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Determination of inorganic chlorine species in kraft mill bleach effluents by ion chromatography

Joseph Sullivan*, Maurice Douek

Pulp and Paper Research Institute of Canada, 570 St. John's Boulevard, Pointe Claire, Quebec H9R 3J9, Canada

Abstract

A sensitive ion chromatography method has been developed for the determination of chlorine dioxide, chloride, chlorite, chlorate and several other anions in kraft mill bleach effluents. The new method overcomes problems found in existing methods, such as low recovery of chlorine dioxide and poor resolution of chlorite from organic anions. The effects of storage time and temperature on the stability of inorganic chlorine species and other ions, in first bleaching, first extraction, final bleaching and combined mill effluent samples were also studied. In addition, the efficacy of ethylenediamine as a preservative for chlorite and its impact on chlorine dioxide in stored samples of final bleaching stage effluent were assessed. © 1998 Elsevier Science B.V.

Keywords: Paper; Kraft mill effluents; Inorganic anions; Chlorine dioxide; Chloride; Chlorate; Chlorite

1. Introduction

Although chlorine dioxide (ClO_2) use in Canadian bleached kraft mills has increased dramatically over the last five years [1], little is known about the effect this has had on the levels of ClO_2 by-products, such as chlorite (ClO_2^-), chlorate (ClO_3^-) and chloride (Cl^-) in bleaching effluents. Moreover, little is known about the stability and/or persistence of these species in the wide array of effluents generated from kraft bleaching operations. Because these species play an important role in corrosion and because of environmental concerns [2], it is important that a rapid and sensitive analytical method be available for quantifying these analytes in a variety of bleaching effluents.

High-performance ion-exchange chromatography (HPIEC or ion chromatography, IC) is a well-established

technique for separating and determining a wide variety of ionic solutes [3,4]. Over the last decade, IC has been used extensively in the pulp and paper industry, and reliable methods have been developed for the determination of sulphur species ([5–7] and references therein) and carbohydrates [8] in wood and process liquors. However, fewer and less comprehensive methods for the analysis of inorganic chlorine species in bleach effluents have been developed [6,9–11]. In addition, many of the methods suffer from limitations in terms of applicability and selectivity. Although sensitive IC methods for determining inorganic chlorine and bromine species in simple matrices such as surface and drinking water have been developed [12–15], many of the methods are somewhat complicated since they specify the use of very weak eluents to achieve adequate resolution of chlorite from interfering species, followed by a post run rinse of the column with a more concentrated eluent to remove

*Corresponding author.

strongly retained ions. This approach precludes the separation and quantitation of other anions in the sample. Moreover, these methods have not been shown to be suitable for determining ClO_2 in kraft mill bleach effluents.

In the current report, we describe a sensitive IC method that is suitable for determining the major inorganic chlorine species and other anions in a variety of bleach effluents. We also examined the effect of storage time, temperature and ethylenediamine (EDA), a reportedly effective preservative for chlorite in water samples, on the stability of these analytes in several effluents.

2. Experimental

2.1. Chromatographic instrumentation and reagents

Ion analyses were conducted on a Dionex Model 4000i ion chromatograph (Sunnyvale, CA, USA) equipped with a quaternary gradient pump module (GPM), conductivity detector (CDM-3), anion self-regenerating suppressor (ASRS) and a Kratos Model 757 UV–Vis detector (Ramsey, NJ, USA). Samples were injected via a Dionex high-pressure injection valve equipped with a 50- μl sample loop. Anions were separated on Dionex IonPac AG12A (25 \times 4 mm) and AS12A (250 \times 4 mm) columns connected in series. The eluent consisted of 25 mM each of H_3BO_3 and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (pH 8.7) and was pumped through the columns at a flow-rate of 1.0 ml/min. Effluent from the columns was first directed through the UV detector, which was set at 205 nm (20 mAUFS) and then through the ASRS and into the conductivity cell. Minimum lengths of polyether ether ketone (PEEK) tubing (130 μm I.D.) were used throughout the chromatographic system. The ASRS was operated in the chemical suppression mode with 10 mM H_2SO_4 as regenerant, delivered at a flow-rate of 5 ml/min. Both the eluent and regenerant were stored in helium-pressurized polypropylene reservoirs (Dionex). Chromatographic data were collected from the detectors with two Hewlett-Packard Model 3396A integrators.

2.2. Chemicals and solutions

Unless specified otherwise, analytical or ACS grade chemicals from Fisher Scientific (Pittsburgh, PA, USA), Aldrich (Milwaukee, WI, USA) and Anachemia (Montreal, Canada) were used to prepare eluent, regenerant and ion standards. Technical grade NaClO_2 (purity: 82.4%, balance: NaCl and NaClO_3) was standardized by iodometry [16]. Dilute mixed standards containing acetate, formate, chloride, chlorate, sulphate and oxalate were prepared daily by dilution of 1000 mg/l solutions of the sodium salt of each reagent in deionized water. Dilute ClO_2^- standards were prepared daily by diluting standard 1000 mg/l stock solutions in water. Aqueous ClO_2 (ca. 6–7 g/l) was obtained from Paprican's bleaching group and was standardized by iodometry [16]. Stock ClO_2^- and ClO_2 solutions were stored in glass containers, in the dark at 4°C to minimize thermolytic and photolytic degradation [17]. Thirty five percent H_2O_2 was diluted to 10% prior to use in ClO_2 reductions. Dilute NaOH (0.1 M) was prepared by dilution of 50% NaOH with deionized water.

2.3. Sample collection and storage

Samples were collected from an eastern Canadian hardwood bleached kraft mill operating with a Dc, Eo, D, E, D (five-stage) bleaching sequence (where D, c, E and o refer to chlorine dioxide, chlorine, extraction and oxygen, respectively), with 75% ClO_2 substitution in the first bleaching stage. The mill was equipped with a clarifier and a settling basin (hydraulic retention time ca. 18 h).

Grab samples of Dc, Eo, final D stages and both untreated and combined bleached kraft mill effluent (BKME, clarifier inlet and outlet) were stored in polypropylene bottles (Nalgene), in the dark at 4 and 25°C. Sufficient EDA was added to the final D-stage sample to give a concentration of 50 mg/l. All samples were analyzed within 4 h of collection and at regular intervals thereafter over a four-week period.

2.4. Sample preparation

Samples destined for ClO_2 analysis were diluted in water containing 0.1 mM NaOH and 12 mM H_2O_2 .

(ambient pH 9–9.5), and then injected into the IC system. The chlorite result obtained in this manner represents the chlorite originally present in the sample plus chlorite formed by the reduction of chlorine dioxide. Chlorite and other anions originally present in the sample were determined in a separate aliquot that had been sparged with He to remove ClO_2 , as described below.

Typically, 50 ml of effluent along with a PTFE-coated stirring bar were placed in a 125-ml gas washing bottle (ACE Glass, Vineland, NJ, USA, cat. No. 7164-06). The apparatus was then placed on a magnetic stirring plate and the sample was mixed vigorously as it was sparged with He at a flow-rate of 200–300 ml/min for 15 min.

3. Results and discussion

3.1. Development of chromatographic conditions

The determination of chlorite and other inorganic chlorine species in bleach effluents is complicated by the presence of relatively high concentrations of acetic, chloroacetic and, in particular, formic acid. Improved resolution and more reliable identification of chlorite and other ions was achieved by performing separations on a recently developed high capacity anion-exchange column [18], in combination with a boric acid–tetraborate eluent and coupled UV–conductivity detection, as illustrated in Fig. 1. As indicated, chlorite and organic acids produce a similar response in the conductivity detector, while the response of the acids relative to chlorite in the UV detector is significantly lower, thus providing a more sensitive and reliable means of identifying chlorite in the presence of high concentrations of formate.

Linear regression results from plots of relative peak height versus concentration for the major ions of interest had correlation coefficients of 0.999, over the concentration range of 0.1 to 10 ppm for ions of interest. Very reproducible retention times and peak heights were obtained for all ions studied, with relative standard deviations (R.S.D.s) in the range of 1 to 2%.

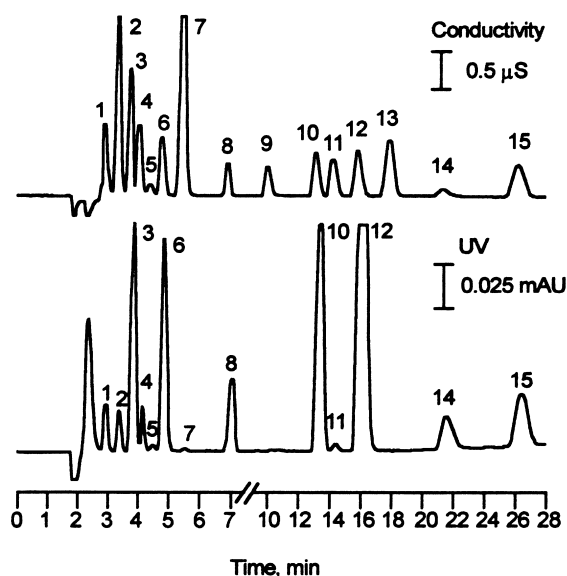
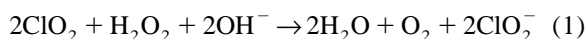


Fig. 1. Separation of anions on IonPac AG12A/AS12A columns using a borate–tetraborate eluent with coupled UV and suppressed conductivity detection. Other conditions as described in Section 2. Each solute present at 2 mg/l (except carbonate, which arises from dissolved CO_2 present in the dilution water). Peaks: acetate (1), formate (2), chlorite (3), chloroacetate (4), carbonate (5), bromate (6), chloride (7), dichloroacetate (8), orthophosphate (9), bromide (10), chlorate (11), nitrate (12), sulphate (13), trichloroacetate (14), oxalate (15).

3.2. Determination of ClO_2

Because ClO_2 is not ionized in solution, it is not amenable to separation by IC, but can be analyzed if some means can be found to reduce it to ClO_2^- prior to or during IC analysis. According to Easty et al. [9], aqueous ClO_2 (in the range of 1–20 mg/l) is quantitatively reduced to ClO_2^- upon injection onto the IC column, via reaction with the ion-exchange resin. However, using the recommended columns (Dionex AG3/AS3) and eluent (Na_2CO_3), we were unable to obtain quantitative conversion of ClO_2 to ClO_2^- at concentrations above 1 mg/l of ClO_2 . Moreover, ClO_2^- yield decreased with increasing ClO_2 concentration. Low yields of ClO_2^- from injected ClO_2 were also observed in our current work when samples were simply diluted in water and injected, which indicates that the problem is independent of column material and the eluent used in the analysis.

We found that hydrogen peroxide was an excellent reagent for converting ClO_2 to ClO_2^- . Under alkaline conditions, H_2O_2 reduces ClO_2 to ClO_2^- according to the following reaction [17,19,20].



The main advantage of using peroxide is that ClO_2 is reduced to ClO_2^- exclusively, and neither the reactants nor the products of the reaction are detrimental to or interfere with the IC analysis. Furthermore, it is only necessary that the solution be moderately alkaline ($\text{pH} > 8$) and thus exact pH control is not necessary, thereby simplifying the sample preparation procedure. It was found that hydrogen peroxide did not produce a response in the conductivity detector, but did possess a significant absorption at 205 nm. Fortunately, H_2O_2 eluted near the void volume (retention time ca. 2.6 min) and hence did not interfere with the determination of chlorite, which eluted at ca. 3.9 min.

The choice of solvent for sample dilution was found to have a significant effect on the efficiency of the reduction of ClO_2 with peroxide, as shown in Fig. 2. Injection of ClO_2 standards prepared in water resulted in about a 70% conversion at the 1 mg/l level and decreased nearly linearly to about 55% at

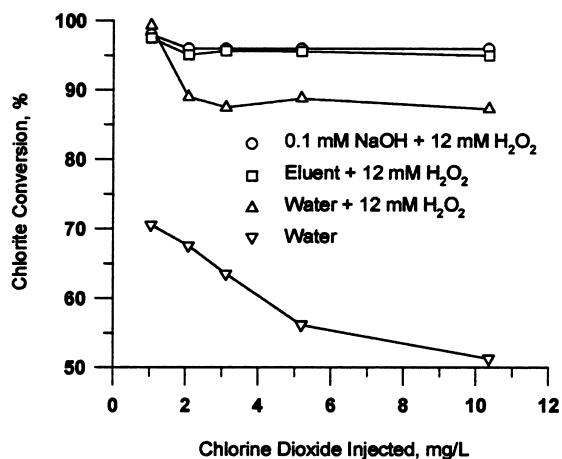


Fig. 2. Effect of dilution medium on the conversion of chlorine dioxide to chlorite. Samples of ClO_2 were prepared in the solvent combinations indicated and injected into the IC system. Results obtained using UV detection at 205 nm, other conditions as described in Section 2.

the 10 mg/l level. Dilution in water containing a stoichiometric excess of H_2O_2 gave 100% conversion at the 1 mg/l level, but dropped to about 90% at levels above 1 mg/l. Dilution in eluent (pH ca. 8.7) with excess peroxide or dilution with 0.1 mM NaOH and excess peroxide (final solution pH ca. 9) produced equivalent results, with conversions of about 95–98% over the entire concentration range. The use of eluent as diluent is not recommended however, since it was discovered that ClO_2^- appears to form a complex with borate–tetraborate. This is supported by the observation that a broader peak with a slightly shorter retention time and a significantly lower peak height was obtained for ClO_2^- standards prepared in eluent. A plot of peak height for chlorite standards prepared in eluent was linear, but as expected, had a lower slope than that obtained for chlorite standards prepared in water. Interestingly, peak areas for chlorite standards prepared in eluent or water were identical, which suggests that uncomplexed and complexed forms of ClO_2^- have the same absorptivity at 205 nm. A literature search for reports on the complexation of chlorite with borate–tetraborate was unfruitful, but did reveal that chlorine dioxide can form a complex with perborate [21]. In view of the structural similarities between the two species, it is not surprising that ClO_2^- also appears to form a complex with borate–tetraborate. Based on these findings, it is essential that standards and samples be prepared in water containing 0.1 mM and 12 mM each of NaOH and peroxide, respectively.

3.3. Analysis of bleach effluents

3.3.1. Dc, BKME and Eo effluents

The initial concentrations of selected ions found in various effluents are summarized in Table 1. As indicated, IC analyses of Dc and BKME effluents (clarifier inlet and outlet) showed that chlorine dioxide and chlorite were not present in either sample. This is due to rapid decomposition of both species during pulp bleaching and through reactions with numerous dissolved organic and inorganic compounds present in both effluents. As expected, relatively high levels of Cl^- and ClO_3^- , the two major by-products of ClO_2 bleaching, as well as formate were present. Lower levels of chlorinated acetates, sulphate, oxalate and traces of phosphate

Table 1
Initial concentrations of selected anions in the effluents examined in the stability study

Sample	[Anion] ^a (mg/l)					
	Formate	Chlorine dioxide	Chlorite ^b	Chloride	Chlorate	Sulphate
Dc-stage	417±8	ND	ND	2378±7	1208±3	132±2
Eo-stage	176±7	ND	27±1	714±7	263±3	34±2
Final D-stage	18±1	27±1	21±1	253±7	205±2	25±2
Clarifier inlet	60±4	ND	ND	325±6	146±3	35±2
Clarifier outlet	ND	ND	ND	362±8	ND	95±3

Results are based on triplicate determinations.

^a Mean±standard deviation.

^b Chlorite results are based on UV detection.

ND=Not detected.

and nitrate were also found. About 400 mg/l of formate was found in the Dc-stage effluent and about 60 mg/l in the BKME sample. Most of the formate found in bleach effluents probably originates from the ClO₂ bleach liquor. This is supported by the work of Hoq and co-workers [22,23], which showed that bleach liquors from commercial ClO₂ generators contain up to 0.3 M formate.

Eo-stage effluent was found to contain significant concentrations of acetate, formate, chlorite, carbonate, chloride and chlorate, with lower levels of trichloroacetate, sulphate, oxalate and a trace of nitrate.

3.3.2. Final D-stage effluent

All four inorganic chlorine species along with several other ions were found in final D-stage effluent as illustrated in Fig. 3. The presence of both chlorine dioxide and chlorite indicates that both species are relatively unreactive toward the dissolved organic and inorganic components present in the effluent. This finding is not surprising, since most of the reactive wood components, such as lignin, have been removed in previous bleaching stages. The level of formate was considerably lower in this effluent, as expected, based on the relatively low charge of ClO₂ used in this bleaching stage.

3.3.3. Recovery of ions from bleach effluents

The quantitative nature of the method was assessed by performing spike-recovery experiments with the four types of effluent. Samples of sparged final D-stage effluent were spiked with three levels of each of the four inorganic chlorine species and

analyzed as described in Section 2. As shown in Table 2, recovery of the four species at each level of spiking ranged between 95±4% and 106±7%. A further spiking experiment was performed with Dc, Eo and BKME effluents. Samples of each effluent were spiked with one level of chloride, chlorate, formate and sulphate. Chlorine dioxide and chlorite were not included in the study (except for Eo effluent which was spiked with ClO₂⁻) because of their instability in Dc and BKME effluents. As shown in Table 3, all analytes were quantitatively recovered

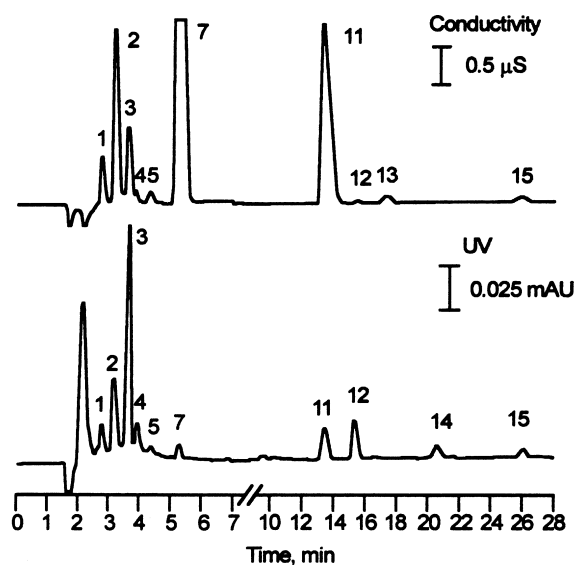


Fig. 3. Separation of anions in a sample of final D-stage effluent sparged with He. After sparging, the sample was diluted 1:25 with water and injected into the IC system. Peak identities as indicated in Fig. 1, other conditions as described in Section 2.

Table 2
Recovery of chlorine species from final D-stage effluent

Analyte	[Analyte] (mg/l)			Recovery (%)
	Original (mean±S.D.)	Added	Found (mean±A.D.)	
Chlorine dioxide	27.0±0.9	10.0	10.6±0.7	106±7
		25.0	24.2±1.2	97±5
		50.0	47.6±1.8	95±4
Chlorite	20.9±0.5	10.0	10.2±0.2	102±2
		25.0	24.6±0.3	98±1
		50.0	48.2±0.5	96±1
Chloride	253±7	100	105±6	105±6
		250	243±7	97±3
		500	493±5	99±1
Chlorate	205±2	100	98±2	98±2
		250	245±3	98±1
		500	491±5	98±1

Results for original and spiked samples are based on triplicate and duplicate determinations, respectively.

S.D. = Standard deviation.

A.D. = Average deviation.

Chlorite results are based on UV detection.

Table 3
Recovery of anions from Dc, Eo and untreated BKME samples

Analyte	[Analyte] (mg/l)			Recovery (%)
	Original (mean±S.D.)	Added	Found (mean±S.D.)	
<i>Dc effluent</i>				
Chloride	2378±7	1000	1017±8	102±1
Chlorate	1208±3	500	513±5	103±1
Formate	417±8	400	392±6	98±2
Sulphate	132±2	100	96±2	96±2
<i>Eo effluent</i>				
Chlorite	27±1	20	19±1	95±5
Chloride	714±7	500	492±6	98±2
Chlorate	263±3	200	205±7	103±3
Formate	176±7	200	209±5	105±2
Sulphate	34±2	25	24±1	96±4
<i>BKME (clarifier inlet)</i>				
Chloride	325±6	250	262±6	105±2
Chlorate	146±3	100	104±4	104±4
Formate	60±4	50	51±3	102±6
Sulphate	35±2	25	24±2	98±6

Results for original and spiked samples are based on triplicate and duplicate determinations, respectively.

Chlorite results are based on UV detection.

from each sample, with recoveries ranging between $95 \pm 5\%$ and $105 \pm 2\%$.

3.4. Stability of chlorine species during storage

Under suitable conditions, both ClO_2 and ClO_2^- are known to react with a wide variety of organic compounds and both species are thermolytically and photochemically degraded in aqueous medium. Moreover, ClO_2 is unstable in alkaline medium and ClO_2^- disproportionates in acidic medium. Recent studies have also shown that ClO_2^- is unstable in water samples containing Fe^{3+} [24] and OCl^- [13,14]. Recent work by Hautmann et al. [13,14] has demonstrated that EDA is effective at stabilizing ClO_2^- in groundwater and reagent water samples stored in the dark at 4°C for up to two weeks. The effectiveness of EDA is due to its ability to form a stable complex with Fe^{3+} and its ability to react with OCl^- to form Cl^- .

It was expected that both ClO_2 and ClO_2^- would be considerably less stable in bleaching effluents due to the presence of numerous organic and inorganic solutes present in these matrices. Consequently, the effects of storage time and temperature on the stability of a number of ions in Dc, Eo, BKME and final D-stage effluents were studied. In addition, the efficacy of EDA as a preservative for chlorite in BKME and final D-stage effluent was assessed.

3.4.1. Dc, Eo and final D-stage effluents

The study revealed that formate, chloride, chlorite, chlorate and sulphate were stable in Dc and Eo effluent samples stored at 4°C over the course of the study period, and thus sample refrigeration is an effective means of preventing ion degradation. As indicated previously, ClO_2 and ClO_2^- were not detected in Dc-stage effluent and Eo-stage effluent was found to contain a relatively low level of ClO_2^- .

As illustrated in Fig. 4, both EDA and temperature had a significant effect on the stability of ClO_2 and ClO_2^- in final D-stage effluent. In the absence of EDA, chlorine dioxide was stable for up to two weeks in samples stored at 4°C and decreased by more than 50% over the same time period in samples stored at 25°C . In the presence of EDA, ClO_2 decreased by about 50% in samples stored for two weeks at 4°C , and was essentially completely de-

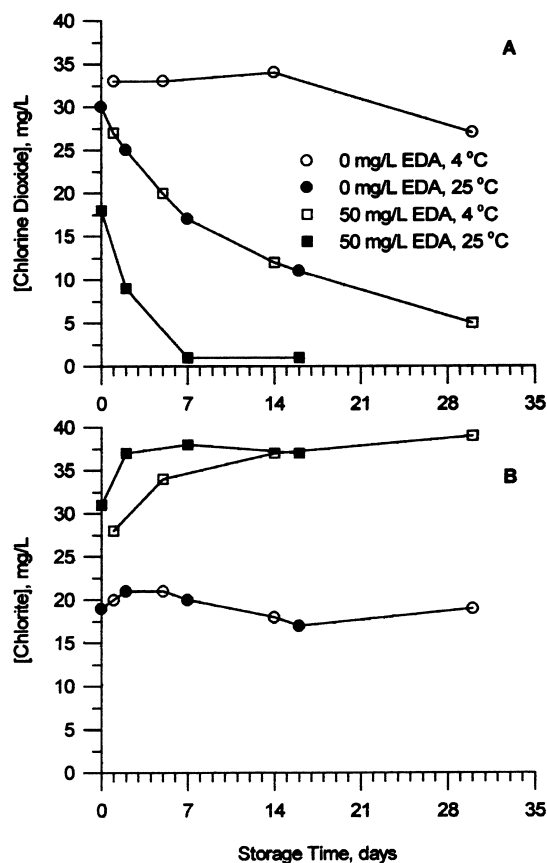


Fig. 4. Effect of storage time, temperature and EDA on the stability of chlorine dioxide (A) and chlorite (B) in final D-stage effluent. Total ClO_2^- , which represents the sum of ClO_2 and ClO_2^- originally present in the effluent, was determined by diluting a sample of unsparged effluent 1:25 in water containing NaOH and H_2O_2 . The ClO_2 result was obtained with a sparged sample of effluent that had been diluted 1:25 with water. The ClO_2^- concentration of the sample is obtained by subtracting the two ClO_2 results. Other conditions as described in Section 2.

composed in samples stored for one week at 25°C . The effect at 4°C was similar to that observed for samples stored at 25°C without EDA present. An examination of the literature revealed that others have reported ClO_2 to be unstable in the presence of EDA as well as tertiary and polyamines [20,25]. In the current work, it appears that ClO_2 reacts with EDA to form ClO_2^- and probably other inorganic chlorine products. Evidence to support the formation of ClO_2^- from the reaction between ClO_2 and EDA is shown in Fig. 4B. As indicated, chlorite levels

increased to about 38 mg/l in both final D-stage samples containing EDA after 1–2 weeks of storage, and then leveled off and remained constant for up to four weeks of storage. The two samples which did not receive EDA remained approximately constant over the same four-week period. The decrease in ClO_2 at 25°C (Fig. 4A), does not result in an equivalent increase in ClO_2^- . This indicates that Cl^- rather than ClO_2^- was produced by the reaction between EDA and ClO_2 during sample storage. Consequently, the addition of EDA to samples containing ClO_2 should be avoided. The most effective means of preserving both ClO_2 and ClO_2^- in final D-stage effluent is simply to store samples at 4°C in the absence of light.

Storage temperature and EDA had little effect on the stability of Cl^- and ClO_3^- in final D-stage effluent. The levels of Cl^- appeared to rise slightly over the first two weeks in samples stored at 4°C with and without EDA present, and remained nearly constant in samples stored at 25°C. Chlorate was approximately constant in samples stored at 4 and 25°C, with and without EDA present.

3.4.2. BKME

Analysis of the BKME effluent revealed that neither ClO_2 nor ClO_2^- were present in either the inlet or the outlet samples. The results also showed that formate and chlorate were less stable in the clarifier inlet sample that was stored at 25°C when compared to the sample stored at 4°C, while chloride and sulfate were about equally stable at 4 and 25°C. An increase in chloride levels found on day 21 in the inlet sample stored at 25°C corresponds approximately to the decrease in chlorate observed in the same sample stored at the same temperature, possibly indicating that microbial or other degradative mechanisms are responsible for the loss of chlorate and formate over an extended period of time. Neither formate nor chlorate were found in the clarifier outlet sample and both chloride and sulfate levels remained constant over the four-week study period. These results suggest that significant degradation of chlorate and organic compounds such as formate are occurring during the ca. 18-h period which the effluent spends in the settling basin.

To illustrate the instability of chlorite in BKME, separate aliquots of clarifier outlet sample were diluted 1:5 with water and spiked with ClO_2^- (2

mg/l) alone, and ClO_2^- (2 mg/l) along with EDA (50 mg/l). Analysis of the chlorite content at regular intervals thereafter showed that in the absence of EDA, ClO_2^- was completely degraded within 30 min. Even in the sample containing 50 mg/l of EDA, the concentration of ClO_2^- decreased by about 50% after 1 h and by about 75% after 2 h. This result indicates that ClO_2^- may be degraded by a wide array of substances, such as suspended solids, wood fibers and inorganic solutes present in BKME. These findings are in sharp contrast to results obtained by NCASI workers, which indicate that as little as 0.1 to 0.4 mg/l each of ClO_2^- and ClO_3^- can be stabilized for up to 48 h in BKME samples that received 50 mg/l of EDA and 80 mg/l NaOH, and were stored at 4°C [11]. One possible explanation for the increased stability of ClO_2 observed in the NCASI study may be due to the use of NaOH, which increases the pH of the effluent considerably. Chlorite is reportedly stable in mildly alkaline solutions for up to a year if care is taken to exclude light [20].

4. Conclusions

A sensitive IC method has been developed for the determination of the major inorganic chlorine species and a number of other anions in kraft bleach effluents. Unlike previous methods reported in the literature, the new method allows for the analysis of the ions of interest in a single isocratic run and eliminates interferences from organic anions, such as acetate, formate and chloroacetate, in the determination of chlorite. A simple procedure, involving dilution of samples in mildly alkaline hydrogen peroxide was developed, to ensure quantitative reduction of ClO_2 to ClO_2^- prior to sample injection. Recovery of ions from spiked samples ranged between 95 and 106% with R.S.D.s between 3 and 7% and all ions were stable for up to three weeks in samples stored at 4°C. The addition of EDA to stabilize chlorite was not suitable for samples containing chlorine dioxide.

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