"Available Chlorine" In Household Bleaches by Using a New and Easy Spectrophotometric Method

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Abstract: In this communication, an alternative method to determine the "available chlorine" in household bleach, based on the reaction of a known quantity of bleach with a standardized $CuSO_4.5H_2O$ aqueous solution is proposed. The alkaline media of the bleach can promote the formation of both hydroxyl cupric sulfate and cupric hydroxide, which form a solid mixture that can be separated by filtration. Since the $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex has a maximum of absorbance at 815 nm, the remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex in solution after the addition of the bleach can be obtained by spectrophotometric analysis. By using these measurements and the stoichiometry of the process, the "available chlorine" concentration in the household bleach can be easily estimated, in a fast and reliable fashion. The values obtained for different samples of commercial household bleaches by using this methodology were compared with those obtained with the standard sodium thiosulfate titration method. The differences between the values obtained, considering the titration method as the true value, were less than 2 %. Consequently, the spectrophotometric method presented in this communication offers the possibility of comparing the results with other well-established methods, and combines elegantly stoichiometry calculations and spectrophotometry measurements in one laboratory activity.

Introduction

Bleaches are used as household chemicals to whiten clothes and remove stains and as disinfectants, primarily in the bathroom and kitchen. Household bleach contains an oxidizing agent known as sodium hypochlorite, NaOCl (an alternative formula is NaClO), which is prepared by bubbling chlorine gas into a sodium hydroxide solution. When household bleach is produced, part of the chlorine gas is oxidized to the hypochlorite ion, $ClO^-_{(aq)}$, and some is reduced to the chloride ion, $Cl^-_{(aq)}$. The excess of the hydroxide keeps the resulting solution strongly basic [1]. An equation describing this process is given below:

$$Cl_{2(g)} + 2\,OH^-_{(aq)} \rightarrow ClO^-_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

The ability of bleach to serve as an oxidizing agent is reported in terms of "available chlorine". Chemically, this is incorrect because the true oxidizing agent in chlorine bleach is the $ClO^-_{(aq)}$ anion, not $Cl_{2(aq)}$. Since both, $ClO^-_{(aq)}$ and $Cl_{2(aq)}$ react with a similar stoichiometry, the term "available chlorine" allows the hypochlorite concentration to be calculated as if $Cl_{2(g)}$ was actually present in the solution.

To determine the "available chlorine", the most commonly used method is the known "iodometric titration" [2–3]. This method is based on a redox titration, taking the advantage that iodide ion $(I^-_{(aq)})$ is a strong enough reducing agent. Consequently, many oxidizing agents can react completely with $I^-_{(aq)}$ to form iodine $(I_{2(aq)})$, which is the targeted compound in iodometric processes. The usual procedure involves the addition of an excess of $I^-_{(aq)}$ to the oxidizing agent analyte. This reaction will produce $I_{2(aq)}$, which can be later titrated with a standard solution of a proper reagent.

In High Schools, the "available chlorine" in household bleach is determined by the reaction of the bleach sample with an excess of potassium iodine solution. In this process, the $ClO^-_{(aq)}$ anion is reduced to $Cl^-_{(aq)}$, and the stoichiometric added $I^-_{(aq)}$ is oxidized to $I_{2(aq)}$. The $I_{2(aq)}$ formed is later titrated with a standardized sodium thiosulfate solution. The iodine-thiosulfate reaction is quite fast, and the equilibrium is far to the product side [4].

In this communication, an alternative method to determine the "available chlorine" in household bleach is proposed based on the reaction of a known quantity of bleach with a standardized $CuSO_4.5H_2O$ aqueous solution. The alkaline media of the bleach can promote the formation of both hydroxyl cupric sulfate and cupric hydroxide, which form a solid mixture that can be separated by filtration. In all cases, the concentration of the initial $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex will be reduced, and this difference can be measured by spectrometric measurements. By using these measurements and the stoichiometry of the process, the "available chlorine" concentration in the household bleach can be easily estimated, in a fast and reliable fashion.

Experimental

Materials and methods. Five commercial household bleaches were identified as A, B, C, D and E, and used as received. Solid reagents were used as received. Sodium thiosulfate solution was standardized with a freshly prepared solution of potassium iodate (KIO_3). A small quantity of soluble starch was dissolved in hot water (1 wt%), under stirring, to obtain the titration indicator. Concentrated acetic acid was used without prior purification. A Turner Model SP-830 Spectrophotometer (Barnstead I Thermolyne Corporation) was employed to obtain the absorbance vs. concentration curves

Preparation of a stock solution of $CuSO_4.5H_2O$ 0.04 M, and measurement of the absorbance vs. concentration of solutions of

CuSO₄.5H₂O. A stock solution of $CuSO_4.5H_2O$ was prepared by dissolving the appropriate amount of the salt in water. Previously, the salt was grinded in the mortar, and then dissolved in water by adding small amounts with spatula. From this stock solution, different solutions of known concentration were prepared by dissolving an exact volume of the stock solution in water, and diluted in the appropriate volumetric flasks. These dilutions were later used for constructing the absorbance vs. concentration curve for the $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex at 815 nm, using distilled water as reference (blank solution).

Standardization of sodium thiosulfate solution. Solid $Na_2S_2O_3$. $5H_2O$ was dissolved in water in order to obtain approximately a 0.1 M solution. After that, approximately 0.5 grams of solid KIO_3 were weighed, and dissolved in water. The solution was transferred quantitatively to a 250 mL volumetric flask, and the exact concentration of this solution was calculated. After that, 10 mL of the KIO_3 were transferred to a 125 mL Erlenmeyer flask. Approximately 15 mL of distilled water was added to the flask followed by 1 g of solid KI. The mixture was stirred until all solids were dissolved. Then, 5 mL of concentrated acetic acid were carefully added, and gently stirred. The mixture turned brown due to the presence of $I_{2(aq)}$. A buret was rinsed with the 0.1 M $Na_2S_2O_3$ previously prepared, and then the Erlenmeyer flask mixture was titrated with this solution until the color changed to pale yellow. At this moment, approximately 3 mL of starch solution was added to the Erlenmeyer flask, and the reaction mixture turned to blue. The mixture was hand swirled in order to rinse any solution adhering to the sides of the flask into the bulk solution. The titration was performed carefully until the blue color disappeared. At this point, the final buret reading was recorded, and the standardization process was repeated many times until a trusted value was obtained (a reproducible titration value was obtained from at least three titration experiences, with differences among them lower than 0.1 mL).

Determination of "active chlorine" in household bleach samples by using titration method. A buret was filled with the standardized sodium thiosulfate solution. Approximately 1 gram of solid KI was added to 45 mL of distilled water in a 125 mL Erlenmeyer flask, and swirled to dissolve the KI. After that, 1 mL of the household bleach sample and 5 mL of acetic acid were added to the flask, and stirred until all of the KI was dissolved. The Erlenmeyer flask was covered with an aluminum foil, and it was placed in the dark for about 5 minutes in order to allow iodine formation. Then, the obtained solution was gently mixed with a magnetic stir bar, and titrated with the standardized sodium sulfate solution. When the color changed from brown to a very pale yellow, 3 mL of starch indicator solution was added. The titration was stopped when the blue color disappeared. The titration was repeated many times until it was reproducible (a reproducible titration value was obtained from at least three titration experiences, with differences among them lower than 0.1 mL).

Determination of "active chlorine" in household bleach samples by using the spectrophotometric method. An appropriate amount of test tubes were filled with 10 mL of standardized 0.04 M $CuSO_4.5H_2O$. Then, a sample of household bleach was added to each tube in steps of 0.1 mL up to 0.8 mL. After the addition, a light blue-green solid suspension was observed in each tube. The mixture was filtered through filter paper, and the liquid solution was collected in order to perform the absorbance measurements of the solution at 815 nm.

Results and Discussion

Laundering white clothes to remove dirt and stains is an everyday chore and is usually accomplished with the aid of bleach. The effectiveness of bleach to whiten and remove stains is related to its oxidizing (bleaching) strength. In most cases, liquid "chlorine" bleaches contain the hypochlorite ion

$ClO^-_{(aq)}$ as the oxidizing agent. This anion can be presented as the sodium (NaClO) or the calcium salt ($Ca(OCl)_2$).

The most common and successful method employed in High Schools to determine the oxidizing strength ("available chlorine") in commercial household bleaches involves a redox titration in an acidic medium. In this process, the $ClO^-_{(aq)}$ from the sample of bleach is converted to $I_{2(aq)}$ by the addition of solid KI [5–6].This process can be described by the following reaction:

$$ClO^-_{(aq)} + 2\,I^-_{(aq)} + 2\,H^+_{(aq)} \rightarrow Cl^-_{(aq)} + I_{2(aq)} + H_2O_{(l)}$$
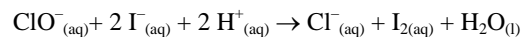
Aqueous iodine ($I_{2(aq)}$) is slightly soluble in water (0.00134 mol/L at 25 ºC) but is soluble in solutions containing $I^-_{(aq)}$ ion. This behavior is explained by the formation of the triiodide complex, $[I_3]^-_{(aq)}$, with an equilibrium constant greater than 500 at 25 ºC [7]:

$$I^-_{(aq)} + I_{2(aq)} \rightleftarrows [I_3]^-_{(aq)}$$
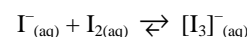
Normally, excess potassium iodide is added to the reaction mixture to increase the solubility of iodine and to decrease its volatility. The $[I_3]^-_{(aq)}$ is pale yellow in diluted solution, and red-brown color in more concentrated solutions. In many textbooks, the $[I_3]^-_{(aq)}$ is referred to as "aqueous iodine", $I_{2(aq)}$.

The $I_{2(aq)}$ formed is titrated with standardized sodium thiosulfate solution.The reaction of $I_{2(aq)}$ with thiosulfate is fast and goes to completion. Iodine oxidizes thiosulfate to the tetrathionate ion, according to the chemical equation given below:

$$I_{2(aq)} + 2\,S_2O_3^{2-}_{(aq)} \rightarrow 2\,I^-_{(aq)} + S_4O_6^{2-}_{(aq)}$$
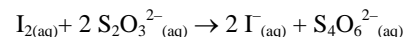
The red-brown color of the $[I_3]^-_{(aq)}$ becomes pale yellow, and eventually the solution will become colorless when all of the $[I_3]^-_{(aq)}$ has reacted to form $I^-_{(aq)}$. Since it is very difficult to see when the pale yellow color becomes colorless, a sharper end-point detection system is needed. Starch forms a dark bluish purple complex with the $[I_3]^-_{(aq)}$ ion in aqueous solutions [8]. Care must be taken to not add the starch until most of the $[I_3]^-_{(aq)}$ has been reacted since at high concentrations, the starch may prevent the $[I_3]^-_{(aq)}$ from reacting. The starch indicator is added just before the end-point of the titration when the solution still has a pale yellow color. The end-point of the titration occurs when the bluish colored starch-$[I_3]^-_{(aq)}$ complex is no longer present in solution due to quantitative reaction, and the solution becomes clear.

By combining all the above-mentioned equations, an overall process for the bleach titration can be described as:

$$ClO^-_{(aq)} + 2\,S_2O_3^{2-}_{(aq)} + H^+_{(aq)} \rightarrow Cl^-_{(aq)} + S_4O_6^{2-}_{(aq)} + H_2O_{(l)}$$
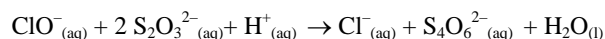
which shows that for every mole of hypochlorite, two moles of thiosulfate are required. Thus, from the volume of the standardized solution of thiosulfate that is required, and from the volume of the bleach sample analyzed, it is possible to calculate the "available chlorine" presented in the sample, according to the equation 1:

$$\frac{V \times C}{2} \times FW_{Chlorine}$$

Table 1. Determination of "available chlorine" in different household bleach samples

Bleach sample	"Available chlorine" (g/L) ± 0.1			
	Student 1	Student 2	Student 3	Average
A	55.3	54.6	57.4	55.6
B	45.3	46.4	46.1	45.9
C	45.7	44.6	46.1	45.5
D	52.5	52.6	52.7	52.6
E	55.0	54.7	55.1	54.9

Table 2. Absorbance dependency on mL of bleach added (values from bleach sample B)

mL of bleach added	Absorbance
0.1	0.423
0.2	0.390
0.3	0.336
0.4	0.303
0.5	0.262
0.6	0.215
0.7	0.202
0.8	0.147

Table 3. Absorbance and remaining and reactive $[Cu(H_2O)_6]^{2+}_{(aq)}$ concentrations after addition of bleach B

V (mL)	A	Remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ $(\times 10^{-4} mol)$	Reactive $[Cu(H_2O)_6]^{2+}_{(aq)}$ $(\times 10^{-4} mol)$
0.1	0.423	3.69	0.31
0.2	0.390	3.44	0.56
0.3	0.336	2.99	1.01
0.4	0.303	2.72	1.28
0.5	0.262	2.38	1.62
0.6	0.215	1.97	2.03
0.7	0.202	1.87	2.13
0.8	0.147	1.37	2.63

Codes: V: mL of bleach added. A: absorbance value at 815 nm.
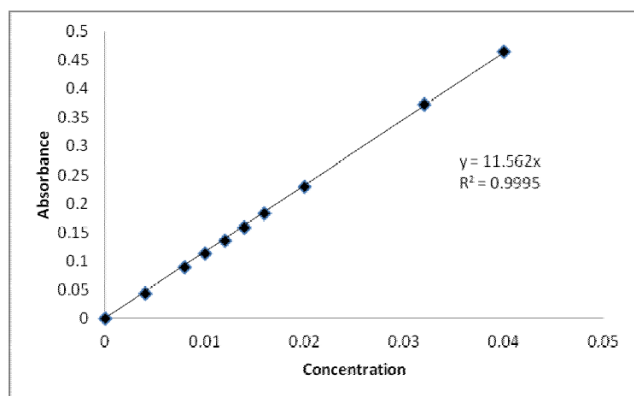
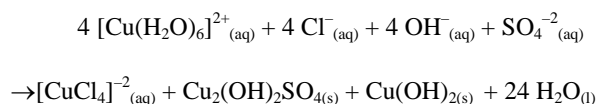**Figure 1.** Absorbance vs. concentration at 815 nm for diluted aqueous solutions of $[Cu(H_2O)_6]^{2+}_{(aq)}$.

in which V is the volume of standardized thiosulfate solution employed in the titration; **C** is its concentration; and FW$_{chlorine}$ is the molar mass of Cl_2 (the factor 2 takes into account the stoichiometry of the process). Accordingly, the results were obtained in grams of "active chlorine" per liter of bleach solution.

This methodology was employed to characterize five different household bleach samples. Three different students

performed the titrations of each sample, and the results obtained are shown in Table 1.

The methodology proposed in this work considers another approach for determining the "available chlorine" in household bleaches, and involves the reaction of the bleach with a solution of cupric sulfate. Diluted aqueous solutions of $CuSO_4.5H_2O$ exhibit a light blue, intense color. This phenomenon is attributed to the presence of the $[Cu(H_2O)_6]^{2+}_{(aq)}$ in solution. By performing appropriate tests, we determined that this complex has a maximum of absorbance at 815 nm. Consequently, for diluted solutions of $CuSO_4.5H_2O$ in water, the Lambert-Beer dependency is observed, as it is displayed in Figure 1.

If one takes a sample of an aqueous solution of cupric sulfate, and slowly adds drop by drop of household bleach, a solid suspension is immediately formed. Although the stoichiometry of the process is complex, the main components in the suspension are a mixture of hydroxyl cupric sulfate and cupric hydroxide. The reaction can be represented by the following chemical equation:

$$4 [Cu(H_2O)_6]^{2+}_{(aq)} + 4 Cl^-_{(aq)} + 4 OH^-_{(aq)} + SO_4^{-2}_{(aq)}$$

$$\rightarrow [CuCl_4]^-_{(aq)} + Cu_2(OH)_2SO_{4(s)} + Cu(OH)_{2(s)} + 24 H_2O_{(l)}$$

Consequently, according to this process the initial concentration of the $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex is reduced, and this reduction should be proportional to the quantity of bleach added to the sample. Since $[Cu(H_2O)_6]^{2+}_{(aq)}$ has a maximum of absorbance at 815 nm, the remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ after addition of the bleach can be easily obtained by spectrophotometric analysis.

Table 2 displays the absorbance at 815 nm of 10 mL of cupric sulfate 0.04 M solution after addition of different quantities of bleach sample B. As it can be observed, the absorbance values for the $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex diminish after the addition of the bleach. This trend is confirmed by Figure 2, in which these values show a lineal tendency.

At this point, it is also worthwhile mentioning that the $[CuCl_4]^{-2}_{(aq)}$ is also formed in the process. Nevertheless, this complex has a maximum of absorbance at 200 nm, and its presence in the analyzed solution does not interfere with the absorbance of the $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex [9].

Taking into account these results, it is possible to calculate the remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ in solution, as well as the "reactive" $[Cu(H_2O)_6]^{2+}_{(aq)}$. This reactive cupric specie can be easily calculated from the initial absorbance value of the solution, and the absorbance value obtained after the addition of the bleach. Since the initial solution of $CuSO_4.5H_2O$ obeys Lambert-Beer Law, and the volumes of bleach added are small, the remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ in solution can be calculated from the analytical curve previously constructed. Under these circumstances, it is not difficult to show that the absorbance of the remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex (and consequently, its concentration) must present a lineal tendency in function of the mL of bleach added, as it is shown in Table 3, and in Figure 3. According to the chemical equation that represents the process, $[Cu(H_2O)_6]^{2+}_{(aq)}$, $Cl^-_{(aq)}$ and $OH^-_{(aq)}$ are in equal molar ratio, but from the chemical equation that explains the oxidation of $Cl_{2(g)}$ in bleach, the stoichiometric relation between $Cl_{2(g)}$ and $OH^-_{(aq)}$ is 2 to 1. Consequently, by taking into account the stoichiometry and the absorbance

Table 4. Obtained values for the "available chlorine" concentration for bleach sample B by using the spectrophotometric method proposed in this communication

Bleach sample added (mL)	"Available chlorine" (g/L) ± 0.1	Average value ± 0.1
0.1	44.0	
0.2	39.5	
0.3	47.8	
0.4	45.4	
0.5	46.6	45.2 g/L
0.6	48.0	
0.7	43.2	
0.8	46.7	

Table 5. Comparison of the "available chlorine" obtained for each bleach sample by using the conventional titration method, and the spectrophotometric method described in this work

	"Available chlorine" (g/L) ± 0.1		
Bleach sample	Titration method	Spectrophotometric Method	Absolute Error %
B	45.9	45.2	−1.53
D	52.6	53,6	+ 1,90
E	54.9	55,0	+ 0.18

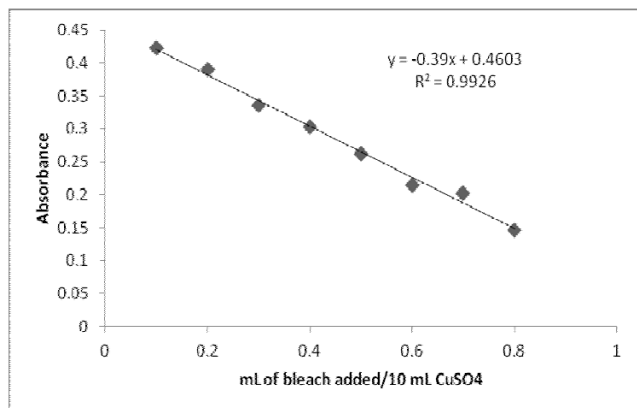**Figure 2.** Absorbance at 815 nm vs. mL of bleach added for a diluted aqueous solution of $[Cu(H_2O)_6]^{2+}_{(aq)}$.

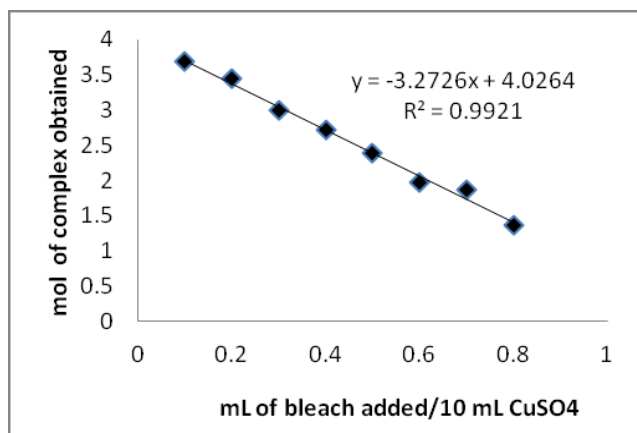**Figure 3.** Absorbance at 815 nm of the remaining $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex after the addition of bleach sample B.

measurements, the following relationship can be deduced for the "available chlorine" for each volume of bleach sample added (Equation 2):

$$2 \times \frac{n \times 1000mL}{v} \times FW_{chlorine}$$

in which n is the concentration of the "reactive" $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex; v is the volume of bleach sample added to the aqueous $CuSO_4.5H_2O$ solution; and $FW_{chlorine}$ is the formula weight of $Cl_{2\,(g)}$. As an example, Table 4 shows the obtained values for the calculation of the "available chlorine" in bleach sample B, according to the results obtained by the equation 2 given above.

By comparing this average value obtained with theaverage value obtained with the titration method (see Table 1), and if we consider that the average titration value obtained is the real value, with the method proposed we obtained less than 1,6 % absolute error, which is more than an acceptable estimation.

The same calculation was performed for other selected bleach samples. Briefly, the "available chlorine" was calculated for each volume of sample bleach added, and then the average value was obtained. This value was compared with the average value obtained for the titration method, and the error percentage was calculated by considering the titration method value as the true value. The results obtained are shown in Table 5.

As it can be seen, the differences between the values obtained by the spectrophotometric and the titration method, considering this last as the true value, are less than ± 2 %. In conclusion, the spectrophotometric method proposed in this communication is simple to manage, and reliable in the values obtained. It is proposed as an alternative methodology for determining "available chlorine" in household bleaches at High School, which combines in a satisfactory fashion both principles: stoichiometry and spectrophotometric measurements.

Conclusions

A new method for determining the "available chlorine" in samples of household bleaches is proposed. This method takes into account the reaction of standardized aqueous cupric sulfate solutions and bleach, and employs a conventional laboratory spectrophotometer as the main tool. By analyzing the differences between the initial and the remaining absorbance of the $[Cu(H_2O)_6]^{2+}_{(aq)}$ complex at 815 nm after the addition of a known volume of the bleach, the corresponding "available chlorine" in the bleach is determined in a simple fashion. In addition, this method offers the possibility of comparing these results with other well-established methods, and combines elegantly stoichiometry calculations and spectrophotometric measurements in one laboratory activity. It is proposed as an alternative method for High School Laboratory experiments.

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