Investigation of Ionic Disinfection Byproducts Presence in Treated Drinking Water Distribution Network Using Ion Chromatography

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Introduction

Water disinfection (e.g. using chlorine, chlorine dioxide, chloramines and ozone) has had tremendous results in terms of killing and deactivating bacteria, viruses and pathogens in drinking water in order to make it safe for human consumption. However, this has not come without any setbacks. Water disinfectants react with natural organic matter (NOM) and inorganic material in water forming disinfection byproducts (DBPs)[1]. These compounds have been shown to have adverse effects to humans as they are carcinogens, mutagens, cause abortion and result into still birth[2]. Many DBPs have been detected and identified in water samples. However, developing countries like South Africa have been merely focusing on organic DBPs such trihalomethanes (THMs)[3]. There is a significant research gap in focusing on inorganic/oxyhalide DBPs and their determination in environmental samples using inorganic analytical techniques in South Africa. This study entails the development and validation of a method to detect and determine oxyhalides disinfection byproducts (bromate (BrO_3), chlorate (ClO_3) and chlorite (ClO_2)) using ion chromatograph in environmental water samples. Moreover, the method is going to be used to determine the presence of these oxyhalide DBPs in drinking water and address UN SDG 6 on the provision of safe and clean water.

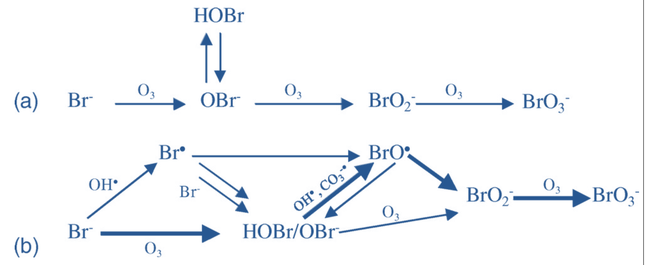
Inorganic DBPs

Bromate forms from ozonation of bromide-containing water as bromide ion (Br^-) is oxidized to bromate (BrO_3^-). For example, bromate (BrO_3^-) which is a potential carcinogen, forms from the residual inorganic bromide's act to rapidly remove ammonia resulting into the formation of hypobromous acid (HOBr) which yields hypobromite (BrO^-) and finally bromate with increased ozone contact time (**Scheme 1**). Chlorate and chlorite result from chlorine dioxide, chlorine and to some extent chloramine (only chlorate) disinfection. Chlorite is the predominant species in the chlorine dioxide decomposition in water and this reaction is favored by alkaline conditions **(Equation 1 and 2)**. Inorganic DBPs are well documented in literature and by the World Health Organization (WHO) to have similar adverse effects to humans as other DBPs. However, they are not reported in the current South African National Standards for drinking water (SANS 0241) of 2015 and there is no/minimal information about them in South African drinking water[4]. The WHO maximum specifications for bromate is 10 ppb, chlorate and chlorite 1000 ppb in drinking water[5].

$$2ClO^- \longrightarrow Cl^- + ClO^-_2 \quad (1)$$

$$ClO^- + ClO^-_2 \longrightarrow Cl^- + ClO^-_3 \quad (2)$$

Equation 1 and 2: Formation of chlorite and chlorate



Scheme 1: Formation of bromate

Aims and objectives

- Develop an IC method to determine bromate, chlorate and chlorite using standards
- Validate the method following prescribed validation guideline using standards and real water samples.
- Apply the developed and validated method to determine presence of bromate, chlorate and chlorite in Rand Water drinking water distribution network.

1. Gilchrist, E. S., Healy, D. A., Morris, V. N., & Glennon, J. D. (**2016**). *Analytica Chimica Acta*.
2. Ding, W., Jin, W., Cao, S., Zhou, X., Wang, C., Jiang, Q., Huang, H., Tu, R., Han, S. F., & Wang, Q. (**2019**). *Water Research*, *160*, 339–349.
3. Mamba, B. B., Krause, R. W., Matsebula, B., & Haarhoff, J. (**2009**). *Water SA*, *35*(1), 121–128.
4. Ngwenya, N., Ncube, E. J., & Parsons, J. (**2013**). *Recent Advances in Drinking Water Disinfection: Successes and Challenges*.
5. World Health Organization **(2010)**. Chemical fact sheets. *Guidelines for Drinking Water Quality*, *Chapter 1*, 296–461.

Instrumentation and conditions

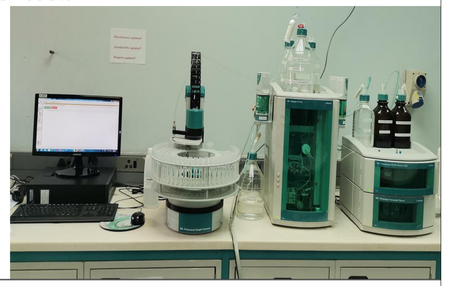
Ion chromatography (IC) offers several advantages over colorimetric techniques as no sample pretreatment is required, low analysis costs and no/less hazardous reagents are required. IC is more accurate, reliable and fast.

Column
- Metrohm A sup 7 – 250/4.0 mm

Test conditions
- Suppressor: 6.2832.000 MSM-A Rotor
- Eluent: 3.6 mmol/L Na_2CO_3
- Flow: 0.700 mL/min
- Temperature: 45.0 ºC
- Pressure: 15.00 MPa
- Sample: BrO_3, ClO_3 and ClO_2
- Sample volume: 50 µL

Instrument
- Metrohm 930 Compact Ion Chromatography Flex

Detection
- Conductivity
- 944 Professional UV/VIS Detector Vario
- 886 Professional Thermostat/Reactor



Preliminary Results and Discussion

Chloride and sulfate were observed to be highly interfering anions in the conductivity detection. This was expected as the water used is disinfected with chlorine. Literature predicts that these can be eliminated by the use of cartridges on-guard -Ag and -Ba and high-capacity columns. Setting the temperature at 45 ºC using isocratic eluent 3.6 mmol/L Na_2CO_3 at 0.7 mL/min yielded peaks of interest in less than 30 min retention time (**Figure 1, Table 1**).

Linearity was determined by preparing 20 ppb standards for individual oxyhalides which was used to calibrate the instrument down to 0.2 ppb. Conductivity detection was able to quantitate oxyhalides to as low as 0.2 ppb. UV/Vis detection was able to only quantitate chlorite and bromate, as expected since chlorate does not react with UV/Vis reagents potassium iodide and antimonyl heptamolybdate.

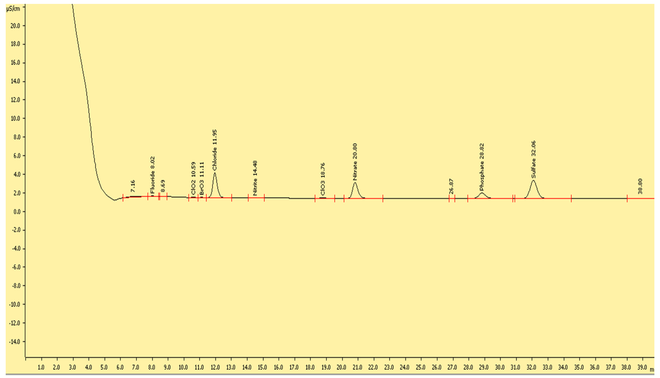


Figure 1: Chromatogram of the 10 ppb calibration standard

Component	Retention time (min)	Concentration (ppb)
BrO_3	11.12 Conductivity	10.206
	11.67 UV/VIS	10.092
ClO_3	18.34 Conductivity	10.064
ClO_2	10.61 Conductivity	10.362
	11.16 UV/VIS	10.607

Table 1: Observed retention time and concentration