

# Liquid-liquid Extraction of Palladium (II) in Acidic Chloride Solutions Using Tri-n-octylamine

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## Abstract

The extraction of palladium in hydrochloric acid solution (200 ppm) using tri-n-octylamine (TOA) as extractant were performed in four different solvents (toluene, xylene, crosin and 1, 2-dichloroethane) via liquid-liquid method. The effect of extraction time and material concentration investigated for Pd ( II ) extraction. The maximum extraction for palladium achieved with 1% TOA in 0.05 M HCl medium in 15 min with toluene. After the extraction, the Pd ( II )-loaded organic phase was stripped with different stripping agents. Results showed that Pd ( II ) stripping is better achieved by 8 M ammonia solution. The percentage stripping of palladium ( II ) was 100% in this condition.

**Keywords:** Extraction; Palladium; Tri-n-octylamine (TOA); Liquid-Liquid; Stripping.Introduction.

## 1. Introduction

Precious metals such as gold, platinum and palladium are important materials for the high technological industries such as decorative materials, dental materials, catalysts, fuel cells and electronic materials [1-5]. Due to the scarcity of these precious metals, the applications of processes for the extraction of platinum group metals (PGM) (ruthenium, rhodium, palladium, osmium, iridium and platinum) become essential [6]. In the attempt to recover the PGMs from the anthropogenic sources, many processes have been employed such as thermal process, leaching, liquid-liquid extraction, ion exchange, etc. [7-10]. This work deal with the liquid-liquid extraction technique.

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Liquid-liquid extraction (LLE), also called solvent extraction (SX), is a process that allows the separation of two or more component due to their unequal solubilities in two immiscible liquid phases [11]. The high prices of precious metals like PGMs have been ensured that there is continued interest in the development of new extractants for the commercial concentration and separation of these metals. The extraction and separation of metals from source materials such as ores or spent catalysts or industrial waste need several multi-step procedures. The final refining stage is often based on hydrometallurgical treatments, which can be achieved by use of ion-exchange/LLE. [12].

Jaree and khunphakdee proposed a method for platinum and rhodium recovery in acidic chloride solution using tri-octylamine (TOA) in toluene. The percentage of extraction for Pt (II) and Rh was 97% and 21% respectively [13]. Shiro kiyoyama reported the extraction of palladium with divinylbenzene microcapsules containing tri-n-octylamine as the extractant in an aqueous hydrochloric solution [14].

For liquid-liquid extraction, different chemicals have been used such as tributylphosphane (TBP), N, N'-dimethyl-N, N'-dicyclohexylthiodiglycolamide (DMDCHTDGA), 3-phenyl-4-acyl-5-isoxazolones and tri-iso-octylamine [15-17]. Amine derivatives are one of the main families of organic compounds that have been extensively considered for PGMs extraction particularly for Pd (II) and Pt (II) [18]. In our previous work, platinum was extracted by tri-n-octylamine in toluene from hydrochloric acid media [19]. In this paper the extraction of Pd (II) in acidic solution was carried out and TOA was used as extractant. Inductively Coupled Plasma (ICP) was applied to measure the amount of palladium.

## 2. Experimental

### 2.1 Materials

All the reagents were analytical grade and used without further purification, unless otherwise mentioned. Stock solution of PdCl<sub>2</sub> (200 ppm) were prepared by dissolving a weighted amount of palladium (II) chloride (Merck) in HCl (0.05 – 4 M). Toluene, xylene, crosin and 1, 2 dichloroethane were used as organic solvents. Tri-n-octylamine (TOA) used as extractant.

Perkin Elmer Precisely-Optima 2100 DV Inductively Coupled Plasma (ICP) used for the determination of trace amount of palladium. Operating conditions for ICP are given in Table 1.

**Table 1:** ICP operating conditions

Plasma view	axial
Analysis time	0.5 s
Plasma gas flow rate	150 L / min
Sample flow rate	1.5 mL / min

## 2.2 Procedure

For the palladium extraction, a required amount of TOA was added into 4 different solvents to form the organic phase. The organic phases and aqueous solution containing Pd ( II ) (200 ppm) were added to a 50 ml beaker. Extraction and stripping experiments were generally carried out by stirring equal volumes of aqueous and organic phases (A/O=1) at room temperature and using a rotation speed between 900-1000 rpm. The agitation period for all the experiments considered between 5-15 min; afterwards, the organic phase and aqueous phase were separated by the use of a centrifuge at 2000 rpm for 5 min. The extraction efficiency (E %) of palladium ion are expressed as the following equation:

$$E\% = \frac{C_{initial,palladium} - C_{aq,palladium}}{C_{initial,palladium}} \times 100$$

The symbols C initial, palladium and C<sub>aq, palladium</sub> represent the initial concentration of palladium ion and the instantaneous concentration in the aqueous phase, respectively. Stripping experiments were always performed for 15 min and different stripped agnates were used to remove the organic phase.

## 3. Results and discussion

### 3.1 Effect of contact time

The contact time was varied from 5 to 15 min at room temperature. The effect of contact time on the extraction percentage (E %) is shown in Figure 1. In order to ensure the complete extraction, 15 min is chosen as the contact time in the following experiments.

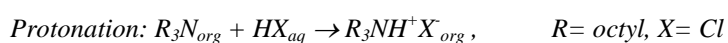
### 3.2 Effect of tri-n-octylamin (TOA) concentration on palladium (II) extraction

The extraction of palladium in different concentration of TOA in 4 different solvents (toluene, xylene, crosin and 1, 2 dichloroethane) over the 5-15 min of extraction time were carried out.

Table 2 illustrates the effect of TOA concentration on palladium extraction. Figure 1 shows the difference between solvents and indicates that toluene is more effective.

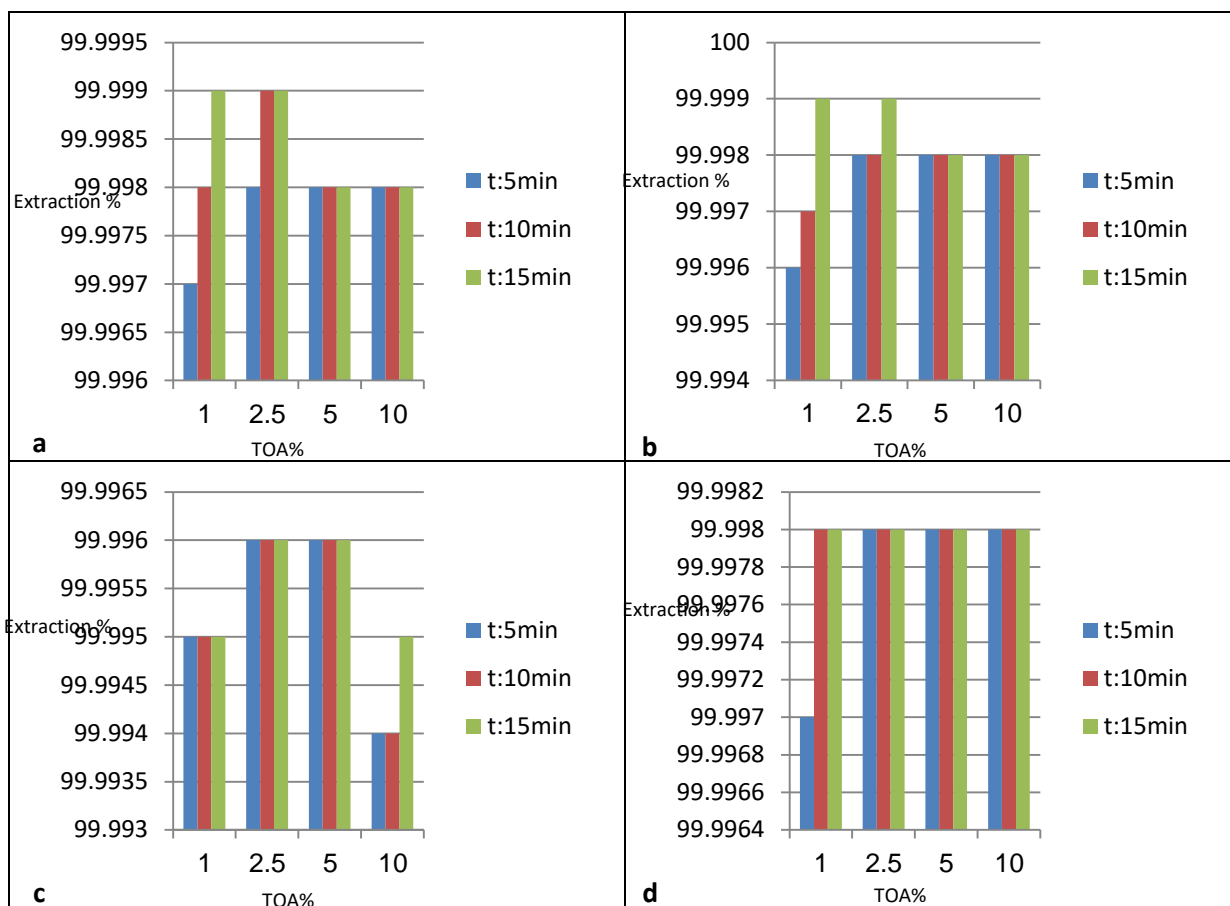
TOA contains a basic nitrogen atom, typically can react with a variety of inorganic and organic acids to form amine salts, which are capable of ion exchange with other anions.

The following reaction, describe the protonation and ion exchange of TOA.



**Table 2:** Effect of TOA% on palladium extraction in different solvents.

TOA%	T ( min )	toluene %	xylene %	crocin %	1, 2 dichloroethane %
1	5	99.997	99.996	99.995	99.997
2.5		99.998	99.998	99.996	99.998
5		99.998	99.998	99.996	99.998
10		99.998	99.998	99.994	99.998
1	10	99.998	99.997	99.995	99.998
2.5		99.999	99.998	99.996	99.998
5		99.998	99.998	99.996	99.998
10		99.998	99.998	99.994	99.998
1	15	99.999	99.997	99.995	99.998
2.5		99.999	99.998	99.996	99.998
5		99.998	99.998	99.996	99.998
10		99.998	99.998	99.995	99.998

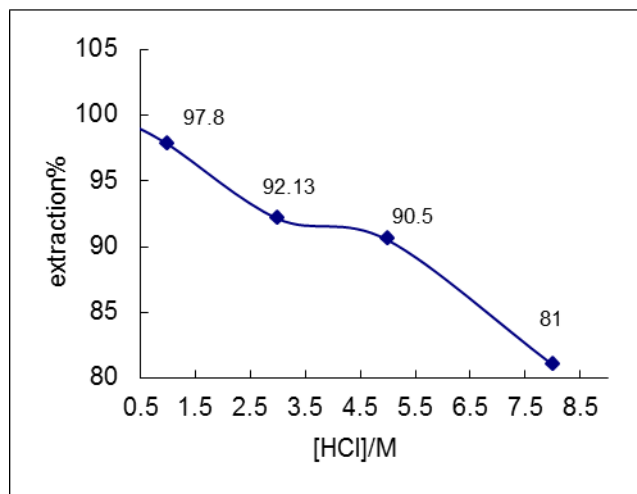


**Figure 1:** Effect of TOA% on palladium extraction in different solvents (a: toluene, b: xylene, c: crocin and d: 1, 2 dichloroethane).

### 3.3 Effect of hydrochloric acid concentration on palladium (II) extraction

Equal volumes of aqueous solutions containing 200 ppm Pd (II) in 0.05 M to 8 M HCl, and organic phases with 1% TOA in toluene, were put in contact for 15 min. The extraction results obtained are displayed in Figure 2

which shows the dependence of Pd (II) extraction on HCl concentration. The extraction of palladium was 97.8% in 0.05 M HCl concentration.



**Figure 2:** Variation of the palladium ( II ) extraction with the HCl concentration (200 ppm Pd ( II ) in 0.05-8 M; 2.5% TOA in toluen; A: O (v/v) = 1; room temperature; 10 min).

### 3.4 Palladium (II) stripping

After the extraction, the Pd (II)-loaded organic phase was stripped with different stripping agents (A/O=1:10 and 15 min contact).

Several stripping agents have been tasted to release Pd (II) from TOA: HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and NH<sub>3</sub> solutions up to 1M, 3M, 5M and 8M.

The overall data achieved are summarized in Table 3. Table 3 shows that 8 M ammonia solution is a quite efficient stripping medium for Pd (II) removal from the TOA organic phase. In Figures 3-5 effect of concentration of stripped agents are shown.

**Table 3:** Effect of different stripped agents

Stripping agents	% Extraction
1 M NH <sub>3</sub>	1.85
3 M NH <sub>3</sub>	96
5 M NH <sub>3</sub>	99
8 M NH <sub>3</sub>	100
1 M HClO <sub>4</sub>	0.02
3 M HClO <sub>4</sub>	0.02
5 M HClO <sub>4</sub>	0.02
8 M HClO <sub>4</sub>	0.02
1 M H <sub>2</sub> SO <sub>4</sub>	0.02
3 M H <sub>2</sub> SO <sub>4</sub>	0.075
5 M H <sub>2</sub> SO <sub>4</sub>	0.02
8 M H <sub>2</sub> SO <sub>4</sub>	0.02

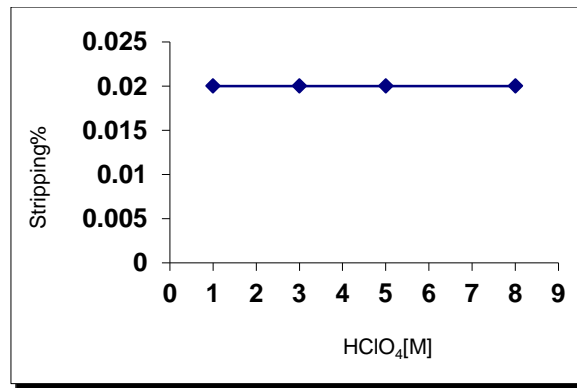


Figure 2: The effect of HClO<sub>4</sub> concentration on stripping

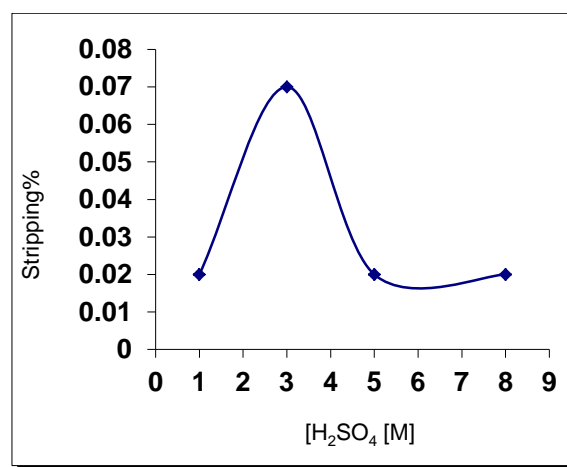


Figure 3: The effect of H<sub>2</sub>SO<sub>4</sub> concentration on stripping

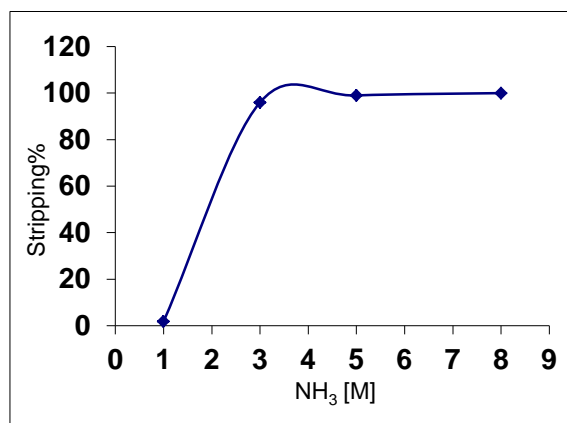


Figure 4: The effect of NH<sub>3</sub> concentration on stripping

## 5. Conclusion

The following conclusions are drawn from the present liquid–liquid extraction of palladium (II) process:

1. Effect of time concluded that 10 min for palladium extraction.
2. The highest extraction of palladium achieved from TOA 1% in toluene with an A/O phase ratio equal to 1 (v/v).
3. Experiments show that 8 M ammonia solution is a quite efficient stripping medium for Pd (II) extraction.
4. This technique can be applied for continuous processes, like spent material or other related solutions.

## References

- [1] Trochimczuk, A.W.; Kabay, N.; Arda, M. & Streat, M. (2004). *Reactive & Functional Polymers*, 59, 1-7.
- [2] Saurat M. & Bringezu, S. (2008). *Journal of Industrial Ecology*, 12, 754-767
- [3] Fu, J.; Nakamura, S. & Akiba, K. (1995). *Separation science & Technology*, 30, 609-619.
- [4] Shams, K.; Beigay, M.R. & Gholampour Shirazi, A. (2004). *Applied Catalysis*, 258, No 2, 227-264.
- [5] Barakat, M.A. & Mahmoud, M.H.H. (2004). *Hydrometallurgy*, 72, 179-185.
- [6] Chen, J. & huang, K. (2006). *Hydrometallurgy*, 182, 164-171.
- [7] Huang, H.; Huang, C.; Wu, Y.; Ding, S.; Liu, N.; Su, D. & Lv, T. (2015). *Hydrometallurgy*, 156, 6-11.
- [8] Juang, R.S. (1988). *Industrial & Engineering Chemistry Research*, 6, 813-820.
- [9] Kumar, J.R. (2004) Ph.D. Thesis, Studies on liquid-liquid extraction of tetravalent zirconium and hafnium, Sri venkateswara University.
- [10] Hundson & Shepherd, M.J. (1985). *Hydrometallurgy*, 14, 23-24
- [11] Jaree, A. & Khunpakdee, N. (2011). *Journal of Industrial & Engineering Chemistry*, 17, 243-247.
- [12] Kiyoyama, S.; Yonemura, S.; Yoshida, M.; Shiomori, K.; Yoshizawa, H.; Kawano, Y. & Hatate, Y. (2007). *Reactive & Functional Polymers*, 67, 522-528.
- [13] Bandekar, S.V. & Dhadke, P.M. (1998). *Separation & Purification Technology*, 13, 129-134.
- [14] Ortet, O. & Paiva, A.P. (2015). *Separation & Purification Technology*, 156, 363-368.
- [15] Lee, J-Y.; J. Kumar, R.; Kim, J-S.; Park, H-K. & Yoon, H-S. (2009). *Journal of Hazardous Material*, 168, 424-429.
- [16] Mirza, M.Y.; Ejaz, M.; Sani, A.R.; Ullah, S.; Rashid, M. & Samdani, G. (1967). *Analytica Chimica Acta*, 37, 402-404.
- [17] Pashdar, H.; Fallah, J.; Marandi, R.; Daneshpajuh, S. & Hajmohammadi, H. (2011). *Journal of Applied Chemical Research*, 17, 37-40.