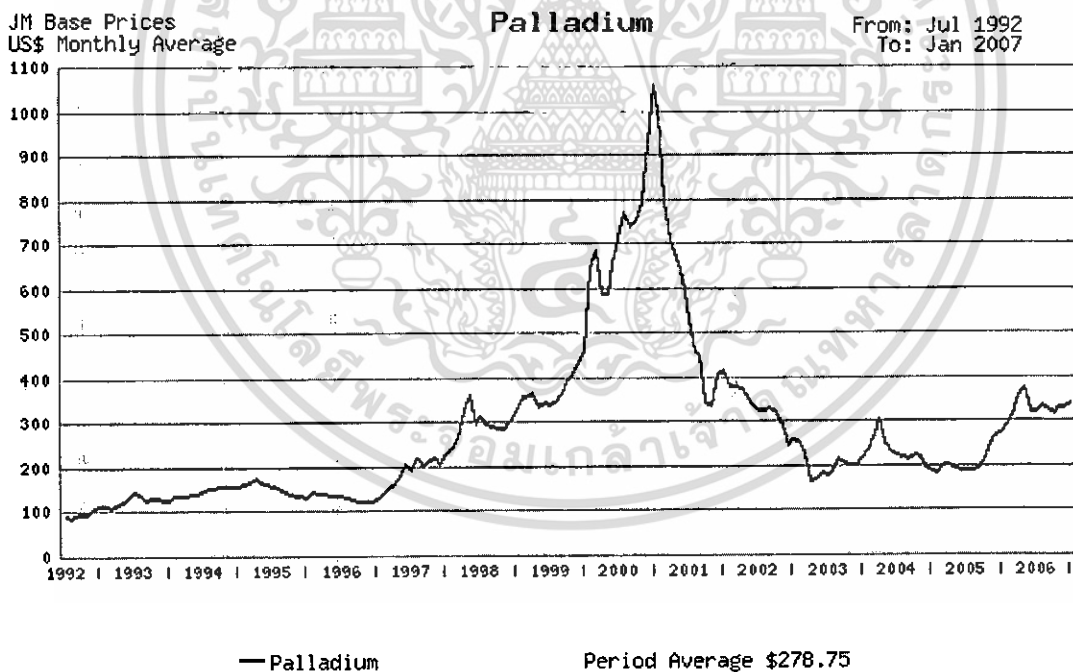


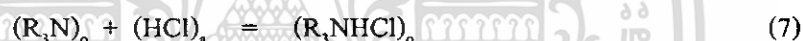
Figure 2.6 Price of palladium from July, 1992 to January, 2007 [8]

2.3 Recycling technology

As part of the automotive recycling industry, the recovery of autocatalysts is not only adding to global environmental conservation but also supporting the global supply of platinum, palladium and rhodium through processing and refining the PGMs obtained from spent autocatalysts. Platinum, palladium and rhodium are highly recyclable – up to 96 percent of the metals in autocatalysts collected for refining are recoverable in the recycling process.

Barakat and Mahmoud (2004) investigated the recovery of platinum from spent catalyst dust arising from the fertilizer industry. The dust was homogenized by thorough mixing and the < 106- μm fraction used. The dust was refluxed with aqua regia prepared by mixing concentrated hydrochloric acid (36%) and concentrated nitric acid (65%) by the volume ratio of 3HCl:1HNO₃. It was used as a leaching agent for the dust to solubilise platinum for subsequent recovery. Two alternative methods were investigated for separation of platinum from the leach solution.

In the first method, solvent extraction used 10% trioctylamine (TOA) in kerosene. An aqueous solution of ammonium hydroxide and ammonium chloride was used as the stripping agent. Trioctylamine (TOA) reacts with HCl to form the chloride species as follows:



Where the subscripts (o) and (a) represent the organic and aqueous phases, respectively.

Platinum (IV) is extracted with TOA by an ion exchange mechanism according to following equations



In the second method, direct precipitation, platinum was precipitated as diammonium hexachloroplatinate, (NH₄)₂PtCl₆, by adding ammonium chloride to the leach solution.

The precipitate was decomposed by ignition at 350 °C to produce platinum powder with purity of 97.9% and 99.9% for direct precipitation and solvent extraction, respectively. A platinum recovery of 97.5% was achieved by both routes.

2.3.1. Liquid-liquid extraction

Liquid-liquid extraction is a mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly immiscible liquid (solvent) that exhibits preferential affinity of selectivity towards one or more of the components in the feed. Two streams result from this contact: the extract, which is the solvent rich solution containing the desired extracted solute, and the raffinate, the residual feed solution containing little solute.

- Solvent selection

Solvents differ in their extraction capabilities depending on their own and the solute's chemical structure. The distribution coefficient and selectivity are the most important parameters that govern solvent selection. The distribution coefficient or partition coefficient for a component (A) is defined as the ratio of concentration of A in the extract phase to that in the raffinate phase. Selectivity can be defined as the ability of the solvent to pick up the desired component in the feed as compared to other components. The desired properties of solvents are a high distribution coefficient, good selectivity towards solute and little or no miscibility with feed solution. Also, the solvent should be easily recoverable for recycle. Designing an extractor is usually a fine balance between capital and operating costs. Usually, good solvents also exhibit some miscibility with feed solution. Consequently, while extracting larger quantities of solute, the solvent could also extract significant amount of feed solution.

Other factors affecting solvent selection are boiling point, density, interfacial tension, viscosity, corrosiveness, flammability, toxicity, stability, compatibility with product, availability and cost.

- Selection of extraction conditions

Depending on the nature of the extraction process, the temperature, pH and residence time could have an effect on the yield and selectivity. Operating pressure has a negligible effect on extraction performance and therefore most extractions take place at atmospheric pressure unless governed by vapor pressure considerations.

Temperature can also be used as a variable to alter selectivity. Elevated temperatures are sometimes used in order to keep viscosity low and thereby minimizing mass-transfer resistance. Other parameters to be considered are selectivity, mutual solubility, precipitation of solids and vapor pressure.

The pH becomes significant in metal and bio-extractions. In bio-extractions (e.g., Penicillin) and some agrochemicals (e.g. Orthene), pH is maintained to improve distribution coefficient and minimize degradation of product. In metal extractions, kinetic considerations govern the pH. In dissociation-based extraction of organic molecules, pH can play a significant role (e.g., cresols separation). Sometimes, the solvent itself may participate in undesirable reactions under certain pH conditions (e.g., ethyl acetate may undergo hydrolysis in presence of mineral acids to acetic acid and ethanol).

Bandekar and Dhadke (1998) investigated the solvent extraction separation of platinum (IV) and palladium (II) by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) in toluene in the presence of stannous chloride. The extraction of platinum with 5×10^{-3} M PC-88A in toluene was carried from a solution of 0.1-5.0 M HCl and was found to be quantitative from 0.5-2.25 M HCl solutions. The extraction of palladium with 6×10^{-4} M PC-88A in toluene was carried out from a solution of 0.1-4.0 M HCl-HClO₄ acid mixture and was quantitative from a solution of 0.75-2.0M HCl- HClO₄ acid mixture. The percentage extraction is 99.21% and 100% for platinum and palladium, respectively. Separation of platinum and palladium from their mixed solution was maintained at 1.0 M HCl, 1.0 M HClO₄, 2.5×10^{-2} M stannous chloride concentration and equilibrated with 6×10^{-4} M PC-88A in toluene. Palladium was extracted in the organic phase. Platinum was determined in the aqueous phase using the stannous chloride method. The percentage recovery is 99.9% and 99.2% for palladium and platinum, respectively.

Residence time is also an important parameter in reactive extraction processes (e.g., formaldehyde extraction from aqueous streams, precious metal extraction from leached solution) and in processes involving short-life components (e.g., antibiotics & vitamins) because the minimum equilibration period required for complete extraction.

- Equipment for extraction

Mixer-Settler, one of equipment for extraction is often used to provide intimate contact between the two liquid phases. One phase is usually dispersed into the other in the form of small droplets. Sufficient time of contact should be provided for the extraction to take place. Small droplets produce large interfacial areas and faster extraction. However, the droplets must not be so small that the subsequent settling time in the settler is too large.

A typical mixer-settler, the mixer or agitator is entirely separate from the settle. The feed of aqueous phase and organic phase are mixed in the mixer, and then the mixed phases are separated in the settle.

Mhaske and Dhadke (2001) investigated the separation of platinum, rhodium and palladium from their mixture, the sample solution was first at 6.0 M HCl, using 7.5 mmol/l Cyanex 921 (tri-octyl phosphine oxide), when Pd (II) was quantitatively extracted. The extracted Pd (II) from the organic phase was stripped with 2.0/2.0 M HCl:HClO₄. The unextracted Rh(III) and Pt(IV) in remaining sample solution was then again with 10 mmol/l Sn₂Cl in 6.0 M HCl, using 10 mol/l Cyanex 921, when only Pt(IV) was extracted. The

extracted Pt (IV) was stripped with 4.0 M HNO₃. The unextracted Rh(III) from the sample solution was again with 250 mmol/l Sn₂Cl in 6.0 M HCl and 75 mmol/l Cyanex 921 and it was recovered from the organic phase by stripping twice with 4.0 M HNO₃ at 60°C. The proposed method is simple and rapid for the extraction and separation of rhodium, platinum and palladium from their mixtures with the recovery of 98%.

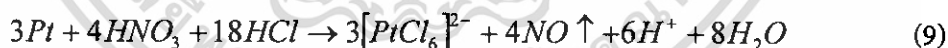
Alam and Inoue (1997) investigated the solvent extraction of platinum group metals such as: Pd, Pt and Rh was carried out from chloride media with Kelex 100 in the absence and presence of a large amount of tin. When tin is absent in the feed solution, the order of extraction follows: Pd > Pt > Rh (at low acidity) and Pt > Pd > Rh (at high HCl acidity). When a large amount of tin is added to the feed solution, the extraction order was changed to: Rh > Pd ≈ Pt (at low acidity) and Rh > Pt > Pd (at high acidity)

Percent stripping of rhodium from the loaded organic solution containing tin can be enhanced greatly by adding three kinds of oxidizing agent as KMnO₄, H₂O₂ and HNO₃ together with the stripping agent. Stripping increases with the increase in the concentration of the oxidizing agents. The order of stripping ability of the oxidizing agents employed in this work was found to be: HNO₃ > KMnO₄ > H₂O₂.

2.3.2 Precipitation

An alternative approach for recovery of precious metals from leached solution is precipitation method.

Platinum is a noble metal, not attacked by dilute or concentrated acids, except aqua regia, which dissolves platinum forming hexachloroplatinate(IV) ions:

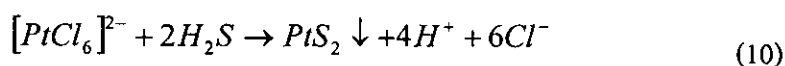


In its compounds, platinum can be mono-, di-, tri-, tetra-, and hexavalent, tetravalent platinum being the most important in analytical practice.

There are many chemical reagents for platinum precipitation as follows.[14]

1. Hydrogen sulphide

Black (or dark brown) precipitate of the disulphide, PtS₂ (possibly containing a little platinum metal), is slowly formed in the cold, but rapidly on warming. The precipitate is insoluble in concentrated acid, but dissolves in aqua regia and also in ammonium polysulphide solution; it is reprecipitate from the latter by dilute acids.

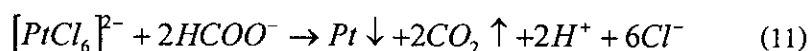


2. Potassium chloride

Yellow precipitate of potassium hexachloroplatinate(IV), $K_2[PtCl_6]$, from concentrated solutions is formed in leached solution. A similar result is obtained with ammonium chloride solution.

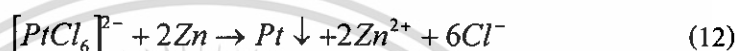
3. Sodium formate

Black powder of metallic platinum is formed from neutral boiling solutions.



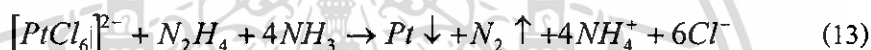
4. Zinc, cadmium, magnesium or aluminium

All these metals precipitate finely divided platinum.



5. Hydrazine sulphate

It is ready reduction in ammonium solution to metallic platinum, some of which is deposited as a mirror upon the sides of the tube.



6. Silver nitrate

Yellow precipitate of silver hexachloroplatinate(IV), $Ag_2[PtCl_6]$, sparingly soluble in ammonia solution but soluble in solutions of alkali cyanides and of alkali thiosulphates.

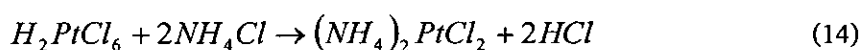
7. Potassium iodide

It is intense brownish-red or red colouration, due to $[PtI_6]^{2-}$ ions. With excess of the reagent, $K_2[PtI_6]$ may be precipitated as an unstable brown solid. On warming, black PtI_4 may be precipitated.

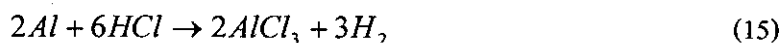
8. Tin(II) chloride

Red or yellow colouration, due to tetrachloroplatinate(IV) ions, $[PtCl_4]^{2-}$ that soluble in ethyl acetate or in ether.

JIN, In-Soo (2004) investigated to recovery method of platinum series metals from automobile waste catalysts or alumina waste catalysts containing the precious metals are comprised of following steps: platinum group metals are extracted by the wet method and filtered. The filtered solution is concentrated. Ammonium chloride solution is added to the solution to precipitate is precious metal, and the precipitated metal is filtered. Precipitation reaction of platinum is as follows.



Solubility of ammonium chloroplatinate is determined based on the amount of ammonia in aqueous solution. Therefore, a large amount of ammonia chloride is needed. Platinum recovered through the precipitation is above 95%. Aluminium scrap is added to the filtered liquid to precipitate precious metal, and the precipitated metal is filtered and recovered. In the above method, about 100% yield of precious metals is obtained without any loss. The above method is implemented based on the following formula.



Aluminium is provided in a ball form because ball has large surface area with respect to the volume. The diameter of aluminium ball is preferably 3 mm. Heat generated in the following precipitation process by aluminium is used through the heat exchanger for a concentration of acid solution having dissolved platinum.

Kayanuma et al. (2003) investigate to recover Rh from the solution obtained by leaching Mg reacted Rh compound with aqua regia. The solution was then heated and dried to remove nitric acid. There are two different methods for recovery rhodium from leach solution.

1. Precipitation method

In the process of Rh recovery by precipitation $NaNO_2$ was added to the solution. The solution was aged at 343-353 K for 1 h, and rapidly cooled in ice water. Saturated NH_4Cl solution was added while cooling. The white precipitate generated was recovered by filtration, and then dried on a hot plate. Rh was recovered as $(NH_4)_2Na[Rh(NO_2)_6]$, and the yield was 86%.

2. Cementation method

In the process of Rh recovery by cementation using zinc powder was added to the solution containing Rh at 323 K, until the solution colour became clear and a black precipitate was recovered by centrifugation, washed by distilled water, 2-propanol and acetone, and then dried in a vacuum dry oven. Rh was almost completely recovered as a mixture with Zn.

CHAPTER 3

Experimental Methods and Equipment

In this chapter, the experimental set-up for liquid-liquid extraction of precious metals (Pt and Rh) is described. Details of all components including the stock solutions for metal, extractant and stripping agent, equilibrium separator, and experimental procedure are follows. The system provides for constant-temperature separation for all conditions investigated.

3.1 Experimental and chemicals

Solvent extraction experiments are performed in a batch reactor provided with good mixing during extraction that uses apparatus and reagent as follows.

Apparatus

- Atomic absorption spectrometer (Spectr AA-300P)
- Magnetic stirrer
- Funnel 250 ml
- Thermometer
- Pipette 1, 5 and 10 ml
- Beaker 50 and 100 ml
- Erlenmeyer Flask 100, 125 and 250 ml
- Volumetric flask 250 ml
- Cylinder 10 and 100 ml
- Conical Funnel
- Droppers
- Stopped watch

Reagent

- Standard solutions of Pt (IV) in 2 M Hydrochloric acid (Merck, Analytical reagent grade)
- Standard solutions of Rh(III) in 1 M Hydrochloric acid (Fluka, Analytical reagent grade)
- Hydrochloric acid (Merck, Analytical reagent grade)

- Nitric acid (Labscan, analytical reagent grade)
- Deionized water
- TOA (trioctylamine) (Merck, Analytical reagent grade)
- Soyabean oil (Morakot , Commercial grade)
- Sunflower oil (Morakot, Commercial grade)
- Palm oil (Morakot, Commercial grade)
- Toluene (Fisher Scientific, Analytical reagent grade)

3.2 Procedure

Figure 3.1 shows a schematic diagram for the experimental procedure in this study. There are 2 steps involved as follows.

Step 1 Extraction

- Mixed solution containing metal in hydrochloric acid solution and TOA in an organic solvent is vigorously stirred using a magnetic stirrer.
- After a certain period of extraction, the two phases are allowed to separate by gravity and the metal concentration in the aqueous phase is determined by an atomic absorption spectrometer (AAS).

Step 2 Stripping

- The metal-loaded organic phase is mixed with 4 M nitric acid as a stripping agent by means of a magnetic stirrer.
- After a certain period of stripping, the two phases are allowed to separate by gravity and the metal concentration in the aqueous phase is again determined by AAS.

3.2.1 Preparation the stock solution

The stock solution of Platinum, Rhodium and mixed Platinum and Rhodium are prepared by dissolving analytical reagent grade 1000 ppm H_2PtCl_6 and 1000 ppm $RhCl_3$ in hydrochloric acid. Platinum and Rhodium are diluted to 80 ppm and 40 ppm respectively with hydrochloric acid and deionized water.

3.2.2 Extraction individual metal from aqueous solution

1. Effect of hydrochloric acid concentration and organic solvent for TOA

Solvent extraction experiments for individual metal are carried out by varying the HCl concentration in the range 0.5-8 M. The stock solution is stirred with an equal- volume of organic phase containing 0.1, 5 and 10 wt% TOA in different organic solvents such as soyabean oil, sun flower oil, palm oil and toluene for 20 minutes and 10 minutes for platinum and Rhodium, respectively at room temperature. A magnetic stirrer is used to provide good mixing. After extraction, the two phases are allowed to separate by gravity and the metal concentration for each metal ion in the aqueous phase is determined by an atomic absorption spectrometer. The metal ion in the loaded organic phase is determined by mass balance.

Once organic solvent for extraction individual metal from aqueous solution are determined, subsequent experiments are set with that condition.

2. Effect of TOA concentration

The extraction efficiency depends on the amount of free electron pairs from amine in TOA to be shared with the metal to form complex compound. Therefore, the experiments are carried out by varying concentration of TOA 0.01- 3 wt% with that condition.

3.2.3 Separation of Pt and Rh from their mixed solution

Solvent extraction experiments for mixed solution which is prepared by mixing equivolume of the standard solutions of Pt (IV) 80 ppm and Rh (III) 40 ppm in hydrochloric acid. The experiment in this section is carried out the same way as those have done in the previous section for studying the extraction of each component. The optimum condition of the previous experiment is applied.

3.2.4 Effect of stripping agent volume

The stripping of metal-loaded organic phase containing metal is tried with stripping agent as 4 M nitric acid by varying volume as equal and twofold volume of organic phase. The metal -loaded organic phase is stirred for 30 minutes at room temperature. A magnetic stirrer is used to provide good mixing. After stripping, the two phases are allowed to separate by gravity and the metal concentration for metal ion in the aqueous phase is determined by an atomic absorption spectrometer.

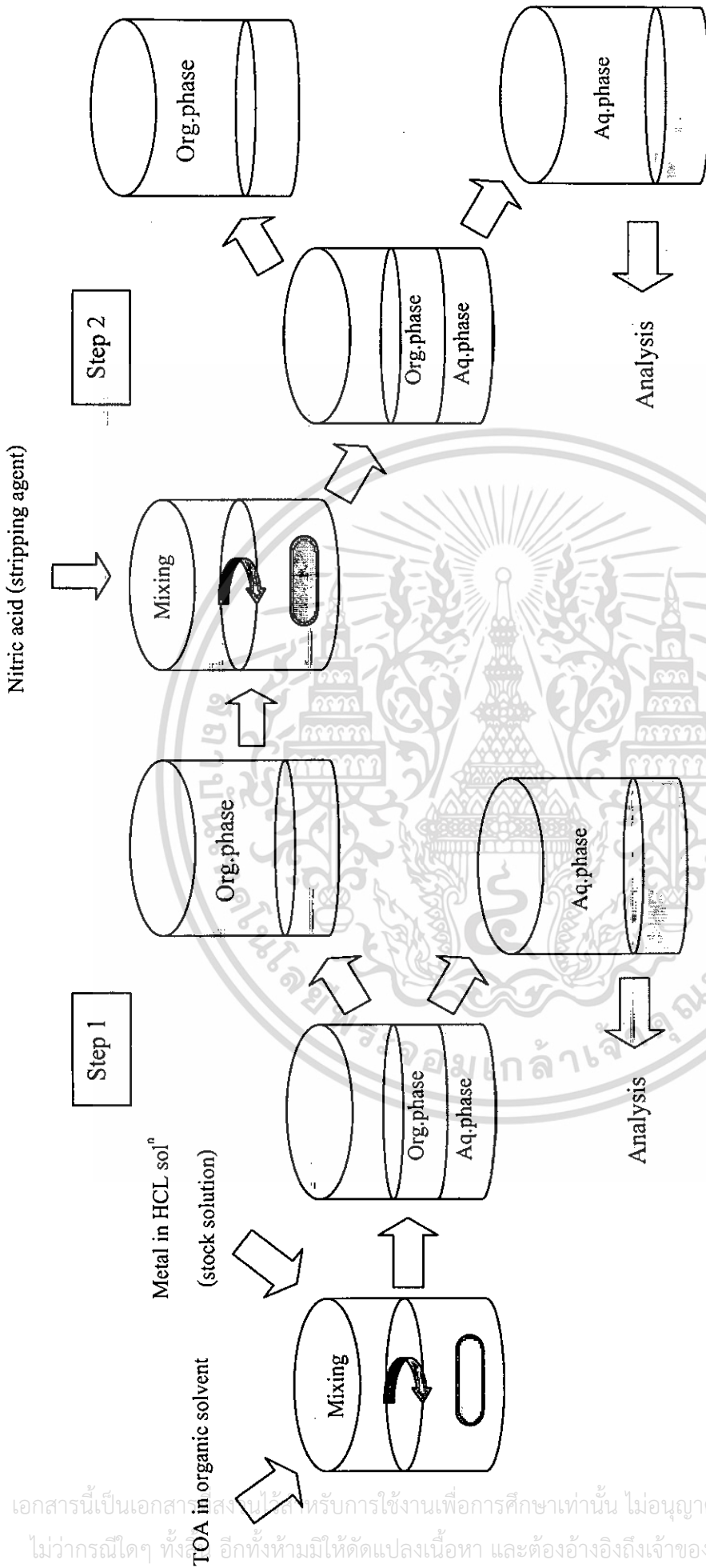


Figure 3.1 Schematics of solvent extraction process

CHAPTER 4

Results and Discussion

In this chapter, experimental results and discussion for extraction of platinum and rhodium metals are provided. The first set of experiments was the investigation of individual metal extraction. The next experiment was the separation of Pt and Rh from their mixed solution. After separation, the Pt-loaded organic phase was stripped by stripping agent. All experiments were carried out at room temperature.

4.1 Extraction individual metal from aqueous solution

4.1.1 Effects of hydrochloric acid concentration and types of organic solvent on platinum and rhodium extraction efficiency

A series of metal extraction experiments was performed using soyabean oil, sunflower oil, palm oil and toluene as organic solvents. Conceivably, the results of such experiments depend on the period of extraction. However, this project is not focused on the transient behavior of the system. Prior to systematically conducting the entire series of experiment, the equilibration time was determined by carrying out liquid extraction experiments with the lowest level of TOA and hydrochloric acid concentrations. It was found that extraction periods of 20 minutes and 10 minutes are adequate for platinum and rhodium, respectively, to establish a steady state. Therefore, all subsequent extraction experiments were performed for extraction period of each metal. To determine the effect of hydrochloric acid concentration for platinum and rhodium extraction, 0.1, 5 and 10 wt% of TOA dissolved in the organic solvents were used to extract 80 ppm of platinum and 40 ppm of rhodium in HCl solution while varying the hydrochloric acid concentration in the range of 0.5-8 M. The results are shown in figures 4.1 (a)-(c) for platinum and figures 4.2 (a)-(c) for rhodium.

It appears that all four kinds of organic solvent used exhibit similar results. At 0.1 wt% TOA, especially with high acid concentration, only part of platinum dissolved in the aqueous phase transferred to the organic phase through the formation of metal complex with TOA. Higher acid concentration keeps platinum in the aqueous phase in form of chloroplatinic acid. Increasing hydrochloric acid concentration in the aqueous phase decreases the percent metal extraction due to mass action. At 5 wt% TOA, nearly all of platinum is transferred into the

organic phase regardless of the kind of oil used. Further increasing the TOA concentration offers no improvement in the extraction performance as shown in figure 4.3.

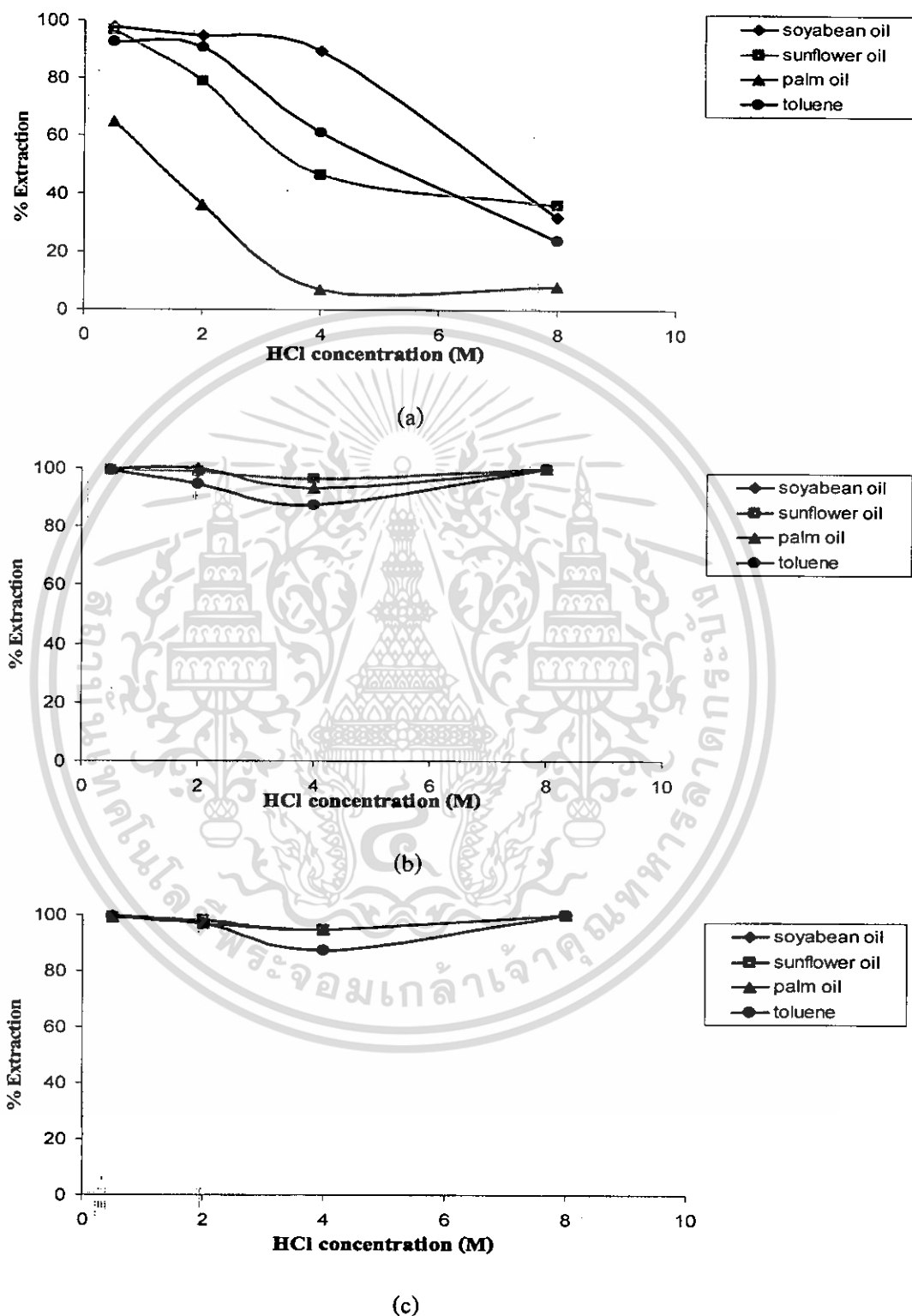


Figure 4.1 Effect of concentration of HCl on efficiency of platinum extraction in various organic solvents (a) TOA 0.1 wt% (b) TOA 5 wt% (c) TOA 10 wt%

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

For rhodium extraction, similar experiments to those for platinum extraction were carried out. It was found that, for the same hydrochloric and TOA concentrations as applied to platinum extraction, rhodium was extracted in much less extent. For 0.1 wt% TOA, at hydrochloric acid concentrations higher than 2 M, the extraction efficiency was virtually zero. Again, high acid concentration causes the shift of the metal ions in the aqueous solution to form complex compound with chloride ions. Increasing TOA concentration to 5 wt% in various kinds of organic solvent results in higher extraction efficiency up to 60% as there are more amine molecules available to share electrons with. However, the effect of TOA concentration quickly subsides with increasing hydrochloric concentration. This trend also continues for 10 wt% TOA. It is noted that all four kinds of organic solvent applied exhibit similar metal extraction performance. These experimental results indicate that it is possible to use vegetable oil i.e. sunflower oil, palm oil, or soyabean oil as an organic solvent in stead of toluene in metal extraction. This is because the major function of it is to dissolve the active component for metal extraction, which is TOA for this project, while at the same time being immiscible liquid to the aqueous solution. Therefore, the risk of using toxic chemicals such as toluene can be avoided. Soyabean oil and sunflower oil were used for subsequent metal extraction experiments.

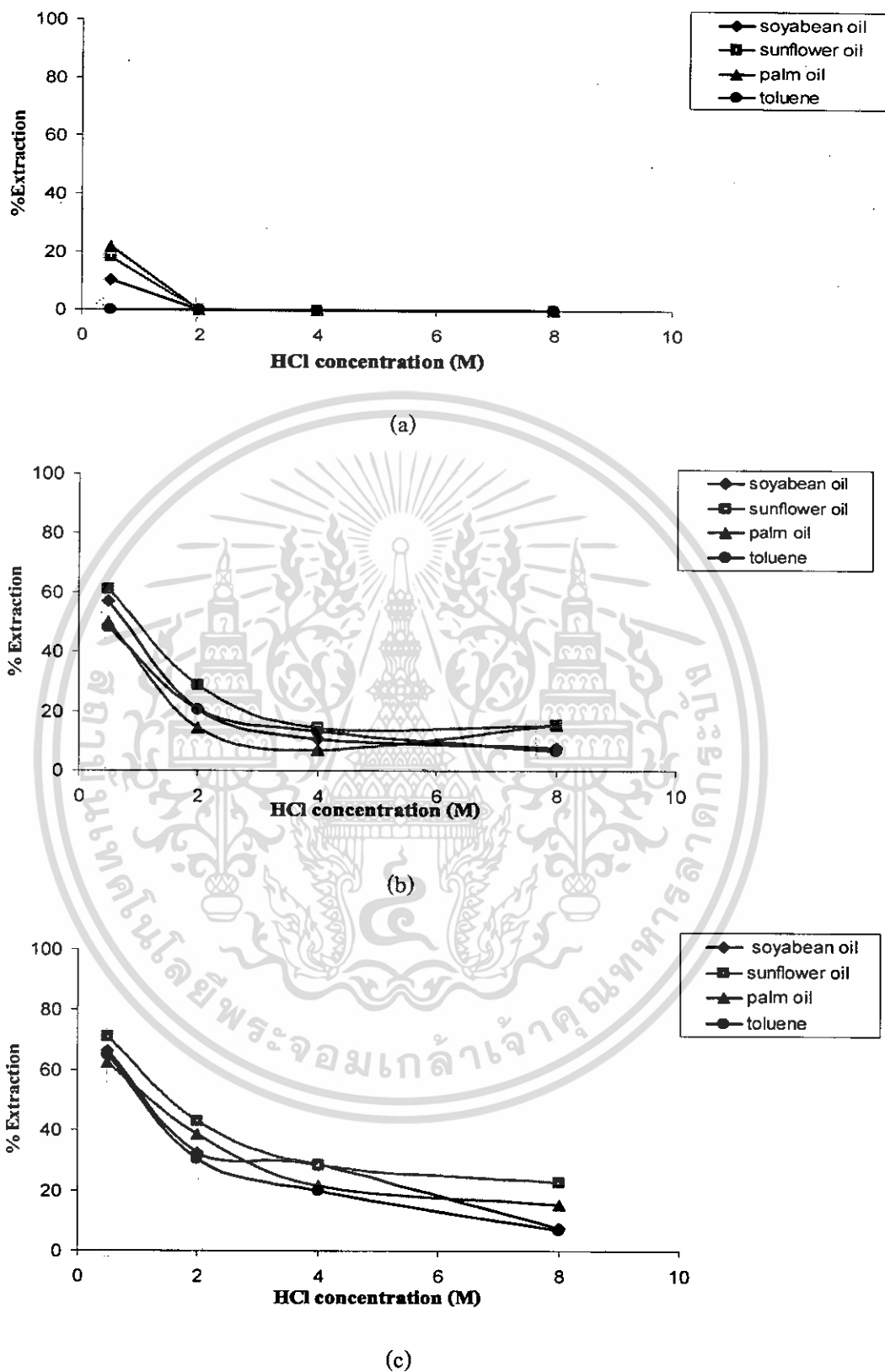


Figure 4.2 Effect of concentration of HCl on efficiency of rhodium extraction in various organic solvents (a) TOA 0.1 wt% (b) TOA 5 wt% (c) TOA 10 wt%

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4.1.2 Effect of TOA concentration on platinum and rhodium extraction efficiency

The individual metal extraction experiments were performed using soyabean oil and sunflower oil as an organic solvent in order to determine the range of TOA concentration suitable for the separation of both metals. Platinum concentration of 80 ppm and rhodium concentration of 40 ppm in 8 M hydrochloric acid was used as a stock solution for platinum and rhodium extraction respectively. Although high concentrations of hydrochloric acid provide less extraction efficiency, it was chosen because leaching the metals out of the catalytic support requires very strong acid. Diluting the leached solution would make the volume of the system larger and more difficult to operate. To determine the effect of TOA concentration for platinum and rhodium extraction, TOA concentration in the range of 0.01 – 10 wt% was used. The results are shown in figures 4.3.

It was observed that both metals are not able to transfer from the aqueous phase into the organic phase when the TOA concentration is 0.01 wt%. The platinum extraction efficiency rapidly increases in the range of 0.01 – 1 wt% concentration of TOA in soyabean oil. Further increasing TOA concentration above 1 wt% TOA gave slightly higher (over 90%) extraction efficiency and complete extraction resulted for over 2.5 wt% TOA. On the other hand, rhodium was not extracted at all in the TOA concentration range of 0.01 -3 wt%. The extraction efficiency was improved marginally by using high TOA concentration up to 10 wt%. Note that rhodium extraction efficiency is zero while that of the platinum is maximum for TOA concentration in the range of 2.5-3 wt%. These results suggested that it is probable to separate platinum and rhodium in hydrochloric acid by using TOA as an active component dissolved in soyabean oil. The same set of experiments was performed using sunflower oil as an organic solvent. The results showed no significant difference to that of the soyabean oil.

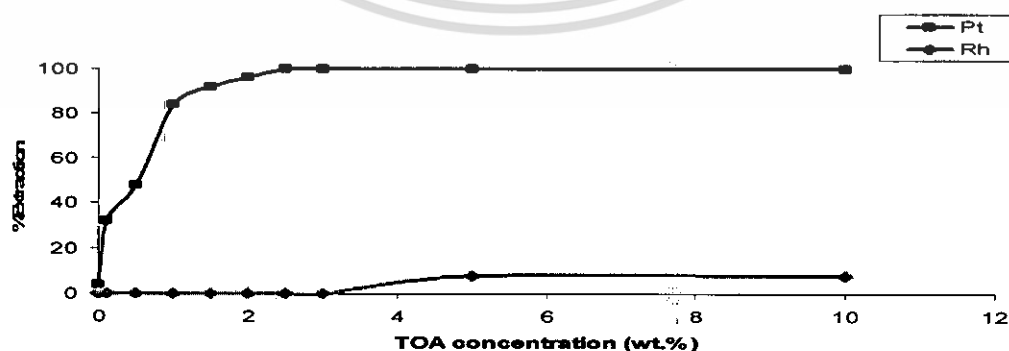


Figure 4.3 Effect of concentration of TOA in soyabean oil on efficiency of platinum and rhodium extraction

4.2 Separation of Pt and Rh from their mixed solution

Again, the metal extraction experiments were performed using soyabean oil as an organic solvent. According to the individual metal extraction results, TOA concentration in the range of 2.5 – 5.5 wt% was chosen to selectively extract platinum out of the aqueous solution containing 80 ppm of platinum and 40 ppm of rhodium in 8 M HCl. Figure 4.8 shows that nearly all platinum (over 95%) was transferred into the organic phase leaving all rhodium in the aqueous phase when using 2.5 wt% TOA in soyabean oil. Further increasing TOA concentration to 3.5 wt% and beyond not only enhanced the platinum extraction, rhodium was also extracted to some extent. That causes the metal separation to be less effective. Therefore, the platinum-rhodium separation by liquid-liquid extraction using TOA was proposed at a concentration level of 2.5 wt%. The extract obtained at this operating condition was later stripped for further purification of platinum.

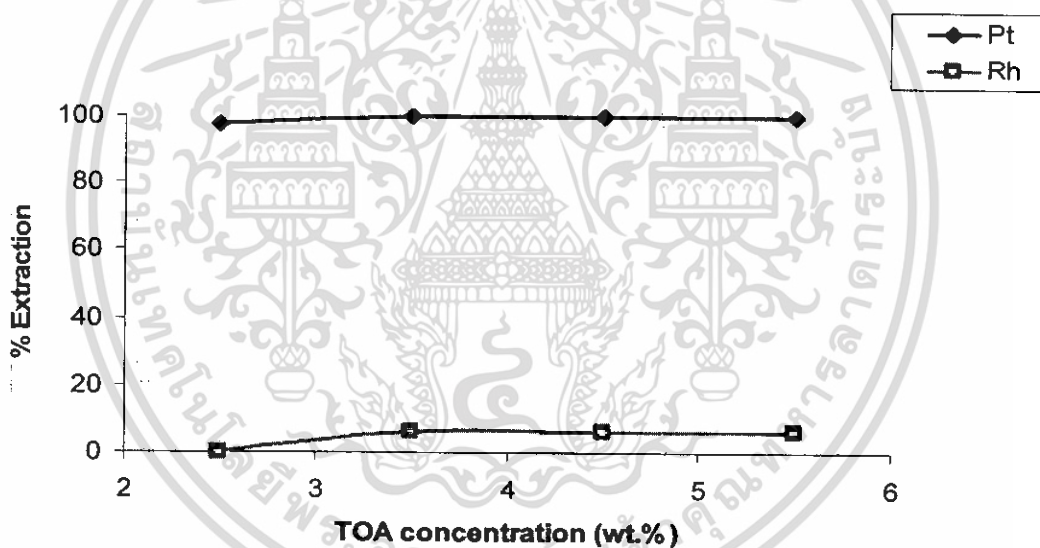


Figure 4.4 Effect of concentration of TOA in soyabean oil on efficiency of platinum and rhodium coexisting extraction

4.3 Effect of stripping agent volume

The prior-extracted solution containing only platinum metal in the form of complex compound with TOA was used to study the effect of volume ratio for stripping. According to the study performed by Chaikla D. et al. [18], using nitric acid as a stripping agent showed much higher stripping performance than hydrochloric acid. In this study, 4.0 M nitric acid was, therefore, used as a stripping agent. To determine the effect of stripping agent volume for platinum stripping, equal and twofold volume of nitric acid phase were mixed with the extract solution containing 2.5 wt% TOA in soyabean oil. The equilibration time was determined by carrying out stripping experiments with the lowest level of 4.0 M nitric acid volume. It was found that an extraction period of 20 minutes is enough for the system to establish a steady state. The results revealed that increasing stripping agent volume significantly increased the percent of platinum stripped, as shown in Table 4.1. Nonetheless, it is also possible to apply higher nitric concentration in less quantity for platinum stripping [18].

Table 1 Stripping results of Pt-loaded organic phase using different stripping agent volume

Stripping agent volume	% Pt stripped
4.0 M HNO ₃ equal-volume of org. phase	68.11
4.0 M HNO ₃ twice folds volume of org. phase	90.81

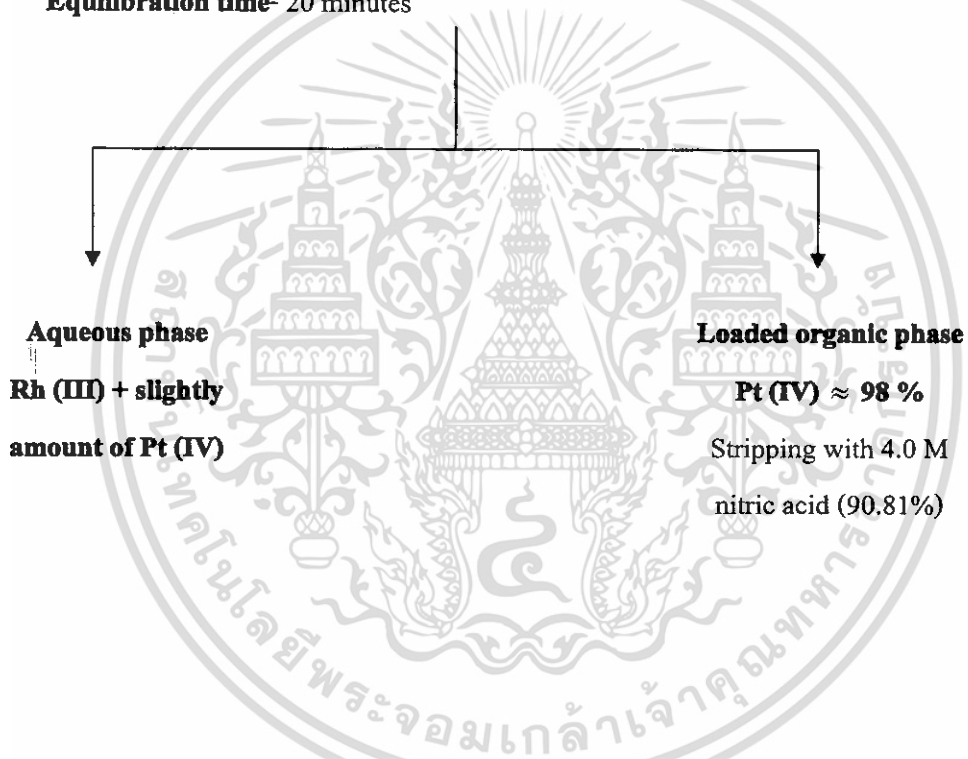
From results of extraction and stripping experiments, a separation process for platinum-rhodium dissolved in hydrochloric solution is proposed in flowsheet 1 below. The aqueous solutions obtained from both sides of the flowsheet are to be treated for precipitation and refinement of metal.

Flowsheet 1 Separation of Pt and Rh from their mixed solution

Aqueous phase- Pt 80 ppm and Rh 40 ppm in 8.0 M HCl

Organic phase- 2.5 wt% TOA in soyabean oil

Equilibration time- 20 minutes



CHAPTER 5

Conclusion and Suggestion

5.1 Conclusion

It was demonstrated that liquid-liquid extraction technique can be used to separate platinum and rhodium from their hydrochloric aqueous solution. TOA was proved to be an effective reagent for extraction of platinum. For equi-volume extraction, only 2.5 wt% TOA was required for complete removal of platinum from the aqueous phase (distribution coefficient = 39.43). Rhodium extraction using TOA was not efficient. The organic solvent investigated in this study (soyabean oil, sunflower oil, palm oil, and toluene) did not significantly affect the extraction performance. Thus, any of them could be used to dissolve TOA and separate from the aqueous solution. Increasing HCl concentration decreased the extraction efficiency for both metals.

The optimized TOA concentration necessary for the separation of both metals was 2.5 wt%. This left all amount of rhodium in the aqueous phase and transferred 97.53% of platinum into the organic phase. By using 4.0 M nitric acid as a stripping agent with the volume ratio of 2 : 1 between the stripping agent and the organic solution, 90.81 % of platinum was stripped out into the aqueous phase.

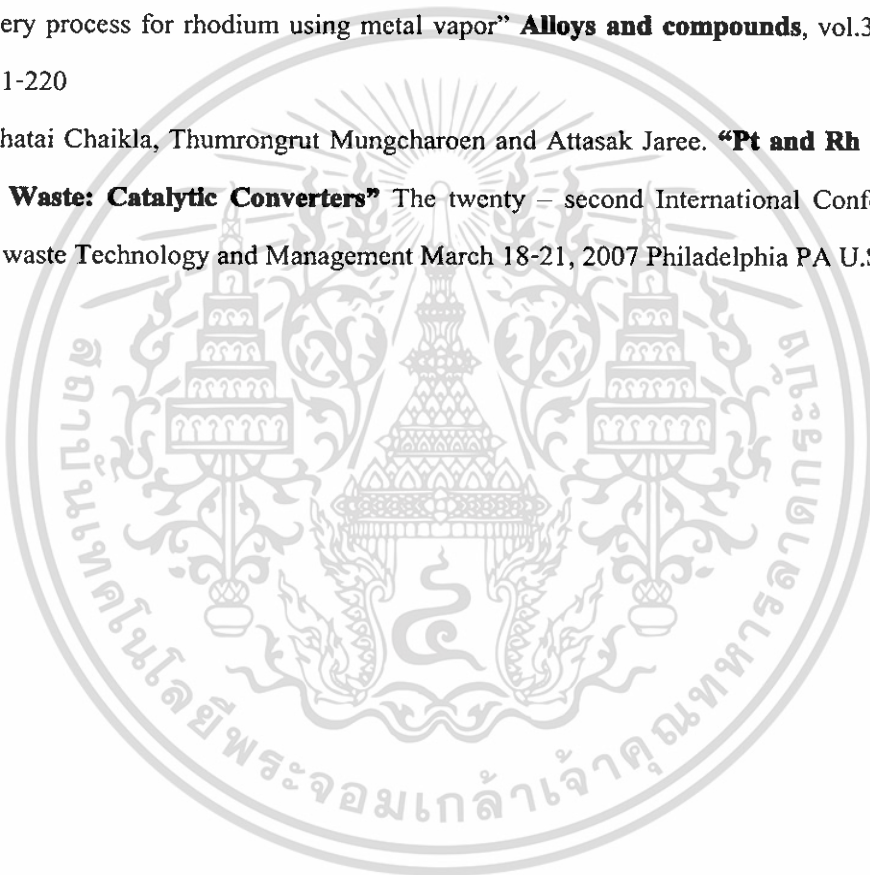
5.2 Suggestion

Future investigation should include the possibility of recycling the vegetable oil in the metal extraction process, the effect of temperature on the extraction and stripping, and the comparison of extraction performance using different active components. Finally, the design of a continuous process of metal separation should be considered.

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Appendix A

Experimental Data

Table A.1.1 Platinum in 0.5 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Pt from AA (ppm)	Concentration of Pt in aqueous phase (ppm)	Concentration of Pt in organic phase (ppm)	% Pt Extraction
soyabean oil	0.1	1.0	1.80	82.80	97.87
	5.0	0.2	0.36	84.24	99.57
	10.0	0.2	0.36	84.24	99.57
sunflower oil	0.1	1.5	2.70	81.90	96.81
	5.0	0.3	0.54	84.06	99.36
	10.0	0.3	0.54	84.06	99.36
palm oil	0.1	16.4	29.52	55.08	65.11
	5.0	0.1	0.18	84.42	99.79
	10.0	0.3	0.54	84.06	99.36
toluene	0.1	3.4	6.13	78.47	92.75
	5.0	0.4	0.66	83.94	99.22
	10.0	0.4	0.66	83.94	99.22

Concentration of Pt in stock solution = 84.60 ppm

Note: The aqueous solution was diluted 1.8 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A1.2 Platinum in 2 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Pt from AA (ppm)	Concentration of Pt in aqueous phase (ppm)	Concentration of Pt in organic phase (ppm)	% Pt Extraction
soyabean oil	0.1	0.5	3.65	69.35	95.00
	5.0	0.1	0.73	72.27	99.00
	10.0	0.2	1.46	71.54	98.00
sunflower oil	0.1	2.1	15.33	57.67	79.00
	5.0	0.1	0.73	72.27	99.00
	10.0	0.2	1.46	71.54	98.00
palm oil	0.1	6.4	46.72	26.28	36.00
	5.0	0.0	0.00	73	100.00
	10.0	0.3	2.19	70.81	97.00
toluene	0.1	0.9	6.64	66.36	90.91
	5.0	0.5	3.93	69.07	94.62
	10.0	0.3	2.19	70.81	97.00

Concentration of Pt in stock solution = 73.00 ppm

Note: The aqueous solution was diluted 7.3 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A1.3 Platinum in 4 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Pt from AA (ppm)	Concentration of Pt in aqueous phase (ppm)	Concentration of Pt in organic phase (ppm)	% Pt Extraction
soyabean oil	0.1	0.6	8.76	75.92	89.66
	5.0	0.2	2.92	81.76	96.55
	10.0	0.3	4.38	80.30	94.83
sunflower oil	0.1	3.1	45.26	39.42	46.55
	5.0	0.2	2.92	81.76	96.55
	10.0	0.3	4.38	80.30	94.83
palm oil	0.1	5.4	78.84	5.84	6.90
	5.0	0.4	5.84	78.84	93.10
	10.0	0.3	4.38	80.30	94.83
toluene	0.1	2.2	32.78	51.90	61.29
	5.0	0.7	10.77	73.91	87.28
	10.0	0.6	8.47	76.21	90.00

Concentration of Pt in stock solution = 84.68 ppm

Note: The aqueous solution was diluted 14.6 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A1.4 Platinum in 8 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Pt from AA (ppm)	Concentration of Pt in aqueous phase (ppm)	Concentration of Pt in organic phase (ppm)	% Pt Extraction
Soyabean oil	0.01	2.4	70.08	2.92	4.00
	0.1	1.7	49.64	23.36	32.00
	0.5	1.3	37.96	35.04	48.00
	1.0	0.4	11.68	61.32	84.00
	1.5	0.2	5.84	67.16	92.00
	2.0	0.1	2.92	70.08	96.00
	2.5	0.0	0.00	73.00	100.00
	3.0	0.0	0.00	73.00	100.00
	5.0	0.0	0.00	73.00	100.00
	10.0	0.0	0.00	73.00	100.00
Sunflower oil	0.01	2.5	73.00	0.00	0.00
	0.1	1.6	46.72	26.28	36.00
	0.5	1.2	35.04	37.96	52.00
	1.0	0.4	11.68	61.32	84.00
	1.5	0.3	8.76	64.24	88.00
	2.0	0.2	5.84	67.16	92.00
	2.5	0.1	2.92	70.08	96.00
	3.0	0.1	2.92	70.08	96.00
	5.0	0.0	0.00	73.00	100.00
	10.0	0.0	0.00	73.00	100.00

Concentration of Pt in stock solution = 73.00 ppm

Note: The aqueous solution was diluted 29.2 folds to analyze metal concentration by an atomic absorption spectrometer.

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Table A1.4 (cont.) Platinum in 8 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Pt from AA (ppm)	Concentration of Pt in aqueous phase (ppm)	Concentration of Pt in organic phase (ppm)	% Pt Extraction
Palm oil	0.1	2.3	67.16	5.84	8.00
	5.0	0.0	0.00	73.00	100.00
	10.0	0.0	0.00	73.00	100.00
toluene	0.1	1.9	55.48	17.52	24.00
	5.0	0.0	0.00	73.00	100.00
	10.0	0.0	0.00	73.00	100.00

Concentration of Pt in stock solution = 73.00 ppm

Note: The aqueous solution was diluted 29.2 folds to analyze metal concentration by an atomic absorption spectrometer.

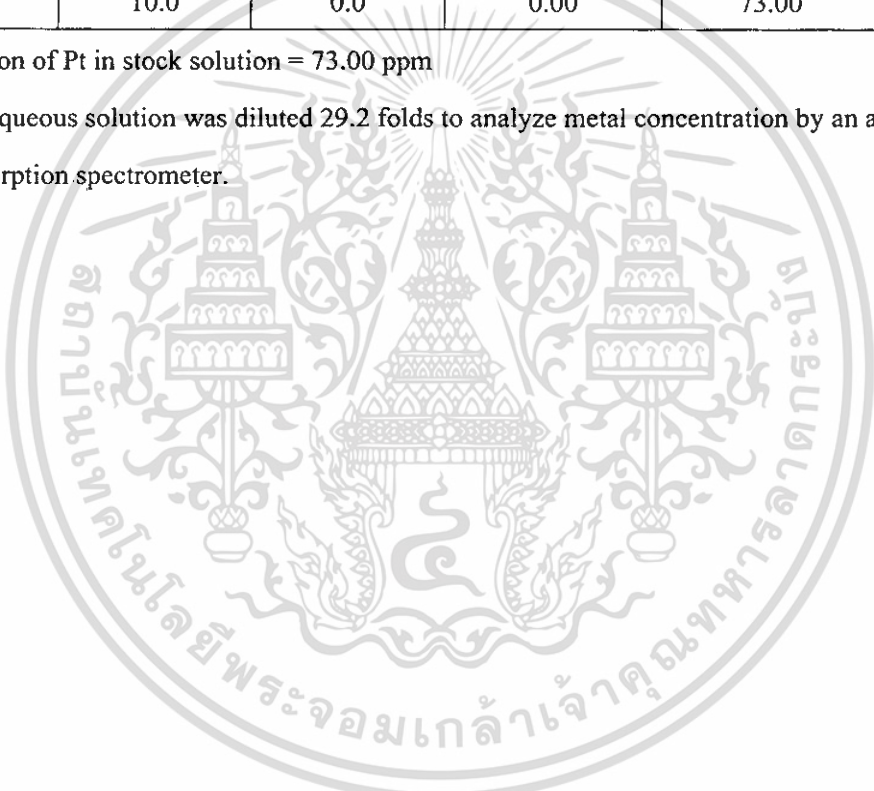


Table A2.1 Rhodium in 0.5 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Rh from AA (ppm)	Concentration of Rh in aqueous phase (ppm)	Concentration of Rh in organic phase (ppm)	% Rh Extraction
soyabean oil	0.1	19.7	35.46	4.14	10.45
	5.0	10.4	18.68	20.92	52.82
	10.0	7.4	13.32	26.28	66.36
sunflower oil	0.1	18.0	32.40	7.20	18.18
	5.0	8.6	15.48	24.12	60.91
	10.0	6.4	11.52	28.08	70.91
palm oil	0.1	17.2	30.96	8.64	21.82
	5.0	11.0	19.80	19.80	50.00
	10.0	8.3	14.94	24.66	62.27
toluene	0.1	22.0	39.60	0.00	0.00
	5.0	11.4	20.51	19.09	48.21
	10.0	7.8	13.97	25.63	64.73

Concentration of Rh in stock solution = 39.60 ppm

Note: The aqueous solution was diluted 1.8 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A2.2 Rhodium in 2 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Rh from AA (ppm)	Concentration of Rh in aqueous phase (ppm)	Concentration of Rh in organic phase (ppm)	% Rh Extraction
soyabean oil	0.1	4.9	35.77	0.00	0.00
	5.0	3.9	28.47	7.30	20.41
	10.0	3.3	24.09	11.68	32.65
sunflower oil	0.1	4.9	35.77	0.00	0.00
	5.0	3.5	25.55	10.22	28.57
	10.0	2.8	20.44	15.33	42.86
palm oil	0.1	4.9	35.77	0.00	0.00
	5.0	4.2	30.66	5.11	14.29
	10.0	3.0	21.90	13.87	38.78
toluene	0.1	4.9	35.77	0.00	0.00
	5.0	3.9	28.47	7.30	20.41
	10.0	3.4	24.82	10.95	30.61

Concentration of Rh in stock solution = 35.77 ppm

Note: The aqueous solution was diluted 7.3 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A2.3 Rhodium in 4 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Rh from AA (ppm)	Concentration of Rh in aqueous phase (ppm)	Concentration of Rh in organic phase (ppm)	% Rh Extraction
soyabean oil	0.1	2.8	40.88	0.00	0.00
	5.0	2.5	36.50	4.38	10.71
	10.0	2.0	29.20	11.68	28.57
sunflower oil	0.1	2.8	40.88	0.00	0.00
	5.0	2.4	35.04	5.84	14.29
	10.0	2.0	29.20	11.68	28.57
palm oil	0.1	2.8	40.88	0.00	0.00
	5.0	2.6	37.96	2.92	7.14
	10.0	2.2	31.75	9.13	22.33
toluene	0.1	2.8	40.88	0.00	0.00
	5.0	2.4	35.43	5.45	13.33
	10.0	2.2	32.70	8.18	20.00

Concentration of Rh in stock solution = 40.88 ppm

Note: The aqueous solution was diluted 14.6 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A2.4 Rhodium in 8 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Rh. from AA (ppm)	Concentration of Rh in aqueous phase (ppm)	Concentration of Rh in organic phase (ppm)	% Rh Extraction
Soyabean oil	0.01	1.3	37.96	0.00	0.00
	0.1	1.3	37.96	0.00	0.00
	0.5	1.3	37.96	0.00	0.00
	1.0	1.3	37.96	0.00	0.00
	1.5	1.3	37.96	0.00	0.00
	2.0	1.3	37.96	0.00	0.00
	2.5	1.3	37.96	0.00	0.00
	3.0	1.3	37.96	0.00	0.00
	5.0	1.2	35.04	2.92	7.69
	10.0	1.2	35.04	2.92	7.69
Sunflower oil	0.01	1.3	37.96	0.00	0.00
	0.1	1.3	37.96	0.00	0.00
	0.5	1.3	37.96	0.00	0.00
	1.0	1.3	37.96	0.00	0.00
	1.5	1.3	37.96	0.00	0.00
	2.0	1.3	37.96	0.00	0.00
	2.5	1.3	37.96	0.00	0.00
	3.0	1.2	35.04	2.92	7.69
	5.0	1.1	32.12	5.84	15.38
	10.0	1.0	30.22	7.74	20.38

Concentration of Rh in stock solution = 37.96 ppm

Note: The aqueous solution was diluted 29.2 folds to analyze metal concentration by an atomic absorption spectrometer.

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Table A2.4 Rhodium in 8 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of Rh from AA (ppm)	Concentration of Rh in aqueous phase (ppm)	Concentration of Rh in organic phase (ppm)	% Rh Extraction
Palm oil	0.1	1.3	37.96	0.00	0.00
	5.0	1.1	32.12	5.84	15.38
	10.0	1.1	32.12	5.84	15.38
Toluene	0.1	1.3	37.96	0.00	0.00
	5.0	1.2	35.43	2.53	6.67
	10.0	1.2	35.43	2.53	6.67

Concentration of Rh in stock solution = 37.96 ppm

Note: The aqueous solution was diluted 29.2 folds to analyze metal concentration by an atomic absorption spectrometer.

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า
ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Table A3 Mixed solution of platinum and rhodium in 8 M HCl extraction data

Organic solvent	TOA concentration (wt%)	Concentration of metal from AA (ppm)		Concentration of metal in aqueous phase (ppm)		Concentration of metal in organic phase (ppm)		% Extraction	
		Pt	Rh	Pt	Rh	Pt	Rh	Pt	Rh
soyabean oil	2.5	0.067	1.6	1.95	46.72	76.89	0.00	97.53	0.00
	3.5	0.00	1.5	0.00	43.80	78.84	2.92	100.00	6.25
	4.5	0.00	1.5	0.00	43.80	78.84	2.92	100.00	6.25
	5.5	0.00	1.5	0.00	43.80	78.84	2.92	100.00	6.25

Concentration of Pt in stock solution = 78.84 ppm

Concentration of Rh in stock solution = 46.72 ppm

Note: The aqueous solution was diluted 29.2 folds to analyze metal concentration by an atomic absorption spectrometer.

Table A4 Stripping of platinum – loaded organic phase data

Stripping agent	Stripping agent volume (ml)	Metal conc. from AA (ppm)	Metal conc. in aqueous phase (ppm)	Metal quantity in aq. phase (μ g)	% metal stripped
4.0 M HNO ₃	10	2.1	52.50	525.00	68.11
	20	1.4	34.99	699.96	90.81

Quantity for Pt in load-organic solution = 770.8 μ g

Note: The aqueous solution was diluted 25 folds to analyze metal concentration by an atomic absorption spectrometer.

Appendix B

Calculation

Percent metal extraction calculation

From platinum in 0.5 M HCl extraction data at 0.1 wt % TOA in soyabean oil is shown in table

A1.1

Organic solvent	TOA concentration (wt%)	Pt conc. from AA (ppm)	Pt conc. in aqueous phase (ppm)	Pt conc. in organic phase (ppm)	% Pt Extraction
soyabean oil	0.1	1.0	1.80	82.80	97.87

Concentration of Pt in stock solution = 84.60 ppm

- Metal concentration in aqueous phase = AA × Number of dilute
= 1.0 × 1.8 = 1.8 ppm

Note: Number of dilute is 1.8 for metal in 0.5 M HCl solution.

Number of dilute is 7.3 for metal in 2 M HCl solution.

Number of dilute is 14.6 for metal in 4 M HCl solution.

Number of dilute is 29.2 for metal in 8 M HCl solution.

- Metal concentration in organic phase

Mass balance

Initial metal conc. in stock solution = Metal conc. in aq. phase + Metal conc. in org. phase

Metal conc. in org. phase = Initial metal conc. in stock solution - Metal conc. in aq. phase

$$= 84.60 \text{ ppm} - 1.8 \text{ ppm}$$

$$= 82.80 \text{ ppm}$$

- Percent metal extraction

% Extraction = (Metal conc. in org. phase / Initial metal conc. in stock solution) × 100

$$= (82.88 / 84.60) \times 100$$

$$= 97.87 \%$$

Percent platinum stripping calculation

From stripping of platinum – loaded organic phase data at 4.0 M HNO₃ is shown in table A4

Stripping agent	Stripping agent volume (ml)	Pt conc. from AA (ppm)	Pt conc. in aqueous phase (ppm)	Pt quantity in aq. phase (μg)	% Pt stripped
4.0 M HNO ₃	20	1.4	34.99	699.96	90.81

Concentration of Pt in loaded-organic solution = 77.08 ppm

- Platinum concentration in aqueous phase = AA × Number of dilute

$$= 1.4 \times 25 = 34.998 \text{ ppm}$$

Note: Number of dilute is 25 for metal stripping by 4 M HNO₃ solution.

- Platinum quantity in aqueous phase

$$\begin{aligned} \text{Pt quantity in aq. phase} &= \text{Pt conc. in aq. phase} \times \text{Aq. phase volume} \\ &= 34.998 \frac{\text{mg}}{\text{l}} \times 20 \text{ ml} \\ &= 699.96 \mu\text{g} \end{aligned}$$

- Quantity for Platinum in load-organic solution

$$\begin{aligned} \text{Quantity for Pt in loaded-org.} &= \text{Conc. of Pt in loaded-org.} \times \text{loaded-org. volume} \\ &= 77.08 \frac{\text{mg}}{\text{l}} \times 10 \text{ ml} \\ &= 770.8 \mu\text{g} \end{aligned}$$

- Percent platinum stripped

$$\begin{aligned} \% \text{ Stripping} &= (\text{Pt quantity in aq. phase} / \text{Pt Quantity in load-organic solution}) \times 100 \\ &= (699.96/770.80) \times 100 \\ &= 97.87 \% \end{aligned}$$