Determination of chloride, chlorite, chlorate and bromate in pool water samples by ion chromatography

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Abstract

Chloride (Cl^-), chlorate (ClO_3^-), chlorite (ClO_2^-) and bromate (BrO_3^-) are anions commonly found in swimming pool water due to treatment with different processes for chlorination and/or bromination. Chloride, chlorate, chlorite, and bromate have potential negative health implications; therefore it is important to monitor these anion levels. Ion chromatography was used to analyze swimming pool water from the pools at Concordia College and Moorhead High School both in Moorhead, MN. Chlorite and bromate were not detected in samples from either pool while a very small concentration of chlorate was detected in the Moorhead High School pool. Safe levels of chloride were found in both pools.

Introduction

Swimming pools are often disinfected through chlorination and/or bromination processes. This can be done through addition of solids (calcium chloride/calcium hypochlorite/calcium hypobromite), liquids (sodium hypobromite/sodium hypochlorite – bleach), and gases (chlorine gas).[1,2] When added to water, these compounds form the anions chloride (Cl^-), chlorate (ClO_3^-), chlorite (ClO_2^-) and bromate (BrO_3^-). This formation of anions is rapid and these compounds are effective sanitizers.[3]

The most cost effective and maintainable method of pool water sanitation and disinfection is through salt addition. For a safe pool, ion levels need to be between 120 and 400ppm.[4] This is preferable because it keeps the water disinfected but does not add a salty taste because humans cannot taste salt until a concentration of around 5000ppm.[2]

Proper concentrations must be kept in order to limit the formation of disinfection byproducts. Examples of these would be chloramines which are irritating substances which can cause red eyes in swimmers and a strong chemical odor sometimes present in pools.[5] Disinfection byproducts are caused by a high concentration of disinfectants, like the ones in this study. Disinfectant concentrations are usually measured and monitered using salt test strips much in the same way pH test strips are used to monitor pH levels. Test strips are cheap and can easily be used by people with little knowledge of chemistry. A problem with the test strips is they are not very accurate.[2]

A more accurate and still fairly simple way to determine concentrations of chloride, chlorite, chlorate, and bromate in pool water is through ion chromatography (IC).[6] Standard solutions of known concentrations of ions can be analyzed to create calibration curves. These calibration curves can aid in the determination of ion levels in samples of unknown concentrations.[3,7]

Experimental

Materials and reagents

Sodium carbonate and sodium bicarbonate for the instrument eluent were purchased from Fisher Scientific. Solid sodium bromate was also purchased from Fisher Scientific and solid sodium chlorate was purchased from Sigma-Aldrich. A 1000 ppm solution of chloride was purchased from Metrohm-Peak and a 1000 ppm solution of chlorite was purchased from SPEX.

Eluent preparation

Eluent was prepared by dissolving 0.339 g of sodium carbonate and 0.085 g of sodium bicarbonate in 1 L of ultrapure degassed water.

Standard preparation

Solutions of 1000 ppm chlorate and bromate were made by dissolving 0.335 g sodium chlorate and 0.295 g sodium bromate into de-ionized water for a final volume of 250 mL each. These solutions were then diluted to 100 ppm to create stock solutions. A 100 ppm stock solution of chlorite was made using a premade 1000 ppm solution. 100 ppm stock solution of chloride was made using a premade 1000 ppm solution. Standard chlorate, chloride and chlorite solutions were prepared by dilution of stock solution to concentrations ranging from 1 ppm to 10 ppm. Standard bromate solutions were prepared by dilution of stock solution to concentrations ranging from 0.25 ppm to 2 ppm.

Sample reparation

Pool water samples were collected from the pools at Concordia College and Moorhead Senior High School on April 4, 2011. Samples were collected poolside in glass jars. For both samples, 5mL portions of pool water were diluted with de-ionized water to 500 mL. Multiple samples were prepared in order to calculate standard deviations.

Instrument preparation

The IC analysis was conducted on a Metrohm ion chromatography system with a conductivity detector. Analytes were separated on a Metrosep A Supp 5-100 column, 4.0 x 100 mm and a particle size of 5.0 μm. The column temperature was 35.0°C, the flow rate was 0.70 mL/min, and the injection loop volume was 1.0 μL.

Results and discussion

Standards and calibration curves

Standards were ran of combined samples of chlorate, chlorite and bromate, but retention times appeared very similar (Fig. 1) having only a range of 1 min. For more precise analysis, standards were made separately and run through the IC.
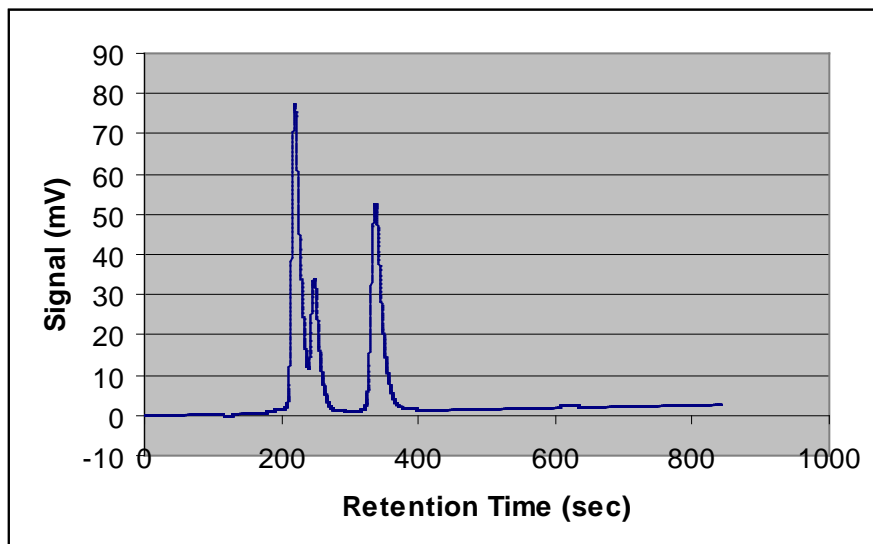

Figure 1. Chromatogram for standard of 10 ppm chlorate and chlorite and 2ppm bromate.

A strong peak with a retention time of 5.6 min was present in all chlorate standard chromatograms (Fig. 2) and was selected as the signal for chlorate analysis. The calibration curve (Fig. 6) was constructed by comparing the peak areas versus the known concentrations of the standards. Linearity was exceptional with a correlation coefficient of 0.9989.
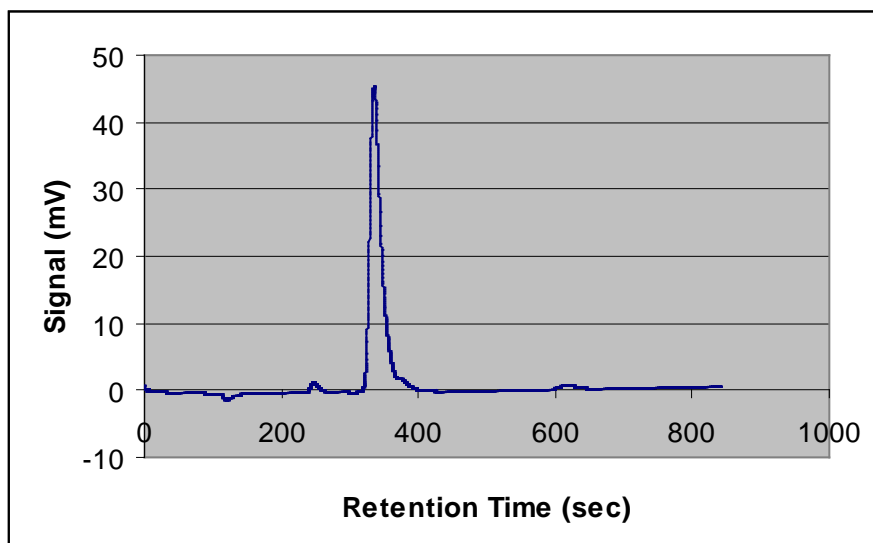

Figure 2. Chromatogram for chlorate standard at concentration of 10 ppm.

A strong peak around retention time of 3.6 min and a weaker peak around 4.1 min was present in all chlorite standard chromatograms (Fig. 3). Calibration curves were constructed for both signals by comparing the peak areas verses the known concentrations of the standards. Further analysis determined that a chloride ion has a retention time of around 4.1 so for analytical purposes, the calibration curve (Fig. 6) for retention time around 3.6 minutes was chosen as the peak for chlorite. The calibration curve produced excellent linearity with a correlation coefficient of 0.9965.
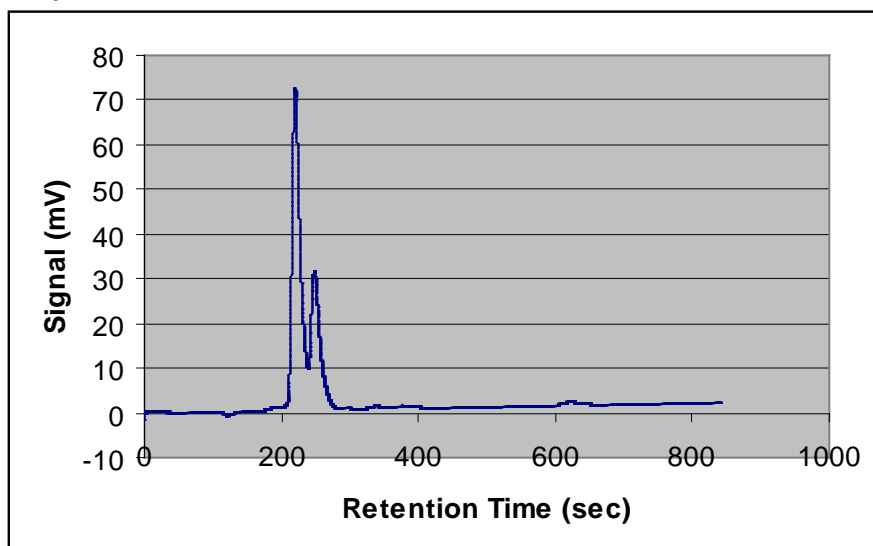

Figure 3. Chromatogram for chlorite standard at concentration of 10 ppm.

A strong peak with a retention time around 3.8 min was present in all bromate standard chromatograms (Fig. 4). The calibration curve (Fig. 7) was once again constructed by comparing the peak areas verses the known concentrations for the standards. Linearity was present in the calibration curve with a correlation coefficient of 0.9952. There was however, a chloride impurity in the samples and retention time was very similar to that of chlorite meaning there would be no separation from chlorite in the samples.
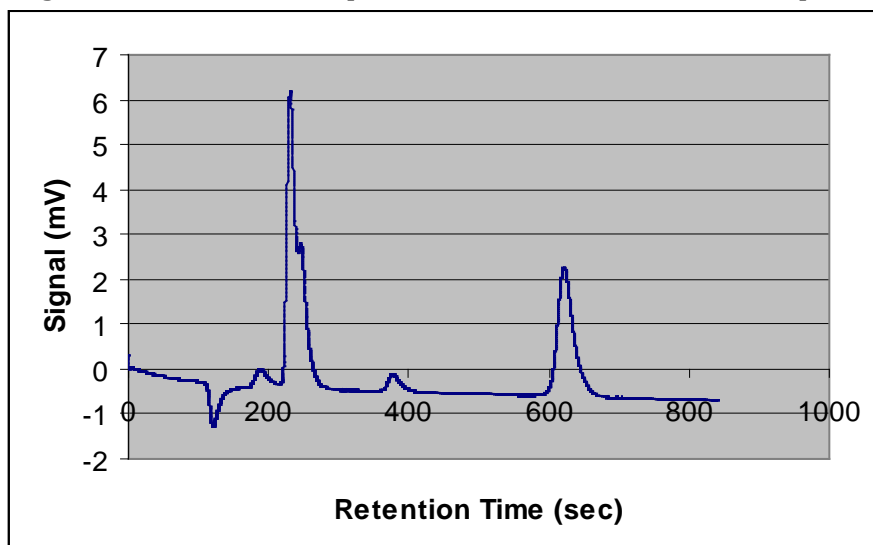

Figure 4. Chromatogram for bromate standard at concentration of 2 ppm.

A peak around retention time 4.1 min was present in all chlorite standard chromatograms (Fig. 2) because the purchased chlorite standard was found to be 80% sodium chlorite and 20% sodium chloride. Chloride standards were therefore run and a strong peak at retention time around 4.1 minutes appeared on the chromatograms (Fig. 5) for all concentrations. Calibration curves (Fig. 6) were constructed from these samples rather than the chlorite samples because concentrations of chloride in the chlorite standards were estimates. The resulting correlation coefficient was 0.9986.
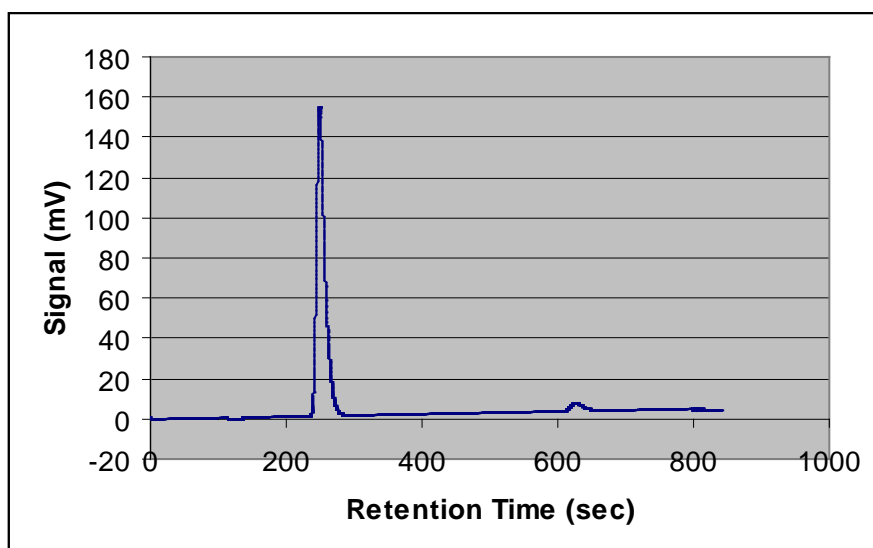

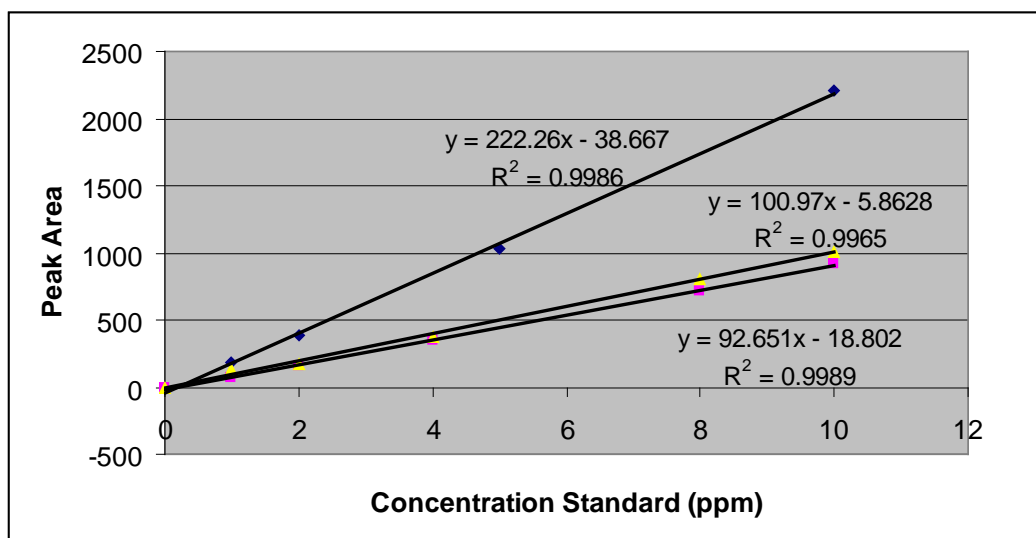Fig. 5. Chromatogram for chloride standard at concentration of 10ppm.

Figure 6. Calibration plots for chloride, chlorate and chlorite standards. Chloride standard concentrations vs. area of peak around 4.1 minutes (♦). Chlorate standard concentrations vs. area of peak around 5.6 minutes (■). Chlorite standard concentrations vs. area of peak around 3.6 minutes (▲).
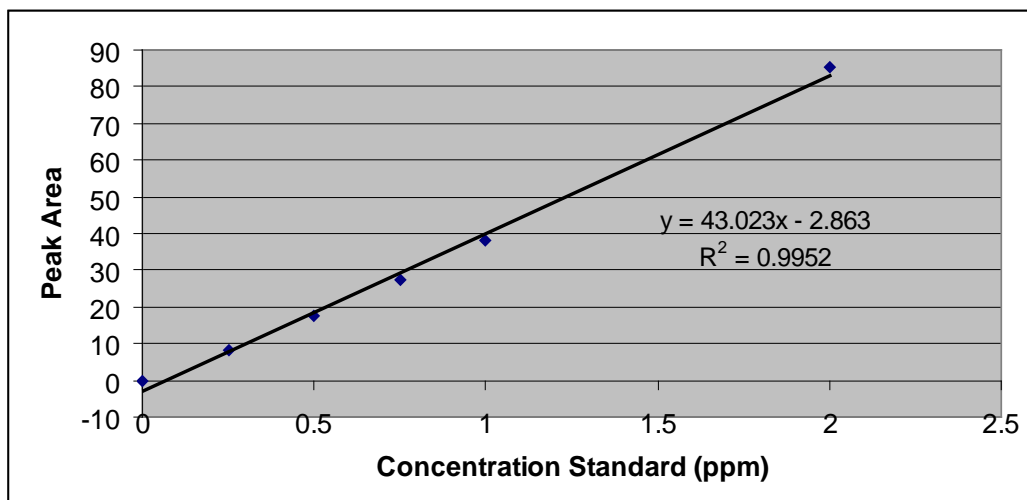
Figure 7. Calibration plots for bromate standard concentrations vs. area of peak around 3.8 minutes.

Analysis of pool water samples

Pool water samples from Moorhead High School were analyzed using IC and the resulting chromatogram (Fig. 8) showed a strong peak at 4.11 min and matched the retention time for the chloride standards. The concentration was determined to be 276.55 (±8.63) ppm. There was a very small peak matching the retention time for the chlorate standards. The concentration was determined to be 0.2657 (±0.0006) ppm. There were no peaks matching the retention times for chlorite or bromate and it is therefore determined that there is no chlorite or bromate in the pool water samples from Moorhead High School.
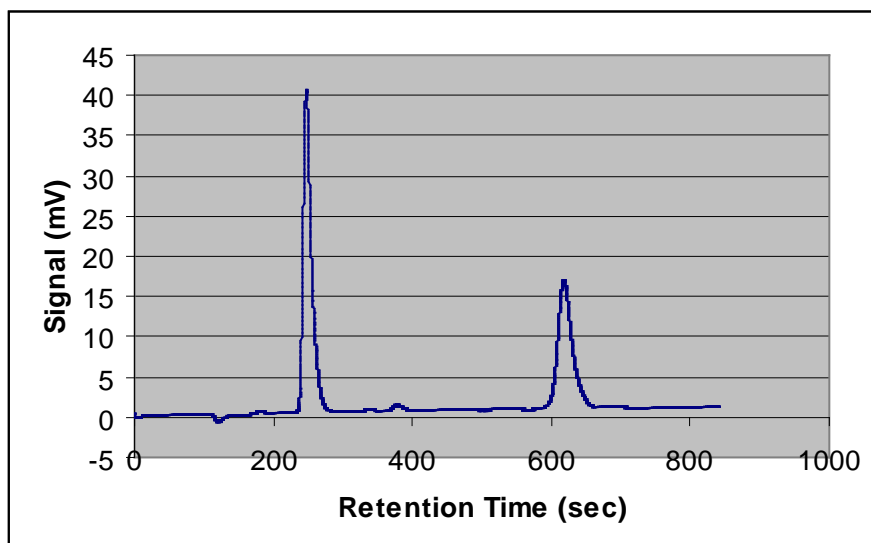

Figure 8. Chromatogram for Moorhead High Pool sample diluted 100 times

Pool water samples from Concordia College were analyzed using IC and the resulting chromatogram (Fig. 9) showed a strong peak at 4.13 min which matched the

retention time for the chloride standards. The concentration was determined to be 413.80 (±5.44) ppm. There were no peaks that matched the retention time for chlorate, chlorite or bromate and it is therefore determined that there is no chlorate, chlorite or bromate in the pool water samples from Concordia College.
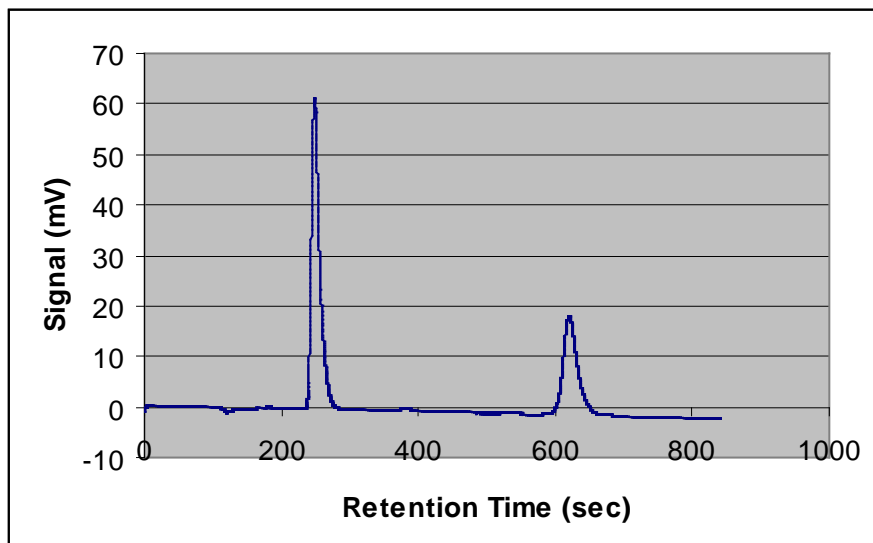

Figure. 9. Chromatogram for Concordia College Pool sample diluted 100 times.

A peak around retention time 10.3 min was present in all chromatograms aquired at verying concentrations. Further analysis is necissary to determine the identity of this peak.

Conclusions

The procedure developed for determining the concentration of chloride, chlorate, chlorite and bromate in pool water samples by ion chromatography is simple and fairly quick involving the dilution of the pool water samples and analyzing the sample using IC and the calibration curves for chloride, chlorate, chlorite and bromate. The procedure could not, however, separate chlorite from bromate. This procedure found no bromate or chlorite present in the water samples from the pools at Moorhead High School and Concordia College. A very small concentration of chlorate was found in the pool water from Moorhead High School but not from in the water from the Concordia College pool. Chloride was found in both pool water samples at normal concentrations. Further investigation is required to determine what type of chlorination is used in the pools to further investigate other possible ion concentrations.

References

1) Pool Treatment 101: Introduction To Chlorine Sanitizing. http://www.americanchemistry.com/s_chlorine/sec_content.asp?CID=1167&DID=4529&CTYPEID=109 (accessed April 17, 2011)
2) Saltwater Chlorine Generators. http://www.poolcenter.com/chlorine_generator.htm (accessed April 17, 2011)

3) Carlson, A.; Kowalski, V. Determination of chlorate and chlorite in water samples by ion chromatography. *Concordia College Journal of Analytical Chemistry 1*, 2010, 9-13.
4) Residential Swimming Poll Water Quality & Safety Information. http://www.oakgov.com/health/info_pub/eh_respool.html (accessed April 17, 2011)
5) Chloramines. http://www.poolcenter.com/ozone_chloramine_poolstor.htm (accessed April 17, 2011)
6) Mathews, B.; Michalski, R. Occurrence of Chlorite, Chlorate and Bromate in Disinfected Swimming Pool Water. *Polish J. of Environ. Stud. Vol. 16, No. 2*, 2007, 237-241.
7) Concordia College Analytical Chemistry Laboratory Manual. Determination of Sulfur in Coal by Ion Chromatography. http://www.cord.edu/dept/chemistry/ analyticallabmanual/ xperiments/ic/intro.html (accessed April 17, 2011)