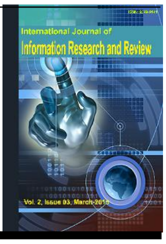
IJIRR

International Journal of Information Research and Review
Vol. 2, Issue, 03, pp. 473-479, March, 2015



Research Article

ULTRAVIOLET-VISIBLE SPECTROSCOPIC METHOD IN DETERMING REACTION RATE CONSTANT FOR THE REDUCTION OF CR (VI) TO CR (III) USING FERROUS SULPHATE ($FESO_4$)

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ARTICLE INFO

Article History:
Received 28th December, 2014
Received in revised form
20th January, 2015
Accepted 26th February, 2015
Published online 31st March, 2015

Keywords:

UV-Vis spectrometer,
HACH Method,
Lambda Series,
Reduction of Hexavalent to Trivalent Chromium,
Ferrous Sulphate ($FeSO_4$).

ABSTRACT

The kinetics of the reduction of hexavalent to trivalent chromium using ferrous sulphate ($FeSO_4$) under acidic condition was studied using two methods of UV-Visible spectroscopy – the HACH and the Lambda Series. Potassium dichromate ($K_2Cr_2O_7$) was used as source of Cr^{6+}. Due to complexity and time consuming steps of the Lambda Series, the HACH Method was employed as screen test. As soon as the trial gave good results from the HACH method, the Lambda series was performed. Comparison of the results was carried out and several differences were noted.

The study was composed of four parts – kinetics of the reduction of potassium dichromate by ferrous sulphate, determination of the rate and order of reaction, analysis of chromium hexavalent using the Diphenylcarbazide Method of HACH and Lambda Series UV-Vis spectrometer and determination of rate constant. There are several trials performed to arrive at the procedure for the reduction of hexavalent chromium via ferrous sulphate presented herein. Same is true with the rate and order of reaction.

At a ratio of 1:10 of potassium dichromate to ferrous sulphate, a good result for the rate and order of reaction was obtained. Results from the procedures showed that the overall rate of reaction is first order – that is zero order with respect to $K_2Cr_2O_7$ and first order with respect to $FeSO_4$. In the kinetic study, a ratio of 3:5 $K_2Cr_2O_7$ to $FeSO_4$ also showed good results in which the rate constant was computed to be 1.7×10^{-4} per second. However this result was only obtained from the HACH Method. Lambda Series showed different results in the computation of rate constant.

INTRODUCTION

One of the problems encountered by many industries utilizing chromium in their process is how to deal with their wastes containing huge concentration of aqueous hexavalent chromium. Companies such as those involved in power generation as wood preservatives in cooling towers, leather production, metallurgy and electronics in the Philippines turn to waste management service providers to handle and dispose of their wastes properly.

Converting hexavalent chromium to the trivalent form must be effective and fast so as to make it cost efficient. To do so, there are several methods that can be applied which are all proven effective, such as the use of:

- Ferrous sulphate under acidic condition;
- Sodium metabisulfite also under acidic condition; and
- Sodium sulphite at pH greater than 6.

There are several ways on how to observe the mechanism of reduction of chromium (VI) (Cr^{6+}) to chromium (III) (Cr^{3+}) via ferrous sulphate. One of which is via spectroscopic methods. Hexavalent chromium absorbs well at 540nm and thus possible to study using an Ultraviolet-visible (UV-Vis) spectrometer (*Diphenylcarbazide Method for Hexavalent Chromium,* 2011). The rate of which Cr^{6+} is converted into Cr^{3+} by Fe^{2+} at a given temperature is well established using the method. At a given time, the concentration of Cr^{6+} can be measured, and depending on the order of reaction, the rate constant can be determined. The study will center on the first option presented above in which the reaction will be carried out at pH 2.0. At this pH, optimum reduction of Cr^{6+} is observed in several studies. Knowing that Cr (VI) is highly toxic, the service provider's basic approach would be to convert it first to a less toxic form – Cr (III), prior to removal, stabilization and eventually re-use or disposal.

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Thus the study is significant in that:

- the rate at which Cr^{6+} is reduced to Cr^{3+} using Ferrous sulphate shall be fully appreciated and be able to apply in real situations;
- the use of more available and cheaper raw material will be maximized – Ferrous sulphate;
- the proper use, handling and disposal of Cr^{6+} will be carried out with ease; and
- reaction rates involving other reactants may also be determined using UV-Vis spectroscopy.

Review of Related Literature

Rate Law

Mathematically, the first goal of a kinetic study is to determine the effect of reactant concentrations to arrive at a rate law (Castellan, 1983). Rate law is given that:

Rate = $k[A]^x[B]^y$ ……………………………… (Equation 1)

where [A] and [B] are the molar concentrations of the reactants while their exponents are the experimentally determined order of reaction. The k is the reaction rate constant which quantifies the rate of chemical reactions. It is a function of temperature for specific reaction, but is completely independent of the concentrations of the reactants.

The Rate Constant

The rate constant is a function of temperature for a specific reaction, but it is completely independent of the concentrations of the reactants. Svante Arrhenius of Sweden relates the temperature dependence with the activation energy and the reaction rate at which the reaction proceeds:

$k = Ae^{-E_a/RT}$ ……………………….. (Equation 2)

where k = rate constant;
A = constant for any particular reaction;
E_a = activation energy;
R = gas constant (8.314 J / mol-K); and
T = temperature in Kelvin.

Taking the natural logarithm of equation 2 will give:

$\ln k = \ln A - E_a / RT$ …………………………..(Equation 3)

A plot of lnk versus 1/T is a straight line with the intercept lnA and a slope equal to $-E_a / RT$.

Plotting the natural logarithm of k versus the reciprocal absolute temperature to find the slope (rise / run) and from the slope, E_a can be calculated as:

$E_a = -R(\text{slope})$ …………………………. (Equation 4)

In Philippine setting, however, treatment of hexavalent chromium takes place under ambient conditions for economic and environmental reasons. Thus in doing this study it is important to take into consideration what is really happening in the actual situations so as to realize its importance at economic level.

Reduction of Hexavalent Chromium

Hexavalent chromium compounds are found to be carcinogenic by inhalation and corrosive to tissue. On the other hand, according to Viamajala S. et.al.(2000), the trivalent form is much less toxic and even essential to human glucidic metabolism, contributing to the glucose tolerance factor necessary for insulin-regulated metabolism (Viamajala *et al*., 2000). Despite the risk, hexavalent chromium is continuously being used in many applications due to lack of suitable substitute. M. Gheju *et al.* (2011) reported that hexavalent chromium can be removed from a solution using scrap iron in a continuous flow system under acidic conditions. Several interpretations of the data are taken at different orders of reaction. Using kinetic model it was found that the removal proceed in two stages, with Cr(VI) removal rates significantly decreasing with increasing elapsed experimental time (Gheju, 2011).

RS Karale, *et al.* (2007) showed from their experiments the reduction rate of Cr (VI) to Cr (III) using various doses of reducing agents – ferrous sulphate and sodium metabisulfite. For ferrous sulphate, it was seen that for a dose varying from 1800 to 2000ppm, the change in %reduction was rapid for the first 30 minutes and then it tapers towards the end. Same was observed for sodium metabisulfite corresponding to the dose of 280 to 340ppm. In case of ferrous sulphate, the reduction process is slow between 45 to 60 minutes. It was concluded in their experiment that the optimum reduction period using ferrous sulphate is 60 minutes and using sodium metabisulfite is 30 minutes (Karale *et al*., 2011). Beukes, *et al.* (1999) investigated the reduction of hexavalent chromium in unbuffered aqueous solution by sulphite as a function of pH, possible dosage and contact time required to reach equilibrium. It was observed that there is a strong dependence of the rate of reaction with the pH of the reaction mixture. The reaction rate decreased with an increase in pH from 2.0 to 5.0. Sulphate concentration which is as high as five (5) times the concentration of Cr (VI) is needed to complete reduction at the indicated pH range. The industrial relevance of the findings was checked using dust collected from a ferrochromium plant. The results clearly indicated that sulphite would be a suitable reductant for Cr (VI) in wastewater under specified conditions Beukes, *et al.* (1999).

MATERIALS AND METHODS

There are three steps involved in determining reaction rate constant. First, the procedure on how the reaction will take place must be established. As stated in the background it has been determined experimentally that the rate of reduction of Cr (VI) to Cr (III) via $FeSO_4$ is 0.11ppm/minute given that the pH is maintained at 2.00 and the concentration of Ferrous sulphate 400x greater than that of the Cr. Second, the overall order of reaction must be determined since the unit of the rate constant depends on it. Third, the concentration of the analyte must be determined in a defined time interval.

Ultraviolet-Visible Spectroscopy

The colorimetric method is useful for the determination of hexavalent chromium in natural or treated water in the range from 100 to 1000ppm. This range can be extended by appropriate sample dilution or concentration and/or use of longer cell path. In Philippine setting, the Department of Environment and Natural Resources – Environment Management Bureau (DENR-EMB) recognize diphenylcarbizide method via UV-Vis Spectrophotometer (Colorimetric Method) as the sole method in determination of hexavalent chromium as stated in its DENR-EMB Administrative Order 93 (DAO 93) (http://emb.gov.ph/laws/general%20environment/dao98-63.html 1998). There are two recognized approaches / systems in hexavalent chromium analysis using the Diphenylcarbazide Method. One is HACH Method which is recognized by United States Environmental Protection Agency (USEPA) and the other one is via Lambda Series UV-Vis Spectrometer. Both methods use UV-Vis Spectrometer and are accepted by Department of Environment Natural Resources – Environmental Management Bureau (DENR-EMB).

The HACH method (Method 8023, CHROMIUM, HEXAVALENT (0 to 0.60 mg/L Cr6+). For water and wastewater, Water Analysis Handbook 4th Edition, HACH) is a more simplified method of hexavalent chromium analysis. It utilizes a prepared pillows of 1, 5-diphenylcarbohydrazide (which is synonymous to 1, 5-Diphenylcarbazide) (http://www.chemblink.com/products/140-22-7.htm, ?) and the HACH UV-Vis Spectrometer. Due to its cheap cost, simplicity and rapid determination it will be used as screening test in all experimental trials then the results will be compared to that of the other method. The limit of detection of this method is 0.60ppm, thus based on the prior knowledge of the Cr^{6+}, the analyte may need dilution to reach the limit. The dilution factor shall be used after the reading is established. The Lambda Series Method (http://www.perkinelmer.com/pdfs/downloads/app_determinationofhexavalentchromium.pdf, ?) on the other one requires tedious sample preparations which may take 16 hours to finish the entire analysis thus making it a very expensive analytical method. With due consideration with cost and time, this method will only be used if HACH Method proves that the procedure presented above is feasible. Results from the two methods will be compared later. Furthermore, the additional steps in removal of interferences such as molybdenum, iron (+3) and copper were no longer carried out since this were only performed to wastewater with unknown compositions. The procedure below will employ de-ionized water and Analytical Grade reagents thus interferences are more likely absent. The limit of detection of this method is 1.00ppm, thus based on the prior knowledge of the Cr^{6+}, the analyte may need dilution to reach the limit. The dilution factor shall be used after the reading is established.

RESULTS AND DISCUSSION

The concentration of Cr^{6+} shall be in µmol/L. Thus the concentration obtained from the HACH Method which is expressed as mg/L shall still be converted into the required unit, using:

Table 1A. Kinetic Rate Constant of the Reduction of Hexavalent Chromium Using Ferrous Sulphate - HACH 1, 5-Diphenylcarbohydrazide Method

Time /sec	Trial 1	Trial 2	Trial 3	Ave	Ave. Con'c, µmol/L	$\ln[Cr^{6+}]$
	$[Cr^{6+}]$, ppm	$[Cr^{6+}]$, ppm	$[Cr^{6+}]$, ppm			
0	302.70	297.90	298.40	299.67	15.58	2.746170
600	297.00	293.60	294.70	295.10	15.35	2.730803
1200	238.30	236.10	238.70	252.70	13.14	2.575691
1800	232.80	231.90	232.10	232.27	12.07	2.491389
2400	203.20	198.60	204.10	201.97	10.50	2.351608

$$\mu mol/L = ppm x\ at.wt.\ Cr^{6+}\ x\ 1mol/1,000,000\mu mol x\ 1,000mg/1g$$

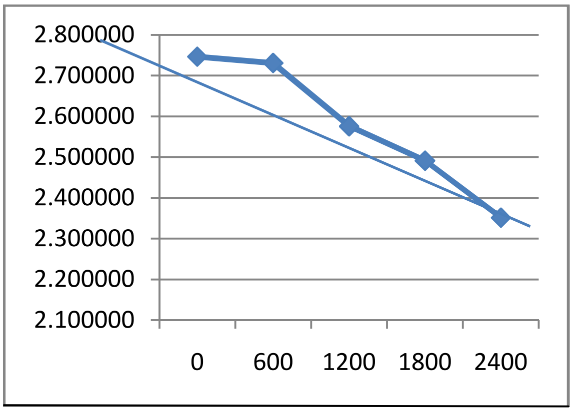

Figure 1. Plot of $\ln[Cr^{6+}]$ against the time in second

Computing the slope of the line using Excel program will give a slope value of -1.7×10^{-4}. However it should be noted that the reaction involves disappearance of Cr^{6+} (as evidence by downward line from the graph) thus the slope is equal to –k (https://www.mcla.edu/Undergraduate/uploads/.../1712.../Section_10.pdf, ?). Thus, k value is equal to 1.7×10^{-4}. Two points from the graph were out of the straight line but by using the Excel program it was able to correct the slope by removing the outliers from the system. The two outliers may have been attributed to the following factors:

- Since powder $FeSO_4$ was used, the reaction after 10 minutes may have not been complete yet as the reactant still needs time to dissolve and fully react with the other reactant; and
- It is noticeable that there is sharp decrease in concentration in the 40th minute thus misaligning the line from the rest which could be caused by sudden reaction of the two reactants.

Table 1B. Kinetic Rate Constant of the Reduction of Hexavalent Chromium Using Ferrous Sulphate – Lambda Series 1, 5-Diphenylcarbazide Method

Time / sec	Trial 1	Trial 2	Trial 3	Ave	Ave. Con'c., µmol/L	$\ln[Cr^{6+}]$
	$[Cr^{6+}]$, ppm	$[Cr^{6+}]$, ppm	$[Cr^{6+}]$, ppm			
0	18.9	61.05	63.40	47.78	2.58	0.91
600	ND	ND	ND	ND	NA	NA
1200	ND	ND	ND	ND	NA	NA
1800	ND	ND	ND	ND	NA	NA
2400	ND	ND	ND	ND	NA	NA

*ND – not detected, as shown by the negative values from the Lambda Series reading (see appendix 1)

As mentioned the HACH Method will become the screening test if whether or not the Lambda Series Method will be performed. The former method showed excellent results thus the latter was done. However, during the conduct of the analysis in which the step by step process was done carefully, results gathered were far different from the expected results. Take for example the value of Cr^{6+} concentration at time = 0, the expected value is 300ppm yet the average results showed only 63.40ppm. Further, the concentration at different time was no longer detectable by the method.

These observations may have been brought about by the following:

- Very limited time to run the entire experimental trial to see repeatability of results using the Lambda Series. While it was proven in several trials using the HACH Method, the Lambda series was just used once due to time consuming steps as well as very expensive cost of analysis. Corrections may have been done if time permits it use.
- In kinetic study, the faster method the better. Since kinetics is a function of time as what was shown in the graph, the method must be able to follow the time requirement. Due to several steps done in Lambda series, the hexavalent chromium may have been reduced fully prior to the analysis thus not detected by the instrument.

Table 2A. Determination of Rate of Reaction Using HACH 1,5-Diphenylcarbohydrazide Method

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 500ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}
1	46.72	17.32	14.76ppm / min
2	48.56	18.11	15.23ppm / min
3	47.73	17.12	15.31ppm / min
Ave	47.67	17.51	15.08ppm / min

Before these date were achieved, several trials transpired which produce inconclusive results using the HACH Method and thus no longer be subjected to Lambda Series. From the report of RS Karale et.al, it would take 45+/-15 min for the hexavalent chromium to be fully reduced by Ferrous sulphate into trivalent chromium at a ratio of 1:400 however, when this was performed in the laboratory, the effect is very fast and took only a matter few minutes to register a zero reading for Cr^{+6}. Thus several adjustments had been made until finally arriving at a ratio of 1:10. The starting concentration of hexavalent chromium used is 50ppm while for ferrous sulphate it is 500ppm at pH = 2.0. Three trials were performed to check accuracy. The concentration at time = 0 were averaged and the result is 47.67ppm which is 4.66% lower than the expected value. This may have been brought about by several transfers. It should be noted that the de-ionized water used in the preparation of the reagents have no significant impurities that may interfere with the reading.

Table 2B. Determination of Rate of Reaction Using Lambda Series 1, 5-Diphenylcarbazide Method

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 500ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}
1	46.40	15.60	15.40ppm/min
2	45.00	15.15	14.93ppm/min
3	45.30	15.15	15.08ppm/min
Ave	45.57	15.30	15.14ppm/min

In a matter of 2 minutes 63.27% hexavalent chromium were converted already into the less toxic trivalent counterpart. From the average of the determinations the change in concentration is 47.67 – 17.51 = 30.16mg/L (ppm) which happen in as short as two minutes therefore, the rate of reaction is 15.08ppm/min. The results obtained herein will be used as baseline for the determination of order of reaction involving HACH Method. Since good results are obtained using this method, the Lambda Series is worth trying. The results obtained between the two methods will be compared later.

Table 3A. Order of Reaction with respect to $K_2Cr_2O_7$ using HACH 1,5-Diphenylcarbohydrazide Method

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 500ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}	New Rate / Average Original Rate
1	98.70	63.38	17.66ppm / min	1.17
2	96.78	61.87	17.46ppm / min	1.16
3	98.12	64.01	17.06ppm / min	1.13
Ave	97.87	63.09	17.39ppm / min	1.15

Comparing the results obtained from the two methods, we can say that they are in unison. However, this method shows lower result than the former that may be attributed to the fact that there are more transfers – from digestion to filtration, that took place as well as more chemicals are used. The method is more prone to human error. When the concentration of potassium dichromate is doubled, it was found out that there is almost no change in the rate of reaction or rate of conversion of Cr^{6+} to Cr^{3+}. If we obtain the ratio between the original rate and the new rate (using similar method), the results obtained is almost 1 thus indicating that doubling the concentration of this reactant has no effect in the rate. From the results it could be concluded that the reaction is zero order with respect to $K_2Cr_2O_7$.

Table 3B.Order of Reaction with respect to $K_2Cr_2O_7$ using Lambda Series 1,5-Diphenylcarbazide Method

Trial	Original Con'c of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 500ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}	New Rate / Average Original Rate
1	107.88	89.00	9.44ppm/min	0.62
2	108.10	84.80	11.65ppm/min	0.77
3	107.72	85.80	10.96ppm/min	0.72
Ave	107.90	86.53	10.69ppm/min	0.71

Similar to the results obtained from the HACH Method, thus further confirms that the order of reaction with respect to $K_2Cr_2O_7$ is indeed zero. The ratio of the new rate vs the original rate is much lower as compared to the other method. There are noticeable differences however in the results obtained from the two methods. Using the average, HACH method deviates 2.13% from the expected concentration of 100ppm. The Lambda Series on the other hand reached 7.9% difference.

Table 4A. Order of Reaction with respect to $FeSO_4$ Using HACH 1,5-Diphenylcarbohydrazide Method

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 1,000ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}	New Rate / Average Original Rate
1	47.58	1.40	23.09ppm / min	1.53
2	46.71	1.36	22.68ppm / min	1.50
3	48.03	1.47	23.28ppm / min	1.54
Ave	47.44	1.41	23.02ppm/min	1.52

Under acidic condition (pH=2), the data shows that the reduction of Cr^{6+} using $FeSO_4$ is very fast. It only required 2 minutes to reduce 97.03% of Cr^{6+} using 1,000ppm of $FeSO_4$. Comparing to 63.27% reduction using 500ppm $FeSO_4$, it could be deduced that the rate reaction was almost doubled and thus the order of reaction with respect to $FeSO_4$ is one or first order. It is said that the overall order of reaction is simply the sum of the order of reaction of the reactants involved. Thus the overall order of reaction is 1 or first order and thus the reaction rate constant should have a unit of per second. The plot should be ln [Cr^{6+}] vs time in second.

Table 4B. Order of Reaction with respect to $FeSO_4$ Using Lambda Series 1,5-Diphenylcarbazide Method

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 1,000ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}	New Rate / Average Original Rate
1	105.39	43.53	30.93ppm/min	2.04
2	105.20	43.70	30.75ppm/min	2.03
3	105.13	43.49	30.82ppm/min	2.04
Ave	105.24	43.57	30.84ppm/min	2.04

The data shows a more pronounced first order reaction with respect to $FeSO_4$. The rate of reaction was clearly doubled when the concentration of $FeSO_4$ was doubled. It was noticeable that as compared to the results obtained from the order of reaction with respect to $K_2Cr_2O_7$, the deviation is lower at 5.24% from the expected concentration of 100ppm.

Conclusions and Recommendations

It has been proven in the experiment via two methods that reduction of hexavalent chromium via ferrous sulphate is a first order reaction overall. There is a noticeable difference between the results given by the two methods however the difference may be compensated by the end results. That is, as we double the concentration of potassium dichromate, there is no effect in the reaction thus zero order for this reactant. The results from the two methods – 1.15 for HACH and 0.71 for Lambda Series proves it. While as we double the concentration of ferrous sulphate the rate of reaction also doubles thus proving that the order of reaction with respect to this reactant is 1 or first order as HACH gave a ratio of 1.52 (rounded to 1 significant digit is equal to 2) and Lambda Series 2.04. While it is safe to say that the rate and order of reaction are true due to the results obtained from the two methods are in agreement with each other, the results obtained for the kinetic rate constant is inconclusive. As good results were obtained from HACH Method, results from Lambda Series provided otherwise. This observation may be due to the fact that the exponential reduction of hexavalent chromium may have been triggered by the heating process during the sample preparation. There might be a process or chemical that can inhibit the reduction while being analysed. If this will be done accordingly, then results that may be obtained could become similar or closer to the HACH value of 1.7 x 10^{-4}per second.

There are several points in which the experiment may be made more conclusive as soon as the following activities were carried out:

- The entire experiment is conducted under ambient conditions, room temperature at 25^0C while the de-ionized water's temperature range is between 24 to 28^0 C. It is said that the rate of reaction and thus the kinetic rate constant are temperature dependent parameters. This has not been incorporated in the study therefore it is a foremost recommendation that the reaction be carried out at different temperatures to determine its effect in the kinetics of reducing hexavalent to trivalent chromium using ferrous sulphate.
- The source of hexavalent chromium in many industries is rather sodium and potassium chromate, the study centers only on potassium dichromate – the more common reagent found in the laboratory. Hexavalent chromium from different sources may react differently with ferrous sulphate and thus a side by side study of the chemicals mentioned shall be considered to eliminate bias.
- Although in the first two parts of the experimental procedures, the results given by the two methods – HACH and Lambda Series, are in unison the latter part showed results with huge variance. As mentioned, to minimize time and expense, the HACH method was use as screen test before Lambda Series is performed. It may have been correct to say that hexavalent chromium is completely reduced prior to analysis due to several steps using Lambda series, but it is still important to know what additional steps must be taken into consideration to prevent this from happening. Due to time constraint, it was no longer included herein the trials that may prevent hexavalent chromium reduction while sample preparations are being done.
- In studying kinetics it is important that the method to be used is fast and accurate as it is a function of time. Finding a more suitable analytical method is highly recommended.
- Although the deionized water used in the experiment do not possess significant amount of impurities that may interfere with the hexavalent chromium determination and iron is known to be the least difficult interference (thus may not give significant effect on the analysis), it is still recommended that the additional steps in interference removal be performed so eliminate doubt in results.
- The ratio of reactants use in determining rate and order of reaction is 1:10 ($K_2Cr_2O_7$ to $FeSO_4$) while for the kinetic study it is 3:5. This ratio was just the result of trial and error experiments conducted. The results may have been different if different ratios are employed.

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Supplementary Materials

Appendix 1. Preliminary Trials Performed in Arriving at the Final Procedures Presented

Note: This serve as screen test / trial and error part and thus only HACH method was employed in hexavalent chromium analysis.

Determination of the order of the reaction

Reagents

a. Potassium dichromate stock solution (50ppm Cr (VI))
- Dissolve 141.345mg $K_2Cr_2O_7$ AR grade in de-ionized water then dilute 1.00 liter.

b. Ferrous sulphate solution (4,400ppm) – Karale et.al[5]
- Dissolve 4.40g $FeSO_4.7H_2O$ in de-ionized water then dilute to 1.00 liter.

c. Concentrated Sulfuric Acid

Order of Reaction of Cr (VI)

a. Pipet 25mL of stock solution in a 250mL volumetric flask then dilute to mark with de-ionized water (results to 5ppm Cr^{6+}). Mix vigorously. Determine the original concentration
b. Transfer solution to 1-L beaker and mix using magnetic stirrer. Acidify to pH 2 using sulphuric acid.
c. Add equal amount of ferrous sulphate solution then mix for 10 minutes before subjecting to hexavalent chromium analysis.
b. Do procedures 1a –c using 50mL stock solution (10ppm Cr^{6+}) instead.

Order of Reaction of Ferrous Sulfate

a. Perform procedure 1a – c.
b. Use 8,800ppm $FeSO_4$ solution for procedure 1d.

Results

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 500ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}
1	4.84	0.00	Not Determined
2	Did not proceed	Did not proceed	Did not proceed
3	Did not proceed	Did not proceed	Did not proceed
Average	NA	NA	NA

It was decided not to pursue trials 2 and 3 here because it was known when the full reduction of Cr^{6+} took place and so is the procedure for order of reaction for ferrous sulphate.

The length of time for the procedure was adjusted from 10 minutes to 5 minutes and 2 minutes but the results obtained are still zero. Therefore this procedure will not be useful in kinetic study.

The concentration of Cr^{6+} was changed to 50ppm but still the results showed 0.00 after reaction with ferrous sulphate at two different reaction time–after 5 minutes and after 2 minutes.

When the ferrous sulphate used was changed from solution to powder, some effects were observed as the following:

Reagents

a. Potassium dichromate stock solution (50ppm Cr (VI))
- Dissolve 141.345mg $K_2Cr_2O_7$ AR grade in de-ionized water then dilute 1.00 liter.

b. Ferrous sulphate, AR grade
c. Concentrated Sulfuric Acid

Order of Reaction of Cr (VI)

a. Transfer 250-mL Cr^{6+} solution to 400-mL beaker and mix using magnetic stirrer. Determine the original concentration. Acidify to pH 2 using sulphuric acid.
b. Add 1,100mg $FeSO_4$ powder then mix for 10 minutes.
c. Repeat procedures a and b using 100ppm Cr^{6+} instead

Order of Reaction of Ferrous Sulfate

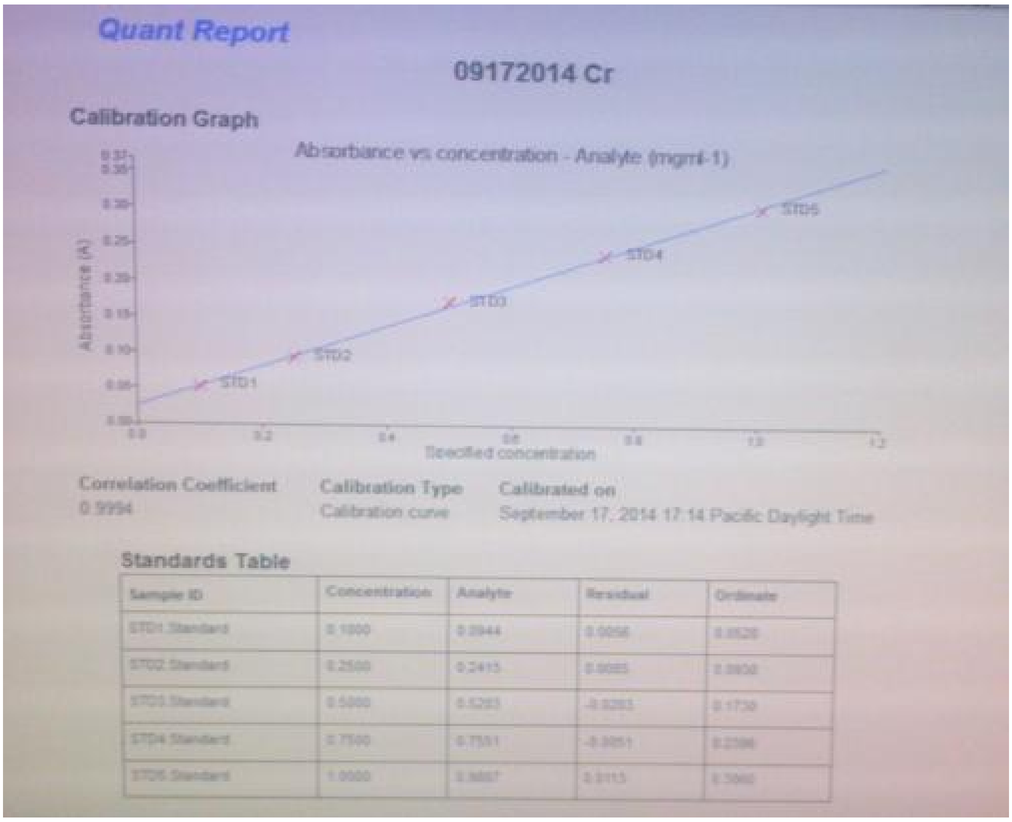
a. Perform procedure 1a – c.
b. Use 2,200ppm $FeSO_4$ solution for procedure 1d.

Results

Trial	Original Concentration of Cr^{6+}	Concentration of Cr^{+6} after 2-minute reaction with 500ppm $FeSO_4$	Rate of Reaction / Rate of Conversion of Cr^{6+} to Cr^{3+}
1	47.99	0.00	Not Determined
2	Did not proceed	Did not proceed	Did not proceed
3	Did not proceed	Did not proceed	Did not proceed
Average	NA	NA	NA

place and so is the procedure for order of reaction for ferrous sulphate. The length of time for the procedure was also adjusted from 10 minutes to 5 minutes and 2 minutes but the results obtained are still zero. Therefore this procedure will not be useful in kinetic study. The concentration of Ferrous sulphate was finally reduced to give a ratio of 1:10 $K_2Cr_2O_7$ to $FeSO_4$.

Appendix 2. Lambda Series Results



Quant Report

09172014 Cr

Calibration Graph

Correlation Coefficient
0.9994

Calibration Type
Calibration curve

Calibrated on
September 17, 2014 17:14 Pacific Daylight Time

Standards Table

Sample ID	Concentration	Analyte	Residual	Ordinate
STD1 Standard	0.1000	0.0944	0.0056	0.0528
STD2 Standard	0.2500	0.2415	0.0085	0.0938
STD3 Standard	0.5000	0.5283	-0.0283	0.1730
STD4 Standard	0.7500	0.7551	-0.0051	0.2398
STD5 Standard	1.0000	0.9887	0.0113	0.3060

Appendix 3. DAO 63 Series of 1998 List of Approved Methods of Analysis

Parameters and Methods for Water and Wastewater Analysis

PARAMETER	METHOD OF ANALYSIS
ARSENIC	Silver Diethyldithiocarbamate Method (Colorimetric)
BOD_5	Azide Modification (Dilution Technique)
BORON	Carmine Colorimetric Method
CADMIUM, TOTAL	Atomic Absorption Spectrophotometry Method (Wet ashing with concentrated HNO_3, + HCl)
CHEMICAL OXYGEN DEMAND	Open Reflux Dichromate Method
CHROMIUM (HEXAVALENT)	DiphenylCarbazide Colorimetric Method
COLIFORM, FECAL AND TOTAL	Multiple Tube Fermentation Technique Membrane, Filter Technique
COLOR	Visual Comparison Method (Platinum Cobalt Scale)
COPPER, DISSOLVED AND TOTAL	Atomic Absorption Spectrophotometric Method (Wet ashing with concentrated HNO_3 and CHl)
CYANIDE, FREE	Specific Ion Electrode Method
DISSOLVED OXYGEN	Azide Modification (Winkler Method), Membrane Electrode Method (DO Meter)
LEAD	Atomic Absorption Spectrophotometry (Wet ashing with concentrated HNO_3 and HCl)
NITRATE AS NITROGEN	Bruccine Method for Saline Waters, specific Ion Electrode Meter for Fresh Water
OIL AND GREASE	Gravimetric Method (Petroleum Ether Extraction)
ORGANOCHLORINE PESTICIDES	Gas Chromatography Method (Electrone Capture Detector)
ORGANOPHOSPHATE PESTICIDES	Gas Chromatographic Method (Flame Photometric Detector)
pH	Glass Electrode Method
PHENOLS	Chloroform Extraction Method
PHOSPHOROUS AS PHOSPHORUS	Stannous Chloride Method
POLYCHLORINATED BIPHENYLS (PCB)	Gas Chromatography (Electron Capture Detector)
SETTLEABLE SOLIDS	Imhoff Cone Method
SURFACTANT (Methylene Blue Active Substances)	Methylene Blue Colorimetric Method
TEMPERATURE	Use of Mercury-Filled Thermometer
TOTAL MERCURY	Cold Vapor Technique, (Mercury Analyzer or Flameless Atomic Absorption Spectrophotometer)
TOTAL SUSPENDED SOLIDS	Gravimetric Method

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