SIMULTANEOUS DETERMINATION OF CHLORINE DIOXIDE AND HYPOCHLOROUS ACID IN BLEACHING SYSTEM

Qiang Wang,[a] Kefu Chen,[a] Jun Li,[a,]* Jun Xu,[a] and Shanshan Liu [b]

This study has demonstrated a rapid spectroscopic method for the determination of chlorine dioxide and hypochlorous acid concentrations in the pulp bleaching processes. It was found that chlorine dioxide and hypochlorous acid have an isosbestic wavelength of 295 nm. The soluble lignin in such a system is the main interference, but can be corrected by determining the absorbances at 295 nm, 380 nm, and 480 nm. Thus, based on the spectroscopic measurements at 295 nm (the isosbestic point wavelength for chlorine dioxide and hypochlorous acid), 380 nm (absorbance wavelength of chlorine dioxide) and 480 nm (the acid soluble lignin absorbance wavelength), the chlorine dioxide and hypochlorous acid concentrations in the bleaching process can be quantified. However, hypochlorous acid was not detected in the real bleaching effluent for its low content. The present method is simple, rapid, accurate, and has the potential for on-line monitoring of the chlorine dioxide bleaching process.

*Contact information: a: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangdong Public Laboratory of Paper Technology and Equipment, Guangzhou, China; b: Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry 210042, Nanjing, China.; *Corresponding author: wangqiang8303@163.co m*

INTRODUCTION

In the paper industry, the so-called elemental chlorine-free (ECF) bleaching technology, i.e., using chlorine dioxide (ClO_2) as the main bleaching chemical has become dominant all over the world in the production of bleached chemical pulps (Barroca et al. 2001; Hamzeh et al. 2007). This shift can be attributed to the high-quality pulp product, low-environmental impact, and reasonable production cost of the process (Brogdon et al. 2005). The residual chlorine dioxide in a pulp bleaching system is one of the most important parameters from the viewpoints of both quality control and process operation (Sullivan et al. 1998). Under the bleaching conditions, chlorine dioxide under-goes disproportionations (Brogdon et al. 2004a), producing hypochlorous acid, chlorite, and chlorate, some of which are not desirable. For example, hypochlorous acid can react with lignin to form organically bound chlorine with lignin (Brogdon et al. 2004b) (determined collectively as absorbable organic halogen, known as AOX). Thus, a good on-line monitoring strategy for the residual chlorine dioxide concentration is critical in operating a successful chlorine dioxide stage.

A number of analytical methods for the determination of the chlorine dioxide concentration have been reported. Spectrophotometric methods that offer simplicity and

***bioresources*.com**

cost-effectiveness have been widely employed (Zhu et al. 2001; Jiang et al. 2005). However, color-fading oxidation reactions of dyes with chlorine dioxide have been reported in several papers (Fletcher et al. 1985; Sweetin et al. 1996; Emmert et al. 2000). Although fluorimetric methods are more selective due to their simultaneous use of excitation and emission wavelengths together, such determinations are indirect, and native fluorescence of organic compounds is required (Jiang et al. 2005; Themelis 2006). Electro-analytical methods have also been applied, including amperometry (Ivaska et al. 1990), differential pulse voltammetry (Quentel et al. 1994), and chlorine dioxide selective electrodes. Chromatographic methods have included high-performance liquid chroma-tography (HPLC) (Watanabe et al. 1998), ion chromatography (IC) (Haddad et al. 2003; Hui et al. 2003), and gas chromatography coupled with mass spectrometric detection (GC-MS) (Shinb 2006). However, the HPLC method tends to be inconvenient for online monitoring, and the IC method relies on the conversion of chlorine dioxide to chlorite, and thus can be considered as an indirect method. The titration method is the dominant method used in industrial practice for the determination of chlorine dioxide. The method is not only time consuming but also has experimental error. Therefore, there has been a need to develop a simple and selective analytical method that can be used for the on-line monitoring of chlorine dioxide and hypochlorous acid concentrations simultaneously.

In this work we have developed a UV spectroscopic method for the determination of residual chlorine dioxide and hypochlorous acid present in the pulp bleaching processes. This method does not need complex sample preparation and can be used for batches test. The dissolved lignin interference can be resolved based on a triple-wavelength measurement technique. The present method is simple, rapid, accurate, and has the potential for on-line process monitoring.

EXPERIMENTAL

Chemicals

The chlorine dioxide used in the experiments was purchased from Weifang Pharmaceutical Co., Ltd., China as a two-part powder product. The chemical composition and mass ratio of the powder was as follows: $NaClO_2$ 36-38%, citric acid 23%-25%, sodium cellulose methyl carboxylate (SCMC) 5%, $MgSO_4$ 10% (as synergist), and $CaCl_2$ (as desiccant) 25%. The product is provided in dual powder packages of powder, wherein the $NaClO_2$ is separately wrapped from the other components. The chemical reaction during preparing process was as follows:

$$5ClO_2^- + 4H^+ = 4ClO_2 + Cl^- + 2H_2O \qquad (1)$$

All other chemicals were from commercial sources. Aqueous chlorine dioxide and hypochlorous acid samples were prepared daily in the laboratory, and their concentrations were determined based on the iodometric method described as below (Zhao et al. 2010). These solutions were stored in glass containers in the dark at 4 $^{\circ}$C to minimize thermolytic and photolytic decomposition.

Titration method

For determination of Cl_2 and ClO_2^-, 200 mL of distilled water was first added into a 500 mL iodine flask, and then buffer was added to make the solution pH stay in the range 7.0 to 8.5. Second, known volumes of ClO_2 and 10 mL KI solution were added to the flask, which was shaken for a while. Third, the solution was titrated with $Na_2S_2O_3$ (0.01mol/L) solution to yellow, and then 1mL starch solution was added. Titration was then continued until the blue coloration faded away. The dosage of $Na_2S_2O_3$ was recorded as A.

For determination of ClO_2, 2.5 mL of HCl solution of 2.5 mol/L was added to the iodine flask; this was placed in a dark closet with stopper for 5 min. The mixture was then titrated with $Na_2S_2O_3$ (0.01mol/L) solution until the blue coloration faded away. Then, the ClO_2 concentration can be calculated by the $Na_2S_2O_3$ solution consumption.

Apparatus

A UV-Vis spectrophotometer (HACH, made in USA, resolution: 1nm) equipped with a 1 cm path length flow cell was used for the experiments.

Acid Solution Lignin and Bleached Effluent

Acid solution lignin was prepared by a pulping process. The raw materials, including *Eucalyptus*, mixed poplar, bagasse, and wheat straw, were milled and subsequently extracted in a benzene-ethanol (2:1) mixture for 8h, then dried under vacuum. The pulping conditions were: NaOH dosage of 10% (on oven-dry material), liquor to solid ratio of 20:1, 170 ^{o}C, and 2 h. The black liquor was filtrated in a Buchner funnel and diluted into acetic acid, then separated by centrifuge at 3000 rpm. The solution was determined for soluble lignin by using a UV-Vis spectrophotometer in wavelength range 190 to 900 nm (Zhang et al. 2010).

Bleached effluent from bagasse pulp was collected from the OD_0EpD_1 bleaching sequence. The condition of each stage was as follows:

- O: an oxygen delignification stage (oxygen pressure 0.5 MPa, 100 ^{o}C, 60 min, consistency 10%),
- D_0 : the first D-stage of chlorine dioxide bleaching (ClO_2 dosage 5% based on o.d. pulp and the same as below, 60 ^{o}C, 60 min, pH 2 to 3, consistency 10%),
- Ep: an alkaline extraction stage (oxygen pressure 0.3 MPa, H_2O_2 0.5%, NaOH dosage 1%, 80 ^{o}C, 60 min, consistency 10%),
- D_1 : the second D-stage of chlorine dioxide bleaching (ClO_2 dosage 1%, 80 ^{o}C, 60 min, pH 3 to 4, consistency 10%).

The bleaching effluent was collected and filtrated through aqueous phase filter membrane of 0.22μL for UV-vis determination.

Procedures

The calibration curve was obtained by preparing a set of standard solutions, i.e., by adding 40, 50, 70, 90, 110, and 130 μL of chlorine dioxide stock solution and 40, 60, 80, 100, 120, and 160 μL of stock hypochlorous acid into 10 mL of distilled water, respectively. The absorbance spectrum for each solution was measured. Distilled water was used as the blank in the UV measurements.

RESULTS AND DISCUSSION

Spectral Characteristics of Chlorine Dioxide and Hypochlorous acid
Principle of chlorine dioxide bleaching

Chlorine dioxide, as a neutral compound of chlorine, is a small, volatile, and highly energetic molecule in the +IV oxidation state. It is a highly selective oxidant for one-electron transfer mechanisms (Tzanavaras et al. 2007)

During the bleaching process, chlorine dioxide is reduced to chloride, including organically linked chlorine and chlorate (Hart and Connell 2008). The transformations of the chlorine atoms of chlorine dioxide to chloride and chlorate follow a complex pattern. The pH value of bleaching process has a major effect on the composition of effluent, and chlorite can be ignored when the final pH is between 2 and 4 (Svenson et al. 2006). Hypochlorous acid is in equilibrium with chlorine, and both species of ClO_2 and $HClO$ would exist in the system (Kolar et al. 1983). The relevant reactions of chlorine dioxide in the bleaching system (Lindgren 1971; Gierer 1986) have been shown to be as follows:

$$ClO_2 + e^- \rightarrow ClO_2^- \tag{2}$$

$$ClO_2^- + 3H^+ + 2e^- \rightarrow HClO + H_2O \tag{3}$$

Spectral characteristics

Based on the principles described above, the UV-Vis spectral absorbances of chlorine dioxide and hypochlorous acid solutions were obtained, and the results are shown in Fig. 1. As shown, the maximum absorbance wavelengths for chlorine dioxide and hypochlorous acid were 360 nm and 292 nm, respectively. They did show a crossing point at a wavelength of 316 nm. A coefficient of 4.609 can be obtained by dividing the ClO_2 concentration by the $HClO$ concentration. By multiplying this factor to the chlorine dioxide's molar concentration, the isosbestic point of chlorine dioxide and hypochlorous acid can be obtained, as shown in Fig. 2.
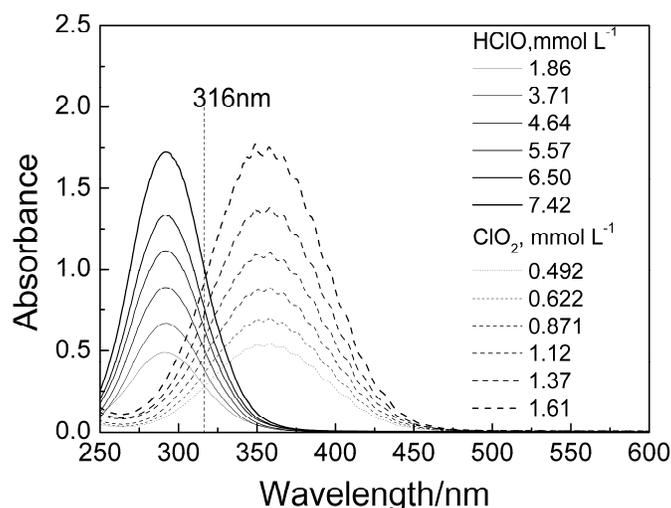

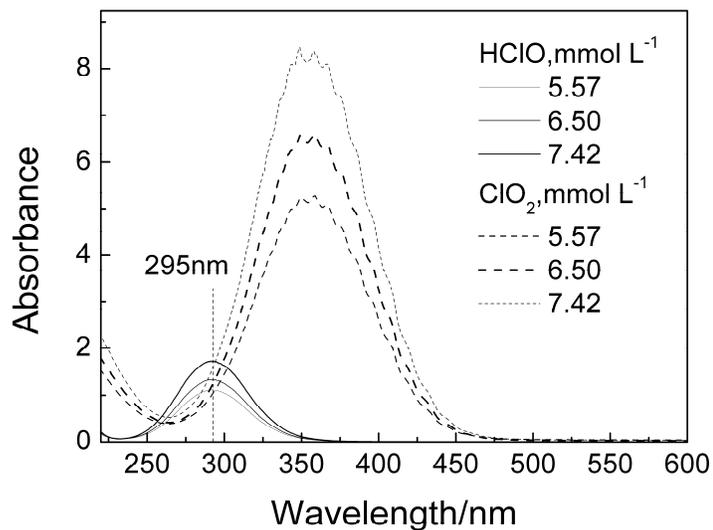**Fig. 1.** UV-Vis spectra of ClO_2 and HClO solutions at different concentrations

Fig. 2. Isosbestic point of ClO_2 and HClO

Based on Fig. 2 it is apparent that chlorine dioxide and hypochlorous acid have an isosbestic point at 295 nm. The absorbance at 380 nm is from chlorine dioxide only, which implies that this wavelength can be used for determination of its concentration.
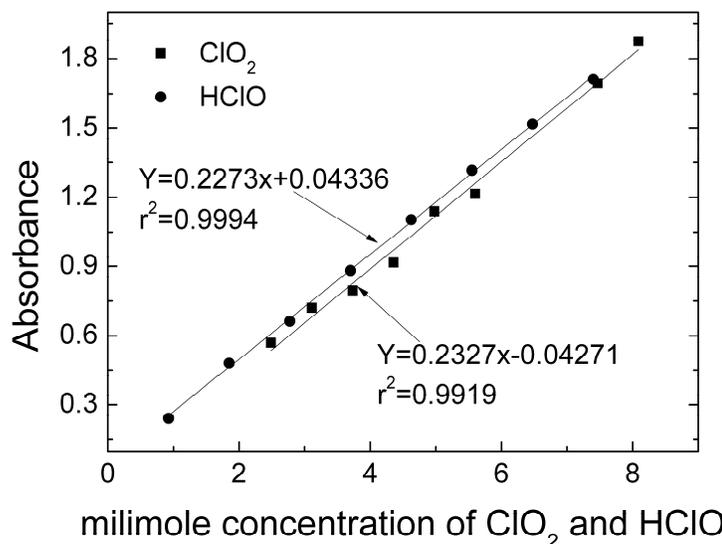

Fig. 3. Absorbance response plot for chlorine dioxide and hypochlorous acid at 295nm

The absorbance response plots for ClO_2 and HClO at 295 nm are given in Fig. 3. As shown, the chlorine dioxide and hypochlorous acid concentrations exhibited linear relationships with their absorbance at 295 nm, and the correlation coefficients were 0.9919 and 0.9994, respectively. Therefore by using the isosbestic point (295nm), and the absorbance at a 380 nm, one could determine the ClO_2 and HClO concentrations.
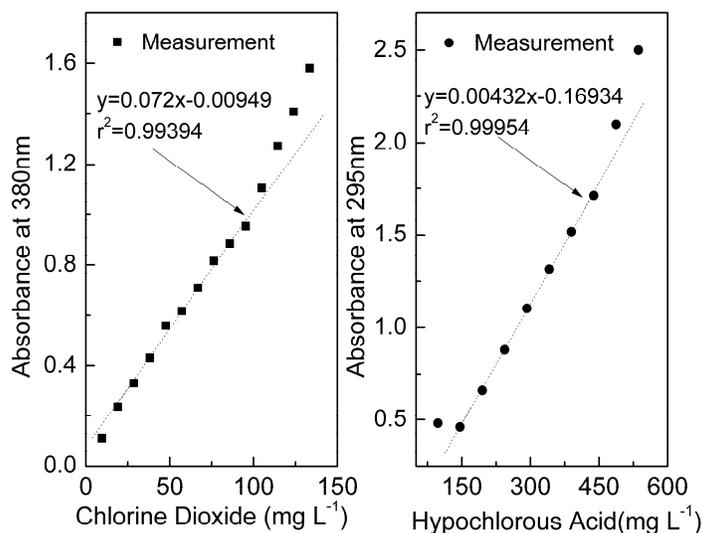
Fig. 4. An absorbance response plot for ClO_2 and HClO determination

Fig. 4 shows the response plot of UV absorbance at 380 nm and 295 nm to the concentration of chlorine dioxide and hypochlorous acid. Linear relationships are shown between UV absorbance at 380 nm or 295 nm and the concentration of chlorine dioxide in the range of 20-100 mg/L (left picture) or the concentration of hypochlorous acid in the range of 150-450 mg/L (right picture).

The absorptivity results for ClO_2 and for HClO at 295 and 380 nm are listed in Table 1.

Table 1. Absorptivities (ε, L/mol cm) of Chlorine Dioxide or Hypochlorous acid at Different Wavelengths

Species	Wavelength/nm	
	380	295
HClO	0	224
ClO_2	837	224

Spectral Interferences and Determination

Spectral interferences

The presence of dissolved lignin in a bleaching effluent can have a strong absorbance in the UV range, as shown in Fig. 5; therefore, it can be expected to interfere with the determination of chlorine dioxide based on the UV spectrophotometry.

A literature report showed (Chai et al. 2004) that the ratio of acid soluble lignin absorbance at 350 nm and 297 nm is a constant, having a value of 0.331. Similarly, one may propose that the ratios of the lignin absorbance at 380 nm, 295 nm, and 480 nm, i.e., A_{380}/A_{480}, A_{295}/A_{480}, may also be constant. In fact, these expectations were confirmed experimentally. Therefore, the spectral contribution from lignin at the wavelength of 295 nm and 380 nm can be corrected by using the lignin absorbance at a 480 nm wavelength.
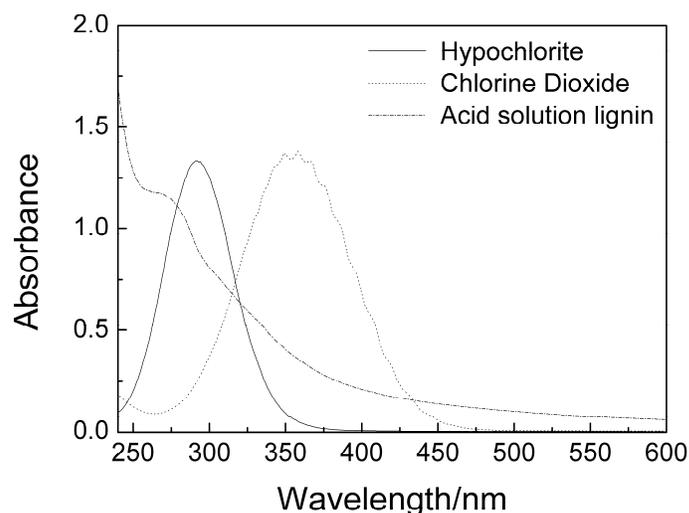
Fig. 5 Spectra of ClO_2 and $HClO$ and the interference of acid soluble lignin

Determination of acid soluble lignin interference

As earlier studied (Wang et al. 2010), the ratio of acidic solution lignin at the maximum absorbance ($A_\lambda{}^x$) of chlorine dioxide and hypochlorous acid, and the result at 295 nm can be calculated as follows:

$$K_x = \frac{A_\lambda^x}{A_{480}} \qquad (4)$$

The absoptivity results for acid-soluble lignin at the selected wavelength and 480 nm are listed in Table 2.

Table 2. K Value of the Raw Materials Selected

	Wood		Non-wood	
	Eucalyptus	Mixed Poplar	Wheat Straw	Bagasse
$K_1 = A_{295}/A_{480}$	7.583	8.172	21.00	24.45
$K_2 = A_{380}/A_{480}$	2.369	2.645	3.647	4.711

A triple-wavelength method

Based on Eq. (4), the absorbance of chlorine dioxide and hypochlorous acid at 295 nm and 380 nm can be determined by correcting the absorbance of soluble lignin. The relationships of absorbance and concentrations are as follows,

$$A_{380} - K_1 A_{480} = \varepsilon_1^1 c_{HClO} + \varepsilon_1^2 c_{ClO_2} \qquad (5)$$

$$A_{295} - K_2 A_{480} = \varepsilon_2^1 c_{HClO} + \varepsilon_2^2 c_{ClO_2} \qquad (6)$$

where A_{295}, A_{380}, and A_{480} are the absorbances at 295 nm, 380 nm, and 480 nm; and K_1 and K_2 are the absorbance ratios of acid-soluble lignin at 295 nm or 380 nm, both versus 480 nm, respectively, i.e. A_{295}/A_{480} and A_{380}/A_{480} (which varies for different raw materials). C_{HClO} and C_{ClO2} are the HClO and ClO_2 concentrations of the diluted samples (mmol L^{-1}). $\varepsilon_1^1, \varepsilon_2^1, \varepsilon_1^2$ and ε_2^2 are the absorptivities of HClO and ClO_2 at wavelengths of 380 nm and 295 nm, respectively.

Based on Eq. (5) and $\varepsilon_1^1 = 0$, C_{ClO2} can be derived as derived as:

$$c_{ClO_2} = \frac{A_{380} - K_1 A_{480}}{\varepsilon_1^2} \tag{7}$$

Furthermore, 295nm is the isosbestic point of HClO and ClO_2. Thus, their absorptivity is equal at this wavelength, i.e.:

$$\varepsilon_2^2 = \varepsilon_2^1 = \varepsilon \tag{8}$$

and $\quad c_T = c_{ClO_2} + c_{HClO} \tag{9}$

Based on Eqs. (6), (8), and (9), the concentration of C_T can be given as:

$$c_T = \frac{A_{295} - K_2 A_{480}}{\varepsilon} \tag{10}$$

and C_{HClO} can be calculated as:

$$C_{HClO} = C_T - C_{ClO_2} \tag{11}$$

Based on Table 2, the content of HClO and ClO_2 can be determined from Eqs. (7) and (11) as follows,

$$W_{HClO} = c_{HClO} M_{HClO} R = 0.1716(A_{295} - k_1 A_{480})R \tag{12}$$

$$W_{ClO_2} = c_{ClO_2} M_{ClO_2} R = 0.08065(A_{380} - k_2 A_{480})R \tag{13}$$

where W_{HClO} and W_{ClO2} are the HClO and ClO_2 concentrations (g L^{-1}), M_{HClO} and M_{ClO2} are the molar mass of HClO and ClO_2, respectively, and R indicates the number of times by which the samples were diluted (dilution factor).

Method Validation

The precision of UV-vis method was evaluated by determining effluent samples contained soluble lignin with different volume of hypochlorous acid and chlorine dioxide. The recovery results are listed in Table 3.

Table 3. Recovery Test of the Method

Sample number	Added (mg*L^{-1})		Measured (mg* L^{-1})		Recovery (%)	
	HClO	ClO$_2$	HClO	ClO$_2$	HClO	ClO$_2$
1	151.42	22.45	158.99	22.67	105	101
2	203.21	33.60	197.11	35.28	97	105
3	249.54	50.40	257.03	50.90	103	101
4	367.46	67.20	352.76	65.92	96	98
5	386.34	84.00	382.48	79.80	99	95

As shown in Table 3, the chlorine dioxide and hypochlorous acid recoveries were in the range of 95.0 to 105%. The repeatability the present method was carried out, and it was found that triplicate testing gave a relative standard deviation (RSD) of 2.96 and 3.96%, respectively for chlorine dioxide and hypochlorous acid.

The validation of the method was carried out on a final D-stage effluent of bagasse pulp, which followed an OD$_0$EpD$_1$ bleaching sequence. The kappa value and brightness of final pulp was 0.64 and 89.0%ISO, respectively. The comparisons of hypochlorous acid and dioxide between the titration and UV-vis method are listed in Table 4.

Table 4. Comparisons of Measured Hypochlorous acid and Chlorine Dioxide Concentration between Titration Method and UV-vis Method

Sample number	HClO (mg*L^{-1})		ClO$_2$ (mg*L^{-1})		Relative difference (%)
	Titration method	UV-vis method	Titration method	UV-vis method	
1	ND[a]	ND	110	120	9.1
2	ND	ND	190	200	-5.3
3	ND	ND	150	150	0

[a]ND: Not detected

As shown in Table 4, the results for chlorine dioxide concentration by UV-vis method were in good agreement with those obtained from the titration method. The hypochlorous acid in the bleached effluent was not detected, which may be due to the quick reaction with lignin residues (Kolar 1983).

CONCLUSIONS

A UV-based method has been developed for the determination of chlorine dioxide and hypochlorous acid concentrations in bleached effluent samples. The method requires absorbance measurements at three wavelength: 295 nm (at which chlorine dioxide and hypochlorous acid have an isosbestic wavelength), 380 nm (where chlorine dioxide has a strong absorbance), and 480 nm (where soluble lignin has an absorbance so that the

soluble lignin effects at 295 nm and 380 nm can be corrected). The new method allows for the simultaneous analysis of chlorine dioxide and hypochlorous acid. The method can be used for the rapid determination and has the potential of on-line monitoring of the chlorine dioxide bleaching system.

ACKNOWLEDGEMENTS

REFERENCES CITED

Barroca, M., Marques, P. J. T., Seco, I. M., and Castro, J. A. A. (2001). "Selectivity studies of oxygen and chlorine dioxide in the pre-delignification stages of a hardwood pulp bleaching plant," *Industrial & Engineering Chemistry Research* 40(24), 5680-5685.

Brogdon, B. N., and Lucia, L. A. (2005). "New insights into lignin modification during chlorine dioxide bleaching sequences (IV): The impact of modifications in the (EP) and (EOP) stages on the D-1 stage," *Journal of Wood Chemistry and Technology* 25(3), 149-170.

Brogdon, B. N., Mancosky, D. G., and Lucia, L. A. (2004a). "New insights into lignin modification during chlorine dioxide bleaching sequences (I): Chlorine dioxide delignification," *Journal of Wood Chemistry and Technology* 24(3), 201-219.

Brogdon, B. N., Mancosky, D. G., and Lucia, L. A. (2004b). "New insights into lignin modification during chlorine dioxide bleaching sequences (II): Modifications in extraction (E) and chlorine dioxide bleaching (D-1)," *Journal of Wood Chemistry and Technology* 24(3), 221-237.

Chai, X. S., Hou, Q. X., Luo, Q., and Zhu, J. Y. (2004). "Rapid determination of hydrogen peroxide in the wood pulp bleaching streams by a dual-wavelength spectroscopic method," *Analytica Chimica Acta* 507(2), 281-284.

Zhao, D.Q., Chen, K.F., Li, J., Mo. L.H., and Xu, J., (2010). "Comparative research on efficiency of chlorine dioxide delignification and oxygen delignification and corresponding bleaching sequences of wheat straw pulp," *CIESC Journal* 4, 988-994.

Emmert, G. L., Coutant, D. E., Sweetin, D. L., Gordon, G., and Bubnis, B. (2000). "Studies of selectivity in the amaranth method for chlorine dioxide," *Talanta* 51(5), 879-888.

Fletcher, I. J., and Hemmings, P. (1985). "Determination of chlorine dioxide in potable waters using chlorophenol red," *Analyst* 110(6), 695-699.

Gierer, J. (1986). "Chemistry of delignification," *Wood Science and Technology* 20(1), 1-33.

Haddad, P. R., Jackson, P. E., and Shaw, M. J. (2003). "Developments in suppressor technology for inorganic ion analysis by ion chromatography using conductivity detection," *Journal of Chromatography A* 1000(1-2), 725-742.

Hamzeh, Y., Benattar, N., Mortha, G., Calais, C. (2007). "Modified ECF bleaching sequences optimizing the use of chlorine dioxide," *Appita Journal* 60(2), 150-154.

Hart, P., and Connell, D. (2008). "Improving chlorine dioxide bleaching efficiency by selecting the optimum pH targets," *Tappi Journal* 7(7), 3-11.

Hui, L., Nonomura, M., and Itoh, N. (2003). "Simultaneous determination of residual chlorine and other anions in water by ion chromatography," *Bunseki Kagaku* 52(9), 819-824.

Ivaska, A., Forsberg, P., and Heikka, R. (1990). "Application of an amperometric sensor to in-line monitoring of pulp bleaching with chlorine dioxide," *Analytica Chimica Acta* 238, 223-229.

Jiang, Z. L., Zhang, B. M., and Liang, A. H. (2005). "A new sensitive and selective fluorescence method for determination of chlorine dioxide in water using rhodamine S," *Talanta* 66(3), 783-788.

Kolar, J. J., Lindgren, B. O., and Pettersson, B. (1983). "Chemical reactions in chlorine dioxide stages of pulp bleaching," *Wood Science and Technology* 17(2), 117-128.

Lindgren, B. O. (1971). "Chlorine dioxide and chlorine oxidations of phenols related to lignin," *Svensk Papperstidn.* 74, 57-63.

Quentel, F., Elleouet, C., and Madec, C. (1994). "Electrochemical determination of low levels of residual chlorine dioxide in tap water," *Analytica Chimica Acta* 295(1-2), 85-91.

Shinb, H. S., and Jung, D. G. (2006). "Determination of chlorine dioxide in water by gas chromatography-mass spectrometry," *Journal of Chromatography A* 1123(1), 92-97.

Sullivan, J., and Douek, M. (1998). "Determination of inorganic chlorine species in kraft mill bleach effluents by ion chromatography," *Journal of Chromatography A* 804(1-2), 113-121.

Svenson, D. R., Jameel, H., Chang, H., and Kadla, J. F. (2006). "Inorganic reactions in chlorine dioxide bleaching of softwood kraft pulp," *Journal of Wood Chemistry and Technology* 26(3), 201-214

Sweetin, D. L., Sullivan, E., and Gordon, G. (1996). "The use of chlorophenol red for the selective determination of chlorine dioxide in drinking water," *Talanta* 43(1), 103-108.

Themelis, D. G., and Kika, F. S. (2006). "Gas-diffusion flow injection assay for the selective determination of chlorine dioxide based on the fluorescence quenching of chromotropic acid," *Microchemical Journal* 82(1), 108-112.

Tzanavaras, P. D., Themelis, D. G., and Kika, F. S. (2007). "Review of analytical methods for the determination of chlorine dioxide," *Central European Journal of Chemistry* 5(1), 1-12.

Wang, Q., Chen, K. F., Li, J., Liu, S. S., and Wang, Z. J. (2010). "A rapid method for determination of silicon content in black liquor by UV spectroscopy," *BioResources* 5(4), 2681-2689.

Watanabe, T., Idehara, T., Yoshimura, Y., and Nakazawa, H. (1998). "Simultaneous determination of chlorine dioxide and hypochlorous acid in water by high-

performance liquid chromatography," *Journal of Chromatography A* 796(2), 397-400.

Zhu,Y. C., Huang, J. L., Shen, Y. L., and Wei, Q. Y. (2001). "Continuous determination of chlorine dioxde in water samples by membrane separation and UV spectro-photometry," *Fenxi Shiyanshi* 20, 58-60.

Zhang, C., Chai, X. S., Luo, X. L., Fu, S. Y., and Zhan, H. Y. (2010). "Rapid method for determination of furfural and 5-hydroxymethyl furfural in pre-extraction stream of biomass using UV spectroscopy," *Spectroscopy and Spectral Analysis* 30(1), 247-250.