

Analysis of Chlorine Species in Chlorine Dioxide Bleaching Liquor and Generation Process by UV-VIS Spectroscopy

Li-Jun Wang¹, Seon-Ho Lee², Byung-Ho Yoon¹

¹Department of Paper Science. & Engineering, Kangwon National. University.

²Dept. of Paper Technology, Yong-In Songdam College

Abstract

In this paper the extinction coefficients of molecule chlorine (Cl_2), chlorine dioxide (ClO_2), hypochlorous acid (HClO), chlorous acid (HClO_2) were determined using a PDA UV-VIS spectrophotometer. Based on these, the concentrations of Cl_2 , ClO_2 , and HClO in general chlorine dioxide bleaching liquor can be measured. The concentrations of Cl_2 , ClO_2 and HClO_2 produced during the generation of methanol based chlorine dioxide generator can also be determined use the same method. The method was thought to be able to give more information in chlorine dioxide bleaching chemistry if combine its use with titration and ion chromatography.

Introduction

It is well know that chlorine dioxide is the most important bleaching agent currently in kraft pulp bleaching, and it is also widely used in water treatment. The determination of the concentration of chlorine dioxide is absolutely necessary in bleaching liquor or effluent, and even in drinking water. However, generally chlorine dioxide bleaching liquor can not be a pure solution, it often contains

certain amount of molecule chlorine¹⁾. This is because chlorine is also produced from most of the generators, and the removal or separation of chlorine from chlorine dioxide is difficult or costly²⁾. Actually in industry, it is yet not necessary to do so. Chlorine dioxide can also decompose itself into chlorine and oxygen during generation. This decomposition also takes place in water solution if it is not properly kept. And also decomposition into chlorite (ClO_2^-) and chlorate (ClO_3^-) should also be considered. Thus, a chlorine dioxide bleaching liquor may contain Cl_2 , HClO (from the hydrolysis of chlorine), CO_2 , HClO_2 and HClO_3 (chloric acid) This made it very difficult to determine all the species when one want to have a fundamental understanding of chlorine dioxide chemistry.

Traditional titration method can only determine the contents of chlorine and chlorine dioxide directly by a dual-pH method³⁾. If the chlorine and chlorine dioxide in a solution are removed by bubbling or vacuum method, the residue chlorite and chlorate can also be determined by titration. But this method is tedious and detection limit is high. Chlorite and chlorate are preferably analyzed by ion chromatography, together with chloride and other ions⁴⁾ if there is any. In addition, the hypochlorous acid can also be analyzed by ion chromatography using an electrochemical detector. If one determines the chlorite, chlorate and chloride ion before and after removing chlorine and chlorine dioxide, the content of chlorine and chlorine dioxide can be determined from the difference. Actually the method has the advantage on determine the contents of ions and hypochlorous acid, but it is not good for

chlorine and chlorine dioxide. no mentioning that the cost of the instrument is high and sample preparation is time consuming.

It is well-known that based on the Lambert-Beer's law, UV-VIS spectroscopy has the advantage of determine the concentration of respective components in a mixture. thus in this paper it was attempted to determine the various chlorine species in chlorine dioxide solution. With the same thought, the species in chlorine dioxide generator was also analyzed.

Experimental

The UV-visible spectrophotometer used was UVS-2100 manufactured by Scinco Co. Ltd. Korea. This spectrophotometer is a single-beamed multi channel system with a PAD (photo diode array detector), and it has the characteristics of fast scan speed (0.02~5 seconds).

All the extinction coefficients were determined at 25°C, using 1cm width cells. The absorbance data were that at wavelengths of 247, 322 and 356nm which are respectively the maximum absorbance wavelengths of HClO, Cl₂ and ClO₂. The extinction coefficients of chlorine and chlorine dioxide were determined in 9N sulfuric acid condition and those of hypochlorous acid in pH 4 CH₃COONa/CH₃COOH buffer solution. Besides, the extinction coefficients of chlorite was determined in water solution and those of chlorous acid by analysing the reaction between chlorite and sulfuric acid.

Results and Discussion

1. Extinction coefficients of chlorine species.

1.1 Extinction coefficients of Cl₂, HClO and ClO₂.

It is known that in water, chlorine hydrolyzes as follows:



The equilibrium constants at 25°C for these two equations are respectively $k_1 = 3.94 \times 10^{-4}$ and $k_2 = 2.90 \times 10^{-8}$.

The contents of Cl₂ and HClO depends strongly on the pH of the solution. From these equations and their equilibrium constants, one may calculate and get the result that at strong acidic conditions (free acid 8~10N) almost only chlorine presents, and at pH 4 almost only hypochlorous acid shows⁵⁾. Thus we used this two conditions respectively to determine the extinction coefficients of Cl₂ and HClO. The spectra were shown in fig. 1 and 2

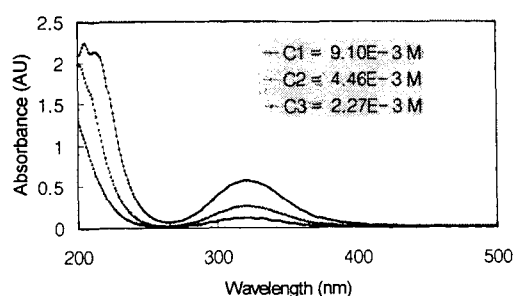


Fig. 1. UV-VIS spectra of chlorine with three concentrations in 9N sulfuric acid.

At 247nm, 322nm, and 356nm, absorbance~concentration straight lines were made, fig. 3. is such an example. The lines were expressed into equations which are listed in Table 1. The coefficients of the equations are the

extinction coefficients in units of $\text{cm}^{-1}\text{M}^{-1}$.

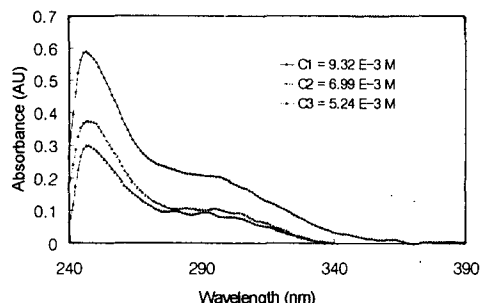


Fig. 2. UV-VIS spectra of hypochlorous acid with three concentrations in pH 4 buffer solution.

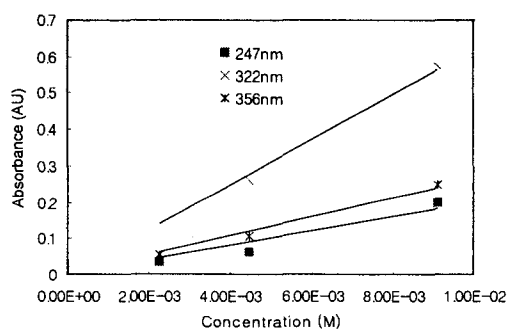


Fig. 3. Calculation of the extinction coefficients of chlorine.

As mentioned above, pure chlorine dioxide solution is not easy to be prepared. Here we used chlorine dioxide and chlorine mixtures in 9N sulfuric acid to determine the extinction coefficients of chlorine dioxide. The concentrations were pre-measured by titration. The spectra of the mixtures were shown in fig. 4.

Since the concentration of chlorine and its extinction coefficients at 247, 322, and 356 nm were known, the absorbance caused by chlorine will be known. Subtract the absorbance by chlorine from the total absorbance will make the absorbance of chlorine dioxide. Then from

the absorbance~concentration data, the extinction coefficients of chlorine dioxide can also be calculated. The result is also listed in Table. 1.

Table 1. Extinction coefficients of Cl_2 , HClO , and ClO_2^- .

| | λ (nm) | Equations | ϵ ($\text{cm}^{-1}, \text{M}^{-1}$) |
|------------------|----------------|--------------|--|
| Cl_2 | 247 | $y = 20.0x$ | 20.0 |
| | 322 | $y = 62.0x$ | 62.0 |
| | 356 | $y = 26.6x$ | 26.6 |
| HClO | 247 | $y = 58.8x$ | 58.8 |
| | 322 | $y = 8.3x$ | 8.3 |
| | 356 | - | 0 |
| ClO_2 | 247 | $y = 104.9x$ | 104.9 |
| | 322 | $y = 632.4x$ | 632.4 |
| | 356 | $y = 938.3x$ | 938.3 |
| ClO_2^- | 247 | $y = 97.2 x$ | 97.2 |
| | 322 | $y = 25.9 x$ | 25.9 |
| | 356 | - | 0 |

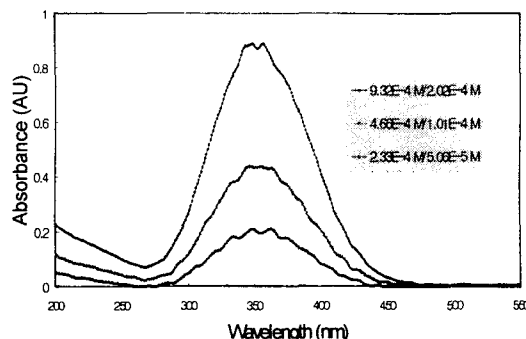


Fig. 4. UV-VIS spectra of ClO_2 and Cl_2 mixture in 9N H_2SO_4 . The concentrations were expressed as ClO_2 concentration / Cl_2 concentration.

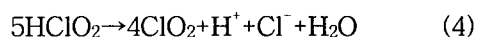
1.2 Extinction coefficients of ClO_2 and HClO_2 .

It is known that HClO_2 dissociates as follows in water:



Its equilibrium constant at 25 °C is $1.1 \times$

10^2 . Because this constant is large, the chlorite in solution can not be omitted. One may suppose to determined the extinction coefficients in high acidic condition as was done in the case of chlorine. However, chlorous acid is very easily decomposed in high acidic condition as follows:



Thus other method was used as follows:

First the extinction coefficients of chlorite were determined easily from neutral pH solutions containing known amount of chlorite concentration. The spectra of chlorite is shown in fig. 5 and extinction coefficients in Table 1.

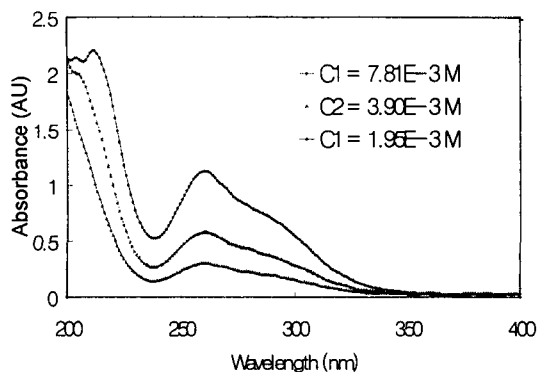


Fig. 5. UV-VIS spectra of sodium chlorite with three concentrations

Then 1.563×10^{-2} M ClO_2 and 0.159 M H_2SO_4 were mixed in same volume and an time-interval experiment was carried out with UV-VIS spectroscopy. This was to check the absorbance of the solution every 20 second for a total of 5 minutes.

Fig. 6. showed the spectra of the original chlorite, as well as that of 12 and 312 seconds, other spectra were not shown in the figure but they are just between this two spectra. One can see the chlorite spectrum changed its shape as soon as

sulfuric acid was added. This is because chlorous acid was formed.

With the time going on, it was also seen that certain amount of chlorine dioxide was generated due to the decomposition of chlorous acid as equation (4) shows.

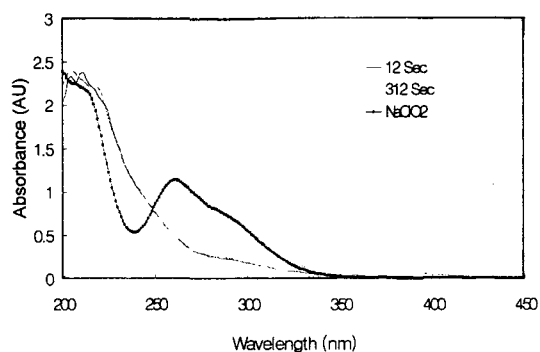


Fig. 6. UV-VIS spectra of $\text{ClO}_2^-/\text{HClO}_2$ by time-interval-experiment.

With the absorbance data one can make the absorbance~time curves which is shown in Fig. 7. The curves were fitted into equations from which the absorbance at zero time, i. e., the time as soon as chlorous acid was formed can be obtained. With the starting concentrations of chlorite and hydrogen ion as $[\text{ClO}_2^-]_0 = 7.82 \times 10^{-3}$ M, $[\text{H}^+]_0 = 0.159$ M and the constant of equilibrium as 1.1×10^2 , one can calculate the concentrations of ClO_2^- , H^+ , HClO_2 at equilibrium to be $[\text{ClO}_2^-]_e = 4.33 \times 10^{-4}$ M, $[\text{H}^+]_e = 0.188$ M, $[\text{HClO}_2]_e = 7.38 \times 10^{-3}$, and since the extinction coefficients of chlorite at 247nm, 322nm, 356nm were known, the absorbance contributed by chlorite at equilibrium can be known. Subtract this part from the total absorbance gives the absorbance by HClO_2 , thus the extinction coefficients of chlorous acid can be calculated. this

process is summarized in Table. 2.

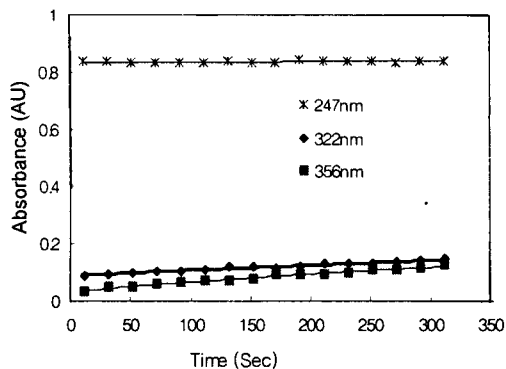


Fig. 7. UV-VIS absorbance of $\text{ClO}_2^- / \text{HClO}_2$ vice time at 247, 322 and 356nm.

Table 2. Calculation of the zero time absorbance in $\text{HClO}_2 / \text{ClO}_2^-$ system.

| λ (nm) | Equations | Abs _{t=0} (AU) | $\epsilon \text{ HClO}_2$ ($\text{cm}^{-1}\text{M}^{-1}$) |
|----------------|--|-------------------------|---|
| 247 | $y = 5\text{E-}08 x^2 - 9\text{E-}06 x + 0.8352$ | 20.04 | 107.5 |
| 322 | $y = 9\text{E-}08 x^2 + 0.0001 x + 0.0897$ | 61.97 | 10.6 |
| 356 | $y = -3\text{E-}07 x^2 + 0.0004x + 0.0311$ | 26.62 | 0 |

Note: $\epsilon_{\text{HClO}_2} = \{ \text{Abs}_{t=0} - [\text{ClO}_2^-]_e \times \epsilon_{\text{ClO}_2} \} / [\text{ClO}_2^-]_e$

2. Determination of Cl_2 and ClO_2 concentrations in ClO_2 bleaching liquor.

Chlorine dioxide bleaching liquor always contains Cl_2 , ClO_2 and HClO , the respective concentration of which can be calculated from the following associated equations:

$$\begin{aligned} \epsilon_{\text{ClO}_2}^{240} \times C_{\text{ClO}_2} + \epsilon_{\text{Cl}_2}^{240} \times C_{\text{Cl}_2} + \epsilon_{\text{HClO}}^{240} \times C_{\text{HClO}} &= A^{240} \\ \epsilon_{\text{ClO}_2}^{322} \times C_{\text{ClO}_2} + \epsilon_{\text{Cl}_2}^{322} \times C_{\text{Cl}_2} + \epsilon_{\text{HClO}}^{322} \times C_{\text{HClO}} &= A^{322} \\ \epsilon_{\text{ClO}_2}^{356} \times C_{\text{ClO}_2} + \epsilon_{\text{Cl}_2}^{356} \times C_{\text{Cl}_2} + \epsilon_{\text{HClO}}^{356} \times C_{\text{HClO}} &= A^{356} \end{aligned}$$

The result from UV-VIS spectroscopy are compared with that from titration in

Table 3. The data showed that the two methods are consistent with each other, however, UV-method has the advantage of knowing another component, that is, hypochlorous acid.

Table 3. Results by titration and UV-VIS spectroscopy. (E-4M)

| | | C_{ClO_2} | C_{Cl_2} | C_{HClO} | $[\text{Cl}_2]$ | $[\text{ClO}_2]$ |
|------------|----|--------------------|-------------------|-------------------|-----------------|------------------|
| UV-VIS | C1 | 12.97 | 6.50 | 4.35 | 10.85 | 12.97 |
| | C2 | 6.40 | 3.21 | 2.16 | 5.37 | 6.40 |
| | C3 | 3.29 | 1.52 | 1.13 | 2.65 | 3.29 |
| | C4 | 2.45 | 1.29 | 0.85 | 2.14 | 2.45 |
| Titra-tion | C1 | 13.30 | 11.0 | - | 11.0 | 13.30 |
| | C2 | 6.65 | 5.48 | - | 5.48 | 6.65 |
| | C3 | 3.32 | 2.74 | - | 2.74 | 3.32 |
| | C4 | 2.49 | 2.05 | - | 2.05 | 2.49 |

Note: $[\text{Cl}_2] = C_{\text{Cl}_2} + C_{\text{HClO}}$ and $[\text{ClO}_2] = C_{\text{ClO}_2}$

3. Determination of Cl_2 , ClO_2 and HClO concentrations during ClO_2 generation.

Here 2ml 10N sulfuric acid, 1.8ml water, $20 \mu\text{l}$ methanol and $20 \mu\text{l}$ 41% sodium chlorate were mixed and the absorbance detected with 30 second time-interval-

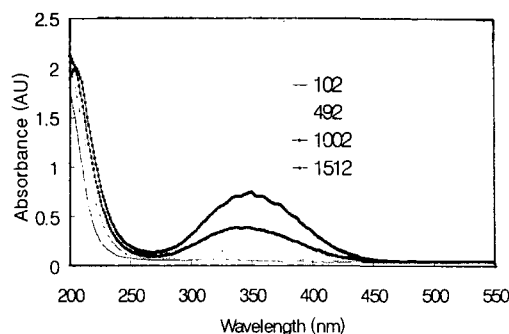


Fig. 8. UV-VIS spectra of mixtures in a simulated chlorine dioxide generator.

experiment. The spectra were showed in fig. 8 taking 100 second, 500 second and 1000 second as the example.

In the generation system, we do not need to consider HClO since it is transferred into chlorine due to the high acidic condition. The concentration of Cl₂, ClO₂ and HClO₂ during generation at each time interval can be calculated by solving the following associated equations.

$$\begin{aligned} \epsilon^{240}_{\text{ClO}_2} \times C_{\text{ClO}_2} + \epsilon^{240}_{\text{Cl}_2} \times C_{\text{Cl}_2} + \epsilon^{240}_{\text{HClO}_2} \times C_{\text{HClO}_2} &= A^{240} \\ \epsilon^{322}_{\text{ClO}_2} \times C_{\text{ClO}_2} + \epsilon^{322}_{\text{Cl}_2} \times C_{\text{Cl}_2} + \epsilon^{322}_{\text{HClO}_2} \times C_{\text{HClO}_2} &= A^{322} \\ \epsilon^{356}_{\text{ClO}_2} \times C_{\text{ClO}_2} + \epsilon^{356}_{\text{Cl}_2} \times C_{\text{Cl}_2} + \epsilon^{356}_{\text{HClO}_2} \times C_{\text{HClO}_2} &= A^{356} \end{aligned}$$

From the above results fig. 9 was made which shows the concentrations of chlorine, chlorine dioxide and chlorous acid during chlorine dioxide generation. Chlorine was the mainly generated specie while chlorous acid remained almost the same concentration and chlorine dioxide was generated after the initial stage. This result coincides with that of carried out by Ni. Y⁶⁾.

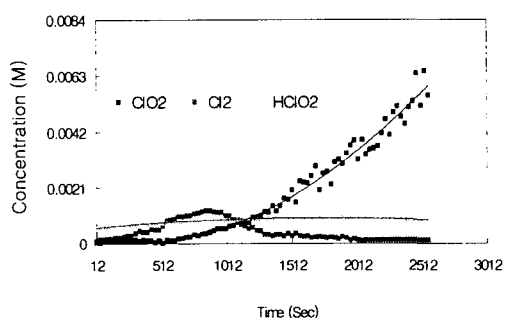


Fig. 9 The developments of chlorine, chlorine dioxide and chlorous acid in simulated chlorine dioxide generator.

Conclusion

Using a PDA UV-VIS spectrophotometer, the extinction coefficients of chlorine, chlorine dioxide, hypochlorous acid, chlorous acid and chlorite ion were determined at 247nm, 322nm, 356nm which belong

respectively to be the maximum absorbance of hypochlorous acid, chlorine and chlorine dioxide. Based on these, the chlorine, hypochlorous acid and chlorine dioxide concentrations can be calculated by resolving three associated equations. The same method can also be used to calculate the concentrations of molecule chlorine, chlorous acid and chlorine dioxide, which may be helpful in understanding the mechanism of chlorine dioxide generation in chlorine dioxide generators. The method was thought to be able to give more information in chlorine dioxide bleaching chemistry if combined with the use of titration and ion chromatography.

References

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