Element-specific examination of volatile halogenated organics in wastewater extracts using GC-ICP-MS.

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Introduction

Water naturally contains differing levels of chloride, bromide, and iodide ions. These ions are typically not harmful to human health at reasonable levels; however, these halides can be incorporated into organic structures when water containing these ions is treated using oxidative processes such as chlorination, ozonation, and chloramination[1, 2]. The oxidative conditions employed in the treatment process can convert these halides into "activated" forms, which can then react with organics present in wastewater to form halogenated disinfection byproducts (DBPs)[3], where many species are largely unidentified[4]. Considering increasing stresses on freshwater resources, many municipalities are considering alternative sources of water for potable supply, including purification of wastewater and ocean desalination. Both wastewater and ocean water have significantly elevated levels of iodide and bromide as compared to most ambient freshwater sources. While some DBPs are regulated in drinking water by the United States EPA, the regulated DBPs are a small list of identifiable compounds[5]. Given that iodinated and brominated DBPs are more toxic than their chlorinated analogs[6-8], it is prudent that occurrence data is acquired quickly in order to better understand the magnitude and prevalence of these emerging DBPs.

Most analytical methods such as EPA method 551.1 employ GC with electron capture detection (GC-ECD) for determining the concentrations of volatile halogenated DBPs in extracts prepared from waters. These methods are limited in their ability to differentiate halogenated species from each other, or from other interfering non-halogenated species. Indeed, methods do exist for determining these species by GC-MS or GC-MS/MS. Unfortunately these forms of molecular MS are limited in their ability to screen a wide array of unidentified molecules for halogen content in a single analysis given due to ionization issues. Chemical Ionization (CI) does not ionize all types of organic molecules, and electron impact (EI) can lead to excessive, undesirable in-source fragmentation. In addition, GC-MS/MS analysis is limited by the inefficient fragmentation of halogenated precursor ions into monatomic halogen product ions (i.e., Br^+ and Br^-).

Instrumentation

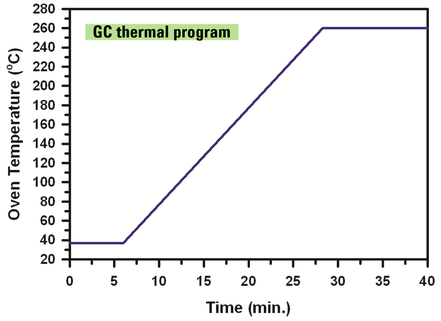
Sample preparation

Municipal wastewater samples were collected from geographically separated areas. Samples were split in two, with one half untreated and the other half treated with aqueous monochloramine. For extraction, 35 mL of these wastewater samples were extracted using 5 mL of MTBE in a modified version of EPA method 551.1. The organic layers were carefully separated and then placed into 2.0 mL amber Agilent GC vials.

Instrument Configuration and Conditions

Gas Chromatograph:

- Agilent 7890A w/ heated ICP-MS transfer line & injector
- Agilent 30 m HP-5 column (320 µm x 0.25 µm)
- 200 °C inlet & 260 °C transfer line/injector temperatures
- Pulsed splitless inection (10 psi until 0.75 min, 5.8 psi afterwards)
- Oven 37 °C for 6 min, then 10 °C/min rise to 260 °C, then hold for 11 min.



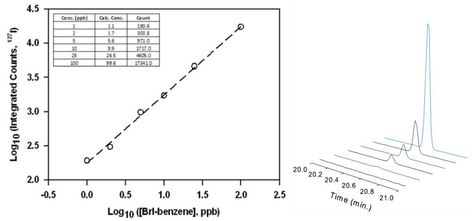
ICP-MS:

- Agilent 7700x ICP-MS operated in No gas mode
- 3.0 mm sample depth, RF power 700 W
- 0.4 L/min dilution gas (Ar) delivered to transfer line
- 0.15 second integrations of m/z 79, 81, and 127
- Calibration standards prepared in MTBE using 1-bromo-4-iodobenzene (0, 1, 2, 5, 10, 25, 100 ng/mL)

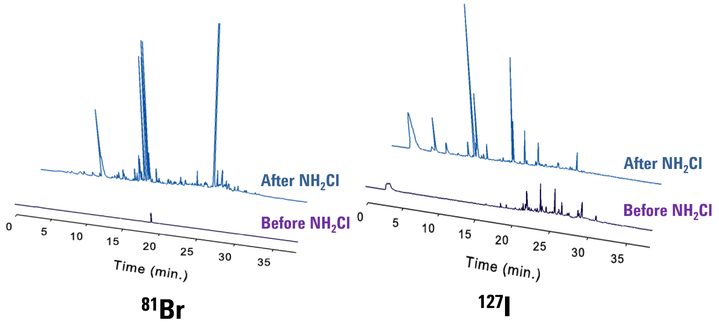
Results and Discussion

Analysis of Calibration Standards & Samples

Using the method described previously, 1-bromo-4-iodobenzene elutes from the column at 20.5 minutes. We have been able to detect iodine in all non-zero calibration standards and bromine in all standards with (compound) concentrations above 5 ng/mL..



Wastewater samples were then examined before and after treatment with monochloramine. The reaction with monochloramine leads to an increase in the concentration of brominated and iodinated species in the extracts. These data reveals several interesting facts. First, there are volatile halogenated organics present in wastewaters prior to chloramination and some of these species are resistant to transformation upon monochloramine treatment while others are consumed (and likely transformed into new halogenated DBPs). Thus it is likely that many non-halogenated organics in untreated wastewaters are converted into new halogenated DBPs, as well.



Summary of Results

The results of our study indicate that the monochloramination of wastewater samples does indeed dramatically change the concentration and speciation of halogenated volatile organics in these waters.. The effects of monochloramination are seen most profoundly in terms of the differences between chromatograms for brominated and iodinated DBPs. There are two reinforcing explanations for this, one dealing with the reactivity of bromide and iodide during oxidative treatments, and the higher sensitivity for detection for I and Br in our assays due to their elemental ionization potentials.

The chloramination of these samples causes clear and profound changes to occur in the concentration and speciation of halogenated organics. The total volatile organohalogen levels increase upon chloramination(as evidenced below) and there is an increased presence of more volatile I-DBPs.

	Blank Extract	Before $ClNH_2$	After $ClNH_2$
Bromine (ppb)	103	1134	98229
Iodine (ppb)	93	490	777

Conclusions

We have succeeded in using an Agilent 7890A coupled to an Agilent 7700x ICP-MS to determine the presence, transformation, and formation of halogenated DBPs in wastewaters that are treated by chloramination. Our instrument configuration allows for easy tuning, chromatographic separation of an array of diverse compounds, and interference-free, high sensitivity analysis for halogens covalently bound within organic molecules. The use of CICs allows us to quantitate the halogen contents of these compounds based on the responses obtained from a commercially available dihaloaromatic. An added benefit to using GC-ICPMS for the analysis of these complex mixtures of halogenated organics is the element-specificity that our ICPMS platform provides over other halogen detection methodologies like GC-ECD. In the near future, we aim to identify these DBPs using GC-QToF and to investigate water treatment technologies that will minimize the formation of iodinated and brominated DBPs.

References

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