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Determination of Chlorite and Chlorate in Chlorinated and Chloraminated Drinking Water by Flow Injection Analysis and Ion Chromatography

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This research investigated the determination of chlorite and chlorate concentrations in drinking water by flow injection analysis (FIA) with iodometric detection and ion chromatography (IC) with conductivity detection. The FIA and IC methods were accurate and effective for reagent water. The IC method was accurate for measurement of chlorite and chlorate concentrations in drinking water even in the presence of other oxidants including chloramines. However, FIA was affected by chloramines and other oxidants in drinking water, resulting in inaccurate determinations. While chlorite concentrations were unstable in chlorinated drinking water, addition of sodium oxalate increased the stability to up to 3 days and addition of ethylenediamine increased stability to up to 18 days. Chlorate concentration were stable in drinking water for up to 18 days with or without a preservative.

INTRODUCTION

Chlorine dioxide (ClO_2) is a widely used disinfectant and bleaching agent that is currently being used by many drinking water treatment utilities in the United States, Canada, and Europe for oxidation and disinfection.[1-3] It is frequently applied as an initial oxidant during treatment, followed by chlorination (gaseous Cl_2 or HOCl) as a final disinfectant. When used as an oxidant, chlorine dioxide reacts to form chlorite (ClO_2^-) and chlorate (ClO_3^-), which have been shown to cause hemolytic anemia in laboratory animals.[4,5] Both ClO_2^- and ClO_3^- concentrations are currently under consideration for regulation by EPA and because of possible adverse health effects will likely be regulated with a maximum contaminant limit of <1.0 mg/L for combined chlorine dioxide, chlorite, and chlorate.[6,7]

Because regulations are imminent and the need exists to protect human health, accurate methods for monitoring these compounds in drinking water are needed. This paper discusses two emerging methods of analysis for low milligram per liter concentrations of chlorite and chlorate in drinking water: a flow injection analysis (FIA) method with iodometric detection and an ion chromatographic (IC) method.

Analysis of individual chlorine-containing oxidants in drinking water has been problematic because other similar oxidant species in drinking water will interfere.[8-11] Possible oxidants in water treated with chlorine dioxide and chlorine include HOCl, OCl^-, ClO_2, ClO_2^-, ClO_3^-, inorganic chloramines (particularly monochloramine, NH_2Cl), and organic chloramines. The chloramines are produced from the reaction of chlorine with ammonia and organic amines naturally present in the water. Under chlorination conditions used for surface waters, the amount of inorganic chloramines produced greatly exceeds the amount of organic chloramines produced.[12] Chloramines have been demonstrated to interfere with amperometric and colorimetric (e.g., *N,N*-diethyl-*p*-phenylenediamine) determination of aqueous free chlorine ([HOCl] + [OCl^-]).[9,10] Consequently, a challenge in measuring chlorite and chlorate in drinking water is to maximize the response of these two species while minimizing the interferences from other oxidants present. Additionally, chlorine and ClO_2^- can react in drinking water to produce ClO_2 which volatilizes and, therefore, changes the concentration of ClO_2^-.[13,14] If a drinking water sample is to be stored prior to analysis, then a preservative is necessary to inactivate chlorine (Cl_2, HOCl, OCl^-), thus preventing reaction between ClO_2^- and chlorine.

FIA is a colorimetric method in which pH and reaction time are controlled to selectively allow certain oxidants to react with iodide to produce iodine. The FIA method for chlorite and chlorate was developed by Gordon and his colleagues.[8,14-17] The FIA method depends upon reproducible reaction rates but does not necessarily require the reaction between the oxidant and iodide to go to completion.

The FIA method for the determination of chlorine, chlorine dioxide, chlorite, and chlorate in one sample is summarized as follows. The processes described, e.g., pH adjustment, iodide addition, sparging, acidification, are performed sequentially on the same sample aliquot. Initially, the sample pH is adjusted to pH >8; combined chlorine and chlorine dioxide is measured. At this pH, aqueous chlorine dioxide and chlorine react rapidly with iodide to form iodine. Chlorite and chlorate ion react too slowly to be detected in the same time frame. The aqueous sample is then treated with either oxalic acid or sodium oxalate to react with the free chlorine

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so that it can no longer react with iodide; chlorine dioxide alone is measured. The chlorine concentration is calculated by difference. Chlorine dioxide is sparged from the sample with nitrogen or helium gas. This oxalate-treated and sparged sample is reacted with iodide at pH 1.1; chlorite reacts rapidly, but chlorate reacts too slowly to be detected. The sample pH is then decreased to pH <1 with concentrated HCl, allowing both chlorite and chlorate to react with iodide.

All species are quantitated relative to standard curves. The concentration of chlorate is calculated by a multiple regression analysis in which the chlorite concentration (measured at pH 1.1) is subtracted from the total chlorate and chlorite concentrations measured at pH <1; the number of electrons transferred and the relative molecular weights of chlorite and chlorate are accounted for in the calculation.[16,18] This method is linear for the detection of chlorite in the range from 0.1 to 10.1 mg/L and chlorate from 0.1 to 8.3 mg/L for combined solutions of chlorite and chlorate in reagent water.[16] If only chlorite and chlorate are to be measured in a drinking water sample, then the chlorine dioxide is sparged with nitrogen, and approximately 300–400 mg/L sodium oxalate is added as a preservative to remove free chlorine, and the sample is stored for >12 h prior to analysis.[14]

An ion chromatographic analysis for chlorite and chlorate in drinking water has been developed.[16,19] Concentrations of 0.05–5.0 mg/L chlorite and 0.05–5.0 mg/L chlorate can be detected in drinking water. Although oxalate can also be used to preserve samples for IC analysis, the oxalate anion has a long retention time under the conditions used for the chlorite and chlorate analyses (approximately 40 min). A nonanionic preservative is preferred for IC analyses. Ethylenediamine can be used as a preservative to inhibit the reaction of chlorine with chlorite and allow drinking water samples to be stored for several days prior to IC analysis.[20,21]

Recent experiments in our laboratory involved analyzing chlorite and chlorate in drinking water field samples obtained from water utilities throughout the United States. Several drinking water samples preserved with sodium oxalate and quality control check samples prepared in reagent water were split and analyzed by both FIA and IC. The expected concentration ranges were 0.5–3 mg/L ClO_2^- and 0.1–1.0 mg/L ClO_3^-. Results indicated that the FIA and IC measurements agreed for concentrations of the check samples. Application of a paired t test to the check sample data demonstrated no significant difference at the 99% confidence level for either chlorite ion ($p = 0.321$) or chlorate ion ($p = 0.250$). There was notable disagreement between the two methods for the analysis of some drinking water samples, including water samples from a utility which applied chloramines. Statistical analysis of the field sample data, using a paired t test, demonstrated that the results were significantly different at the 99% confidence level for both ClO_2^- ($p = 0.001$) and ClO_3^- ($p = 0.001$). The FIA method yielded values for chlorite up to 2 mg/L higher than those determined by IC for the same drinking water sample. The chlorate values by FIA were up to 0.8 mg/L lower than those determined by IC. Additionally, the chlorate values measured by FIA were frequently negative by several tenths of a mg/L. The disagreement between the two methods was most pronounced at concentrations <1.5 mg/L ClO_2^- and 1 mg/L ClO_3^-. At concentrations of chlorite near 3 mg/L ClO_2^-, the methods were in close agreement.

The current research investigated the performance of FIA and IC analysis methods for chlorite and chlorate concentrations in drinking water. The effect of preservative type, chemical matrix of the water, and analytical method on the determination of chlorite and chlorate in drinking water were investigated. Experiments were designed to evaluate the long-term effects of the sodium oxalate and ethylenediamine preservatives, the ability of FIA and IC to quantitate check samples when standard curves prepared in different water matrices were used, and the effect of drinking water oxidants and chloramines on FIA and IC measurements of chlorite and chlorate.

EXPERIMENTAL SECTION

Reagents. The following certified ACS-grade chemicals were purchased from Fisher Scientific (Pittsburgh, PA): sodium borate, boric acid, potassium iodide, potassium chlorate, sodium oxalate, sodium hypochlorite, and concentrated (~12.1 N) hydrochloric acid. Anhydrous ethylene diamine (99.9%) was also purchased from Fisher Scientific. Ultrapure sodium chlorite was purchased from Novatec (Oxford, OH) and stored in a desiccator over phosphorus pentoxide until use. Reagent water consisted of distilled water which was processed through a Milli-Q water purification unit (Millipore Corporation, Milford, MA). Reagent water samples were not sparged with helium or nitrogen prior to determination of chlorite of chlorate ion.

Drinking water used for preparation of laboratory solutions was obtained from a conventional water treatment plant which treated river water. The treatment process consisted of prechlorination, lime addition, fluoridation, coagulation by polyaluminum chloride, flocculation, sedimentation through rapid sand filters, and then post chlorination with a target concentration of 1 mg/L chlorine. No chlorine dioxide or chlorite was used in the treatment train; therefore, these samples were not sparged with either helium or nitrogen prior to determination of chlorite or chlorate. Typical fluoride, chloride, and nitrate concentrations were 1, 6, and 1 mg/L respectively.

FIA Method. A Tecator FIAstar Model 5020, with a photometer (Novatek s-1000-200), 1 cm path length cell (18 μL), and 360-nm filter (Tecator 5024) was used in all analyses. Tubing diameters were 3.5-mm i.d. for delivery of sample, buffer, and KI solutions, with 0.5-mm i.d. throughout the remainder of the FIA system. The flow rate through each 3.5-mm i.d. tube was 0.9 mL/min.[14] A 0.3 M KI solution was used in all analyses. The sample volume was 200 μL, and triplicate measurements were made of each sample. The average of these three measurements was used in analysis of data. Sodium oxalate was used as a preservative for FIA analyses.

A pH 8 buffer solution consisting of 8.75 mM sodium borate and 65 mM boric acid was used for Cl_2 and ClO_2 measurements. For ClO_2^- measurements at pH 1.1, the buffer solution was pH 1.1 HCl. Reaction coils of 30 cm for the buffer solution and 30 cm for the KI solution were used for the determination of chlorine, ClO_2, and ClO_2^-. For ClO_3^- measurements at pH <1, the buffer solution was 12 M HCl used directly from the reagent bottle. Reaction coils of 2 and 3 m were used for mixing the buffer and KI solutions, respectively.

Chlorine and chlorite were quantified by comparison of sample absorbance to standard curves prepared from analysis of four or five samples of known concentration. Chlorate was quantified by a multiple regression procedure which involved analysis of 18 standard solutions containing chlorate only, chlorite only, and chlorate plus chlorite to generate a standard curve (see Table I for concentrations).[16]

IC Method. A Dionex Ion Chromatograph 2010i (Sunnyvale, CA) with a conductivity detector, AS9 analytical column, AMMS1 suppressor, and 50- or 100-μL sample injection loop was used for all analyses. The eluant developed for this research consisted of 2.8 mM bicarbonate and 0.4 mM carbonate at 2.0 mL/min; the suppressor used with the carbonate eluant was 0.025 N H_2SO_4 at 4.0 mL/min. A four- or five-point standard curve was developed and the peak height vs concentration regression was used to quantify unknown concentrations. The average retention time for chlorite was 1.4 min while that for chlorate was 3.4 min. The average retention times for fluoride, chloride, and nitrate, were 1.08, 1.8, and 3.8 min, respectively. Both sodium oxalate and ethylenediamine were used as preservatives for samples analyzed by IC.

Stability Study. The stability of ClO_2^- and ClO_3^- in solution was evaluated by periodic analyses of solutions prepared in waters of different matrices and stored for 2.5 weeks at 7 °C. Drinking-water solutions, some with either 350 mg/L sodium oxalate (NaOx) or 50 mg/L ethylenediamine (ED), and some without

Table I. Concentrations of Chlorite and Chlorate Used To Prepare Standard Curves for Analyses of Check Samples

series 1, ClO_2^- only, mg/L	series 2, ClO_3^- only, mg/L	series 3, combined	
		ClO_2^-, mg/L	ClO_3^-, mg/L
0.2	0.2	0.2	0.2
0.5	0.3	0.5	0.3
0.7	0.5	0.7	0.5
1.0	0.7	1.0	0.7
2.0	1.0	2.0	1.0
3.0	2.0	3.0	2.0

preservative, were prepared and stored headspace-free for 20 h prior to the addition of chlorite and chlorate. Then ClO_2^- and ClO_3^- were added to produce concentrations of 1.0 and 0.5 mg/L, respectively. A control sample was prepared from the same drinking water that was used in the preparation of the chlorite and chlorate solutions.

A solution containing 1.0 mg/L ClO_2^- with 0.5 mg/L ClO_3^- was prepared in reagent water. This reagent solution was divided into six aliquots, two preserved with 350 mg/L NaOx, two with 50 mg/L ED, and two without preservative. A reagent water blank sample containing no ClO_2^-, ClO_3^-, or preservative also was prepared. All samples were stored at 7 °C. The samples were analyzed by IC at approximately 2, 12, 28, 48, 72, 95, 120, 144, 216, and 413 h. At each time interval, fresh standard curves were prepared in reagent water from chlorite and chlorate salts. Each sample's concentration was plotted against time in order that changes might be observed. Regression analysis was performed on all data within an experimental treatment to determine which lines had slopes significantly different from zero.

Evaluation of Check Samples by FIA and IC. The FIA and IC methods were compared for analysis of check samples containing chlorite (0.25–2 mg/L ClO_2^-) and chlorate (0.25–1.36 mg/L ClO_3^-). The quality control check samples were prepared in reagent water by an independent analyst. The check samples were quantitated against standard curves prepared in reagent water and drinking water; the standards were preserved with sodium oxalate when analysed by FIA and ethylenediamine when analyzed by IC. This approach permitted the use of the same check sample for both FIA and IC analyses, since the standard curves, and not the check samples, contained preservatives. All samples were analyzed within 72 h of preparation.

Solutions for standard curves were prepared in reagent water and drinking water (which contained 1.2 mg/L chlorine, as Cl_2, as measured by a Fisher Scientific Model 450 computer aided titrimeter) by appropriate dilutions of 100 mg/L stock of ClO_2^- or ClO_3^- in reagent water (Table I). The drinking water used for the preparation of chlorite and chlorate standards was dosed with the appropriate preservative (either sodium oxalate or ethylenediamine) and stored for 20 h at 7 °C prior to adding ClO_2^- or ClO_3^-. This was done to inactivate the chlorine and prevent its reaction with chlorite to form chlorine dioxide.

The accuracies of the FIA and IC methods were determined by a comparison of the actual concentrations to the measured concentrations. A two-way ANOVA was performed to compare variations among the two methods and two matrices. A Tukey HSD multiple comparison test was performed to analyze pairwise comparisons.

Chloramine Study. In order to assess possible interferences from other oxidizing species, chlorite and chlorate solutions were prepared in drinking water containing chloramines and analyzed by both FIA and IC. The drinking water was determined to contain an average free chlorine concentration of 1.2 mg/L and 0.1–0.2 mg/L as monochloramine by a computer-aided titrimeter. Drinking water containing chloramines was prepared by treating chlorinated drinking water with ammonium chloride in a ratio of three parts ammonia to one part chlorine (weight to weight ratio). The solutions were mixed, allowed to react for 25 min, and then reanalyzed for chlorine and monochloramine by computer-aided titrimeter.

Samples for analysis by FIA were preserved by adding 350 mg/L sodium oxalate to drinking water containing 0.29 mg/L HOCl (as Cl_2) and 1.02 mg/L monochloramine. Samples for analysis by IC were prepared by adding 50 mg/L ethylenediamine to drinking water containing 0.20 mg/L HOCl (as Cl_2) and 1.00 mg/L monochloramine. These preserved, chloramine-containing waters were stored for 22 h and then used to make chlorite and chlorate solutions as indicated in Table I.

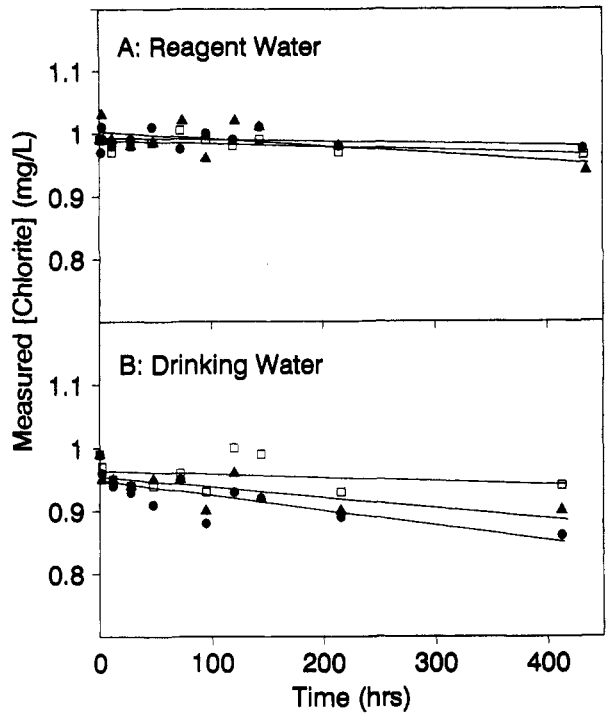

Figure 1. Stability study for chlorite. Top (A) is in reagent water, bottom (B) in drinking water: ● indicates control with no preservative, □ indicates ethylenediamine added, and ▲ indicates sodium oxalate added.

FIA was used to measure chlorite at pH 1.1, chlorate at pH <1, and the residual absorbance at pH 8 after sodium oxalate had been added to inactivate chlorine. Only chlorite and chlorate were measured by IC. Solutions were prepared to the concentrations listed in Table I. Standards prepared in reagent water were analyzed simultaneously. All samples were analyzed within 72 h of preparation.

Regression analysis fitting measured values to actual values was performed on each matrix and method comparison. Each curve was tested for a slope significantly different from 1 and an intercept significantly different from 0.

Statistics. All statistical analyses were performed using SYSTAT, version 5.0.

RESULTS AND DISCUSSION

Stability Study. The stability data for chlorite and chlorate during a 2-week period are shown in Figures 1 and 2, respectively. The IC method was used for analysis of chlorite and chlorate for all data presented in these two figures. Regression analyses for chlorite indicated that only the slopes for the drinking water with no preservative and drinking water with sodium oxalate were significantly different from zero at the 99% confidence level ($\alpha = 0.01$). Chlorite was stable in reagent water with or without a preservative and stable in drinking water when ethylenediamine was added as a preservative. The chlorite concentration in unpreserved drinking water declined to approximately 95% of the initial value within 12 h, to 88% of initial within 96 h, and continued to decline throughout the study. The significant drop in the first 96 h, followed by a slower decline over the next 300 h, may have been due to dissipation of the free chlorine in the water. In the drinking water with sodium oxalate matrix the chlorite concentration did not significantly change within the first 75 h (99% confidence level); the chlorite concentration began to decline after 75 h. Thus, the data indicate that sodium oxalate was useful as a short-term preservative. Day to day

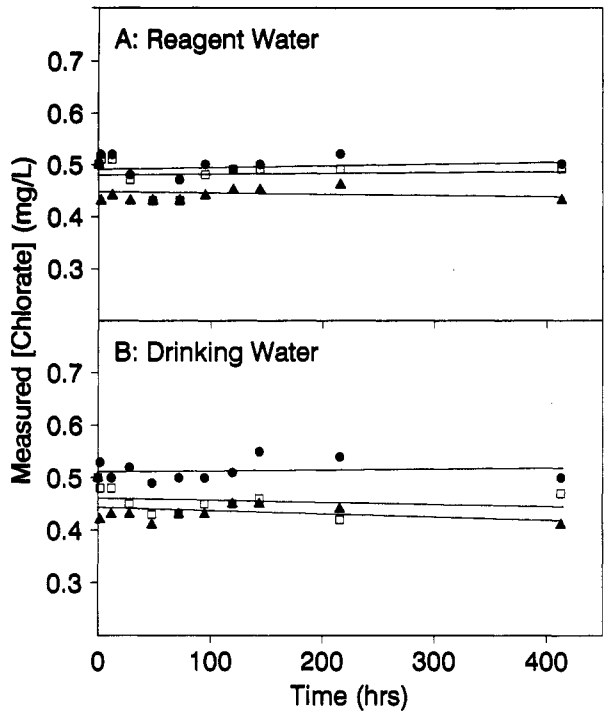

Figure 2. Stability study for chlorate. Top (A) is in reagent water, bottom (B) in drinking water: ● indicates control with no preservative, □ indicates ethylenediamine added, and ▲ indicates sodium oxalate added.

fluctuations shown in parts A and B of Figures 1 likely resulted from the daily preparation of new standard curves each day and normal variation in the performance of the IC instrumentation.

Chlorite instability in drinking water has previously been demonstrated,[6] and chlorite is predicted to react with chlorine.[13] The extent of chlorite disappearance is a function of the chlorine concentration in the water, and, therefore, could be greater or less than that observed. Both sodium oxalate and ethylenediamine inhibit the degradation of chlorite in this chlorinated drinking water. Sodium oxalate was an effective preservative for up to 3 days, whereas ethylenediamine was effective for up to 18 days.

Variation in the day-to-day concentrations for chlorate were greater than those for chlorite. This observation was consistent with other experiences in our laboratory, namely that the variability in replicate IC determinations of chlorate was always greater than those of chlorite.

The data in Figure 2 indicate that chlorate was stable for 2.5 weeks in solutions prepared either with or without a preservative in both reagent or drinking water. Regression analyses demonstrated that none of the slopes for chlorate were significantly different than zero at a 99% confidence level. Thus chlorate was stable in all the solutions tested. Chlorate has been reported to be stable for up to 30 days in chlorinated drinking water without a preservative,[6] and our results for chlorate in unpreserved reagent and drinking water support those data.

FIA and IC Comparison. Check samples containing both chlorite and chlorate were prepared in reagent water; for quantitative analysis of the check samples, standard curves were prepared in reagent water containing the appropriate preservative and drinking water containing the appropriate preservative. The differences between the actual concentrations and the measured concentrations of chlorite and chlorate in the check samples are reported in Tables II and III, respectively.

The analysis of variance (ANOVA) among the chlorite concentrations showed that the analytical method (FIA or IC),

Table II. Mean Differences for Check Samples Containing Chlorite: Samples Quantitated Using Standard Curves Prepared in Reagent or Drinking Water[a]

	matrix	
method	reagent water	drinking water
FIA[b]	+0.00	+0.62
	(sd[d] = 0.01)	(sd = 0.15)
	(n = 6)	(n = 7)
IC[c]	−0.03	+0.03
	(sd = 0.03)	(sd = 0.01)
	(n = 9)	(n = 4)

[a] $([ClO_2^-]_{actual} - [ClO_2^-]_{measured})$ reported in mg/L ClO_2^-. [b] Standard curves for FIA contained sodium oxalate. [c] Standard curves for IC contained ethylene diamine. [d] sd = standard deviation. [e] n = number of elements in data set.

Table III. Mean Differences for Check Samples Containing Chlorate: Samples Quantitated Using Standard Curves Prepared in Reagent or Drinking Water[a]

	matrix	
method	reagent water	drinking water
FIA[b]	+0.03	−0.50
	(sd[d] = 0.05)	(sd = 0.41)
	(n^e = 5)	(n = 7)
IC[c]	−0.05	+0.04
	(sd = 0.04)	(sd = 0.07)
	(n = 9)	(n = 4)

[a] $([ClO_3^-]_{actual} - [ClO_3^-]_{measured})$ reported in mg/L ClO_3^-. [b] Standard curves for FIA contained sodium oxalate. [c] Standard curves for IC contained ethylene diamine. [d] sd = standard deviation. [e] n = number of elements in data set.

water matrix (reagent or drinking water), and the interaction between method and matrix were all highly significant ($p < 0.001$). Similarly, a significant effect of the interaction of matrix and method ($p = 0.005$) was observed among the chlorate concentrations. The variability of the data was higher for chlorate than chlorite as indicated by the higher standard deviations for chlorate measurements (Table III).

A Tukey HSD multiple comparison was performed to determine which combination of method and matrix had the greatest impact on determinations of chlorite and chlorate. This statistical test performs a pairwise comparison of the mean concentration differences. It can indicate whether the differences between actual and measured concentrations are significantly influenced by a particular combination of matrix and method. For chlorite, the differences among values in drinking water analyzed by FIA were significantly different than the other three combinations—FIA/reagent, IC/drinking water, IC/reagent—at the 99% significance level ($\alpha = 0.01$). For the other pairwise comparisons not involving FIA/drinking water, the p value associated with the next most significant combination was 0.679. Recall that the smaller the p values, the more significant the effect. The chlorate results were similar to those for chlorite. For chlorate, FIA/drinking water was again significantly different from the other three combinations at the 99% significance level. For the other pairwise comparisons not involving FIA/drinking water, the p value associated with the next most significant combination was 0.914.

Thus, the measured concentrations of chlorite in drinking water analyzed by FIA were significantly greater than those actually present, and measured chlorate concentrations were lower than those actually present. The concentrations measured by FIA/reagent, IC/drinking water, and IC/reagent were not significantly different.

Chloramine Study. This study was undertaken to evaluate the effect of inorganic chloramines on quantitation of

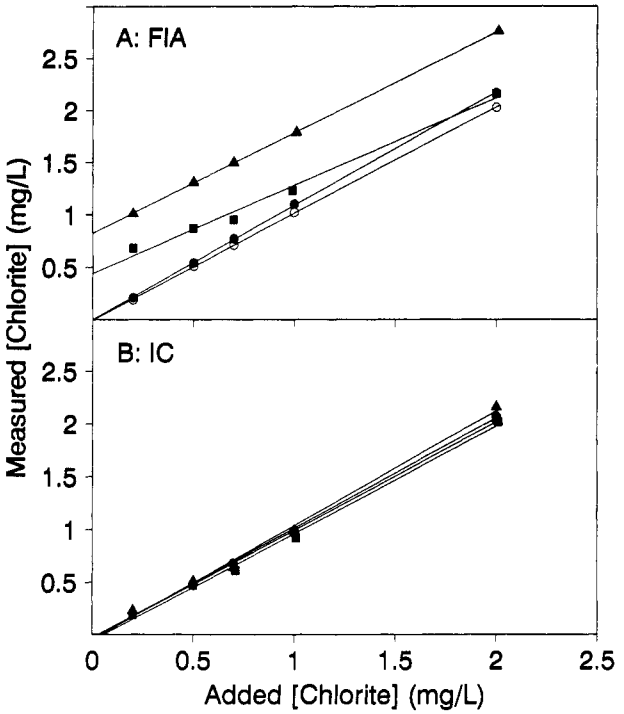

Figure 3. Analysis of chlorite in different water matrices. Top (A) is measured by FIA, bottom (B) is measured by IC: O indicates reagent water, ● indicates reagent water with appropriate preservative (ED for IC, NaOx for FIA), ■ indicates drinking water with the appropriate preservative, and ▲ indicates drinking water with added chloramines and the appropriate preservative.

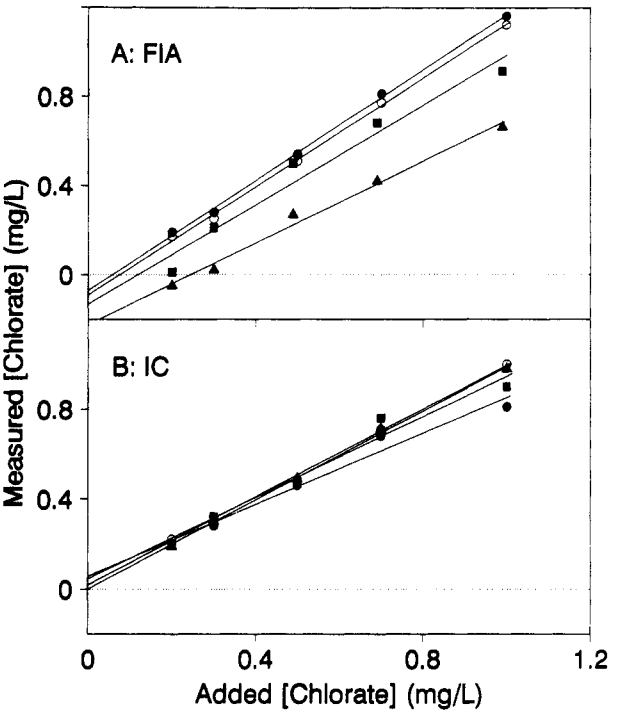

Figure 4. Analysis of chlorate in different water matrices. Top (A) is measured by FIA, bottom (B) is measured by IC: O indicates reagent water, ● indicates reagent water with appropriate preservative (ED for IC, NaOx for FIA), ■ indicates drinking water with the appropriate preservative, and ▲ indicates drinking water with added chloramines and the appropriate preservative.

chlorite and chlorate by FIA or IC. Solutions containing various chlorite and chlorate concentrations were prepared in different water matrices and quantitated against standards prepared in reagent water only.

The results for the quantitation of chlorite solutions by FIA in reagent water with and without sodium oxalate, drinking water with sodium oxalate, and drinking water with 1.02 mg/L chloramine and sodium oxalate are presented in Figure 3A. Regression analysis indicated that the slope and intercept for the reagent water matrix were not significantly different from 1 and 0 at the 99% significance level (slope value was 1.02). Thus the measured and actual concentrations were statistically the same. When NaOx was added to the reagent water, the intercept remained at 0 but the slope increased very slightly to a value of 1.09. Although this slope was significantly different from 1 at the 99% significance level, the change in the slope was minor (0.07). The drinking water and NaOx sample indicated an intercept near 0.5 mg/L, and a slope significantly less than 1 at the 99% significance level. The measured values were too high at lower ClO_2^- concentrations, but agreed more closely at chlorite concentrations ≥2 mg/L (see Figure 3A; additionally, a drinking water data point not shown on the graph had x, y coordinates of (3.0, 3.12), further indicating that the drinking-water interference is minimized at higher chlorite concentrations). When chloramines were added to the drinking water, the intercept increased to 0.8 mg/L, but the slope was not significantly different from 1.

Figure 3A shows that while the FIA-measured concentrations of chlorite in drinking water were generally higher than the actual concentrations, the interference was not constant. At low added-chlorite concentrations, the interference was great, but as the added chlorite concentration approached 2 mg/L, the interference was negligible. These data indicated that some oxidant(s) in the chlorinated drinking water interfered with the quantitation of chlorite by FIA, and that this interference was neither constant nor removed by NaOx. This was consistent with our initial observation concerning FIA measurement of ClO_2^- in drinking water samples from throughout the U.S.

The data suggest that interferences other than monochloramine were present in the chlorinated drinking water tested. As noted earlier, these interferences were more pronounced at lower chlorite concentrations.

Figure 3B presents the results for the IC analysis of chlorite in reagent water with and without ED, drinking water with ED, and drinking water with 1.00 mg/L chloramine and ED. For all four matrices, the concentrations measured by IC were nearly identical to the actual prepared concentrations. Thus, the presence of chloramines or other oxidants in this drinking water did not interfere with IC chlorite quantitation. None of the curves was significantly different from the others at a 99% significance interval. All the slopes were not significantly different from 1 and the intercepts were not significantly different from 0.

Figure 4A presents data for the quantitation of chlorate in reagent and drinking water matrices. The FIA measured concentrations of chlorate were consistently less (about 0.1–0.4 mg/L) than the actual concentrations for both drinking water and drinking water containing 1.02 mg/L chloramines. The regression analysis indicated that the intercepts were −0.09 and −0.25 mg/L, respectively. Both are significantly different from 0 at the 99% significance level. The slopes for all the regressions were not significantly different from 1. Thus, there was an interference from both drinking water and chloramines that resulted in low chlorate concentrations as determined by FIA.

From this study, the magnitude of the interference appeared similar when drinking water was analyzed both with and without a high concentration of chloramines. Due to the method of calculating chlorate concentrations, the measured chlorate concentrations were low, even in the presence of chloramine compounds that are known to react with iodide to produce iodine. Chlorate concentrations were calculated by difference; chlorite and chlorate were measured together

at pH <1, then the measured chlorite concentration was subtracted to determine the amount of chlorate in the sample. Thus, if the measured chlorite concentration was too high (due to presence of interfering chloramines), then the chlorate concentration likely would be low because too much was subtracted.

Data for the IC analysis of chlorate in reagent and drinking water matrices are presented in Figure 4B. Statistical analysis demonstrated that there were no significant difference between the four matrices at the 99% confidence interval.

During our FIA analysis of drinking-water samples from water utilities throughout the U.S., we noticed high residual absorbances at pH 8 in some samples, even after chlorine dioxide had been sparged from the sample and sodium oxalate had been added to inactivate chlorine. The absorbance was particularly high when chloramines were present in the water sample. A residual absorbance present at pH 8 indicated response to some oxidant other than chlorine or chlorine dioxide since these oxidants had been either inactivated or removed. The residual absorbance was not due to chlorite or chlorate because these species do not respond at pH 8. A correction based on this residual pH 8 absorbance was tested. The absorbance was treated as Cl^+ in terms of oxidizing potential (and thus could account for monochloramine). The correction factor converted the residual pH 8 absorbance to mg/L Cl_2 using a chlorine standard curve. This oxidant concentration as Cl_2 was subtracted from chlorite and chlorate concentrations after adjustments both for molecular weight and number of electrons transferred during the reaction with iodide were incorporated.[18] The adjusted chlorite concentration was used in the multiple regression to calculate chlorate values.

In general, the correction lowered the measured values of chlorite, and, thus, the corrected values agreed better with the actual values than the uncorrected values. However, regression analysis demonstrated that the slope of the drinking water with NaOx was still significantly lower than 1, and the intercept of the standard curve derived from analysis of drinking water with NaOx and added chloramines was near 0.17 mg/L, which was significantly different from 0. Thus, the correction factor improved the accuracy, but did not remove all the interferences. For chlorate, the results did not change significantly from the uncorrected results. Although lower chlorite values would increase the measured chlorate concentrations, the correction factor did not significantly alter the chlorate concentrations.

Interpretation. The data presented from the analysis of check samples (Table II; ANOVA results reported above) and from the analysis of standard curves prepared in different matrices (Figures 3A and 4A) indicated that the accuracy of the chlorite analysis in reagent water (with or without preservative) was about the same regardless of the method used for the analysis. The accuracy of chlorate was similar for both FIA and IC in reagent water based on results from the check sample study (Table III). Thus the preservatives, either NaOx or ED, had no effect on the determination of chlorite and chlorate by FIA or IC.

The accuracy of the IC method for analysis of chlorite or chlorate was not affected by either the drinking-water matrix or the presence of chloramine (Tables II and III; Figures 3B and 4B). Conversely, the results of the analyses in drinking water (Tables II and III; Figures 3A and 4A) demonstrated that in drinking water alone, which contained about 0.2 mg/L chloramines, and in chloraminated water which contained about 1 mg/L chloramines, the FIA method was inaccurate and prone to interferences from chloramines and other oxidants present in drinking water. These interferences are analogous to those in other techniques (e.g., amperometric titration, *N,N*-diethyl-*p*-phenylenediamine) which measure individual oxidants in solutions containing multiple oxidants without prior separation of the oxidant species.[9-12]

The ion chromatographic method for analysis of chlorite and chlorate separated these ions in time and space prior to detection; this approach is desirable for analysis of oxidants in the complex matrix of drinking water. Similarly, a recent method for analysis of inorganic and organic chloramines uses reverse-phase HPLC methods with electrochemical detection or postcolumn reaction with iodide to overcome the problems of measuring individual organic and inorganic chloramines in solutions containing multiple oxidants.[12,22] Although the FIA method does not separate individual oxidants in time and space, the method does attempt to enhance the response of individual drinking-water oxidants by controlling the kinetics of the reaction with iodide and using oxalate to inhibit the reaction of chlorine and iodide. The published FIA method which was used in this research is being revised to compensate for interferences from chloramines and other oxidants, and thus when modified may be a viable method for analysis of chlorite and chlorate in drinking water.[23] Nonetheless, the FIA method is a difference method for the analysis of chlorate. Difference methods are subject to cumulative errors in accuracy and precision.[11]

The results of this research further emphasize the need to separate oxidants in mixtures prior to the measurement of individual oxidant species. Both methods have their own respective advantages for drinking-water analysis. FIA can be used for both ionic and nonionic oxidants such as chlorine, chlorine dioxide, inorganic chloramines, chlorite, and chlorate. Ion chromatography, on the other hand, can be used to analyze for oxidant and nonoxidant ionic species such as chlorite, chlorate, chloride, bromate, nitrate, and other common anions.

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Temperature Programming in Capillary Zone Electrophoresis

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A new type of selectivity in capillary zone electrophoresis (CZE) based on temperature programming is presented. By using a buffer system with a large temperature coefficient, e.g. Tris buffer, the pH within the capillary can be adjusted in situ by simply controlling the temperature of the capillary. The electromigration behavior of weak acids is found to be influenced by both temperature-induced pH changes and viscosity changes. The effect of pH on the electrophoretic mobilities of analytes is most significant if the range of pH change matches the acidity constants, pK_a, of the analytes. The implementation of temperature programming in both temporal and positional modes in CZE are illustrated by the separation of a mixture of fluorescent organic acids.

INTRODUCTION

Over the past decade, capillary zone electrophoresis (CZE) has proven to be one of the most powerful techniques for the separation of complex mixtures, particularly in the area of biology and biochemistry. CZE is generally characterized as a separation method of extremely high efficiency and fast speed; generation of more than 10^6 theoretical plates in less than 20 min has been demonstrated.[1,2] Separation in CZE is achieved mainly via differences in mobilities of analytes under a high electric field. Both electroosmotic flow of the bulk solution and electrophoretic mobilities contribute to the observed migration behavior of each analyte in the capillary.[2,3] Since the electrophoretic mobility of an ion is directly proportional to its charge,[4] which in turn is strongly affected by pH, manipulation of the buffer pH becomes one of the key strategies in optimizing a separation. This is particularly true in the separation of proteins and peptides by CZE.[5,6] However, for mixtures of acids and bases possessing similar ionic mobilities and/or acidity constants (pK_a), it is sometimes difficult to find a suitable pH which enables a fast and efficient separation. A pH gradient as a function of position, as that commonly employed in isoelectric focusing[7] and free-flow electrophoresis,[8] may be used to solve this problem.

To date, only a few pH gradient methods in CZE have been reported. Bocek et al.[9,10] first developed a three-pole separation column for dynamic (temporal) programming of pH in the capillary. The actual operational buffer inside the capillary was generated by the simultaneous electromigration of various ionic species of the same polarity from two separate buffer chambers. Using a syringe-type pump, Sustacek et al.[11] created a dynamic pH gradient in CZE through the continuous addition of a modifying electrolyte into the buffer chamber at the injection of the capillary. This method was applied to the separation of nucleic bases and their derivatives. Recently, Foret et al.[12] used the same technique to generate a step change of pH in the separation of proteins by CZE. A substantial improvement on the resolution of protein mixtures was demonstrated. All pH gradient methods reported involve the continuous variation of electrolyte composition in the buffer chamber at the injection end of the capillary through an electrical or a mechanical means.

In this paper, a new method for manipulating selectivity in CZE is presented. Using a buffer system with a large temperature coefficient (dpH/dT), e.g. Tris buffer, a pH step or gradient can be generated in situ simply by varying the temperature of the capillary as a function of time or as a function of position during electrophoresis. Temperature programming has been a routine technique to solve general elution problems in gas chromatography for many years. Improvement of both speed and efficiency in liquid chromatographic separations through temperature-controlled or gradient techniques has also been demonstrated.[13,14] In CZE, temperature control was often used to provide efficient heat removal.[15-17] Manipulation of chemical equilibria such as metal chelation and micelle partitioning[18,19] within the capillary through temperature control has also been reported. The generation of a positional pH gradient by using a buffer system with a large dpH/dT has been demonstrated in isoelectric focusing.[20] In this research, effects of temperature-induced pH changes and viscosity changes on the electromigration behavior of analytes in CZE are studied. Improvements in the efficiency of separation by employing a dynamic (time dependent) or static (position dependent) temperature step or gradient technique are also demonstrated.

EXPERIMENTAL SECTION

The CZE system is similar to that described previously.[21] A high-voltage power supply (Glassman High Voltage, Inc., Whitehouse Station, NJ; Model PS/EH40R02.5) was used to generate the potential across the capillary. Fused-silica capillaries (Polymicro Technologies, Phoenix, AZ) of 50 μm i.d. and 360 μm o.d. were used in this study. Of the 60-cm total length, a 40-cm region

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