Hydrogen Detection using Platinum Nanoparticles

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Introduction: Significance of Hydrogen Sensors

Finding new ways to detect Hydrogen is vital for the future of clean energy and the further development of chemical and clinical Hydrogen sensors. Hydrogen is a valuable clean energy source because it produces no waste and can easily be reused. While Hydrogen is the most abundant element in our solar system, it is rare in it's elemental form because it makes bonds easily with other molecules. Being able to detect Hydrogen producing sources is an important step in finding new ways to utilize the amazing energy capabilities of Hydrogen gas. While Palladium and Platinum are known to absorb Hydrogen and are often utilized in electrical sensors, Hydrogen remains difficult to detect without electrical systems because theses metals do not change in appearance or pH. Electrical Hydrogen detecting systems pose a risk because Hydrogen is a highly flammable gas that can combust in the presence of sparks. The developments of sensors that do not require electricity increases both the safety of Hydrogen sensors and the usage of Hydrogen sensors to detect new sources of Hydrogen from biological agents such as algae and bacteria. The goal of this project was to discover which oxidizing agents can best be used with platinum nanoparticles to absorb Hydrogen and release it as Hydrogen ions and produce visible results. After determining the viability of different agents, the next goal was to discover how they could be manipulated to create the most visible reaction in order to function as a optical sensor. The eight agents chosen for experimentation were selected based on their chemical structure and strong oxidizing capabilities. It was predicted that these agents would be most likely to detect Hydrogen because they are strong oxidizers that were likely to oxidize the Hydrogen ions absorbed by the platinum nanoparticles and react with them visibly. After experimenting to determining viable agents, it was later hypothesized that acidic forms of Potassium Ferricyanide would produce the best results.

Materials and Methods: Experimental Design and Process

The question of which oxidizing agents would be best used with platinum nanoparticles to detect the presence of Hydrogen required much experimentation and revision based on the knowledge gained from each test. Each successive test had the purpose of narrowing down results to find the most successful oxidizing agent in optimal conditions that would show visible change in reaction to Hydrogen gas. In the preliminary test, eight oxidizing agents were chosen: Potassium Ferricyanide, Potassium Ferrocyanide, Ammonium Persulfate, Ammonium Dichromate, Ammonium Nitrate, Potassium Permanganate, Potassium Dichromate, and Potassium Chlorate. They were chosen for testing based on their chemical structure and known oxidizing characteristics. The molar solution concentration of these agents were then calculated using their molar weight to determine how many grams would be needed for 0.02 liters. Solution of 20 ml were created for each agent and divided evenly into two test tubes. To absorb Hydrogen, platinum is commonly used, however it does not show visible signs of detection and is often used in electrical Hydrogen sensors. Ten microliters of platinum nanoparticles were added to each test tube in the prediction that the oxidizing agents would pull the Hydrogen ions away from the platinum nanoparticles after they absorbed it and react visibly in color. Hydrogen gas was bubbled for ten seconds into the eight test tubes containing each oxidizing agent. The remaining test tubes did not receive Hydrogen and served as the control group. The results were not immediate and had to be observed after a period of about 12-24 hours. At this stage, it became apparent that Potassium Ferricyanide and Potassium Ferrocyanide had visibly changed by becoming faintly darker compared to their controls. The remaining oxidizing agents were not altered visibly compared to their controls and it was decided that Potassium Ferricyanide and Potassium Ferrocyanide would continue to be tested to see if the visibility of the reaction could be enhanced.

After narrowing the viable oxidizing agents down to Ferricyanide and Ferrocyanide, the next question to be tested was whether manipulating the pH of the solutions could enhance the detection of Hydrogen. To test this, new molar solution concentrations were calculated for 0.05 liters at a concentration of 0.05 molar to increase the amount of solution available for experimentation compared to the preliminary experiment. Potassium Ferricyanide and Potassium Ferrocyanide were each separated into two beakers, one beaker to create a basic solution and one to create and acidic solution. The pH of the solutions was manipulated by using a pH probe and NaOH and HCl to artificially change the pH of the solutions. Each solution was placed on a magnetic mixer to ensure that the probe could measure the pH of the solutions accurately. To create acidic solutions of Ferricyanide and Ferrocyanide, HCL was gradually added until the pH of the solutions were no less than 4. Similarly, basic solutions were created by adding NaOH until the pH of the solutions were no more than 9. At this stage, it was discovered that the pH of these oxidizers was very difficult to stabilize at a specific value and prefered to be either very acidic or very basic. It was noted for future testing that a buffer might be used to better manipulate pH values. After manipulating the pH of Potassium Ferricyanide and Potassium

Ferrocyanide, there was one extremely acidic and one extremely basic form of both Potassium Ferricyanide and Potassium Ferrocyanide. Ten milliliters of each solution were placed in labeled test tubes, with half being the control group tubes that would not receive Hydrogen. Ten microliters of platinum nanoparticles were added to each test tube, including the control group tubes. Hydrogen was bubbled into each of the experimental test tubes for ten seconds and observations were made after 12-24 hours.

At this stage, observations suggested that basic forms of both Potassium Ferricyanide and Potassium Ferrocyanide were not viable for visibly detecting Hydrogen because there was no difference between the their experimental and control groups. From observations, it was determined that the acidic solution of Potassium Ferricyanide were most effective in the detection of Hydrogen by changing in color to a dark greenish brown. Acidic Ferrocyanide was less effective and did not show an obvious change in color compared to the control group. This helped in narrowing the processes of experimentation further, allowing Ferricyanide to be isolated as the most viable oxidizing agent for the detection of Hydrogen using platinum nanoparticles and continuation in the experimental process.

After obtaining results from the previous test, further testing on potassium Ferricyanide was performed. The new testable question became: Do more acidic or basic levels of Ferricyanide best detect the presence of Hydrogen using platinum nanoparticles? In addition, after discovering the instability of the pH of Ferricyanide in previous testing, a buffer was needed to better control the pH of each solution. In this third test, the addition of the TRIS buffer allowed pH’s from 5-9 to be created in Ferricyanide solutions by neutralizing small amounts of added acids and bases in order to stabilize the pH level of the solution. Five beakers with 0.80

grams of Potassium Ferricyanide, 5 ml of TRIS, and 45 ml water were created and labeled 5-9. The pH probe was used to monitor the pH of each solution as either NaOH and HCl were added. The TRIS buffer was successful in stabilizing the changing pH of the solutions, allowing the solutions to come within 0.5 units of the target pHs.

After manipulating the pH of the solutions 5-9, ten experimental test tubes were filled with each pH so that there were two of each pH, one for the control group and one for the experimental group. The pH number and group type were labeled and ten microliters of platinum nanoparticles were added into each test tube and thoroughly mixed. Hydrogen was bubbled into the experimental group and observations were recorded after 12-24 hours.

At this stage, the hypothesis that more acidic solutions of Potassium Ferricyanide would be effective in detecting Hydrogen was confirmed. The pH's of 5 and 6 with Hydrogen added turned dark greenish brown while the basic pH's of 7-9 did not change in color compared to the control groups. In order to determine the numerical significance of the color change, the absorbance units of the experimental group was measured at wavelengths from 400-700 at intervals of 20 and compared to the control group using a spectrometer. The peak wavelength that showed the most difference, found in the first test of pH 5, was used as the wavelength of testing for the remaining pH values. The differences in absorbance value between the solutions in the first group (G1: the original solutions made without adding platinum particles or Hydrogen) and the experimental(G3) and control groups(G2) were recorded and analysed.

Graphs and Statistical Analysis of Data

______Much of the date collected throughout the experimentation process was qualitative, being based on the color and appearance of the solutions. In all of the experiments, pH was an independent variable that was used to change the dependent variable of color. To ground the outcome of this experiment numerically, a spectrometer was used to measure the difference in color between Potassium Ferricyanide solutions at different pH levels without platinum or Hydrogen (G1), with platinum and no Hydrogen (G2) and with both platinum and Hydrogen added (G3). This method of data collection yielded quantitative results that supported the qualitative observations that had been made while also providing support for interesting conclusions.

For the first spectrometer test, (See Figure 1) Potassium Ferricyanide at a Ph of 5 with added platinum nanoparticles and Hydrogen (G3) was compared to the control group (G2) and the difference between the two was graphed. The pH of 5 G3 showed a peak absorbance level of 0.206 at a wavelength of 560 hertz. The graph shows that the absorbance capacity of the solution was about equal on either side of the peak, forming a parabola like trend. For example, both wavelengths of 540 and 580 had absorbance units of 0.198. The absorbance peak of 560 hertz also reveals that the pH5 G3 solution was absorbing more green yellow light, which was significant because the solution itself appeared brownish green and it had been predicted that the peak absorbance would occur in the blue and red wavelengths and that yellow and green wavelengths would not be absorbed. This prediction was the opposite to the results and encouraged an investigation into the wavelengths best absorbed by the color brown.

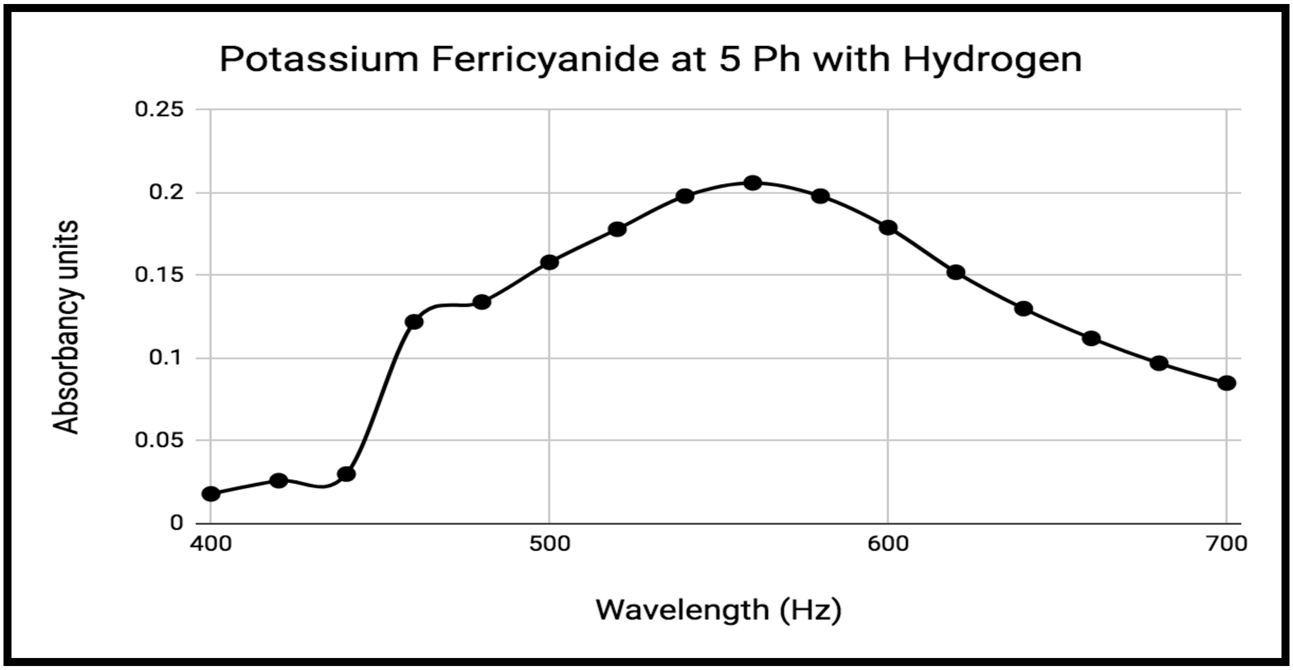


Figure 1

For the second spectrometer test shown in Figure 2, three separate groups were used. G1 represents the solutions of Potassium Ferricyanide without platinum nanoparticles or Hydrogen added. The solutions in G1 were used as base values and the bars on the graph below show the difference in absorbance compared to G1 for each pH value. The G2 group was the control group that had platinum nanoparticles but no Hydrogen. While all of the control groups looked the same visibly compared to each other and their respective G1 solutions, the graph shows that each pH has a difference in absorbance compared to the G1 groups (except G2 pH 7) . This may be due to the addition of platinum, found in the G2 solutions but not the G1 solutions, which could have had an effect on absorbance. Solutions of different pHs are also at different absorbance levels and it may be possible that the different pH's affected the absorbance of each solution. In addition, this graph supports the qualitative data that the acidic values of 5 and 6 changed the most in the presence of Hydrogen. The G2 values for pH's 5 and 6 eliminate the possibility that the platinum alone causes the dramatic color change since the G2 group received platinum but no Hydrogen. The G3 pH of 5 has an absorbance of 0.211 while the G3 pH of 6 has an absorbance of 0.203. This suggests that even more acidic forms of Ferricyanide might absorb more wavelengths of 560, causing it to become even darker.

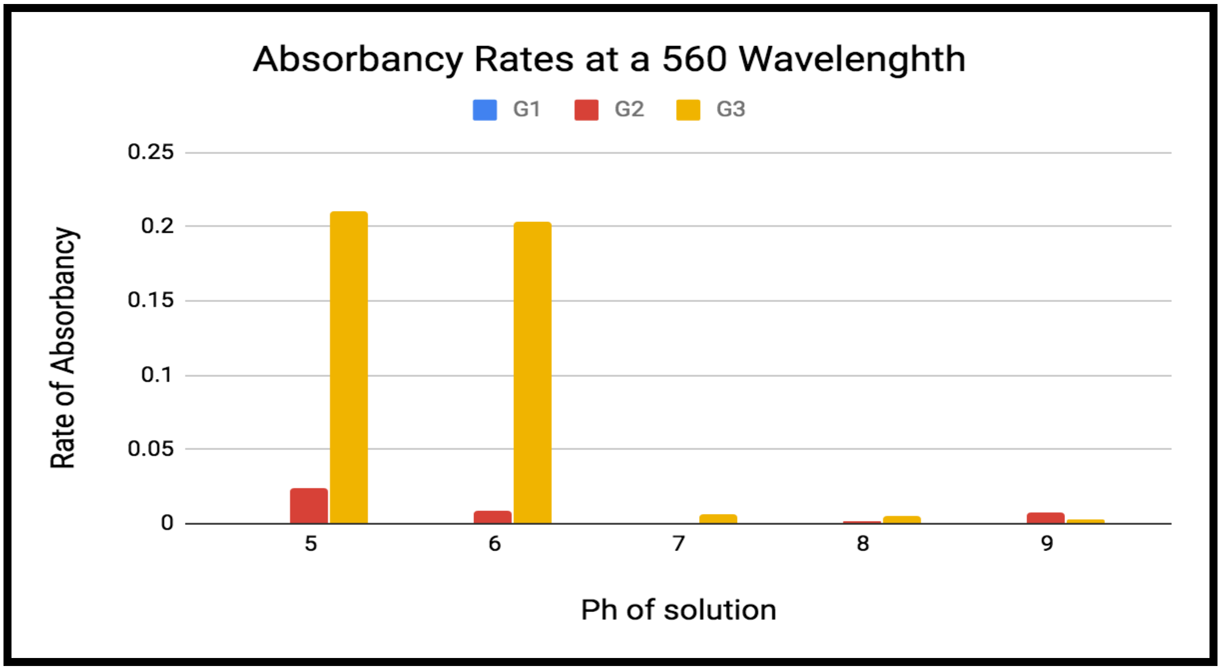


Figure 2

Statistically, the more acidic solutions of 5 and 6 had a higher absorbance value (Figure 2).The average of the acidic solutions is 0.207 absorbance units. This contrasts to the average absorbance units of the basic solutions, 8 and 9, at 0.004. This statistical analysis reveals how the acidic solutions of Potassium Ferricyanide, on average, have an absorbance value of 0.203 units more than basic solutions when exposed to Hydrogen. This further confirms that the qualitative color change observed in the acidic solutions is quantitatively significant and valid.

Discussion

The need for optical Hydrogen sensors is well known within scientific communities and many studies have been carried out to find effective ways in which Hydrogen can be detected. Currently, one of the most common methods of detecting Hydrogen is the use of palladium or platinum in electrical sensors that detect the absorbance of Hydrogen within the lattice of the metal (Wadell). This form of sensing poses a risk because electrical readout sensors can generate sparks and pose a risk in “explosive Hydrogen environments” (Wadell). Recently, sensors have been developed by Ngene et al. that "rely on the change in reflection or transmission of light from/through a metal film as a hydride". (Wadell) In this study, a Pd-capped yttrium film was used to create a sensor that produced a distinct color change due to hydride formation (Wadell). The results of this study were similar to my own in that the mode of detection was a distinct color change. However, my study made use of aqueous metal oxidizing agents, such as Potassium Ferricyanide, to detect Hydrogen rather than a metal film. In addition, palladium (Pd) nanoparticles were used to absorb Hydrogen in the study by Ngene, while platinum (Pt)nanoparticles were used within my experiment.

In one study “ Pd nanowires were nanofabricated on top of a Au film covered by a MgF2 spacer layer" (Wadell et al.). This design was structured to allow a near perfect absorption of a specific wavelength of light. As the palladium nanowires absorbed the Hydrogen, the wavelength could no longer be perfectly absorbed and more light was reflected from the surface. This study was able to measure "the reflection of the single wavelength where perfect absorption occurs", creating a sensor that could detect the presence of Hydrogen with high sensitivity (Wadell et al.). Similarly to my experiment, this study used simple visual changes in order to create an optical sensor. However, in contrast, this study did not make use of aqueous oxidizing agents and used palladium nanowires rather than the platinum nanoparticles to absorb Hydrogen. Interestingly, the addition of gold film found in this study has been shown to enhance Hydrogen sensors in many other studies and it has been found to work best at room temperature (Delft)

My study found that acidic levels of Potassium Ferricyanide were able to detect Hydrogen using platinum nanoparticles and produce a distinct color change. This study has similar results to many other studies focused on creating optical sensors by changing the wavelength of light absorbed such as in the two studies mentioned previously. However, my experiments on Potassium Ferricyanide raised many questions involving the manipulation of pH levels, a variable that was not mentioned within previous studies. In addition, none of the optical sensing methods researched used aqueous solutions of oxidizing agents or studied the uses of Potassium Ferricyanide as a Hydrogen sensor. My findings are unique because they revealed a relationship between pH and the ability of an oxidizing agent to detect Hydrogen using platinum nanoparticles. This relationship could be further tested on the other oxidizing agents to determine if they could also function as Hydrogen sensors in acidic environments. Some of the original oxidizing agents chosen for the experiment that did not show visible change may have been too basic and might show a reaction if they were artificially manipulated to be more acidic.

As in any experiment, possible sources of error must be recognized. Possible errors may have occurred if the TRIS buffer interfered with the results or if the addition of NaOH or HCl affected the results by chemically reacting with the Hydrogen or Potassium Ferricyanide. Various other acids and bases should be used to manipulate the pH of the solutions to ensure that the pH level itself is the main cause of detection rather than the specific acids or bases. This would also ensure that the alkaline nature of the solution is inhibiting the detection of Hydrogen rather than NaOH alone. In addition to possible error, the some of the data varied between repeated observations. In the first experiment, Potassium Ferricyanide only produced a slight color change in reaction to Hydrogen. The normal pH of Potassium Ferricyanide is slightly less than a pH of 7, so the Ferricyanide in the first experiment was just acidic enough to produce a slight reaction. By decreasing the pH further to 6 and 5, a more visible reaction resulted, accounting for the variation of data between repeated observations.

Some uncontrolled events that may have affected the data are also possible. The results may have been affected by the amount of time between observations, the exact number of drops of NaOH and HCl added to manipulate the pH of each solution, or the temperature of the environment. None of these factors were specifically controlled during the experiment and may have affected the results. If this experiment was repeated, I would account for the previously uncontrolled events by timing the reactions, determine the exact amount of drops needed to manipulate the pH of each solution, and controlling the temperature of the environment in which the experiment takes place in.

In future studies, it would be beneficial to experiment using different types of acids and bases to manipulate the pH. This would help confirm the results and provide further insights on the effect of pH. In addition, some studies have shown that the size of platinum or palladium nanoparticles can impact the results of Hydrogen sensors (Wadell). In future studies, the size of the platinum nanoparticles could be tested in an effort to speed up the reaction time of color change. Studies on the original eight oxidizing agents should be conducted to see if their natural pH inhibited their ability to react visibly to Hydrogen, but if more acidic or basic forms might act as Hydrogen sensors. Lastly, many studies on optical Hydrogen sensors make use of palladium as well as palladium and gold alloys to detect Hydrogen. Comparing the use of palladium nanoparticles to platinum nanoparticles with potassium Ferricyanide could also produce beneficial insights in the ultimate viability of Potassium Ferricyanide as a Hydrogen sensor. Once this is determined, it would be interesting to see if Potassium Ferricyanide could be incorporated into a film, or if it must be aqueous to create a reaction. Other questions remain, such as what level of Hydrogen is being detected, how much time it take to detect Hydrogen, and if higher pH levels can detect lower amounts of Hydrogen. One concern that has been brought to my attention through further research is the reaction between potassium ferricyanide and hydrochloric acid to produce Hydrogen cyanide gas. It should also be noted that potassium ferricyanide under extreme acidic conditions can evolve into Hydrogen cyanide gas as well. Under normal conditions, potassium ferricyanide is not toxic. These safety concerns were not known prior to experimentation, and in future experiments a fume hood should be utilized to minimize risks.

Conclusion

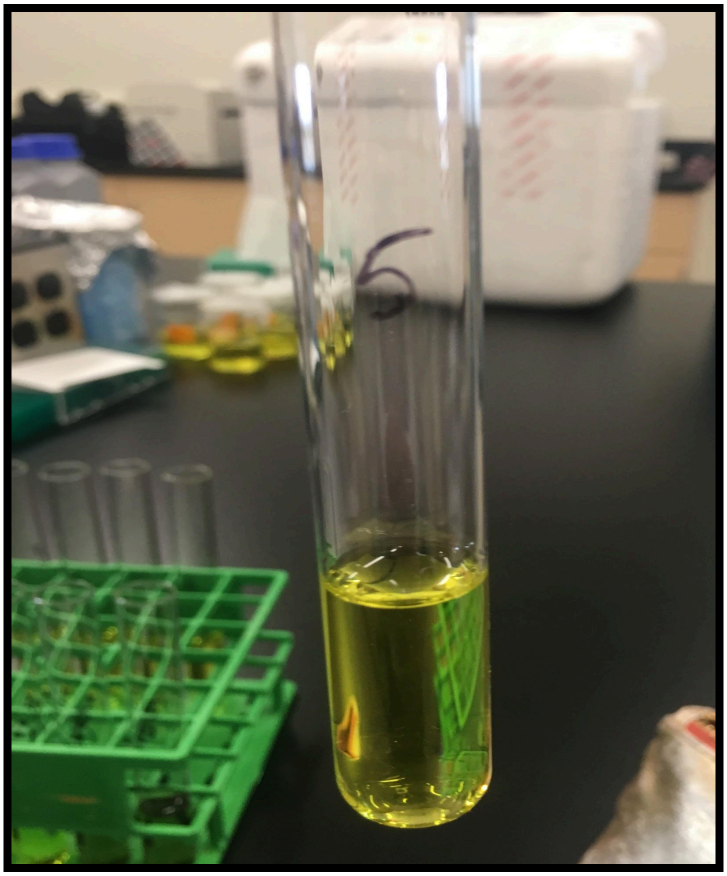
Hydrogen is a valuable, clean energy source that could one day replace fossil fuels. Hydrogen sensors are imperative in detecting sources of Hydrogen, both for industrial purposes as well as for finding novel sources of Hydrogen such as bacteria or algae. The experiments conducted in this study have lead to a discovery of acidic Potassium Ferricyanide as a optical Hydrogen sensor. As a optical Hydrogen sensor, Potassium Ferricyanide has the potential to replace dangerous electrical readout systems that can cause sparks in highly explosive Hydrogen environments.

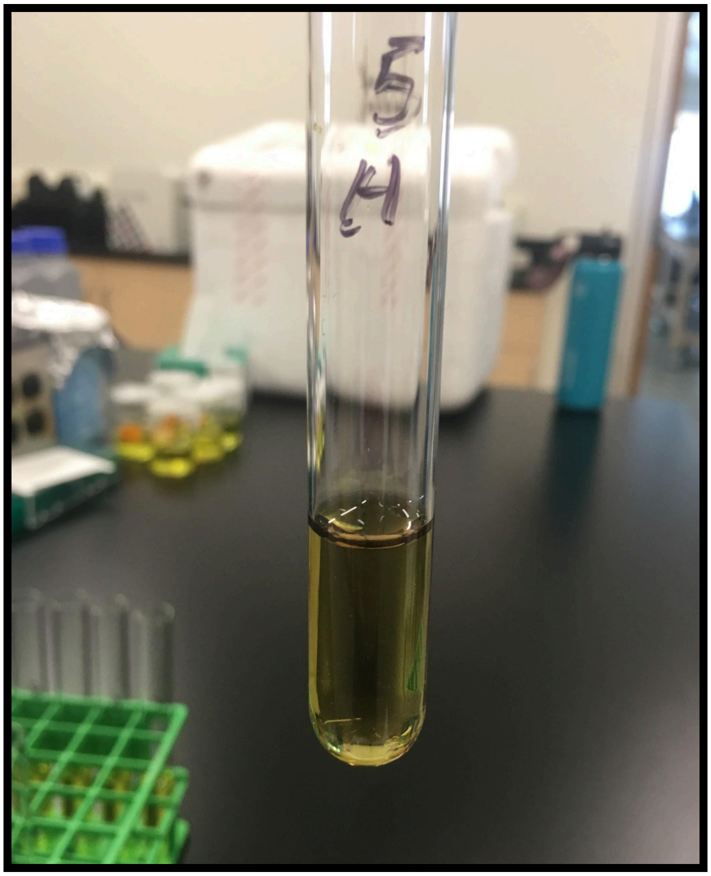
Out of eight original oxidizing agents chosen for experimentation, Potassium Ferricyanide and Potassium Ferrocyanide showed the most visible change in reaction to the addition of Hydrogen and platinum nanoparticles. Potassium Ferricyanide and Potassium Ferrocyanide were then manipulated into separate acidic and basic solutions in order to test the effect of pH in enhancing their ability to detect Hydrogen. It was found that acidic Potassium Ferricyanide was more effective in detecting Hydrogen than basic Potassium Ferricyanide or acidic or basic Potassium Ferrocyanide. After experimenting with different levels of pH in solutions of Potassium Ferricyanide, it was concluded that acidic solutions were most successful in detecting Hydrogen using platinum nanoparticles. On average, acidic solutions of Potassium Ferricyanide absorbed 0.203 more absorbance units than basic solutions of Potassium Ferricyanide.

In conclusion, this study has shown that acidic levels of Potassium Ferricyanide are effective in detecting Hydrogen using platinum nanoparticles. Future studies can be done to gain knowledge on the effect of pH on Hydrogen detecting agents as well as perfect the performance of Potassium Ferricyanide as a Hydrogen sensor. Thank you to all who contributed their time and knowledge to this project. This study could not have been done without the generous assistance and mentorship of Professor Mark Osterlund and the resources of Rocky Mountain College.

Appendix

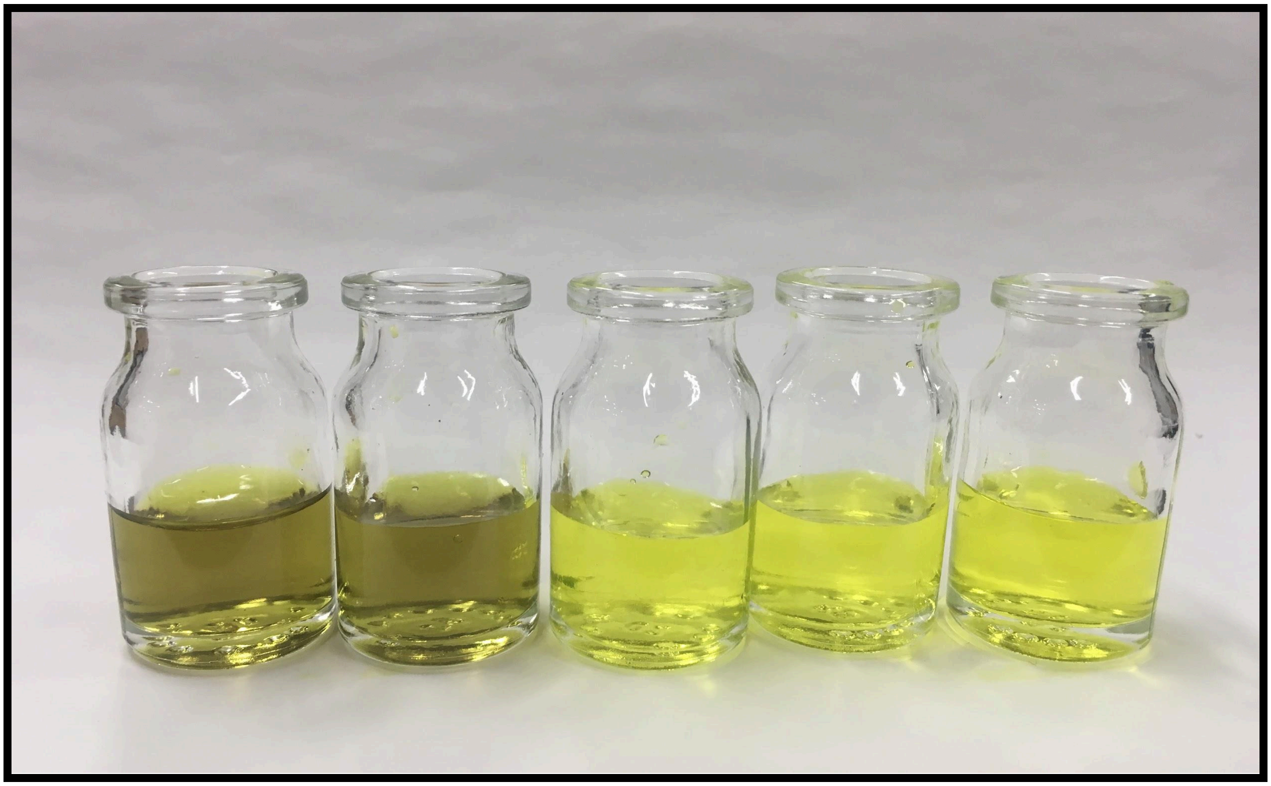
1. Below shows the result of Potassium Ferricyanide at a pH of 5. Left shows the control group of Potassium Ferricyanide (without Hydrogen) and the right shows the experimental group in which Hydrogen was added.





2. Below shows the results of manipulating the pH of Potassium Ferricyanide and adding platinum nanoparticles without adding Hydrogen (G2). In order of pH of 5 on far left to pH of 9 on far right.

3. Below shows the results of manipulating the pH of Potassium Ferricyanide, adding platinum nanoparticles, and adding Hydrogen (G3). In order of pH of 5 on far left to pH of 9 on far right.



4. Raw Data for Figure 1 on the absorbance units of Potassium Ferricyanide at a pH of 5.

   Note peak wavelength is 560 hertz

Wavelength (hz)	G3 Ph5 absorbance units
400	0.018
420	0.026
440	0.03
460	0.122
480	0.134
500	0.158
520	0.178
540	0.198
560	0.206
580	0.198
600	0.179
620	0.152
640	0.13
660	0.112
680	0.097
700	0.085

5. Raw data for Figure 2 showing the results of the second spectrometry test with each pH solution measured at the peak wavelength of 560 from the first spectrometry test (see Appendix #4). G1 is used as a base with G2 and G3 values representing the difference from G1.

pH of solution	G1 (absorbance units)	G2 (absorbance units)	(G3 absorbance units)
5	0	0.024	0.211
6	0	0.009	0.203
7	0	0	0.006
8	0	0.002	0.005
9	0	0.008	0.003

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