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Individual Reactions of Permanganate and Various Reductants

Student Report to the DOE ERULF Program for Work Conducted May to July 2000

Amber M Gauger
Richard T Hallen

September 2012

Pacific Northwest
NATIONAL LABORATORY

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Richland, Washington 99352

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PREFACE

Amber M. Gauger, as a chemistry student at Lewis Clark State College, participated in the DOE ERULF summer intern program at Pacific Northwest National Laboratory in the summer of 2000. Richard T. Hallen was the PNNL mentor for the research conducted as part of Amber's internship. This report is an account of the research conducted by Amber, and as reported to the DOE ERULF program on July 28, 2000 in partial fulfillment of the program requirements. Correspondences in regard to this report should be directed to richard.hallen@pnnl.gov.

ABSTRACT

Tank waste on the Hanford Site contains radioactive elements that need to be removed from solution prior to disposal. One effective way to do this is to precipitate the radioactive elements with manganese solids, produced by permanganate oxidation. When added to tank waste, the permanganate, Mn(VII), reacts quickly producing manganese (IV) dioxide precipitate. Because of the speed of the reaction it is difficult to tell what exactly is happening. Individual reactions using non-radioactive reductants found in the tanks were done to determine reaction kinetics, what permanganate was reduced to, and what oxidation products were formed. In this project sodium formate, sodium nitrite, glycolic acid, glycine, and sodium oxalate were studied using various concentrations of reductant in alkaline sodium hydroxide solutions. It was determined that formate reacted the quickest, followed by glycine and glycolic acid. Oxalate and nitrite did not appear to react with the permanganate solutions. The formate reactions quickly reduced permanganate, Mn(VII), to manganate, Mn(VI), and then to manganese (IV) dioxide. These reactions oxidized formate to carbonate and water. The glycolic acid was oxidized slower producing oxalate, water, and manganate, which would disproportionate to permanganate and manganese (IV) dioxide solids. The rate at which Mn(VI) disproportionates is usually slower than the rate at which Mn(VII) is reduced to Mn(VI), however in this case the rates were about equal. The glycine reactions formed some ammonia in solution, oxalate, and water. They reacted similar to the glycolic acid reactions, producing manganese dioxide precipitate before the solution turned totally green from Mn(VI). The formate reactions consumed one mole of hydroxide for every 3 moles of formate, while the glycolic acid and glycine reactions consumed 7 moles of hydroxide for every 3 moles of reductant. These reactions should help to determine the majority of products found in a mixture of these solutions.

INTRODUCTION

There are 177 underground storage tanks on the Hanford Site containing a variety of radioactive and chemical products. Some of these tanks contain waste that needs to be treated to remove Strontium (Sr) and the Transuranium (TRU) elements, before the liquid fraction (supernatant) can be disposed of as low-activity waste. One of easiest ways to do this is by the addition of a reagent that would react with these elements and precipitate them out.

Previous studies with Hanford waste examined the use of Strontium and Iron addition to precipitate out radioactive Sr and TRU elements, but the precipitates are difficult to filter. (SRTC, 2000). More recent studies suggest that permanganate treatment is a comparable alternative (Hallen; et al, 2000a,b) that produces precipitates more readily filtered than the Sr/Fe combination. However, when manganese is added to simulant tank waste, the reaction occurs quickly, and is difficult to characterize what is happening. The tank waste contains many different reducing chemicals that can account for the observed reaction when permanganate is added. Some of these include formate, glycolate, amine complexants (EDTA, HEDTA, etc.), oxalate, and nitrite. Controlled reactions combining these reductants with permanganate need to be performed to determine the rate at which each reacts, to what the permanganate is reduced to, and what products are created.

Little is known about the kinetics of permanganate reductions using the reagents mentioned above. The chemical potentials of manganese when reduced to its different oxidation states are what is known. When permanganate undergoes reduction by another compound, the different oxidation states are easy to identify by their distinct color differences. Permanganate, Mn(VII), solutions are characterized by a dark purple to almost black color. Manganate, Mn(VI), solutions are a dark green color, where hypomanganate, Mn(V), are a blue color. A dark brown or sometimes black precipitate characterizes manganese dioxide, the common form of Mn(IV).

Manganese (III), usually in the form of manganese hydroxide $Mn(OH)_3$, is a red solution, or a red-brown precipitate. Manganese(II), in the form of MnO, or $Mn(OH)_2$, is a blue solution, or a gelatinous white precipitate.

The pH of the solution largely determines what oxidation states permanganate will be reduced to. In alkaline conditions manganese (V), (III), and (II) are especially unstable and do not exist long, if at all. Therefore, the main reduction of manganese in alkaline solution occurs from permanganate, going to manganate, and manganate reacting with itself to form more permanganate and manganese (IV) dioxide. Eventually, all permanganate is converted to manganese dioxide, the dark brown precipitate. In acidic solutions the green manganate, Mn(VI), is unstable and quickly disproportionates to permanganate and manganese dioxide. Because most of the tank waste on site is alkaline, with a large amount of hydroxide, reactions need to be performed in a higher pH solution.

By using higher pH solutions Mn(VII), Mn(VI), Mn(IV), are the oxidation states mainly encountered. These solutions are easily scanned in the ultraviolet-visible, UV/Vis, spectrometer. Distinct peaks at 546 nanometers, and 526 nanometers characterize manganese (VII), or the purple permanganate color. Peaks at 606 and 439nm are characteristic of manganese (VI), which represent the green color in solution. When all permanganate and manganate have reacted and all the precipitate is settled to the bottom, the resulting UV/Vis spectrum shows the absence of all peaks. This is congruent with the loss of the color of the solution, turning it clear and colorless, which is also the result of excess reductant. When the reductant is the limiting reagent, the excess permanganate exists either as permanganate or as manganate. This depends on how much the pH of the solution changed throughout the reaction. If the pH is still above 12, it is likely that all manganese will exist as manganate, a green solution. But if enough of the hydroxide was consumed, and the pH is below 12, the manganese will exist as permanganate, changing the solution back to purple.

Using the spectral data, one can select the optimal wavelengths to study the different oxidation states of manganese. Given the absorbance of an analyte at a specific wavelength, one can determine the extinction coefficient of that analyte using Equation 1:

$$A = \in cl \qquad (1)$$

Where A is the absorbance at a particular wavelength, $\in$ is the extinction coefficient of that analyte at that concentration, c is the molar concentration of the analyte, and l is the path length, or the internal length of the cell the solution is analyzed in (Parikh, 1974). Extinction coefficients have been determined for solutions containing permanganate, and manganate ions (Stewart, 1965). These extinction coefficients make it easier to determine an absorbance value that comes close to the experimental value, given a known concentration and cell length. This allows for a ballpark figure of what an absorbance value is at a certain concentration. Given these extinction coefficients, one can calculate how much of one analyte, such as permanganate, is contained in a solution consisting of both permanganate and manganate.

The purpose of my research will be to analyze the kinetics of reactions between permanganate and various reductants. I will also calculate extinction coefficients, comparing them to literature values. I will also try to determine products of the various reactions, and determine the amount of products produced and reactants consumed.

METHODS AND MATERIALS

The first step to starting the reactions between permanganate and other reducing agents was to construct a calibration curve to determine the optimal wavelength at which to analyze the reaction. The target zone was to get the absorbencies between 0 and 1. I first made up solutions of potassium permanganate at various concentrations, from 0.00005 molar to 0.001 molar.

Using a scanning UV/Vis Spectrometer, the different concentrations of potassium permanganate were analyzed, first doing a full scan to find the λmax, or the wavelength at which permanganate absorbed the most light. From there I scanned all the other concentrations at that wavelength, and determined the optimal concentration of permanganate for samples in the UV/Vis spectrometer.

From here, the experiments began. My mentor advised me to use formate as a good reducing agent, followed by nitrite, glycolate, and glycine. He suggested glycine for use as a simple model compound for an amine complexant such as EDTA or HEDTA. I ran various experiments using these reductants, while varying the concentration of both the reductant and the permanganate. Table 1 shows all the different reactions performed, showing the concentrations of both the reductant and the permanganate. Some of the reactions were allowed to react, and then when finished reacting, samples were taken out from the reaction and diluted to a concentration of permanganate in the region of the calibration curve. Table 2 shows the dilutions used and the final concentrations of the dilutions that were analyzed in the UV/Vis. Some of the reactions were sampled while the reaction was taking place to determine at what time some of the peaks were maximized, so that this data would be used to calculate extinction coefficients.

Another area we wanted to analyze was how much of the hydroxide was being consumed in a give reaction. Using an Auto Titrator, some of the reaction solutions that contained an excess of the reductant, thus making the end solution clear were analyzed to see how much of the initial hydroxide was consumed. This could be calculated by taking a known concentration of the solvent, sodium hydroxide, and titrating a given volume to calculate how much hydroxide was actually contained in the sample. Then the reaction solutions could be tested to see how much hydroxide was left by seeing the difference in the amount of titrant used from the amount used in the known concentration. Also, by titrating solutions of possible products, and mixtures thereof, I can also establish what products might be contained in the reaction supernatants.

RESULTS

All the reactions except the nitrite reactions, Reactions #: 5, 6, and 7, appeared to react and form various colored solutions and precipitates. On reactions 1 through 14, I waited until a color change occurred, then I took a sample and ran it in the UV/Vis. On these experiments, I wanted to determine what was being formed, and if the end result changed after the initial reaction. Table 4 shows, for reactions 1 through 14, what was observed and if it changed after the first sample was taken.

In reactions 15 through 33, samples were taken of the reaction mixture at given time intervals while the reaction was taking place. These samples were then diluted and ran in the UV/Vis. From the data obtained one can see the appearance of the manganese(VI) peaks, with the disappearance of the manganese(VII) peaks, and then the reappearance later on. Figure 1 shows an example of one reaction where the permanganate peaks at 546nm, and 525nm decrease while the manganate peaks at 606nm, and 439nm increase, and then in Figure 2, the decrease of the manganate peaks and the increase in the permanganate peaks. These experiments allowed me to calculate extinction coefficients for manganese (VI) and manganese (VII) at their distinctive wavelengths. Using Equation 1, the extinction coefficient, $\in$, can be calculated. The Absorbance, A, used is equal to the maximum absorbance of the solution at a particular wavelength. The path length is 1cm, the inside diameter of the cell used in all of these experiments. Lastly, the concentration is the concentration of manganese in the dilution solution. Table 4 shows the extinction coefficients calculated. Stewart reports some of the extinction coefficients for Mn(VII), Mn(VI), and Mn(V), (See Table 5).

In some of my reactions, especially those using formate, the extinction coefficients of the manganese(VI) ions turned out to be pretty close to the literature values reported by Stewart. This means that at one point during the reaction all, or close to all of the permanganate was converted to manganate. However, this was not the case in the reactions using glycolic acid and glycine. Some of the reactions, Reactions 27-33, never totally turned green, and contained purple permanganate ions. Thus the extinction coefficients never even came close to the literature values. The extinction coefficients reported in Table 4, for the λ max.'s of 546 and 526, are not actually the maximum values for those wavelengths, but the values calculated for the same sample numbers as reported for the 606 and 439 peaks, where the green peaks are the maximum. It is assumed that this is when there is very little or no permanganate ions in solution, so then the signal is entirely made up of manganate ions. This helps us determine how much permanganate is in a given sample subtracting the signal given by the manganate ions. In Reaction 26, the extinction coefficients display what the values are when manganate is at a very low concentration. Reaction 26 with oxalate did not react, and so the UV/Vis spectrum of it showed that there were only permanganate ions in solution.

In reactions 34 thru 39, reactions were done so that the permanganate was completely reduced to manganese dioxide, a brown precipitate, and the supernatant of the solution was titrated to discern products of the reaction and the amount of hydroxide, the solvent that was consumed. In order to find what products were contained in the supernatant of these solutions, several titrations were done using various solutions of chemicals thought to be the products. Solutions of sodium hydroxide, sodium formate, sodium carbonate, sodium oxalate, glycolic acid, and glycine were titrated. And also various mixes of these solutions were titrated. Table 6 shows the endpoints of these titrations, and at what pH these endpoints occurred. Then these endpoints, especially at the pH values where they occurred are compared to the pH values of the endpoints of the titration of the reactions solutions. Table 7 shows the endpoints of the reaction solutions 34 thru 39, and at what pH the endpoints occurred. From the endpoints, at their respective pH's, the concentration of each of the suspected products of the reaction solutions can be determined, also calculating the amount of hydroxide consumed in the reaction. Table 8 displays the products of the reaction solutions and the concentration of the products, which were calculated using the Equation 2:

$$\left(\frac{\text{mL titrant used}}{\text{g Reaction sltn used}}\right)\left(\frac{\text{density of sltn (g)}}{\text{(mL)}}\right)\left(\frac{\text{M of titrant (mol)}}{\text{(L sltn)}}\right)\left(\frac{\text{mol product}}{\text{mol HCl}}\right)\left(\text{L sltn}\right) = \text{mol. product}$$

The end product is the molarity of the analyte in the solution, or the molarity of hydroxide left in solution. Table 8 also shows the amount of hydroxide consumed, the difference between the original concentration of hydroxide and the ending concentration of hydroxide.

DISCUSSION AND CONCLUSIONS

From experiments 1-14, it can be said that formate reacts the quickest with permanganate to form manganate, the green colored solution. Glycolic acid and glycine react a little slower but also react within an hour with permanganate. Nitrite doesn't appear to react with the permanganate, giving no precipitate, or at least over a reasonable amount of time. Oxalate, which was reacted with permanganate to see if it was stable, or if it reacted, did not react which confirmed beliefs that oxalate could be a product of the oxidation of glycolic acid and glycine. From experiments 15-33, the kinetics of the reactions between formate and permanganate can be determined. The original reduction of permanganate to manganate by formate happens quickly until there is little or no limiting reagent left. So, when manganate ions reach their maximum, the extinction coefficients calculated are closest to the literature values, Tables 4 and 5. Three manganate, Mn(VI), ions disproportionate, and overall produces two more Mn(VII) ions, and one manganese (IV) dioxide molecule. This process is displayed in more detail by the following equations:

$$Mn^{+6} + Mn^{+6} \Rightarrow Mn^{+7} + Mn^{+5} \qquad (2)$$

$$Mn^{+5} + Mn^{+6} \Rightarrow Mn^{+7} + Mn^{+4} \qquad (3)$$

From there the permanganate ions react further with formate if there is still reductant in solution to form more manganate. The reaction continues until all manganate is reduced to manganese dioxide or is converted back to permanganate in the case of excess permanganate to begin with. The reactions using glycolic acid and glycine show that the reaction speed of the oxidation of permanganate to manganate is just slightly more than, or equal to, the reaction of manganate with itself to form permanganate and manganese dioxide. This means that the green color never fully forms, and solids are being formed before the manganate can be fully formed from permanganate. Which explains why the extinction coefficients of these reactions are much lower than the ones where formate was the reductant. Experiments 34-39 showed us how much hydroxide was consumed, and how much of particular products were produced. This helps to establish balanced equations that help to predict future outcomes of reactions. For formate the reaction equation was found to be:

$$2MnO_4^- + 3HCO_2^- + OH^- \Rightarrow 2MnO_2 + 3CO_3^{2-} + 2H_20. \qquad (4)$$

For sodium glycolate (since basic solution) the reaction equation is:

$$2MnO_4^- + 3HO\text{-}CH_2\text{-}CO\text{-}O^- + 7OH^- \Rightarrow 2MnO_2 + 3^-O\text{-}CO\text{-}CO\text{-}O^- + 8H_2O. \qquad (5)$$

For glycine the equation is:

$$2MnO_4^- + 3NH_2\text{-}CH_2\text{-}CO\text{-}O^- + 7OH^- \Rightarrow 2MnO_2 + 3^-O\text{-}CO\text{-}CO\text{-}O^- + 5H_2O + 3NH_{3.} \qquad (6)$$

These equations correspond to the amount of hydroxide consumed in the reactions and also the amount of products created. All of the different isolated reactions show that when adding permanganate to tanks containing these reductants, formate would probably react first oxidizing permanganate to manganate, and then quickly reduced to manganese dioxide. I would guess that with an excess of permanganate, all formate would be oxidized to carbonate, and less of the glycolate and glycine would be oxidized unless there was enough excess permanganate. The tank would probably become less alkaline, given that hydroxide is consumed.

More studies should be done on other reductants that are present in tank waste. Combinations of the different reductants should be used also, to confirm which products react first, second, etc. Then these solutions should also be titrated to see what products exist and what concentrations of the original reagents are still present.

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APPENDICES

Table 1. Reaction conditions used for experiments.

Reaction #	Reductant	Conc. Reductant (M)	Conc. KMnO4 (M)	Solvent
1	Sodium Formate	0.004350767	0.00869235	NaOH
2	Sodium Formate	0.00833897	0.008330169	NaOH
3	Sodium Formate	0.00833897	0.008330169	Water
4	Sodium Formate	0.012008116	0.007996962	NaOH
5	Sodium Nitrite	0.004365469	0.00869235	NaOH
6	Sodium Nitrite	0.00836715	0.008330169	NaOH
7	Sodium Nitrite	0.004365469	0.00869235	Water
8	Sodium Formate	0.015395021	0.007689387	NaOH
9	Glycolic Acid	0.004407855	0.00869235	NaOH
10	Glycolic Acid	0.008448389	0.008330169	NaOH
11	Glycolic Acid	0.004407855	0.00869235	Water
12	Glycine	0.004355355	0.00869235	NaOH
13	Glycine	0.008347764	0.008330169	NaOH
14	Glycine	0.004355355	0.00869235	Water
15	Sodium Formate	0.025016909	0.049981013	NaOH
16	Sodium Formate	0.005003382	0.009994937	NaOH
17	Sodium Formate	0.002501691	0.004997468	NaOH
18	Sodium Formate	0.005003382	0.009994937	NaOH
19	Sodium Formate	0.004002705	0.007995949	NaOH
20	Sodium Formate	0.010006764	0.009994937	NaOH
21	Sodium Formate	0.005003382	0.004997468	NaOH
22	Sodium Formate	0.002001353	0.003997975	NaOH
23	Sodium Formate	0.001000676	0.000999494	NaOH
24	Sodium Formate	0.002001353	0.000999494	NaOH
25	Sodium Formate	0.005003382	0.000999494	NaOH
26	Sodium Oxalate	0.000499405	0.000999494	NaOH
27	Glycolic Acid	0.002534517	0.009994937	NaOH
28	Glycine	0.002504329	0.009994937	NaOH
29	Glycolic Acid	0.012672584	0.049974684	NaOH
30	Glycolic Acid	0.010138067	0.009994937	NaOH
31	Glycine	0.010017317	0.009994937	NaOH
32	Glycolic Acid	0.005069034	0.009949367	NaOH
33	Glycine	0.005008659	0.009994367	NaOH
34	Sodium Formate	0.045030437	0.029984807	NaOH
35	Sodium Formate	0.045030437	0.029984807	NaOH
36	Sodium Formate	0.045030437	0.029984807	NaOH
37	Sodium Formate	0.022515218	0.014992404	NaOH
38	Glycolic Acid	0.022810651	0.014992404	NaOH
39	Glycine	0.011269542	0.014992404	NaOH

Table 2. Dilutions of reactions and ending concentration of $KMnO_4$.

Reaction #	Dilutions	Conc. Of Dilutions (M)
1	0.3mLRxn:10mLNaOH	0.000253175
2	0.3mLRxn:10mLNaOH	0.000242626
3	0.3mLRxn:10mLH_2O	0.000242626
4	0.3mLRxn:10mLNaOH	0.000232921
5	0.3mLRxn:10mLNaOH	0.000253175
6	0.3mLRxn:10mLNaOH	0.000242626
7	0.3mLRxn:10mLH_2O	0.000253175
8	0.3mLRxn:10mLNaOH	0.000223963
9	0.3mLRxn:10mLNaOH	0.000253175
10	0.3mLRxn:10mLNaOH	0.000242626
11	0.3mLRxn:10mLH_2O	0.000253175
12	0.3mLRxn:10mLNaOH	0.000253175
13	0.3mLRxn:10mLNaOH	0.000242626
14	0.3mLRxn:10mLH_2O	0.000253175
15	0.3mLRxn:10mLNaOH	0.001455758
16	0.5mLRxn:10mLNaOH	0.000499747
17	0.3mLRxn:5mLNaOH	0.000282876
18	0.3mLRxn:10mLNaOH	0.000291115
19	0.3mLRxn:10mLNaOH	0.000232892
20	0.3mLRxn:10mLNaOH	0.000291115
21	0.32mLRxn:5mLNaOH	0.0003006
22	0.75mLRxn:5mLNaOH	0.000260737
23	1.5mLRxn:3.5mLNaOH	0.000299848
24	1.5mLRxn:3.5mLNaOH	0.000299848
25	1.5mLRxn:3.5mLNaOH	0.000299848
26	1.5mLRxn:3.5mLNaOH	0.000299848
27	0.15mLRxn:5mLNaOH	0.000291115
28	0.15mLRxn:5mLNaOH	0.000291115
29	0.03mLRxn:5mLNaOH	0.00029806
30	0.2mLRxn:5mLNaOH	0.000384421
31	0.2mLRxn:5mLNaOH	0.000384421
32	0.2mLRxn:5mLNaOH	0.000382668
33	0.2mLRxn:5mLNaOH	0.000384399
34	N/A	N/A
35	N/A	N/A
36	N/A	N/A
37	N/A	N/A
38	N/A	N/A
39	N/A	N/A

Table 3. Observations from reactions 1-14.

Reaction #	Observed Reaction:	Change Over Time? (Yes/No)	Changed to?
1	Solution turned green in about 5 minutes.	Yes	Solution turned back to purple over the course of 5 days.
2	Solution turned green in less than 2 minutes.	Yes	Precipitate (ppt.) formed, and solution returned to purple.
3	Solution turned dark red.	Yes	Solution formed a fine brown ppt., and solution turned back to purple.
4	Solution turned green in less than 2 minutes.	Yes	Ppt. Formed, and solution turns clear by next day.
5	No change in color.	No	N/A
6	No change in color.	No	N/A
7	No change in color.	No	N/A
8	Solution turned green in 1 minute.	Yes	Brown ppt. formed and solution turned clear in about six hours.
9	Solution turned green in 45 minutes with the formation of ppt.	Yes	Solution eventually turned a more dilute purple with brown ppt. (over 5 days)
10	Solution turned green in about 35 minutes with ppt. forming.	Yes	Solution turned clear and colorless, with brown ppt.
11	Solution turns a magenta color in 45 minutes, no ppt.	Yes	An orange solution, with fine brown ppt. making it hard to get a spectrum.
12	Turned a blue color, in 40 minutes, with ppt.	Yes	Turns back to purple but there is both brown ppt., and white looking crystals at the bottom.
13	Turned green in 30 minutes with brown ppt.	Yes	Turned clear, colorless with brown ppt., and some of the clear white crystals at the bottom.
14	No change in color over 45 minutes	Yes	Turned an orange brown color, really dark in about 5 days.

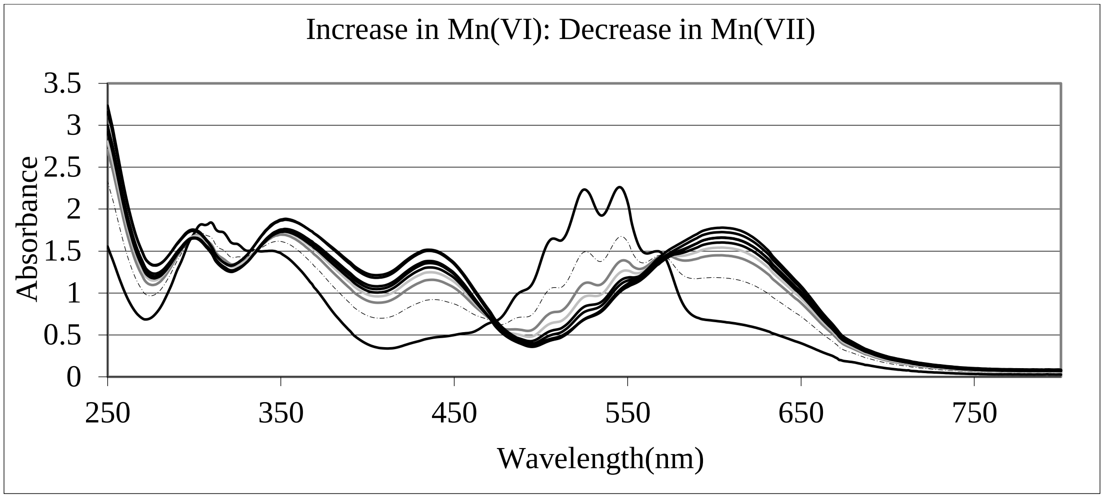

Figure 1. Increase of Manganese (VI) peaks at 606nm and 439nm. Decrease of Manganese (VII) peaks at 546nm and 526nm.

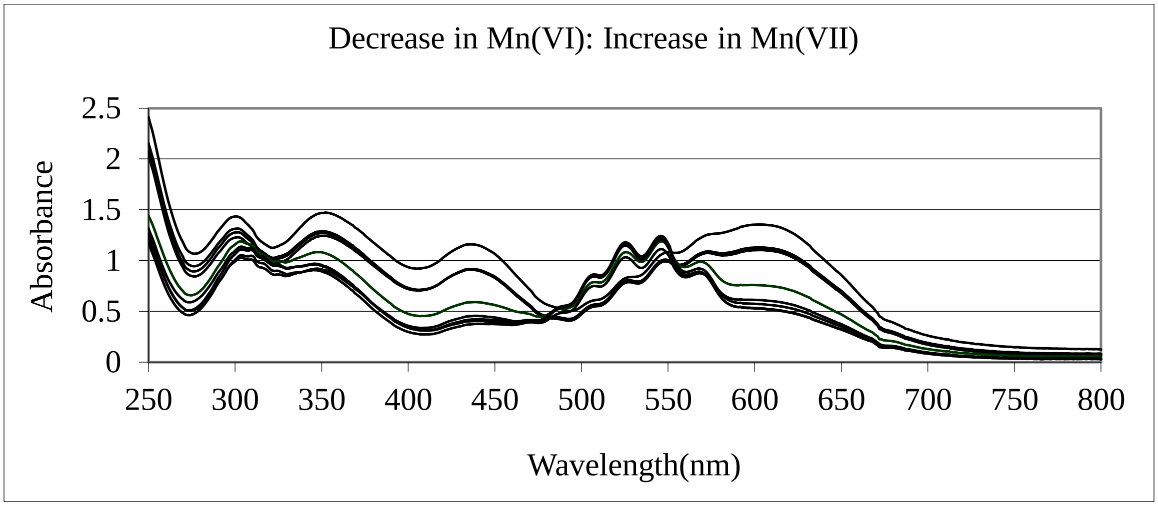

Figure 2. Increase in Manganese (VII) peaks at 546nm and 526nm after original oxidation of permanganate has taken place. Decrease in Manganese (VI) peaks at 606nm and 439nm.

Table 4. Extinction coefficients calculated for reactions 15-33.

Reaction 15		**Reaction 16**		**Reaction 17**		**Reaction 18**	
λ max	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**
606	1.681	606	1.661	606	1.471	606	1.729
546	2.815	546	1.020	546	0.884	546	1.077
526	2.629	526	0.697	526	0.609	526	0.742
439	1.475	439	1.373	439	1.296	439	1.431
Reaction 19		**Reaction 20**		**Reaction 21**		**Reaction 22**	
λ max	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**
606	1.686	606	1.948	606	1.652	606	1.570
546	1.388	546	1.058	546	0.873	546	0.791
526	1.072	526	0.693	526	0.541	526	0.478
439	1.345	439	1.817	439	1.367	439	1.324
Reaction 23		**Reaction 24**		**Reaction 25**		*****Reaction 26*****	
λ max	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**
606	1.698	606	1.566	606	1.569	606	0.256
546	0.887	546	0.783	546	0.758	546	2.345
526	0.548	526	0.472	526	0.438	526	2.407
439	1.427	439	1.325	439	1.263	439	0.121
***Reaction 27**		***Reaction 28**		***Reaction 29**		***Reaction 30**	
λ max	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**
606	1.151	606	1.233	606	0.947	606	1.398
546	1.260	546	1.268	546	1.367	546	1.200
526	1.073	526	1.078	526	1.245	526	1.012
439	1.065	439	1.103	439	0.819	439	1.392
***Reaction 31**		***Reaction 32**		***Reaction 33**			
λ max	**∈ x 10^3**	**λ max**	**∈ x 10^3**	**λ max**	**∈ x 10^3**		
606	1.519	606	1.375	606	1.431		
546	1.219	546	1.196	546	1.193		
526	1.042	526	0.989	526	0.991		
439	1.599	439	1.304	439	1.380		

* Reactions where Manganese (VI) did not reach the maximum concentration.

Table 5. Extinction coefficients reported in literature, (Stewart, 1965).

Manganese (VII)		**Manganese (VI)**		**Manganese (V)**	
λ max	**$\in$ x 10^3**	**λ max**	**$\in$ x 10^3**	**λ max**	**$\in$ x 10^3**
546	2.38	606	1.71	667	0.90
526	2.40	439	1.38	313	3.90
311	1.80	347	1.83		
		299	1.66		

Table 6. Endpoints of titrations for miscellaneous mixtures of products.

Titration Solutions	Mixture Ratio (g - g - g)		EP1	EP2	EP3	EP4	EP5	EP6
NaOH	5.0756	mL	2.259	2.412				
Sodium Hydroxide		pH	10.49	5.84				
$NaCO_2H$	5.0168	mL	None.					
Sodium Formate		pH	None.					
Na_2CO_3	5.0651	mL	2.486	4.909				
Sodium Carbonate		pH	8.14	3.85				
$Na_2(CO_2)_2$	5.0121	mL	2.4					
Sodium Oxalate		pH	2.81					
$NH_3CH_3CO_2H$	5.056	mL	None.					
Glycine		pH	None.					
$NaCO_2H$: NaOH	5.0255 - 5.0283	mL	2.244	2.371	4.754			
Formate: Hydroxide		pH	10.5	7	2.65			
Na_2CO_3: NaOH	5.0617 - 5.0360	mL	2.248	4.697	4.81	7.011	7.292	
Carbonate: Hydroxide		pH	11.38	8.74	8.16	5.46	3.54	
$Na_2(CO_2)_2$: NaOH	5.0363 - 5.0383	mL	2.237	2.381	4.791			
Oxalate: Hydroxide		pH	10.64	7.23	2.82			
$NH_3CH_3CO_2H$: NaOH	5.0017 - 10.0966	mL	2.139	4.775				
Glycine: Hydroxide		pH	11.24	5.48				
$HOCH_2CO_2H$: NaOH	5.0038 - 8.0566	mL	0.825	1.067	3.735			
Glycolic Acid: Hydroxide		pH	10.97	8.58	2.79			
$NaCO_2H$: Na_2CO_3	5.0146 - 5.0409	mL	2.506	4.852	7.236			
		pH	7.97	5	2.68			
$NaCO_2H$: Na_2CO_3: NaOH	5.0112 - 5.0260	mL	2.227	4.652	4.82	5.625	7.187	9.582
	-5.0138	pH	11.3	8.71	7.88	6.83	5.01	2.75
Na_2CO_3: $Na_2(CO_2)_2$: NaOH	2.5197 - 5.0730	mL	1.001	2.318	2.822	3.612	6.116	
	-2.4823	pH	11.28	8.32	6.63	5.3	2.77	

Table 7. Endpoints of Reaction # 34 - 39 supernatants.

Reaction #	Amount titrated (g)	Endpoints	EP1	EP2	EP3	EP4
34	4.9919	mL:	0.366	1.556	2.476	2.681
		pH:	11.19	8.09	5.72	3.84
35	5.0426	mL:	0.365	1.588	2.749	
		pH:	11.17	8.14	4.2	
36	5.0635	mL:	0.347	1.549	2.522	2.69
		pH:	11.32	8.35	5.79	4.44
37	5.0072	mL:	1.243	1.918	2.518	
		pH:	11.23	8.42	4.69	
38	5.0095	mL:	0.9	1.117	1.236	1.822
		pH:	11.11	8.72	6.3	3.02
39	5.0647	mL:	1.511	1.939	2.066	
		pH:	10.95	7.8	5.12	

Table 8. Amount of Hydroxide consumed in reactions 34-39, and suspected products and their respective concentrations.

Reaction #	Amount of OH consumed (mol)	Product #1	Conc. #1	Product #2	Conc. #2	Product #3	Conc. #3
34	0.000825799	CO_3^{2-}	0.047677	HCO_3^-	0.03686	HCO_3^-	0.045073
35	0.000829541	CO_3^{2-}	0.048507	HCO_3^-	0.046048		
36	0.000844956	CO_3^{2-}	0.047477	HCO_3^-	0.038432	HCO_3^-	0.045068
37	0.000571267	CO_3^{2-}	0.026961	HCO_3^-	0.023965		
38	0.000577312	NaOH	0.044595	NaOH	0.049346	Oxalate	0.023396
39	0.000596937	NH_3	0.00544	Oxalate	0.007981		

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)
www.pnl.gov