

**Variability of Chlorate Levels in Sodium Hypochlorite
Feedstock and Finished Drinking Water in New Jersey**

R. Lee Lippincott*, NJDEP Division of Science and Research,
C.N. 409, 401 East State Street, 1st floor, Trenton, N.J. 08625
1-(609) 984-4699
FAX 1-(609) 292-7340

Bernard Bubnis, Novatek, *A Division of EBB, Inc.*, Oxford, OH

Gilbert Gordon, Miami University, Oxford OH

ABSTRACT

The common oxidation chemicals used to disinfect drinking water include chlorine gas, liquid bleach (sodium hypochlorite or dissolved solid calcium hypochlorite), chlorine dioxide, chloramines, and ozone. Because chlorine gas costs are increasing and new safety regulations placed on its transportation, storage, and use are proposed, many utilities are converting their treatment processes to use liquid bleach. During the storage of liquid bleach, hypochlorite ion decomposes to form chlorate ion (at pH > 10, rate = $k[\text{OCl}^-]^2$).

Because chlorate ion is planned for future regulation, the variability of chlorate ion levels in commercially available liquid bleach and finished drinking water in New Jersey was investigated as part of the State's effort to comply with the federally promulgated Disinfection By-product Rule (DBP).

INTRODUCTION

Recent and proposed legislation¹ is forcing water suppliers to comply with regulations enacted to reduce the concentration of inorganic disinfection by-products (chlorite, chlorate, and bromate ions) in the public water supply. Studies^{1,2} have clearly shown that chlorate ion (ClO_3^-) concentrations ranging from 0.1 to 0.5 mg/L (ppm) can be found in finished water treated with liquid bleach (hypochlorite ion, liquid hypochlorite). The objective of this research was to assess various New Jersey utilities that

apply liquid bleach for chlorate ion in their raw water, the bleach stock solutions, and their finished water distribution samples.

Because the finished water product produced at drinking water utilities is to be consumed by the general public, chemicals used for treatment should be at a minimum, "food grade" purity. In practice, an American National Standards Institute (ANSI)/American Water Works Association (AWWA) standard¹ does exist, however ANSI/AWWA B300-92 for hypochlorite purity, falls short of controlling the level of chlorate ion that is present in the bleach delivered to drinking water purveyors. Section 1.4 of the standard specifies that the burden of product purity is the responsibility of the "purchaser's test". Because section 3 of this standard does not specify a chlorate ion declaration, the chlorate ion concentration in the bleach is not specified and in general not measured. The standard does specify a minimum trade percentage of chlorine strength (Sec 2.3.3) and that the bleach solution "shall be a clear liquid containing not more than 0.15 percent insoluble matter by weight" (Sec 2.2.4). However, in the field, these standards are commonly found to be ignored.

Our data indicates that an expansion is needed to section 2.4 (Impurities) to include language regarding a maximum chlorate ion concentration. This adjustment offers a drinking water purveyor the option of signing an Affidavit of Compliance (Section 1.3) with the bleach manufacturer, and thus control the purchased bleach quality and strength. This research investigated the residual chlorate ion problem on two levels:

- A. An assessment was made to understand the awareness of New Jersey utility operators with respect to liquid bleach purchase, storage, and application. A 10 minute survey similar to that used in a recent American Water Works Association Research Foundation (AWWARF) was developed and distributed to participating drinking water purveyors. The survey also provided some information about liquid bleach suppliers operating in the state of New Jersey.
- B. A biannual sample collection and analysis effort was initiated for nine New Jersey drinking water systems. Five of the drinking water purveyors use groundwater (GW) sources: GW1, GW2, GWUI1, GW3, and GWUI2. Of these, two groundwater systems were classified as under the influence (GWUI) of surface water (GWUI1 and GWUI2). Two consecutive systems (CS) participated in this study; one bulk purchasing consecutive system uses all of their water from the supplier and further disinfects the finished water with liquid bleach (CS1), and one bulk purchasing consecutive system which receives only some of their water from the supplier and further disinfects the finished water with liquid bleach (CS2). Two surface supplied (SW) drinking water purveyors also participated in this study, one with multiple open reservoirs where post chlorination occurs before entry into the distribution system (SW1), and one with a conventional treatment system and two separate surface water intake locations (SW2).

MATERIALS AND METHODS

Measurements

Potentiometric titration was used to determine the FAC concentration in concentrated NaOCl¹. The NaOCl solutions were analyzed directly for ClO₂⁻ and ClO₃⁻ by ion chromatography² using a Dionex Dx-100 system. The chromatographic conditions are listed in Table 1.

Following preparation, the sample was injected directly onto the chromatographic column either the same day or within 48 hours. The standard curves for ClO₂⁻ and ClO₃⁻ had a minimum correlation coefficient of 0.9990. To insure the integrity of the calibration curves as a function of analysis time, a quality control (QC) standard containing both ions was analyzed at a minimum every ten sample injections. The relative chromatographic areas for these QC standards deviates less than ± 3%.

Quality Assurance

The quality of the results obtained during this study was ensured at all stages of the experimental and data handling protocols, including collecting raw water samples, storing samples, performing the experiments, analyzing samples, entering data, verifying data and reporting data.

Sampling

The raw water samples should were collected before the addition of any chemicals either at the treatment plant influent or at other locations upstream of the plant. If plant sampling taps were used, the standing water in the pipes was bled for several minutes

before sample collection. Liquid hypochlorite samples were drawn from storage vessels that were to be used within one week.

Sample Preservation and Storage

A sampling instruction sheet and a chain-of-custody document was provided to NJDEP. After filling the sampling container, the samples were immediately packed into a cooler containing frozen blue ice and shipped via overnight delivery to Novatek in Oxford, Ohio. Upon arrival at Novatek, each sample was identified and a file created on the Novatek data base. Sample preservatives and holding times conformed to official USEPA protocols.

Sample Analysis. QA/QC procedures for the analytical methodology involved daily standardization of reagents, calibration of analytical instruments, replicate and control experiments, use of reagent blanks, cross checking between analytical methods, and protocols for calculating reporting levels and control limits.

Survey

The survey took approximately 10 minutes to complete. If a district operated multiple systems, we asked that the questionnaire be completed for either each system or one or two typical systems. The questions focused on gathering information outlined below.

General Information

How many systems does your district operate?

What type of source water is treated by your system?

What volume of water is typically treated by your system each day?

What is your typical total applied chlorine dosage?

Do you use liquid or solid hypochlorite ion?
What is the method of hypochlorite production used by your supplier?
Do you generate hypochlorite on-site?

Hypochlorite Storage

What is the labeled % active ingredient of your hypochlorite stock when purchased?
Do you dilute your hypochlorite stock prior to storage? If yes, by what dilution factor?
How often do you measure the concentration of your hypochlorite stock solution?
What is the temperature of the your storage facility?
What is your typical time of storage before using purchased hypochlorite stock?
If you dilute your hypochlorite, what type of dilution water is used?
Are different hypochlorite shipments routinely mixed?

Hypochlorite Application

Do you calculate the % active ingredient in order to determine the daily applied dosage?
Do you apply hypochlorite at the raw water source?
Do you currently analyze for chlorate ion (ClO_3^-) in your finished water

Sample Collection

All raw water and finished water samples were collected in 40 mL glass vials with teflon lined caps. Duplicate samples were collected at each sampling location to address the method precision and verify the validity of the sample collection and analysis process.

All raw water samples were collected without preservatives with the following exceptions;

- where a chlorine residual was detected in the raw water,
- when a consecutive system chlorinates at the point of entry into the distribution system, and
- when a purveyor has open storage/balancing reservoirs with post chlorination at the point of entry into the distribution system.

In the USEPA draft DBP/ICR Analytical Methods Guidance Manual³, method performance criteria were published for the determination of inorganic disinfection

byproducts by USEPA Method 300.0. These criteria were used as data quality objectives in this study. They include:

- The response must be within ten percent of the predicted response for check standards at a batch rate of 10% for each 8 hour shift.
- The method blank must be less than 10 µg/L for a single analyte at one per batch.

RESULTS

Utility Survey

The initial focus of this contract was to develop a questionnaire that could be used to gather specific information about the facilities in New Jersey using liquid bleach. A prerequisite of this document was that it be similar to that used in the AWWARF contract so that comparisons could be made between New Jersey facilities and facilities located throughout the United States. The New Jersey questionnaire contains all of the elements of the AWWARF survey in addition to asking specific questions regarding the bleach supplier, bleach specifications, and hypochlorination points.

The compiled responses to the questionnaire indicate that the respondent New Jersey utilities closely resemble other utilities across the country in terms of bleach purchase, storage, and application.

In general, the chlorate ion issue has not been addressed. The most effective approach to minimizing chlorate ion in finished water is to limit its formation in the stock liquid bleach. It is recommended that a set of minimum liquid bleach specifications be developed to help utilities purchase bleach having the proper pH, and a low initial

concentration of chlorate ion and transition metal ions (i.e. at the time of delivery). This means that measurements need to be made by the manufacturers, storage conditions must be controlled prior to delivery, and the utilities should receive freshly made product within 1 week of manufacture.

Upon receipt of a liquid bleach shipment, utilities should at least measure the FAC content, the pH, and the chlorate ion concentration. If temperature is a problem, dilution strategies should be implemented for storage.

The Gordon/Adam Predictive Model developed at Miami University was used to predict the number of days that the individual utility liquid bleach stock solutions could be used before reaching the nominal 0.2 mg/L maximum contaminant level goal (MCLG).

Groundwater Systems

GW2

An initial sampling from the GW2 system included: 1 source water, 3 bleach stock solutions, and 1 finished water. Chlorate ion was not detected in the source water. The average measured chlorate ion concentration in the finished water was 24 $\mu\text{g/L}$.

An end of summer analysis indicated that the source water for the GW2 systems contains a chlorate ion residual in the Gist system prior to chlorination. The liquid bleach analysis shows a increase in chlorate ion and less FAC strength compared to the liquid bleach analysis for the Park system in the spring.

GW3

An initial sampling from the GW3 system included: 1 source water, 1 bleach stock solution, and 1 finished water. Chlorate ion was detected in the source water (average = 11 $\mu\text{g/L}$). The average measured chlorate ion in the finished water was 67 $\mu\text{g/L}$. The source water contained a small amount of chlorate ion that contributes to the residual chlorate ion found in the finished water.

An end of summer analysis indicated that the source water for the GW3 system did not contain a chlorate ion residual prior to chlorination. The liquid bleach analysis shows a bleach stock that contains more chlorate ion and less FAC strength compared to the liquid bleach analysis in the spring. The chlorate ion residual found in the finished water is 3 times that found in the earlier analysis but still below the "proposed" chlorate ion action level of 0.2 mg/L.

Systems Using Groundwater Under the Influence of Surface Water

GWUI1

An initial sampling included 4 samples: 2 source waters, 1 bleach stock solution, and 1 finished water. Chlorate ion was not detected in one source water and was measured to be an average of 14 $\mu\text{g/L}$ in the second sample. The average measured chlorate ion in the finished water was 33 $\mu\text{g/L}$. The source water contained a small amount of chlorate ion that probably contributes to the residual chlorate ion found in the finished water product.

An end of summer analysis indicated that the source water did not contain a chlorate ion residual prior to chlorination. The liquid bleach analysis showed a bleach stock that contained significantly more chlorate ion and less FAC strength compared to the liquid bleach analysis in the spring. The chlorate ion residual found in the finished water is 2 times that found in the earlier analysis but still below the "proposed" chlorate ion action level of 0.2 mg/L.

Sayreville

An initial sampling from the Sayreville system included: 3 source waters, 2 bleach stock solutions, and 2 finished waters. Chlorate ion was not detected two of the source waters, however the third showed a trace of chlorate ion. The average measured chlorate ion concentrations in the finished water were 70 and 102 $\mu\text{g/L}$ respectively.

An end of summer analysis indicate that the source water for the Sayreville system do not contain a chlorate ion residual prior to chlorination. The liquid bleach analysis showed a bleach stock that contains more chlorate ion and less FAC strength compared to the liquid bleach analysis in the spring. The chlorate ion residual found in the finished water is to 5 times found in the earlier analysis.

Consecutive Water Systems

CS1

An initial sampling from the CS1 system included: 1 source water, 1 bleach stock solution, and 1 finished water. A resample was undertaken and 1 source water, 2 bleach

stocks and 1 finished water were also analyzed. Chlorate ion was detected in both the initial and the resampling of this source water (average #1 = 35 $\mu\text{g/L}$, average #2 = 30 $\mu\text{g/L}$). The average measured chlorate ion in the finished water was 65 $\mu\text{g/L}$ in the original and 34 $\mu\text{g/L}$ in the resampling. The source water contained chlorate ion that contributes to the residual chlorate ion found in the finished water.

An end of summer analysis indicates that the source water for the system contained a chlorate ion residual prior to chlorination. The chlorate ion residual found in the finished water was comparable to our initial measurements.

CS2

An initial sampling from the CS2 system included: 3 source waters, 3 bleach stock solutions, and 3 finished waters. Chlorate ion was not detected in 2 of the source waters.

Chlorate ion was detected in the purchased source water (average = 16 $\mu\text{g/L}$). The average measured chlorate ion in one of the finished waters was 349 $\mu\text{g/L}$. This level is considered high and is most likely a result of the 5 mg/L chlorine dose that is applied at this treatment point per the survey. The average measured chlorate ion in the second finished water was 33 $\mu\text{g/L}$. The third finished water had an average measured chlorate ion concentration of 36 $\mu\text{g/L}$.

An end of summer analysis indicated that the source water for the CS2 system did not contain a chlorate ion residual prior to chlorination in two of three facilities. The third facility (purchased source water) contained 35 $\mu\text{g/L}$ chlorate ion. The liquid bleach analysis showed that the each of the systems bleach stock contained more chlorate ion and

less FAC compared to the analysis in the spring. The chlorate ion residual found in the finished water increased in each of the 3 systems.

Surface Supply Systems

SW1

An initial sampling from the SW1 system included: 6 source waters, 8 bleach stock solutions, and 11 finished waters. Chlorate ion was detected in each of the source waters in both the original sampling and the resampling ranging from a concentration of 21 to 236 $\mu\text{g/L}$.

An end of summer analysis indicated that the source water for the SW1 systems contained a chlorate ion residual prior to chlorination with the exception of a single system. The liquid bleach analysis shows the chlorate ion and FAC strength to be similar to those analyzed previously.

SW2

An initial sampling from the SW2 system included: 2 source waters, 1 bleach stock solution, and 1 finished water. A trace of chlorate ion was detected in both the source waters. The average measured chlorate ion in the finished water was 33 $\mu\text{g/L}$.

An end of summer analysis indicated that the source water did not contain a chlorate ion residual prior to chlorination. The liquid bleach analysis shows a bleach stock that contains more chlorate ion and less FAC strength compared to the liquid bleach analysis in the spring. The chlorate ion residual found in the finished water is 3 times that

found in the earlier analysis but still below the "proposed" chlorate ion action level of 0.2 mg/L.

Summary

Table 2 presents the source water analyses that were made for chlorate ion. The initial analysis showed a typical low level chlorate ion residual that can be as high as 0.050 mg/L. The final analysis performed at the end of the summer did not show a significant change overall. In many of the utility source waters chlorate ion could not be detected (ND). The SW1 samples continued to show a slightly high chlorate ion residual in the source water.

The bleach decomposition data clearly shows an increase in the bleach stock chlorate ion concentration for most of the utilities submitting samples. This fact is supported by the increase in finished water chlorate ion concentration measured in the final sampling shown in Table 3.

Stock Solution Variability

The analytical results of the bleach stock solutions give an indication of possible causes of low, delivered bleach, FAC concentrations. If a bleach stock solution is expected to contain 15% FAC (wt) but the analysis indicates a lower concentration, either

the bleach has decomposed (indicated by a high concentration of chlorate ion) or the delivered bleach did not meet the FAC specification.

To properly assess the impact of the stock chlorate ion concentration, these data must be evaluated knowing the bleach stock FAC content. For example, if the stock has a high chlorate ion concentration (> 8,000 mg/L) but also has a high FAC concentration, the amount of stock needed to maintain the desired FAC residual is less and thus, less chlorate ion is added to the finished water. Conversely, if a bleach stock contains a relatively low FAC and some chlorate ion concentration, more FAC must be added to maintain the FAC residual. Thus, increased amounts of chlorate ion can be unknowingly added to the finished water and exceed the proposed action level of 0.2 mg/L. For this reason, the Gordon/Adam computer model was used to evaluate each utility stock solution.

Table 4 presents the liquid bleach analyses that were made for chlorate ion. The initial analysis showed a number of utility stock solutions containing greater than 10,000 mg/L chlorate ion and clearly show an increase over time (indicating bleach decomposition) in the stock chlorate ion concentration for most of the utilities submitting samples.

Temperature Effect TO BE COMPLETED

(I have plotted a 3-D surface projection from the NY and VA data, we may need to mention or include consultant as coauthor???) Include the analysis and description of GWUI2 storage facility as an example.

Worst Case Summer Sampling - TO BE COMPLETED

GW1

Model Projections

The predictive model is based on long-term bleach decomposition and chlorate ion formation results gathered for numerous commercial bleach products from various manufacturers. The important parameters evaluated by the model are: FAC concentration, pH, temperature, initial chlorate ion concentration, and chloride ion concentration. The predictive model is constructed so that estimates of chlorate ion concentration, liquid bleach specific gravity, and chloride ion concentrations can be made and used if actual measurements are not available.

Many of the utilities state the pH of the liquid bleach stock to be 10. At pH levels below 11, decomposition by the much faster acid catalysis pathway becomes a concern and the half-life of the stored liquid bleach is greatly decreased. This means that utilities storing bleach at $\text{pH} < 11$ will experience a faster bleach decomposition and more chlorate ion formation than shown in Table 5.

An average temperature of 80°F was used in many cases where temperature was not specified. This assumption does not take into account the warmer summer months when the temperature of storage facilities can easily reach 90°F or more. This means that in the summer months, bleach decomposition and chlorate ion formation can be expected to be greater. Thus, the lifetime of the bleach is less than that presented in the table.

The estimate was made based on a single set of conditions and does not take into account any cumulative effect that may exist due to hypochlorination at multiple points.

DISCUSSION - TO BE COMPLETED

CONCLUSIONS - TO BE COMPLETED

RECOMMENDATIONS

The results of this project indicate that New Jersey utilities need to become more aware of the strategies and practices that help to minimize chlorate ion in finished water. The most effective approach to minimizing chlorate ion is to prevent its formation in the stock liquid bleach.

It is recommended that a set of minimum liquid bleach specifications be developed to help utilities purchase bleach having the proper pH, and a low initial concentration of chlorate ion and minimum transition metal ion levels at the time of delivery. This means that measurements need to be made by the manufacturers, storage conditions must be controlled prior to delivery, and the utilities should receive freshly made product within 1 week of manufacture.

Upon receipt of a liquid bleach shipment, utilities should at least measure the FAC content, the pH, and the chlorate ion concentration. If temperature is a problem, dilution strategies should be implemented for storage.

Additional precautions can be taken to reduce liquid bleach chlorate ion concentrations including seasonal or periodic cleaning of the liquid bleach holding tanks, regular calibration of the liquid bleach injection pumps, and the requirement that bleach manufacturers provide a certificate of analysis for each bleach stock delivered to a New Jersey utility.

ACKNOWLEDGEMENTS

The authors would like to thank the following organizations for contributing to this research: New Jersey Department of Environmental Protection, American Water Works Association Research Foundation, Miami University, and Malcolm-Pirnie Engineering, Inc.

REFERENCES

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1. potentiometric titration
 2. USEPA Method 300
 3. EPA 814/P-94-001 January 1994

Table 1
Ion Chromatographic Experimental Conditions

Guard/Separator Columns	Dionex MFC/AG9/AS9
Detection	Dionex CDM-2 Conductivity
Suppressor	Dionex AMMS, Anion Micromembrane
Suppressor Regenerant	25 mN H ₂ SO ₄
Regenerant Flow Rate	10 mL/min
Sensitivity	1 μS full-scale
Background	6-10 μS
Eluent	20 mM NaOH / 100 mM H ₃ BO ₃
Eluent Flow Rate	1 to 2 mL/min
System Back-pressure	950-1150 psi (@ 1 mL/min)
Injection Loop Volume	25 or 50 μL

Table 2
Source Water Analytical Summary - Chlorate Ion (mg/L)

Facility	Site	Winter	Resample	Summer
GWUI2	Well Field	not detected		not detected
	Lagoon	not detected		
	Morgan Well Field	trace		not detected
GWUI1	Cassion Wells 9	not detected		not detected
	Cassion Wells C1	0.014		not detected

	Cassion Wells C2			not detected
SW2	D & R Canal	trace		not detected
	Lawrence Brook	trace		not detected
GW3	Plant 2	0.011		not detected
CS2	Well 10			not detected
	Well 11	not detected		not detected
	Browntown	not detected		not detected
	Middlesex	0.016		0.036
CS1	Stonybrook	0.035	0.030	0.078
GW2	Raw	not detected		
	Plant			not detected
	Park			0.007
	Gist			0.015
SW1	Plant			0.120
	Pompton River	0.170	0.044	
	Levine	0.046	0.117	0.144
	Great Notch	0.024		not detected
	New Street	0.090		0.043
GW1	Abeel Rd			not detected
	Poss Hollow			not detected
	Mystic Lane			0.043
	Rossmoor GC			not detected
	Middleton			not detected
	Perrineville			not detected

Table 3
Finished Water Analytical Summary - Chlorate Ion (mg/L)

Facility	Site	Winter	Resample	Summer
GWUI2	Well Field	0.070		0.350
	Morgan Well Field	0.102		0.362
GWUI1	Cassion Wells	0.033		0.066
SW2	D&R / Lawrence Brook	0.033		0.101
GW3	Plant 2	0.067		0.094
CS2	Wells	0.349		0.258
	Browntown	0.033		0.085
	Middlesex	0.036		0.060
CS1	Stonybrook	0.065	0.034	0.080
GW2	Plant	0.024		0.122
	Park			0.045
	Gist			0.060

SW1	Plant	0.044	0.089	0.090
	Levine	0.081	0.130	0.163
	Great Notch	0.039	0.082	0.110
	New Street	0.092	0.090	0.160
GW1	Abeel Rd			0.062
	Poss Hollow			0.195
	Mystic Lane			0.039
	Rossmoor GC			0.257
	Middleton			0.059
	Perrineville			0.053

Table 4
Liquid Bleach Summary - Chlorate Ion (mg/L)

Facility	Site	Winter	Resample	Summer
GWUI2	Well Field	2,720		5,255
	Morgan Well Field	4,092		10,573
GWUI1	Cassion Wells	1,995		22,177
SW2	D&R / Lawrence Brook	1,515		5,369
GW3	Plant 2	12,479		13,260
CS2	Wells	3,905		5,149
	Browntown	4,441		5,323
	Middlesex	14,987		4,774
CS1	Stonybrook	9,626	3,102	919
	Old Stock		13,089	
GW2	Plant	3,508		9,633
	Park	10,954		8,831
	Gist	11,351		9,206
SW1	Plant	3,813	4,513	5,289
	Levine	4,115	6,112	2,636
	Great Notch	3,967	5,577	5,957

GW1	New Street	2,872	6,398	4,737
	Abeel Rd			13,601
	Poss Hollow			15,510
	Mystic Lane			14,857
	Rossmoor GC			19,494
	Middleton			10,329
	Perrineville			9,443

Table 5

Estimated Days Before Reaching 0.2 mg/L ClO_3^-
in Finished Water (Spring/Summer Sampling)

Utility/Type	PWS ID	Days
SW2	1214001	35
CS2	1209002	4
CS1	721001	80
GW1	1213002	210
GWUI1	1811001	42
GW3	1326001	49
GWUI2	1219001	49
GW2	717001	180
SW1	1605002	80
