

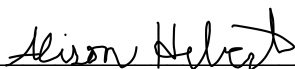
Downstream Processing: Catalyst Separation

A Major Qualifying Project

Submitted to the Faculty
of the

WORCESTER POLYTECHNIC INSTITUTE
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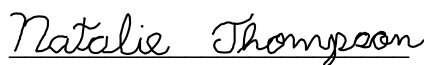
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Abstract

The catalysis of reactions has become a prevalent practice in the pharmaceutical industry. Two methods for organometallic rhodium catalyst recovery from a waste stream were investigated: electro dialysis and solvent combustion. Burning the solvent and dissolving the ashes in acids proved to be the most effective method. Based on the three acids and four molarities tested, 12M HCl proves to be the best acid to dissolve the ash in to create RhCl. This rhodium salt can then be further separated.

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Introduction

The pharmaceutical industry is one of the largest and fastest growing markets in the world. As advancements in medicinal science occur more frequently, the pharmaceutical economy continues to grow. The United States holds over 45 percent of the global pharmaceutical market. In 2016, this share was valued around 446 billion U.S. dollars (Laporte, 2016). The U.S. pharmaceutical market utilizes many techniques to be able to effectively create their products. One of the major techniques utilized is catalysis. The use of catalysis enables “economical and environmentally-sound manufacturing processes” for the many companies that create their own specialized drugs (Busacca, Fandrick, Song, & Senanayake, 2011). Many of the catalysts utilize precious metals to drive the creation of the product. Rhodium is one metal that has grown in use for the pharmaceutical industry. Rhodium, being ten times more expensive than gold, is used by a local pharmaceutical company to make one of their products (Kidwell, 2008). However, a problem occurs in the process of this company where the rhodium catalyst is degrading over time as it is pulled into the waste stream of the system. Our team’s project is focused on finding a way to recover the rhodium that is lost in the waste stream.

Background

The catalysis of reactions has become a prevalent practice in the ever-growing pharmaceutical industry. The use of catalysts in pharmaceutical processes enables economical and environmentally-sound manufacturing (Busacca, Fandrick, Song, & Senanayake, 2011). Viable catalytic processing for industrial scales is complex, and with that, there are many ways that the catalysts become the core of many processes. Over 90% of chemicals derive from catalytic processes in some way (“Recognizing the Best in Innovation”, 2005).

Rhodium as an Organometallic Catalyst

Rhodium is a rare earth metal in the platinum group. It appears as a gray powder on its own and is extremely flammable (“Rhodium”, 2016). As the organometallic catalyst the team worked with, the substance appears as an orange powder. The catalyst is soluble in alcohols, reacts with water, and is incombustible (“Rhodium Catalyst”, 2012). Rhodium catalysts can be used in the synthesis of compounds that apply to many different pharmaceuticals, including OCD, PTSD, eating disorders, generalized anxiety disorder, and major depressive disorder (Zhao et. al., 2016).

Rhodium catalyst recovery is very important for companies that utilize rhodium, as the cost is roughly \$2,080 per troy ounce, or per 31.1 grams (“Rare Metals Prices and Charts”, 2018). Some of the rhodium catalyst used in the process gets lost in the waste stream of the batch reaction, and due to the cost of rhodium per ounce, recovery of at least some of the lost rhodium is highly lucrative. The team investigated a couple of ways to make the Rhodium easier to recover in a reasonable and, hopefully, usable concentration, including combustion of the waste stream and an electrodialysis machine.

Separation Processes

Combustion of Waste Stream

Combustion of organic solvents to produce solid ash of precious metals is a fairly common practice. Its uses include the separation of organic liquids from the precious metals, such as gold and rhodium, in order to recycle and reduce the wasting of these metals (Cole-Hamilton & Tooze, 2006). This combustion technique can be highly exothermic, so the proper environment is necessary to ensure safety. The ash also then has to be further manipulated in some way to recover the metal on its own to recover the metal separate from any carbon deposits made during combustion.

Electrodialysis

Electrodialysis is another technique that can be used for ion separation within solutions. It uses a recycling technique, along with membrane and electric charges to draw the smallest anions and cations to opposite sides of the machine. Generally, there are multiple pore sizes that the membranes have so that the largest molecules stay towards the center of the stream, while the smaller particles get the highest level of separation, as seen in Figure 1 below. This allows the ions to become more highly concentrated in various streams, and thus allows a better chance for higher yields in any subsequent testing performed on the solutions. One of the most common uses for electrodialysis is sea-water desalination, but it can also be extremely useful for separating salts from acidic solutions (“Electrodialysis: Moving Ions in Water by Electric Current”, 2016).

The team used a Medimat tabletop electrodialysis machine from Ionics Corporation, from 1985. The water treatment company, Ionics Corporation, has since been acquired by General Electric in 2004 (“General Electric Agrees to Acquire Ionics”, 2004). The Medimat machine uses three separate solutions that get recycled and separated after running for about 20 to 25 minutes into electrolyte, waste, and product collections. The original use of the machine is salt ion separation from water, and the original membranes came in a cartridge that allowed for containment and free flow of the solutions.

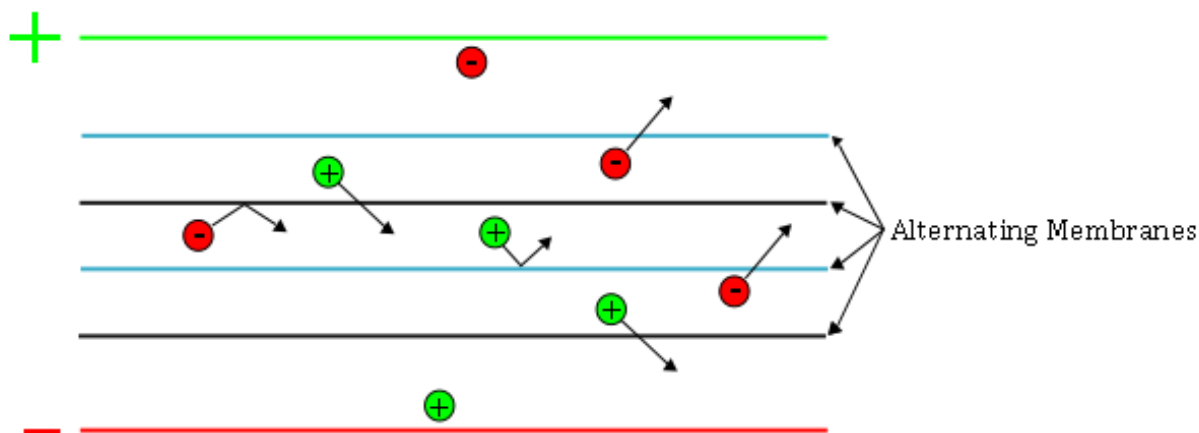


Figure 1: Electrodialysis Membrane and Ion Separation

Waste Stream Composition

The test waste stream consisted of the organometallic rhodium catalyst, methanol and isopropanol. The slurry has 0.18 weight percent Rhodium, which is in the catalyst form, 41.7 g of methanol, which was used to dissolve the catalyst, and 203.5 g isopropanol, which was the original reaction solvent. This is the mock of the solution of the waste stream from the

pharmaceutical process the team is analyzing. The actual waste stream produced from the pharmaceutical process also includes about 20 g of the substrate.

ICP-OES Testing

An Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) tests inorganic solutions using excited argon gas that forms a plasma. The plasma then excites the sample that is injected into the chamber, which gets up to temperatures of 5000 to 7000 K. Emission rays of the excited sample show the intensity of the emission spectrum in the range that was predetermined based off of what the user desires to analyze for (“Principle of ICP Optical Emission Spectrometry”, n.d.).

Methodology

Retrofitting the ED Machine

As mentioned previously, using electro dialysis to separate the catalyst from the waste stream held promise as a feasible process. In order to test this hypothesis, the team took the Medimat 5 and retrofitted it to fit this process' needs. Being an older unit, finding the appropriate materials and making certain adjustments to the machine brought forth unforeseeable difficulties.

To begin the testing of the ED machine the team wanted to validate the the electrical leads on the machine still worked. To do so, the team borrowed a multimeter from the shop to test that there was current going through the machine. The multimeter that was used validated that there was a current going through the electrical leads and the voltage read 11.2 V. Additionally, the built-in current meter on the ED machine went from 200 mAmps initially to 700 mAmps over time as the current was sent through the membranes.

Tubing

The tubes that were used for the electro dialysis machine were MasterFlex© tubing from Cole-Palmer. Both tubes were the same material and the lengths were cut to the sizes needed to function properly with the equipment. The tubing that was put around the peristaltic pump was 1/8" inner diameter and the tubing that was used to bring the solution to the pump was 1/16" inner diameter. The pump tubing had to be flexible and thin enough to be manipulated to stretch and push forward the liquid. Tubing was tested with different lengths to make sure that the tension around the peristaltic pump was correct.

Membranes

On the topic of correct pieces, there was one major problem that our team ran into when looking to use this machine. Before Ionics was bought out by GE, there was a catalog that could be used to order replacement parts for the Medimat 5. In this catalog one would find replacement cartridges to hold the membranes that were used for electro dialysis. Because this company no longer exists, the team was forced to find membranes to use. The hunt for the correct membranes was difficult because of both a lack of benchtop ED machines as well as a lack of knowledge of what was within these replacement cartridges. After searching for electro dialysis membranes for a benchtop unit for a period of time the team refined our search for simply benchtop membranes. This thought process led the team to research fuel cell membranes and see how those might be able to used for our needs. To check the feasibility of retrofitting fuel cell membranes for this purpose, the team realized the need for a cation and anion membrane set. The team purchased

Nafion® XL cation exchange membranes and Fumapem FAA-3-50 anion exchange membranes. Both of these membranes were “middle-of-the-road” models that could be tested and if too much or too little transfer occurred, the team could hypothesize if there was a need for a smaller or bigger membranes. The membranes were between 25 - 50 μm thick and had to be cut to fit the ED machine electrode plates which measured 7” by 4.5”.

Based on our understanding of how electrodialysis works, the team decided to put 3 sets of membranes back to back. This would only take up a fraction of an inch, and because of this needed to fill the remaining space by other means. In order to fill the entire space the team knew that it would be not feasible both economically and practically. In order to make up the distance in between the electrode plates, the team thought to add a plastic spacer. This space had to be made of a material that would not corrode or interact with the solution that would be run through it. This spacer was made out of lexan, had a thickness of ¼”, and was machined to allow the solution through it and the membranes.

The team knew that putting the spacer onto the guides in between the electrode plates increased the possibility of a leak to form. This could occur if the seal between the spacer, the walls of the unit, and the membrane was not strong enough. In order to make sure there were no leaks due to the spacer, the electrode plate was taken off the machine and the spacer was put behind it. Securing the plate with screws with the spacer behind it allowed for a perfect seal and cut out the possibility of leaks occurring due to the spacer. In addition to the spacer, to make up space in between the electrode plates, the team found that the ramped screws that were used to fasten the electrode plates together could, in fact, be tighter than originally thought. By adding washers to the outside of the plate the team was able to tighten the electrode plates more than before thus cutting out some of the leakages.

Burning the Catalyst

As mentioned before, the possibility of burning the catalyst was definitely promising as a way to separate the rhodium from the solution it was in. Because it was mostly within organic liquids it was quite easy to burn. The methanol and isopropanol that the rhodium catalyst was in were both very volatile and simply needed a spark to set them off. In order to burn the catalyst a flint spark torch igniter was used to spark the vapors coming off of the solution. To burn the rhodium solution the team placed the solution into a ceramic crucible to burn, knowing that the heat of combustion would not exceed the breaking point of the ceramic.

First Runs

To begin, a 25 mL ceramic crucible was used to burn small amounts of the solution bit by bit. As the solution was burned, then added, then burnt again, an ash built up on the bottom of the crucible. The ash could then be scraped off of the bottom of the crucible, at which point the ash could start dissolving in acid and other solvents. The team first ran tests to see if the ash

could redissolve in the solvents it was originally in. This included methanol, isopropanol, and DI water. The ash did in fact change the color of the solvent which leads us to believe that there was some part of the ash that was dissolved. The loadings of the solvents can be found below in Table 1.

	IPA		MeOH		DI Water	
Volume of liquid	10	mL	10	mL	10	mL
Mass dissolved	0.0092	g	0.0039	g	0.0023	g

Table 1: Loadings of First Run

Second Runs

The second tests that were run were completed with a different method. After testing the amount of ash that was given off in the previous test, the team decided to burn more of the solution to allow for more ash production. With the scale up, the team decided to use a mortar and pestle to grind the ash in order to get a finer powder for more uniformity. On this series of tests, the mortar and pestle used were made of porcelain, which was also determined safe to burn the solution in. Burning the solution within the same container as grinding it allowed for a lower possibility of losing ash from changing containers multiple times. 10 mL of the solution were placed into the mortar to burn. When sparked through the same process as before and the solution burned in the same matter; however, this time it burnt for much longer. Additionally, even before the ash was ground the ash seemed to be finer. To make sure the powder was as uniform as possible, the team then ground the ash into a fine powder to maximize the contact when the ash was put into the solvents. The ash was finely ground but also was stuck in the small crevices that existed in the mortar. It was at this point the team realized that some of the ash would be lost in the mortar if there were no way to get it out of the mortar. By scraping the bottom of the mortar with a metal scoop, and by using acetone to wash the ash into one area of the mortar, the acetone then evaporated off and left a more concentrated and sizable pile of ash. After the acetone evaporated, more scraping was done to collect the remaining ash. Overall, about 100 mg of ash was collected from the 10 mL of solution to dissolve in acid.

As mentioned before, from literature and guidance of the advisor, the team found that other precious metals are recovered in industry by burning a solution, and then dissolving the ash in an acid to form a complex that is much easier to work with. The team chose to start with hydrochloric acid based on the hypothesis that rhodium (III) chloride hydrate could form from the rhodium that was in the ash interacting with free Cl⁻ ions floating in the solvent. The team decided to dilute 12.14 molar (M) HCl to 12 M, 8 M, 5 M, and 1 M. The thought process behind this was to see if the concentrations would allow more rhodium to become dissolved in the acid. About 2 mg of ash was then measured to be put into 10 mL of each of the acids. After the ash was put into the solution and sat for a period of time, a filtration funnel and paper was used to

separate the solid particles that were left in the acid solution from the pure solution that contained the dissolved rhodium. The loadings of the acids can be found below in Table 2.

	1 M HCl		5 M HCl		8 M HCl		12 M HCl	
Volume of liquid	10	mL	10	mL	10	mL	5.5	mL
Mass dissolved	0.0026	g	0.0019	g	0.0026	g	0.0018	g

Table 2: Loadings of Second Run

Third Runs

The third set of tests that were run followed much of the same approach as the second test. Once again, 10 mL of solution was burnt in the mortar. There were 100 mg of ash collected in this set of experiments as well. The difference on this run was that the team wanted to create “loaded” and “unloaded” samples of hydrochloric acid, nitric acid, and sulfuric acid. “Loaded” refers to doubling the concentration of the ash by adding double the amount of ash (4 mg) to the same amount of liquid (10 mL). This experiment tests whether adding more ash to the acid would allow for more to dissolve in acid as opposed to the “unloaded” solution with only 2 mg of ash. As for the second variable that was changed for this experiment, the acid solvent was also changed to test the ability of other acids to dissolve rhodium. The loaded and unloaded acids can be found in Table 3.

Nitric Acid

Unloaded	1 M Nitric		5 M Nitric		8 M Nitric		12 M Nitric	
Volume of liquid	10	mL	10	mL	10	mL	10	mL
Mass dissolved	0.0019	g	0.0025	g	0.0016	g	0.0015	g

Loaded	1 M Nitric		5 M Nitric		8 M Nitric		12 M Nitric	
Volume of liquid	10	mL	10	mL	10	mL	10	mL
Mass dissolved	0.0047	g	0.004	g	0.0043	g	0.0055	g

Sulfuric Acid

Unloaded	1 M Sulfuric		5 M Sulfuric		8 M Sulfuric		12 M Sulfuric	
Volume of liquid	10	mL	10	mL	10	mL	10	mL
Mass dissolved	0.0024	g	0.0021	g	0.0019	g	0.0025	g

Loaded	1 M Sulfuric		5 M Sulfuric		8 M Sulfuric		12 M Sulfuric	
Volume of liquid	10	mL	10	mL	10	mL	10	mL
Mass dissolved	0.008	g	0.0036	g	0.0034	g	0.0051	g

Hydrochloric Acid

Unloaded	1 M HCl		5 M HCl		8 M HCl		12 M HCl	
Volume of liquid	10	mL	10	mL	10	mL	5.5	mL
Mass dissolved	0.0026	g	0.0019	g	0.0026	g	0.0018	g

Loaded	1 M HCl		5 M HCl		8 M HCl		12 M HCl	
Volume of liquid	10	mL	10	mL	10	mL	10	mL
Mass dissolved	0.0063	g	0.0032	g	0.0051	g	0.0035	g

Table 3: Loadings of Third Run

Results and Discussion

Our initial testing was on the electro dialysis machine to ensure that it was in proper working order. The machine leaked through various places. The leakage was collected and tested with an ICP machine. Due to the amount of organic solvent in the sample, it extinguished the

plasma needed to run the ICP machine. Based on this, the team was unable to obtain data from the separation process of electro dialysis.

However, burning the solution and recovering the ash was effective. The solution was easily lit with a flint lighter. The ashes were recovered and added to methanol, isopropanol, and distilled water. The ashes did not appear to dissolve in these solutions. Next, the ashes were added to hydrochloric acid (HCl) at four different molarities: 12, 8, 5, and 1 M. After running these solutions through the ICP, the 12 M HCl had the best absorbance at a Rh concentration of 2.792 ppm. These results can be seen in Figure 2.

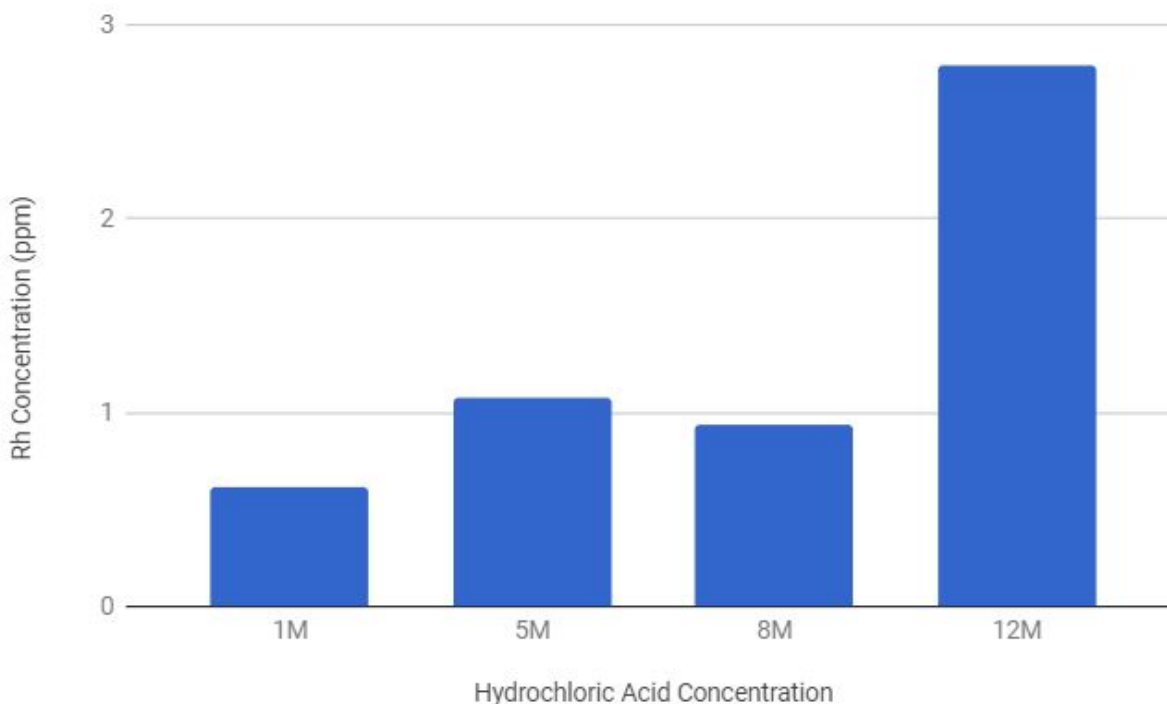


Figure 2: Concentration of Dissolved Rhodium in Hydrochloric Acid, First Run

When the ashes were first ground up using a mortar and pestle and then dissolved, the absorbance increased for each of the HCl concentrations. For each different molarity of HCl tested, two different amounts of the ash were used. In each case, the higher the quantity of ash added to the acid resulted in a higher concentration of Rh. The only outlier to these experiments was the 12 M HCl. Two runs of higher amounts of ash added were performed. As can be seen in Figure 3, the higher the concentration of HCl, the higher the absorbance of Rh. Therefore, the 12 M HCl is the best molarity to dissolve Rh in, with a concentration of 26.41 ppm.

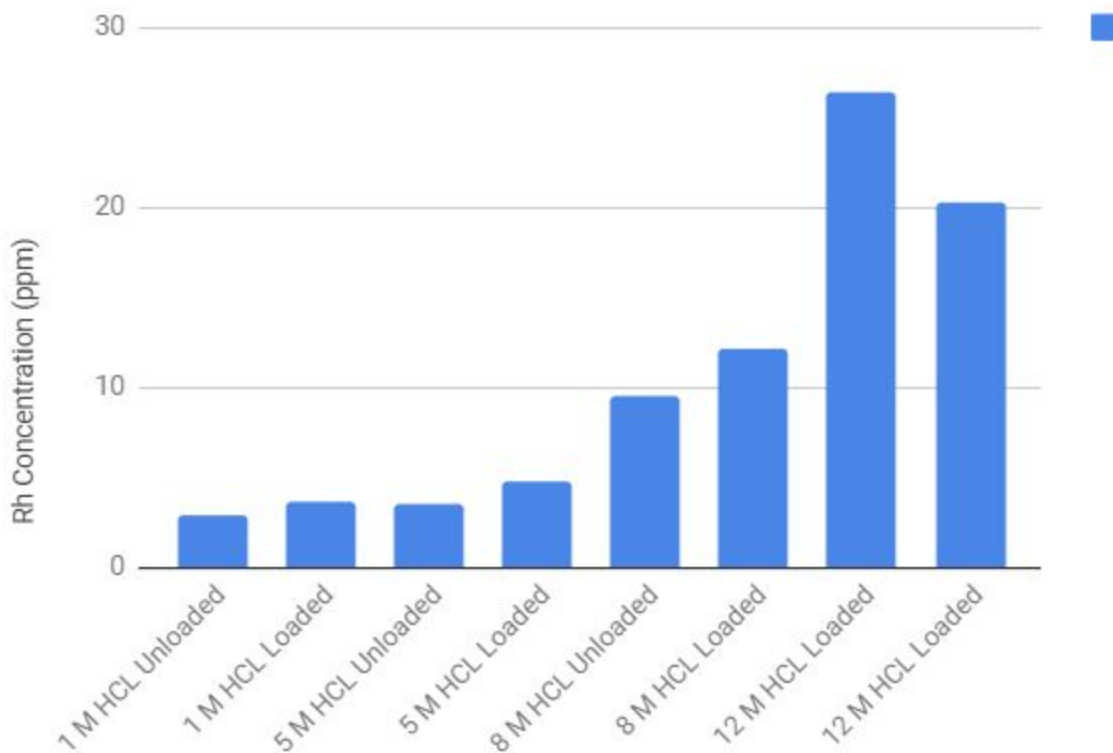


Figure 3: Concentration of Dissolved Rhodium in Hydrochloric Acid, Third Run

When the same quantities of ash were put into H_2SO_4 and HNO_3 , the Rh absorbance was much less in comparison to that of the HCl. The absorbances of these acids did not follow a general trend from lower molarities to higher ones. In general, the loaded version of the acid resulted in a higher concentration of Rh. The only outlier of this trend is the 8 M H_2SO_4 . The concentration data for H_2SO_4 and HNO_3 with each amount of Rh can be seen in Figures 4 and 5, respectively.

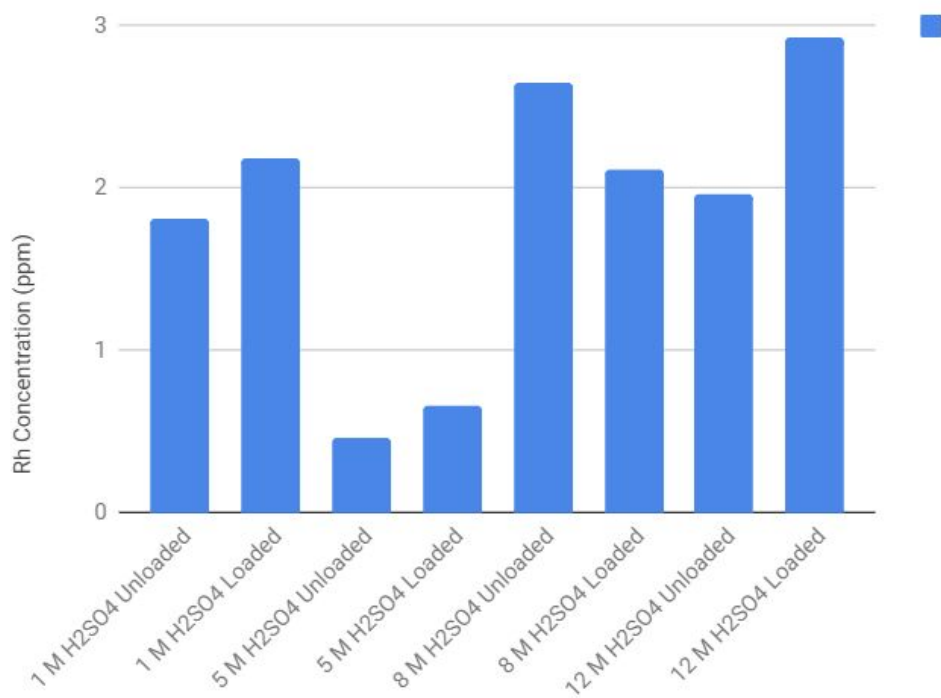


Figure 4: Concentration of Dissolved Rhodium in Sulfuric Acid, Third Run

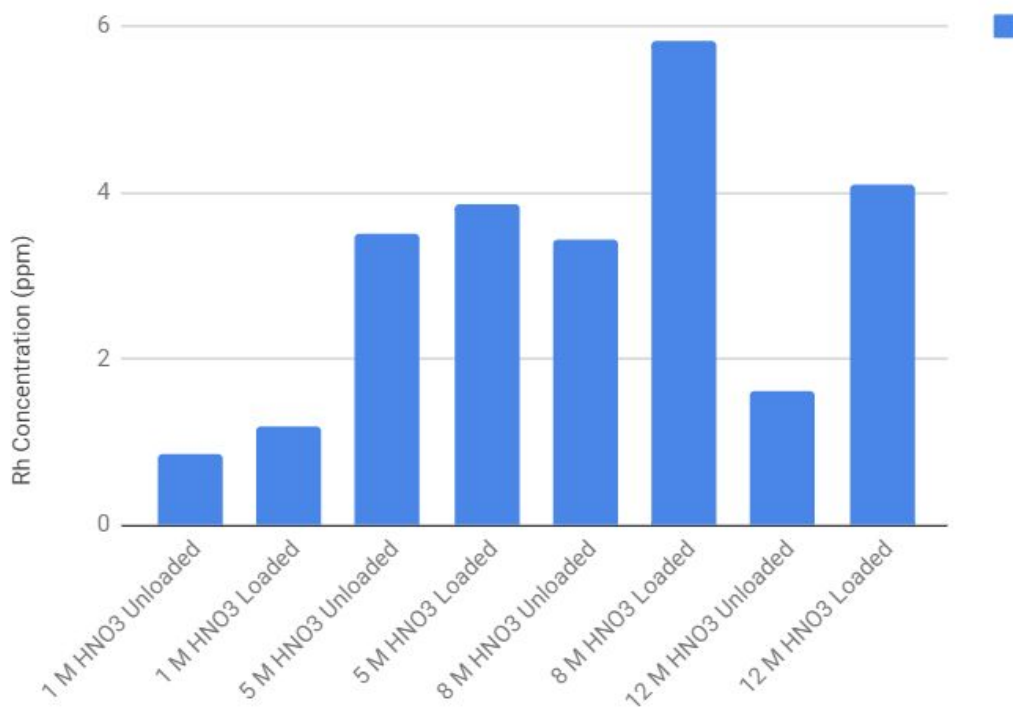


Figure 5: Concentration of Dissolved Rhodium in Nitric Acid, Third Run

Conclusion

Through the scope of this project, the team determined that a valid method of recovering the organometallic Rh catalyst used by a pharmaceutical company in Massachusetts is through the process of burning the substance and dissolving the ashes. Based on the three acids and four molarities tested, 12 M HCl proves to be the best acid in which to dissolve the ash. Dissolving the ash in the 12 M HCl solution creates RhCl, a rhodium salt. This salt can be separated from the solution via conventional separation methods.

The team also determined that electrodialysis is a feasible method for separating Rh from the original catalyst solution. However, the full application of this process is out of scope of this project. Our team has come up with the following recommendations for this project to be taken further.

Recommendations

A full analysis of electrodialysis and its uses in this particular experiment was unfeasible in this project due to a broken electrodialysis machine that our team was unable to fix in the time constraints. Therefore, the team recommends that electrodialysis be fully examined with either a new machine, or time be spent on fixing the current tabletop machine.

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Appendix

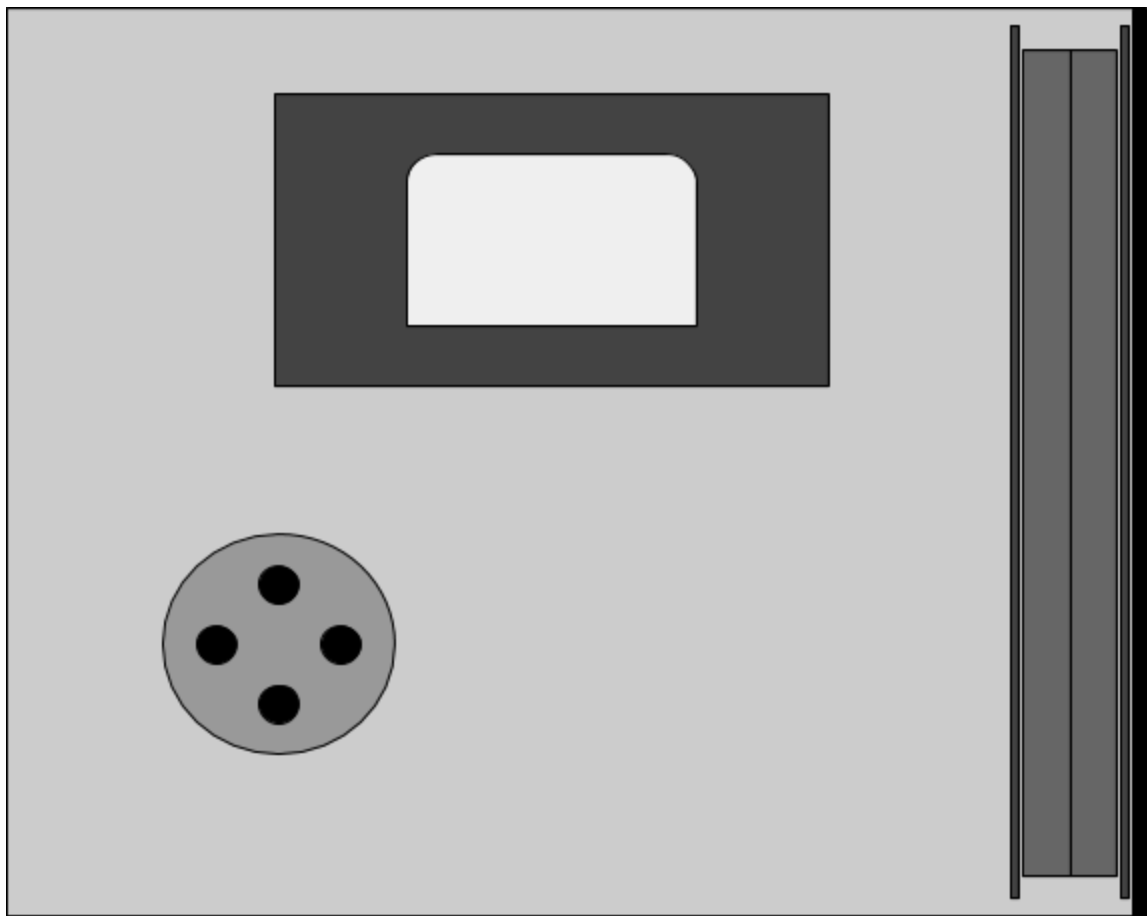


Figure 6: Electro dialysis Machine Side View

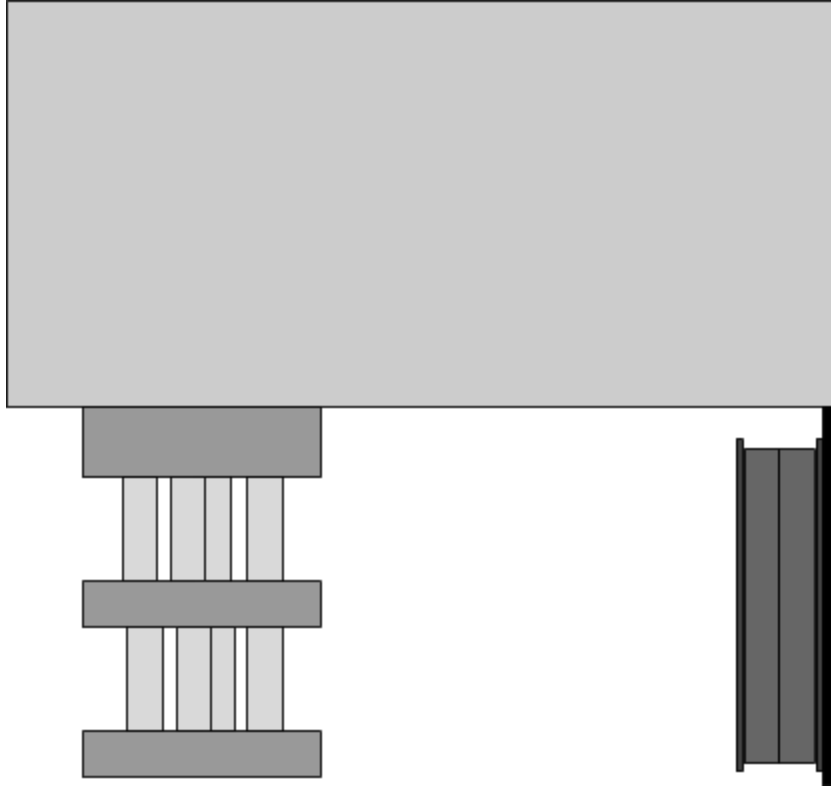


Figure 7: Electro dialysis Machine Aerial View

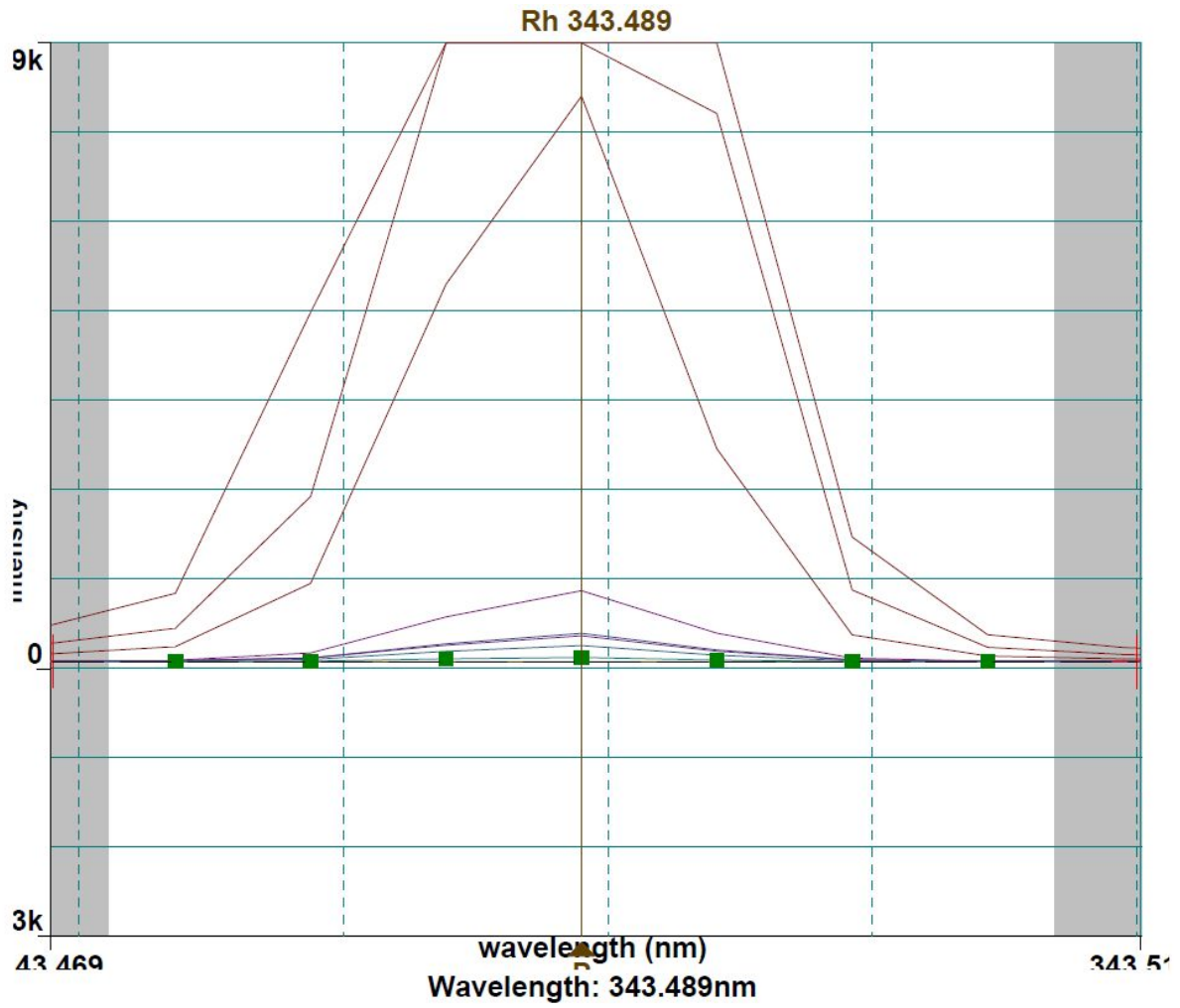


Figure 8: ICP graph for HCl at 12M, 8M, 5M, and 1M

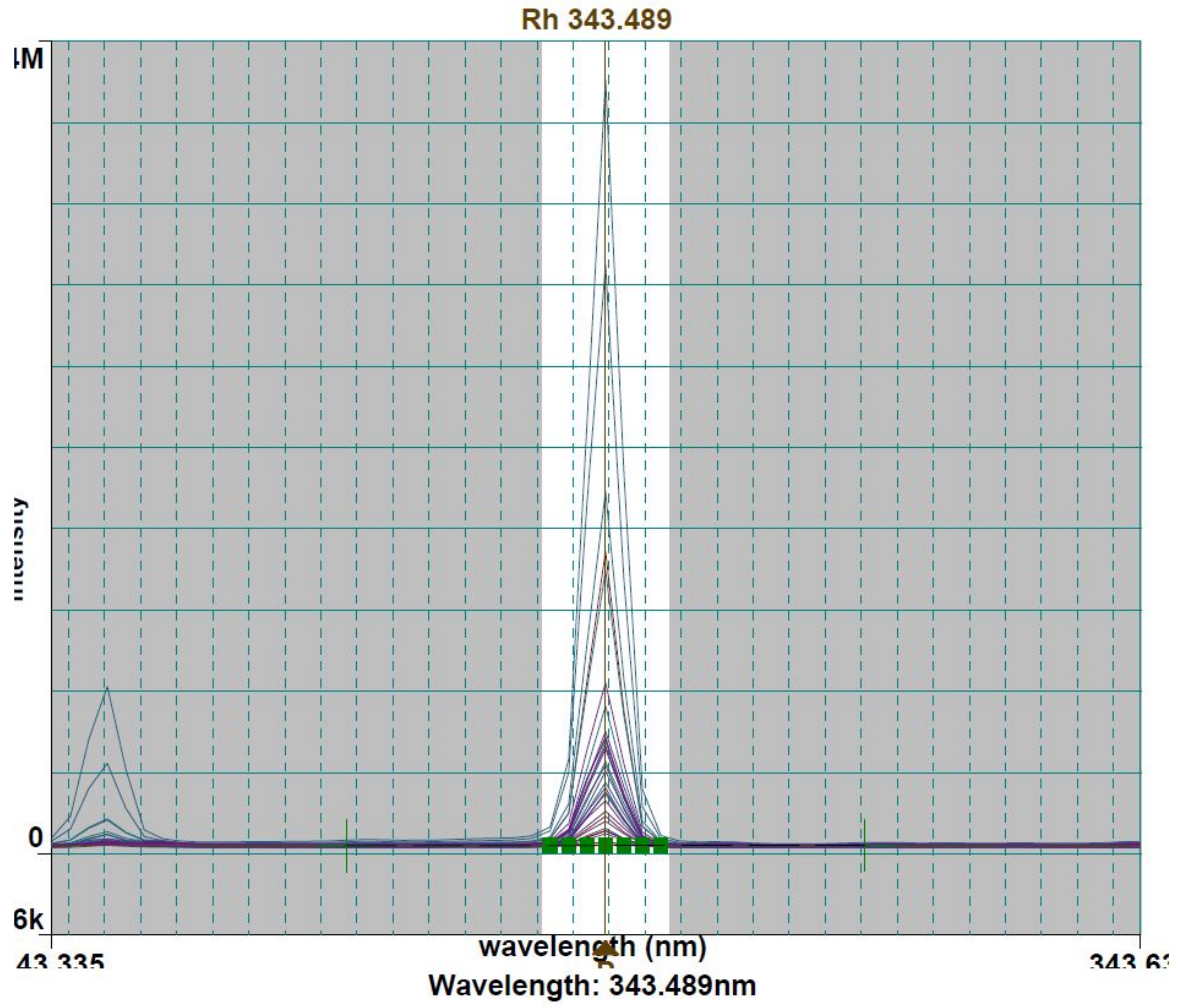


Figure 9: ICP results for H_2SO_4 , HNO_3 , and HCl at 12M, 8M, 5M, and 1M.