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Oxidizability of Common Halides and Applicable Masking Agents in the Dichromate Chemical Oxygen Demand Determination

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Abstract

This study was conducted for the purpose of evaluating the oxidizability of common halides and finding other complexing agents, which can effectively suppress chlorides, bromides and iodides and at the same time minimize the usage of mercuric sulfate. To compare the extent of oxidation of chloride, bromide and iodide, freshly prepared solutions of different concentrations were used in order to see the variations due to concentration. The following are the findings of the study: In the extents of oxidation,(1) chloride was 48.20% oxidized, (2) bromide was oxidized up to 99.40% and (3) iodide was unusual at 553.4% level of oxidation. But, the oxidizabilities of chloride is just about half of the current literature value of 0.226mg oxygen per mg of chloride indicating an overestimation of earlier studies. As far as the masking effectiveness of the complexing agents,(1) mercuric sulfate was effective in totally masking chloride at 760mg but ineffective in totally masking bromide; (2)aluminum sulfate was effective in totally masking chloride at approximately 1930mg but ineffective in totally masking the other halides;(3)ferric sulfate was ineffective in totally masking the three halides even at the maximum amount used of 2500mg;(4)mercuric-aluminum sulfate mixture was ineffective in totally masking the halides;(5)mercuric-ferric sulfate mixture was very effective in totally masking chloride at approximately 380mg but ineffective in totally masking bromide; and(6)aluminum-ferric sulfate was effective in totally masking chloride at approximately 2180mg but again ineffective in totally masking bromide.

Keywords: oxidizability, complexing agents, masking

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1. Introduction

In the industries, one of the most important parameters for assessing the pollution strength of wastewaters (Fah *et al.*, 2003 and EPA, 1995) and natural waters in terms of concentrations of chemically oxidizable substances in water is Chemical Oxygen Demand (COD). The most preferred method is the potassium dichromate because of its superior oxidizing ability for a large variety of samples. However, the test also oxidizes certain inorganic compounds, which may be present in the water samples, which will result, to erroneous COD values (Belkin *et al.*, 1992 and Ebuña *et al.*, 2005). In the study of Xianjuan, M. and Yang, G. , the addition of $AgNO_3$, Cr^{3+} and Al^{3+} were some masking agents added to eliminate chloride interferences in saline wastewater.

In the standard Chemical Oxygen Demand test, mercuric sulfate ($HgSO_4$) is added as a masking agent for minimizing the chloride interference. Other than having an undesirable effect on the environment, mercuric sulfate exhibit unsatisfactory result in minimizing bromide interferences. This study has been conducted for the purpose of evaluating the oxidizability of common halides and finding other complexing agents, which can effectively suppress chlorides and bromides and at the same time minimize the usage of mercuric sulfate. The masking effect of the standard mercuric sulfate was compared to other possible complexing agents on 2000ppm chloride solution with 500ppm glucose and 2000ppm bromide solution with 500ppm glucose. As we head into the 21st century, awareness and education will most assuredly continue to be the most important way to prevent water pollution and save mother earth.

2. Methodology

The study used the experimental type of research. An experimental approach is suitable to study the extent of oxidation of different concentrations of chlorides and bromides. It is also suitable to test the extent of masking of different complexing agents and their combinations at varying doses. To compare the extent of oxidation of chloride and bromide, freshly prepared solutions of different concentrations were used in order to see the variations due to concentration. These concentrations were expressed in molarity (moles/liter) namely: 0.1000 M, 0.0750 M, 0.0500 M and 0.0250 M. Every batch of samples includes one each of chloride and bromide of the same concentration and with its own reagent blank. The COD values were then computed and tabulated for comparison.

The masking effect of mercuric sulfate was tried using three kinds of solutions: one solution containing 2000ppm chloride and 500ppm glucose; another solution containing 2000ppm bromide and 500ppm glucose and another solution containing 2000ppm iodide and 500ppm glucose. A series of COD analyses were carried out for each solution using increasing amounts of mercuric sulfate added to the mixture prior to refluxing. The results were then compared with the expected value when no masking took effect. The same tests were done on the five other masking agents, namely, aluminum sulfate, ferric sulfate and the 50:50 mixture of mercuric sulfate and aluminum sulfate; mercuric sulfate and ferric sulfate and aluminum sulfate and ferric sulfate. Seven trials were carried out for the extent of oxidation and three trials for the extent of masking. Figures 1 and 2 show the schematic diagrams of the extent of oxidation of four different concentrations of chloride, bromide and iodide and the Dichromate Chemical Oxygen Demand (COD) Determination, respectively.

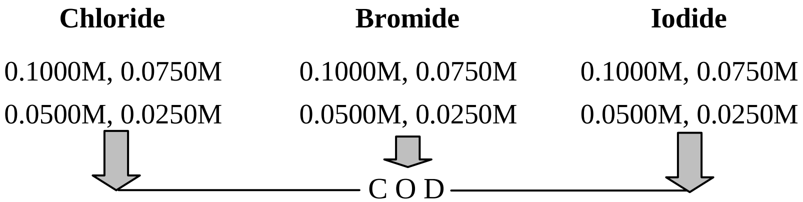

Figure 1. Oxidation of common halides of four different concentrations

3. Results and Discussion

The COD values were calculated through obtained experimental volume of standardized ferrous ammonium sulfate hexahydrate. Calculated concentrations of common halides were obtained from COD values by dividing the COD obtained in mg/L by 8000mg/mol. The actual concentrations were based on the actual preparation data for the solutions. Finally, the percentages of oxidation of halides were obtained by dividing the calculated concentration by the actual concentration (both in molarity) and multiplying by 100.

From the findings it can be inferred that (1) chloride ions even at elevated temperature and strongly acidic medium, are partly resistant to oxidation being oxidized to the extent of only about 50%, (2) bromide ions are relatively easier to oxidize completely into the free bromine, it is oxidized to an average of 99.4% and iodide is oxidized to an average of 553.4 %. The overall trend more or less coincides with the generally understood relative oxidizabilities of halides. However, the oxidizabilities of chloride is just about half of the current literature value of 0.226mg oxygen per mg of

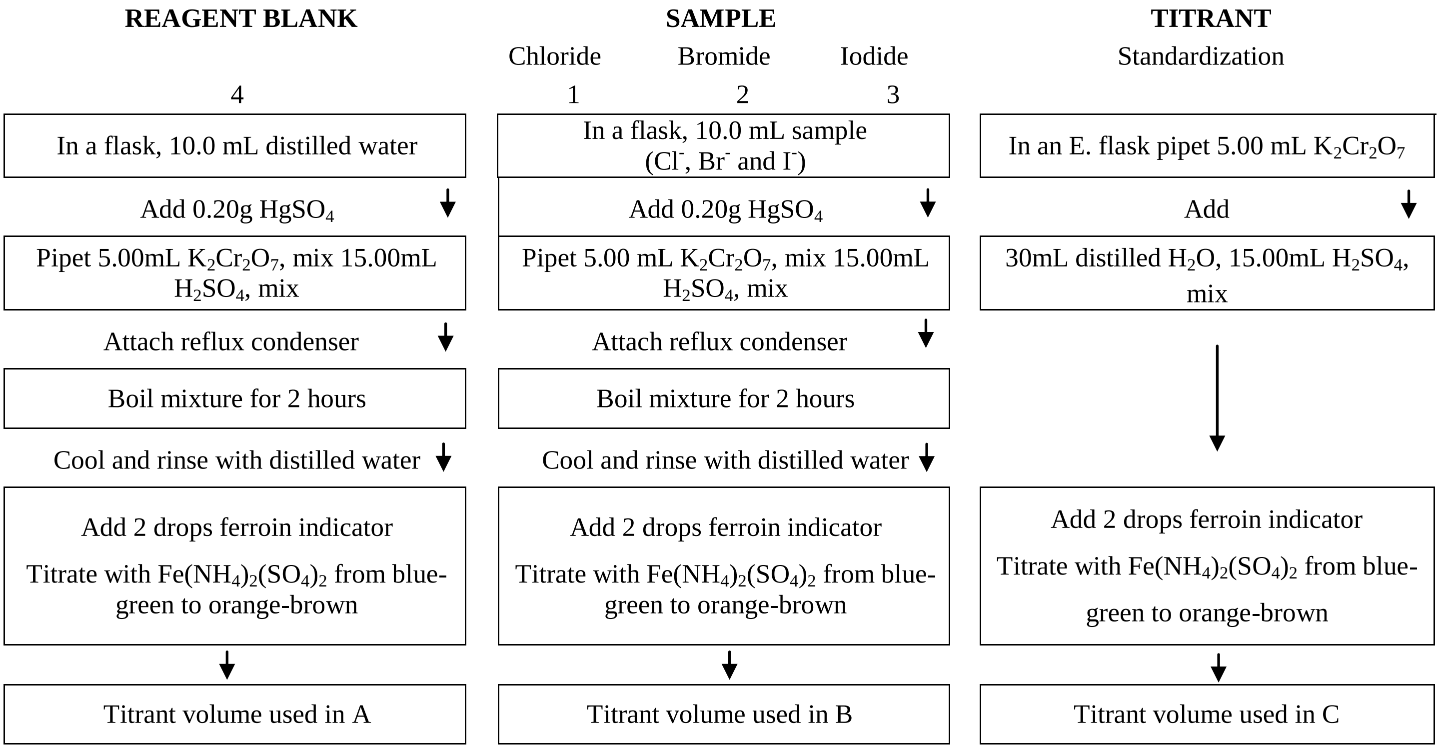

Figure 2. Schematic diagram of the dichromate COD determination

chloride, indicating an overestimation of earlier studies.

The outcome of the results can be explained by the oxidizing ability of halogens. Higher halogen in the group can oxidize the ions of the one lower to it. Chlorine has the ability to take electrons from both bromide and iodide ions. However bromine and iodine cannot get back the electrons from the chloride ions formed. This means that chlorine is the strongest oxidizing agent of the three halogens. Similarly, bromine is a stronger oxidizing agent than iodine. This also explains the decreasing oxidizing ability of halogen down the group. The trend in reactivities of the halogens as against a strong oxidizing agent dichromate can also be explained by comparing the standard reduction potentials for the reduction of halogens. The electrode potential of the reaction of the halogens with dichromate reflects the decreasing oxidizing strength of the element as against the dichromate.

In the masking effect of six complexing agents, Table 1 shows the summary of COD values for the 2000ppm chloride solution with 500ppm glucose with varying amounts of mercuric sulfate, aluminum sulfate, ferric sulfate, mercuric-aluminum sulfate, mercuric-ferric sulfate and aluminum-ferric sulfate in 2000ppm chloride with 500ppm glucose. As shown in Table 1 and through interpolation of data obtained, total masking of chloride interference occurred at the following concentrations: 760mg of mercuric sulfate, approximately 1930mg of aluminum sulfate, 380mg of mercuric-ferric sulfate mixture and 2180mg of aluminum-ferric sulfate mixture. The effectiveness of masking chloride interference by the six complexing agents depends on the stability of forming stable metallic complexes with the chloride.

Table 1. Summary of COD values for the 2000ppm chloride solution with 500ppm glucose with varying amounts of $HgSO_4$,$Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $HgSO_4$-$Al_2(SO_4)_3$, $HgSO_4$-$Al_2(SO_4)_3$, and $Al_2(SO_4)_3$-$Fe_2(SO_4)_3$.

Amount added in mg	COD value obtained in ppm					
	$HgSO_4$	$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	$HgSO_4$-$Al_2(SO_4)_3$	$HgSO_4$-$Fe_2(SO_4)_3$	$Al_2(SO_4)_3$-$Fe_2(SO_4)_3$
0.0	573	573	573	573	573	573
50.0	564	538	564	567	579	548
100.0	522	530	571	539	545	548
200.0	507	532	563	535	534	554
300.0	508	528	569	539	511	549
400.0	506	527	541	530	497	544
1000.0	496	508	522	516	494	520
1500.0	497	503	521	516	496	521
2500.0	494	496	510	507	497	490

Table 2 shows the summary of COD value obtained for the 2000ppm bromide solution with 500ppm glucose with varying amounts of mercuric sulfate, aluminum sulfate, ferric sulfate, mercuric-aluminum sulfate, mercuric-ferric sulfate and aluminum-ferric sulfate. Data shows that the six complexing agents were able to masked bromide to some extent but not effective in totally masking the bromide interference even to the maximum amount of complexing agents used in the study. COD values obtained were greater than the 500ppm COD value of glucose alone. The results on bromide interferences were also supported by the study of Belkin, *et al.* (1992), which states that bromide oxidation is more difficult to prevent than that of chloride.

Table 2. Summary of COD values for the 2000ppm bromide solution with 500ppm glucose with varying amounts of $HgSO_4$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $HgSO_4$-$Al_2(SO_4)_3$, $HgSO_4$-$Al_2(SO_4)_3$, and $Al_2(SO_4)_3$-$Fe_2(SO_4)_3$.

Amount added in mg	COD value obtained in ppm					
	$HgSO_4$	$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	$HgSO_4$-$Al_2(SO_4)_3$	$HgSO_4$-$Fe_2(SO_4)_3$	$Al_2(SO_4)_3$-$Fe_2(SO_4)_3$
0.0	750	750	750	750	750	750
50.0	662	665	674	683	667	672
100.0	643	655	663	679	647	658
200.0	639	643	667	691	650	668
300.0	636	644	649	701	648	662
400.0	641	646	649	662	623	651
1000.0	638	636	635	635	620	646
1500.0	619	631	638	631	607	642
2500.0	618	626	635	612	597	601

Table 3 shows the summary of COD value obtained for the 2000ppm iodide solution with 500ppm glucose with varying amounts of mercuric sulfate, aluminum sulfate, ferric sulfate, mercuric-aluminum sulfate, mercuric-ferric sulfate and aluminum-ferric sulfate in 2000ppm iodide with 500ppm glucose.

Table 3. Summary of COD values for the 2000ppm iodide solution with 500ppm glucose with varying amounts of $HgSO_4$,$Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $HgSO_4$-$Al_2(SO_4)_3$, $HgSO_4$-$Al_2(SO_4)_3$, and $Al_2(SO_4)_3$-$Fe_2(SO_4)_3$.

Amount added in mg	COD value obtained in ppm					
	$HgSO_4$	$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	$HgSO_4$-$Al_2(SO_4)_3$	$HgSO_4$-$Fe_2(SO_4)_3$	$Al_2(SO_4)_3$-$Fe_2(SO_4)_3$
0.0	1211	1211	1211	1211	1211	1211
50.0	1165	1087	1150	1215	1100	1196
100.0	1173	1087	1150	1215	1043	1188
200.0	1110	1051	1117	1207	1002	1023
300.0	1055	1036	1150	1158	1018	1040
400.0	1044	1024	1078	1108	998	1064
1000.0	1040	993	1070	1067	990	1061
1500.0	985	938	1070	1067	998	1030
2500.0	985	911	1008	1043	975	939

Comparison of COD values can also be shown graphically. Figure 3 shows the COD values obtained in nine varying amounts of mercuric sulfate on 2000ppm chloride solution with 500ppm glucose as against the COD values obtained on 2000ppm bromide solution with 500ppm glucose and 2000ppm iodide solution with 500ppm glucose.

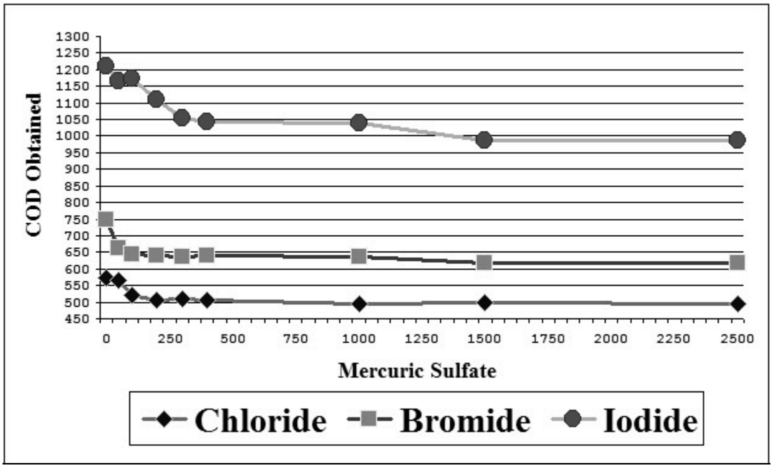

Figure 3. Graph of COD values with varying amounts of mercuric sulfate added.

To minimize the usage of mercuric sulfate, Figures 4 and 5 show the COD values obtained using aluminum sulfate and aluminum sulfate-ferric sulfate mixture as masking agent, respectively. These two complexing agents are just two of the five probable substitutes used in the study.

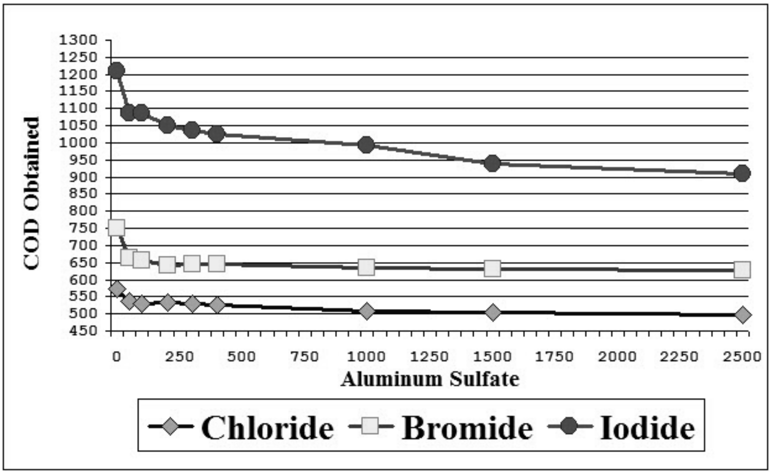

Figure 4. Graph of COD values with varying amounts of aluminum sulfate added.

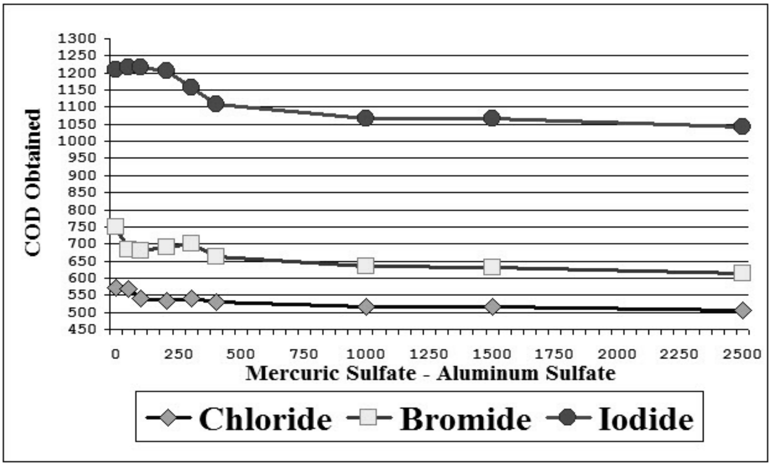

Figure 5. Graph of COD values with varying amounts of aluminum sulfate-ferric sulfate.

As far as the masking effectiveness of the complexing agents, (1) mercuric sulfate was effective in totally masking chloride at 760mg but ineffective in totally masking bromide; (2) aluminum sulfate was effective in totally masking chloride at approximately 1930mg but ineffective in totally masking bromide; (3) ferric sulfate was ineffective in totally masking the halides even at the maximum amount used of 2500mg; (4) mercuric aluminum sulfate mixture was ineffective in totally masking the halides; (5)

mercuric-ferric sulfate mixture was very effective in totally masking chloride at approximately 380mg but ineffective in totally masking bromide; and (6) aluminum-ferric sulfate was effective in totally masking chloride at approximately 2180mg but again ineffective in totally masking bromide.

Based on the stability constant values of metallic complexes, mercury (II) will form stable complexes with iodide than with bromide and chloride, while ferric ions will form stable complexes with chloride than with bromide; and aluminum (III) experimentally forms stable complexes with chloride. The COD values obtained on chloride and bromide solutions with glucose, even without masking were below the expected COD values based on their percent oxidizability. These were due to the fact that 150mg of silver sulfate was added per 10mL water sample. Silver ion will also form stable complexes with the interfering halides. The efficient masking effect of silver ion in chloride interferences is also shown in the study of Vaidya, *et al*. (1997) with the use of bismuth-based absorbents.

4. Conclusion and Recommendation

At elevated temperature and strongly acidic medium, chloride ions are partly resistant to oxidation, being oxidized to the extent of only about 50%. Bromide ions are relatively easier to oxidize completely into the free bromine, and iodide ions are most easily oxidizable to even five times more than is expected from complete oxidation to free iodine. The overall trend more or less agrees with the generally understood relative oxidizabilities of the three halides. However, the oxidizabilities of chloride is just about half of the current literature value of 0.226mg oxygen per mg of chloride, indicating an overestimation in earlier studies. On the other hand, the extremely high extent of oxidation of the iodide is most likely indicative that it is not just oxidized to free iodine but to one with a much higher oxidation state.

As far as the extent of masking the common halides, mercuric sulfate is effective in masking chloride but ineffective in masking bromide and iodide. Aluminum sulfate is effective by itself and a little better when combined with ferric sulfate but not with mercuric sulfate. Ferric sulfate is the least effective but becomes better when combined with other metallic salts. Mercuric sulfate-ferric sulfate mixture is effective in masking chloride as compared to the standard mercuric sulfate. Industrial and commercial establishments, which constantly use the standard dichromate method of

COD determination, should come to know that other halides can interfere in the COD analysis and that suitable masking agents may have to be employed not only for better masking affects but also for an environmentally friendly procedure. Aside from halides, interferences by ammonia can also affect COD values according to the study of Kim (1989).

5. Acknowledgement

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