Development of an Innovative Procedure for the Analysis of Bromate and Other Oxy-halides in Drinking Water

Project Scope

Drinking water treated by chlorine commonly contains a mixture of disinfection byproducts (DBPs). One important class of DBPs is inorganic oxyhalides, which form when residual disinfectant reacts with natural organic substances present in the source water. Bromate is an important inorganic oxyhalide DBP that has mostly been associated with ozonation of drinking waters containing background bromide. Ozonation requires a secondary disinfectant to maintain a residual in the distribution system. Bromate has also been identified as a contaminant in liquid hypochlorite, a commonly used disinfectant. Bromate is classified as a Group B2 carcinogen (probable carcinogen) by the U.S. EPA and is regulated under the 1998 Stage 1 Disinfectants and Disinfection Byproducts Rule with a Maximum Contaminant Level (MCL) of 10 µg/L (10 parts per billion [ppb]) in treated drinking water. However, toxicological studies suggest that drinking water concentrations as low as 0.05 ppb may result in lifetime cancer risks of 10^{-6}.

The goal of this research project was to develop a simple, user-friendly, and reliable analytical method for sub-ppb levels of bromate in drinking water. The method was also extended for the analysis of other oxyhalide DBPs, including iodate, chlorite, and chlorate. It was applied to a variety of synthetically prepared water samples, and to natural waters from several drinking water treatment plants using ozonation and/or hypochlorite that would not otherwise be suspected to contain bromate. The results and implications of research conducted under this grant are summarized below.

Project Results and Implications

Method Development and Optimization: The researchers developed a novel approach for analyzing oxyhalides in drinking water. The method involved chromatographic (IC) separation

Grant Title and Principal Investigators

Development of a New, Simple, Innovative Procedure for the Analysis of Bromate and Other Oxy-halides at Sub-PPB Levels in Drinking Water (EPA Grant #R825952)

Howard S. Weinberg and Philip C. Singer, University of North Carolina, Chapel Hill

Key Findings and Implications

Analytical Accomplishments:

- Developed a practical, sensitive, and selective technique for use by the drinking water industry to detect sub-parts per billion (ppb; µg/L) levels of bromate in waters using ion chromatographic separation followed by a post-column reaction to produce a stable tribromide species that is quantified by ultraviolet absorbance.
- Found bromate levels in the range of 0.1 to 3 ppb, with an average level of 0.94 ppb, in 20 U.S. drinking water plants that use hypochlorite.

Implications of Research and Impacts of Results:

- Demonstrated that bromate levels in finished drinking waters will commonly exceed 0.05 ppb, which corresponds to a lifetime 10^{-6} cancer risk, due to hypochlorite use alone.
- Showed that regardless of drinking water treatment, a long-term goal of 0.05 ppb for bromate may also be unattainable based on levels found in some source water.
- Provides a tool to help fulfill the goals of the EPA Information Collection Rule (ICR) regarding the development of a nationwide database on disinfection by-product (DBP) occurrence in drinking water and for the future development and revision of DBP drinking water regulations.

Publications include 3 peer reviewed journal articles and 2 conference/symposium presentations.

Project Period: September 1997 to August 1999

Relevance to ORD's *Drinking Water Research Multi-Year Plan* (2003 Edition)

This project contributes directly to two of three Long-term Goals for drinking water research: (1) By 2010, develop scientifically sound data and approaches to assess and manage risks to human health posed by exposure to regulated waterborne pathogens and chemicals, including those addressed by the Arsenic, M/MDP, and Six-Year Review Rules; and (3) By 2009, provide data, tools and technologies to support management decisions by the Office of Water, state, local authorities and utilities to protect source water and the quality of water in the distribution system.

This research has led to the development of a practical, sensitive, and selective technique for use by the drinking water industry to measure sub-ppb levels of the bromate in waters treated by ozone and/or hypochlorite. It will provide more meaningful exposure data that can be compared to dose-response values for bromate. The method can be applied in support of bromate monitoring and exposure assessment efforts. Results of sub-ppb bromate monitoring can also be used to inform future development and revision of DBP drinking water regulations.

with no pretreatment, followed by a post-column reaction (PCR) to produce a stable tribromide species that is subsequently detected by ultraviolet (UV) absorbance at 267 nm. The method utilizes a high capacity anion exchange column that allows large volume samples (up to 1 mL) to be tested, increasing the sensitivity of the analysis.

The IC-PCR-UV method was tested and optimized for the analysis of iodate, chlorite, chlorate, and bromate in a variety of aquatic matrices. These included drinking waters from systems employing a number of treatment processes, and simulated drinking water samples containing different mixtures of inorganic ions and organic matter, subjected to varying levels of ozonation. Varying ozone exposure, total organic carbon (TOC) dose, alkalinity, pH, and bromide allowed researchers to investigate relationships between bromate production (at sub-ppb levels) and specific treatment parameters and matrix characteristics. The method was subsequently applied to the determination of bromate in a pilot ozonation plant treating surface water with low-level bromide (<50 ppb) at several ozone to TOC doses. The results demonstrated the applicability of this method to the measurement of sub-ppb levels of bromate in ozonated waters that contain low bromide. The method was found to be very sensitive, with a quantitation limit of 0.05 ppb for bromate, 0.06 ppb for iodate, 0.10 ppb for chlorite, and 70 ppb for chlorate. It was also very selective, in that commonly occurring anions in drinking water samples (e.g., chloride, sulfate, phosphate, and nitrate) are invisible to the UV-PCR detector and therefore do not interfere with the assay.

Application of Method: Following optimization and testing, the method was subsequently applied to samples taken from treatment facilities that ozonated water with low bromide concentrations and/or used hypochlorite to treat water. Previous research has shown that many source waters in the U.S. have ambient levels of bromate on the order of 0.5 ppb; this finding was confirmed using IC-PCR-UV. In addition to bromate present in source water, ozonation of waters that have "low levels" of bromide (< 10 ppb) has been shown to elevate bromate concentrations to upwards of 2 ppb; this finding was also confirmed by this research. Bromate levels in treated water were analyzed from a number of systems where source water bromide was below 10 pbb. Treatment processes included ozone followed by hypochlorination and/or chloramination, or hypochlorination alone. The researchers found that—depending on the dosage of, and number of points of hypochlorite addition during treatment—bromate levels at 20 plants surveyed nationwide ranged from 0.1 to 3 ppb, with an average level of 0.94 ppb. Because bromate levels varied at plants employing similar hypochlorite doses, the researchers suggest that the level of bromate contamination in hypochlorite varies by manufacturer. Such variation may impede future efforts to reduce bromate in systems employing hypochlorite treatment.

Summary and Implications of Research: Research under this grant contributed to the development of a practical technique for use by the drinking water industry to measure sub-ppb levels of bromate in source waters, and in water treated by ozone and/or hypochlorite. For example, it provides EPA and the broader water quality monitoring community a tool to help fulfill the goals of the EPA Information Collection Rule (ICR) regarding the development of a nationwide database on DBP occurrence in drinking water, and for the future development and revision of DBP drinking water regulations. The method uses existing IC instrumentation typically found onsite at drinking water treatment facilities with simple add-on accessories. This research has also demonstrated that if commercially produced hypochlorite solutions continue to be used for secondary disinfection, bromate will continue to be added as a contaminant. In this regard, the researchers concluded that bromate levels in finished waters due to hypochlorite use alone may frequently exceed 0.05 ppb, a concentration associated with a lifetime 10^{-6} cancer risk. Although modifications to the manufacturing process of hypochlorite solutions might reduce the levels of bromate contamination, cost and technological feasibility are major issues of concern to the hypochlorite chemical manufacturing industry, in that water utilities are only a very small portion of their market. Therefore, the researchers concluded that it might be more cost-effective to develop a technology for removing bromate from finished waters that have been treated by ozone and/or hypochlorite. Further bench-scale and pilot-scale studies would be needed to evaluate feasible bromate removal technologies. Regardless of treatment, reducing bromate levels to 0.05 ppb may not be attainable, based on levels found in some raw waters.

Investigators

H.S. Weinberg, University of North Carolina, Chapel Hill
P.C. Singer, University of North Carolina, Chapel Hill

For More Information

NCER Project Abstract and Reports:

http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/199/report/0

Peer Reviewed Publications

Weinberg, H., and Yamada, H. 1998. Post-ion-chromatography derivatization for the analysis of oxyhalides at sub-PPB levels in drinking water. Analytical Chemistry 70(1):1-6.

Weinberg, H., Yamada, H., and Joyce, R. 1998. A new, sensitive and selective method for determining sub-µg/l of bromate in drinking water. Journal of Chromatography A804:137-142.

Delcomyn, C.D., Weinberg, H., and Singer, P.C. 2001. Use of ion chromatography with post-column reaction for the measurement of tribromide to evaluate bromate levels in drinking water. Journal of Chromatography A920:213–219.