Journal of Chemical Health Risks

www.jchr.org

JCHR (2024) 14(6), 991-994 | ISSN:2251-6727

Significance of Regular Monitoring of Inorganic Oxyhalides in Water

Abdullah Siddiqui, Ayeda Matar Ali Al Hosani, & Premanandh Jagadeesan*

Technical Affairs Division, Central Testing Laboratories,

Quality and Conformity Council

P.O Box 853, Abu Dhabi, United Arab Emirates

(Received: 16 September 2024 Revised: 11 October 2024 Accepted: 04 November 2024)

KEYWORDS

Regular Monitoring, Inorganic Oxyhalides

ABSTRACT:

Introduction: The process of disinfection to prevent the colonization of harmful microorganism results in disinfection byproducts particularly during the desalination of sea water. Formation of inorganic oxyhalides such as bromate during chlorination and ozonation needs to be monitored as they found to have health implications.

Objectives: This report presents the status of inorganic oxyhalides in Abu Dhabi water

Methods: Ion Chromatography System equipped with a conductivity detector was utilized to determine the ionic species using a conductivity detector for selective separation of ClO_2^-, BrO_3^- and ClO_3^- ions.

Results: A total of 102 water samples were assessed in this study. Of the 3 oxyhalides investigated, only bromate was found to breach the regulatory threshold while chlorate and chlorite were below the detection limit.

Conclusions: In conclusion, ion chromatography is an effective method to monitor disinfection by products and regular monitoring is very important particularly while converting sea water into drinking water for remedial measures.

1. Introduction

The process of inactivating microorganisms is generally referred as disinfection. It is an essential step to ensure safe water which may otherwise have the potential to cause health implications. In general, disinfection is achieved through ultraviolet light exposure or by using chemical agents such as chlorine and its derivatives (Ramirez et al., 2023). Chlorine is an effective disinfectant applied to reduce the risks of waterborne infections. The oxidizing potential, residual effect, large availability, and cost effectiveness make them preferred choice of disinfectants (Kali et al., 2021). However, chlorine reacts with naturally occurring organic and inorganic matter in water to form byproducts known as disinfection byproducts (DBPs). For instance, free chlorine reacts with natural organic material over an extended contact time resulting in the formation of trihalomethanes which includes chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. These compounds pose serious health threat having the potential to cause cancer (Mishaqa et al., 2022). Inorganic oxyhalides are molecules with oxygen, halogens and another element, usually a metal. The halogen in these compounds is usually bonded to oxygen, forming an anionic complex. Examples of inorganic oxyhalides include chlorate (ClO_3^-), bromate (BrO_3^-), and iodate (IO_3^-) which are often formed as by-products during water treatment processes, particularly in chlorination and ozonation. Prolonged exposure to inorganic oxyhalides in drinking water, at high levels can cause various health problems. According to the International Agency for Research on Cancer (IARC), bromate is categorized as class 2B chemical having carcinogenic potential in humans (IARC, 2019). Likewise, prolonged exposure to chlorite and chlorate can destroy red blood cells and subsequently cause methemoglobinemia and hemolytic anemia (Sorlini *et al.*, 2014). To minimize the health risks associated with disinfection by products, the World Health Organization (WHO), have established guidelines and maximum contaminant levels (MCLs) and regulatory authorities in

Journal of Chemical Health Risks

www.jchr.org

JCHR (2024) 14(6), 991-994 | ISSN:2251-6727

many countries have established rigorous monitoring to ensure the safety of water.

As far as Abu Dhabi, United Arab Emirates (UAE) is concerned, it relies on desalination and groundwater resources to secure freshwater needs. About 84% of desalinated water in Abu Dhabi is produced either by multi-stage flash (MSF) distillation technology or through multiple-effect distillation technology (MED) to convert sea water to drinking water. Nevertheless, long distance transmission channels at a relatively higher temperature have been a concern due to the formation of disinfection by-products over time (Alhamzah *et al*., 2023). Thus, regular monitoring is very crucial to assess the quality status of water distributed through such channels. The department of energy is the regulatory authority for setting policy, standards and regulation for water (DOE, 2021) which prescribes maximum concentration of disinfection byproducts.

2. Objectives

This report presents the status of inorganic oxyhalides in water based on the data assessed during the present study.

3. Methods

One hundred and two water samples were collected using grab sampling technique (APHA 2005). Briefly, one liter of discrete water sample from each location was collected using a hand-held sampler. The samples were labelled and transported in insulated containers to the laboratory for further processing.

Anion analytical reference standards such as Chlorate (CAS# 14866-68-3), Chlorite (CAS# 14998-27-7), and Bromate (CAS# 15541-45-4) were used in this study. Working standards were prepared using deionized ultra-pure water. The calibration curve was obtained using 5 calibration levels (5, 10, 25, 50, and 100ppb). The limit of detection of the assay was determined by applying the mean value of 10 independent replicates of lowest spiked concentration.

Samples with a conductivity ≤1000 µS/cm were injected directly into the auto sampler while those exceeding this value were diluted to bring the final sample conductivity to approximately ≤1000 µS/cm and injected. One hundred micro liter of sample was injected using an AS-AP autosampler and targeted analytes (Chlorate, chlorite and bromate) were separated at 30 °C using a KOH eluent, in gradient mode, at a flow rate of 0.380 mL min^{-1} within a total run time of 30 minutes. Thermo Scientific Dionex ICS-5000 Ion Chromatography System equipped with a conductivity detector was used. Chromatographic separation was achieved using a Dionex IonPac AS19 (4 x 250 mm) chromatographic column with AG19 (4 x 50 mm) guard column. Data collection and processes were conducted using the Thermo Scientific Dionex Chromeleon™ 7 Software. The instrument conditions are provided in table. 1.

Parameters	ICS-5000 Equipment
Sample loop size	100 µL
Injection Volume	100 µL
Guard column	AG19-HC (2X50 mm)
Main Column	AS19-HC (2x250 mm)
Temperature	30°C
Eluent	KOH
Eluent Flow rate, ml/min	0.25
Eluent Generator Mode	Gradient: 0-10 min → 10 mM 10-25 min → 10 mM 25-25.1 min → 45 mM 25.1-35 min → 10 mM
Detection	Suppressed Conductivity Detector
Suppressor	Anion Self-Regenerating Suppressor (AERS_2mm
Applied Suppressor Current	28 mA
Regenerant	Auto regenerant de-ionized water

Table. 1. Ion chromatography instrument conditions

4. Results and Discussion

Ion chromatography (IC) is ideally suited for elemental speciation analysis. It determines ionic species mainly using a conductivity detector through selective separation of ClO2–, BrO3– and ClO3– ions.

The assay calibration was obtained using five-point calibration curve (Fig. 1). The correlation coefficients (R2) were in the range 0.999 with good accuracy. The chromatographic retention time is presented in table. 2. The percentage of overall recovery of spike samples were found to lie between 80-120% and the limit of detection (LOD) for Chlorate, Chlorite and Bromate were 0.46, 2.28 and 0.8 ppb, respectively.

Journal of Chemical Health Risks
www.jchr.org
JCHR (2024) 14(6), 991-994 | ISSN:2251-6727

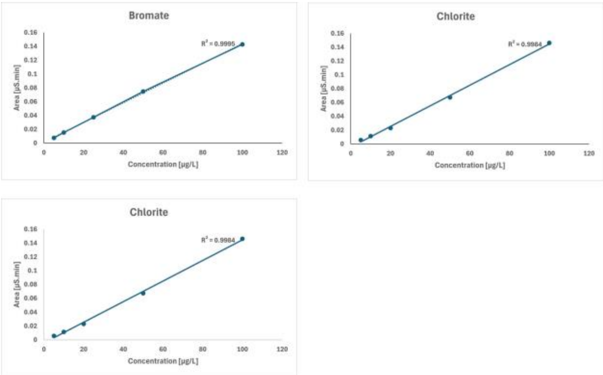

Fig.1. Calibration curve for Bromate, Chlorite and Chlorate

A total of 102 water samples were assessed in this study. Of the 3 oxyhalides investigated, only bromate was detected in the studied samples while chlorate and chlorite were below the detection limit. About 32% of the studied samples found to contain a concentration ranging from 14.2 to 65.7 µg/L. These levels were exceeding the prescribed regulatory value of 10 µg/L. Our results corroborate with Alomirah and coworkers (2020) from Kuwait who reported a relatively higher concentration of up to 89.3 µg/L from tap water in their study.

Test Name	Nominal value	RT	n	Spiked amount (µg/L)	Mean Recovered amount (µg/L)	Recovery %
Bromate (Low)	10	6.353	15	5	4.6600	93.30
Chlorite (Low)	5	6.523	15	10	8.5200	85.22
Chlorate (Low)	10	9.36	15	10	8.2800	82.80

Table. 2. Chromatographic retention time and recovery percentage of spike

One of the reasons for opting thermal desalination over reverse osmosis is associated with a low concentration of disinfection by products (Alhamzah et al., 2023). Nevertheless, the current study confirms the previous finding that thermal desalination does not completely remove disinfection by product precursors (Elshorbagy & Abdul Karim, 2006). Further, it signifies the crucial role of regular monitoring so that control measures can be employed. Since bromine is a natural constituent of seawater, chlorination results in generating hypobromous acid and hypobromite, and there is no control over bromate formation (Ramírez et al., 2023). It is dependent on initial concentration of bromine and low concentration takes relatively longer time for conversion. Therefore, care must be taken to minimize the initial concentration of bromine. For instance, an initial concentration threshold of less than 100 µg/L of bromine was found to keep the bromate formation below the regulatory limits (Morrisson et al., 2023).

In conclusion, ion chromatography is an effective method to monitor disinfection by products and regular monitoring is very important particularly while converting sea water into drinking water for remedial measures.

Acknowledgments

The authors gratefully acknowledge the support and encouragement of the Abu Dhabi Quality and Conformity Council. Gratitude is also extended to the management of Central Testing Laboratories (CTL) for invaluable support.

References

1. Ramírez, Á., de la Morena, A., Sánchez, N., Peñuela, L., Carretero, A. S., · Muñoz, M., and Llanos, J. 2023. Formation of disinfection by-products within the drinking water production system and distribution network of a real case study. *Appl Water Sci*, 13:186.

2. Kali, S., Khan, M., Ghaffar, M.S., Rasheed, S., Waseem, A., Iqbal, M.M., Niazi, M.B.K., Zafar, M.I. 2021. Occurrence, influencing factors, toxicity, regulations, and abatement approaches for disinfection by-products in chlorinated drinking water: A comprehensive review. *Environ Pollut*, 281:116950.

3. Mishaqa, E. I., Radwan, E.K., Ibrahim, M.B.M., Hegazy, T. A., and Ibrahim, M.S. 2022. Multi-exposure human health risks assessment of trihalomethanes in drinking water of Egypt. *Environmental Research*, 207: 112643.

4. IARC. List of classifications: agents classified by the IARC Monographs, Volumes 1–124, IARC Monographs on the Evaluation of Risk to Humans. IARC2019.

5. Sorlini, S., Gialdini, F., Biasibetti, M., and Collivignarelli, C. 2014. Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation. Water Research, 54:44-52.

6. Alhamzah, A.A., Alofi, A. S., Abid, A. A., and Fellows, C. M. 2023. Control of Bromate Formation in Desalinated Seawater Production and Transmission with Ammoniation. *Water*, *15*: 3858.

Journal of Chemical Health Risks

www.jchr.org

JCHR (2024) 14(6), 991-994 | ISSN:2251-6727

7. American Public Health Association (APHA) 2005. Standard methods for the examination of water and wastewater, 21st edn. APHA/ American Water Works Association and Water Environment Federation, Washington.

8. Ramírez, Á., de la Morena, A., Sánchez, N. *et al.* 2023. Formation of disinfection by-products within the drinking water production system and distribution network of a real case study. *Appl Water Sci* **13**, 186.

9. Morrison, C. M., Hogard, S., Pearce, R., Mohan, A., Pisarenko, A. N, Dickenson, E.R.V., von Gunten, U., and Wert, E.C. 2023. Critical Review on Bromate Formation during Ozonation and Control Options for Its Minimization. Environ Sci Technol, 57(47):18393-18409.