An Examination of the Presence, Formation, and Transformation of Volatile Halogenated Organic Species in Wastewater Extracts Using GC-ICP-MS

Application Note

Environmental

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Abstract

The presence and transformation of volatile halogenated organics in wastewaters after treatment with monochloramine have been examined using an Agilent 7890A GC coupled to an Agilent 7700x ICP-MS. The element-specific bromine and iodine content in this diverse set of organic species have been determined using compound-independent calibrations (CICs) that are based on the elemental responses obtained from a calibration curve prepared from the commercially available dihaloaromatic compound, 1-bromo-4-iodobenzene.

Introduction

Water naturally contains differing levels of chloride, bromide, and iodide ions, which are typically not harmful to human health at reasonable levels. However, these halides can be incorporated into organic molecules 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 organic molecules present in wastewater to form halogenated disinfection byproducts (DBPs) [3], of which many species are largely unidentified [4].

Considering the increasing stresses on freshwater resources, many municipalities are contemplating 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 compared to most ambient freshwater sources. While some DBPs are regulated in drinking water by the United States Environmental Protection Agency (EPA), the regulated DBPs comprise a small list of identifiable compounds [5].

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Since iodinated and brominated DBPs are more toxic than their chlorinated analogs [6-8], it is prudent that occurrence data is acquired quickly 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) to determine 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 nonhalogenated species. Indeed, methods do exist for determining halogenated DBPs by GC/MS or GC/MS/MS. However, these forms of molecular mass spectrometry are limited in their ability to screen a wide array of unidentified molecules for halogen content in a single analysis, 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 (that is, Br^+ and Br^-).

This application note describes a novel approach for detecting and quantifying the presence of halogenated organic compounds using an Agilent 7890A GC coupled to an Agilent 7700x ICP-MS. In this work, we prepared calibration curves for iodine and bromine using the commercially available 1-bromo-4-iodobenzene. Compound-independent calibrations (CICs) were then used to quantify the halogen content of various halogenated organics in our extracts. As compounds elute from the GC column, the high temperature of the ICP-MS source quantitatively converts halogenated organics into organic fragments and halogen ions. The dry plasma conditions used in our approach minimized the formation of oxide-based interferences and allowed operation without use of the collision cell.

Experimental

Chemicals and standards

Calibration standards of 1-bromo-4-iodobenzene (Alfa Aesar) were prepared in HPLC grade methyl tertiary butyl ether (MTBE, Fisher Scientific) with concentrations of intact compound being 0, 1, 2, 5, 10, 25, and 100 ng/mL.

Instrumentation

This study was performed using an Agilent 7890A GC coupled to an Agilent 7700x ICP-MS. The instrument conditions used are listed in Table 1.

Table 1. GC and ICP-MS Instrument Parameter Conditions

GC conditions	
Precolumn	None
Analytical column	Agilent J&W HP-5, 30 m × 0.32 mm, 0.25 µm (p/n 19091J-413)
Inlet temperature	200 °C
Injection mode	Pulsed splitless (10 psi until 0.75 minutes, 5.8 psi afterwards) constant pressure mode
Injection volume	1 µL
Oven program	6 minutes at 37 °C 10 °C/min to 260 °C Hold at 260 °C for 11 minutes
Initial column flow	1.2 mL/min
Carrier gas	UHP helium
ICP-MS transfer line injector temperatures	200 °C
GC run time	39 minutes
ICP-MS conditions	
Mode	No collision gas mode; time resolved analysis (TRA) for masses 79, 81, and 127
Integration time	0.15 seconds for each ion over a 38 minute acquisition window
RF forward power	700 W
Dilution gas flow	Argon at 0.39 L/min
Sampling depth	3.0 mm

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 preformed aqueous monochloramine such that the initial concentration of monochloramine in the mixture was 0.08 mM, and the reaction time was 4 hours. A 35 mL aliquot of each treated and untreated sample was then extracted using 5 mL of MTBE in a modified version of EPA method 551.1. For each sample extraction, the MTBE organic layer was carefully separated and placed into a 2.0-mL amber Agilent GC vial.

Results and Discussion

Detection of iodine and bromine

Using this method, 1-bromo-4-iodobenzene elutes from the column at 20.6 minutes. An iodine-containing peak was detected in all nonblank calibration standards (Figure 1), and a bromine-containing peak was detected at calibration standard (intact compound) concentrations higher than 5 ng/mL. Background (non-peak) signal levels for both ^{127}I and ^{81}Br are very low (~30 cps) throughout each of the chromatograms and show no appreciable dependence on oven temperature, indicating minimal presence of hydride-based interferences ($^{126}XeH^+$ and $^{40}Ar_2H^+$, respectively).

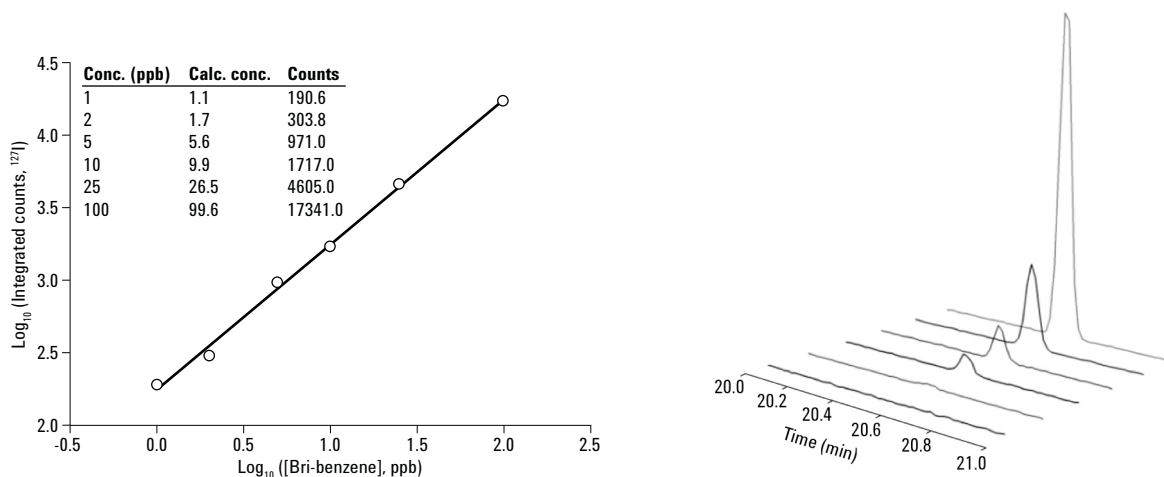| Conc. (ppb)	Calc. conc.	Counts
1	1.1	190.6
2	1.7	303.8
5	5.6	971.0
10	9.9	1717.0
25	26.5	4605.0
100	99.6	17341.0

Figure 1. Log/log plot of a calibration curve for ^{127}I prepared from 1-bromo-4-iodobenzene (left panel) and an overlay of ^{127}I peak intensities for calibration standards (ranging from 0.0 to 25 ppb) analyzed in this work, including a calibration blank (right panel). The retention time for this compound is 20.6 minutes. Chromatograms are not background-subtracted.

Wastewater sample analysis

Wastewater samples were examined before and after treatment with monochloramine. The chromatograms reflect a substantial increase in the concentration of brominated and iodinated species, as well as a change in organohalogen species following treatment (Figures 2 and 3). Indeed, there are some halogenated organics present in wastewaters prior to chloramination. In addition, many non-halogenated organics in untreated wastewaters are converted into new species of halogenated DBPs upon chloramination. Moreover, some of the brominated and iodinated species present before disinfection treatment are resistant to transformation upon monochloramine treatment, while others are consumed (reacted) and are likely transformed into new halogenated DBPs (Figure 3).

The increase in halogenation and changes in halogenated species are due to the high reactivity of bromide and iodide during oxidative treatments. A decrease in argon-based interferences on $^{79/81}Br$ (namely $^{38}Ar^{40}ArH^+$ and $^{40}Ar_2H^+$, respectively) can be attributed to the lower RF power of the dry plasma; at lower RF power the ionization of argon
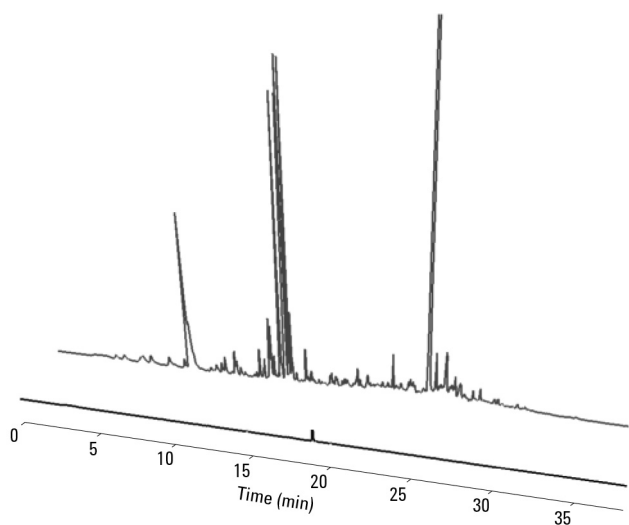

Figure 2. ^{81}Br GC-ICPMS chromatograms obtained from MTBE extracts prepared from a representative wastewater sample before chloramination (purple line, front) and after chloramination (blue line, behind). Intensity scales are identical for both plots. Chromatograms are not background-subtracted.
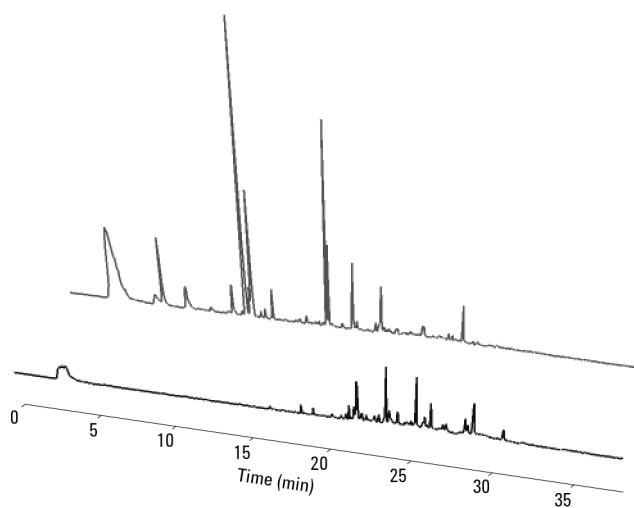

Figure 3. ^{127}I GC-ICPMS chromatograms obtained from MTBE extracts prepared from a representative wastewater sample before chloramination (purple line, front) and after chloramination (blue line, behind). Intensity scales are identical for both plots. Chromatograms are not background-subtracted.

(IP1 = 15.8 eV) is suppressed more than the ionization of bromine (IP1 = 11.8 eV). Despite the existence of a xenon-based hydride interference ($^{126}XeH^+$), essentially interference-free measurements at m/z 127 (^{127}I) can be performed due to the low levels of Xe in the argon supply and the low isotopic abundance of ^{126}Xe (0.09%) compared to the isotopic purity of the iodine in these samples (as evidenced by the 18 cps steady level in the blank). The data generated using this method were highly reproducible, as all continuing calibration verifications (CCVs) were within 10% of bromine and iodine values for the initial calibration.

Many halogenated organic species were detected, some of which are shown in Table 2, before and after chloramination. These data show that the levels of most halogenated organic species increased dramatically after chloramination in all three wastewater samples (Table 2). Compound-independent calibrations (CICs) were used to estimate the concentrations of these unidentified DBPs. While the use of CICs is a well-validated practice in ICP-MS, the quantitative determination of unknowns in our experiments is only an approximation due to the changing He carrier gas flow on our GC (using constant inlet pressure mode) as a result of the oven temperature program. Whereas, the concentrations of most organohalogens increase following chloramination, two exceptions are seen in the case of the unidentified halogenated compounds Br-2 and I-3 in Sample 1 (highlighted in yellow in Table 2). In these cases, the detected levels of both compounds decrease after chloramination, illustrating the ability of these compounds to be transformed into new and perhaps increasingly more halogenated DBPs.

Conclusions

GC-ICP-MS analysis using the Agilent 7890A GC coupled to the Agilent 7700x ICP-MS is an effective tool in determining the presence, formation, and transformation of halogenated DBPs in wastewaters treated by chloramination. The instrument configuration enables easy tuning, chromatographic separation of an array of diverse compounds, and essentially interference-free, high sensitivity analysis for halogens covalently bound to organic molecules. The use of CICs allowed us to approximately quantify the halogen content of these compounds based on the responses obtained from a commercially available dihaloaromatic compound. This technology also enables determination of the total concentrations of volatile brominated and iodinated organic species in a sample. A further benefit of using GC-ICP-MS for the analysis of these complex mixtures of halogenated organics is the element specificity that this ICP-MS platform provides over other halogen detection methodologies such as GC-ECD. We plan to identify these DBPs in the future using GC-Q-TOF and to investigate water treatment technologies that will minimize the formation of iodinated and brominated DBPs.

Table 2. Elemental Halogen Concentrations (in PPB) Present in Various Organohalogens

	Compound name	Br-1[†]	Br-2[†]	Br-I-benzene*	Br-3[†]	I-1[†]	I-2[†]	Br-I-benzene*	I-3[†]
	Retention time (min)	15.4	19.0	20.6	25.2	12.2	12.6	20.6	29.0
	Measured isotope	^{81}Br	^{81}Br	^{81}Br	^{81}Br	^{127}I	^{127}I	^{127}I	^{127}I
Standards	Br-I-benzene* 1ppb							0.5	
	Br-I-benzene 2 ppb							0.8	
	Br-I-benzene 5 ppb			1.2				2.5	
	Br-I-benzene 10 ppb			3.0				4.4	
	Br-I-benzene 25 ppb			7.1				11.9	
	Br-I-benzene 100 ppb			28.3				44.7	
Samples	MTBE Blank		2.5		4.2	1.2	0.6		0.6
	Sample 1 before	1.1	346.8	3.2	15.6		1.3	4.6	26.0
	Sample 1 after	3315.0	293.7		44558.0	169.9	103.4		1.6
	Sample 2 before	3.5	3.2		19.0	0.1	0.6	0.7	1.3
	Sample 2 after	4819.9	1254.7	1377.7	121428.9	23.5	34.8	18.5	6.6
	Sample 3 before	15.4	37.9		100.1	4.1	2.6	1.3	14.8
	Sample 3 after	3388.6	1130.8		126629.7	31.9	103.6	28.5	29.7

*1-bromo-4-iodobenzene (concentrations in standards' names are in ppb of intact compound).
[†]Unidentified halogenated organic compound

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