ANALYSIS OF IODINATED HALOACETIC ACIDS IN DRINKING WATER USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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INTRODUCTION

Iodoacetic acid (MIAA) has been reported to be the most toxic disinfection by-product (DBP), with a $\%C^{1/2}$ (~LC_{50}) value of 2.95 µM. For example, the genotoxicity of MIAA has been reported to be 523.3x higher in *S.typhimurium* than chloroacetic acid (MCAA). In most surveys, low concentrations of HAAs have been detected especially when chloramine (NH_2Cl) has been used as disinfectant. Chloramination has been extensively used in the past decade because of its long term stability in distribution systems and its lower production of DBPs compared to chlorination. In contrast to the chlorinated and brominated DBPs, it has been demonstrated that the formation of I-DBPs is favoured when NH_2Cl is used as oxidant. NH_2Cl reacts with iodide initially present in natural water to form active iodine HOI that can react with natural organic matter (NOM) to form I-DBPs. If NH_2Cl is used as disinfectant, HOI is stabilised in solution because the oxidizing power of NH_2Cl is not sufficiently strong to oxidise active iodine to iodate which is the desired sink of iodine in water treatment.

Only chlorinated and brominated haloacetic acids are regulated. The US EPA has established a guideline of 60 mg/L for the total concentration of 5 haloaetic acids (HAAs) (MCAA, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA)). The presence of I-HAAs was reported for the first time in US drinking waters by Krasner *et al*. The occurrence of MIAA (and other iodoacetic acids) has already been detected and quantified at a maximum level of 1.7 mg/L for water containing between 0.4 to 104.2 µg/L of iodide in the US. A recent survey in Western Australia shows some source waters contain significant concentrations of iodide, greater than those reported in the US study, highlighting the fact that iodoorganic compounds should be quantified and considered for guideline values along with their chloro and bromo analogues. Furthermore, the increasing water demand due to climate change and population growth induces potential overuse of fresh water resources which may lead to seawater intrusion into the groundwater in coastal regions, leading to increasing concentrations of iodide in groundwater. In waters containing relatively high concentrations of iodide, elevated concentrations of I-DBPs may be formed even if low concentrations of regulated DBPs are observed, thus it is important to be able to quantify the presence of I-HAAs (and I-DBPs in general) at very low concentrations, and develop methods to control their concentrations, to prevent subsequent health effects due to water consumption. The formation of iodo-organic compounds is starting to attract some attention in Australia, as it has been recently discussed within the Australian Drinking Water Guideline (ADWG) committee.

In this study, we developed a simple and sensitive (ng/L level) method to analyse four I-HAAs (MIAA, chloroiodoacetic acid (CIAA), bromoiodoacetic acid (BIAA) and diiodoacetic acid (DIAA)) by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

METHODOLOGY/ PROCESS

The LC-MS/MS measurements were performed using an Agilent 1100 HPLC system (Palo Alto, CA, USA). For detection, the LC was coupled to a Micromass Quattro Ultima Triple Quadrupole (Manchester, UK) system fitted with an ESI operated in negative ion mode.

RESULTS/ OUTCOMES

HAAs are currently analysed following the US EPA method 552: this method is highly sensitive and allows detection at the ng/L range for the regulated chloro and bromo HAAs. Basically, HAAs are extracted from the water samples by liquid-liquid extraction using methyl *tert*-butyl ether. Due to the very low pKa of HAAs (0.63-2.9), the sample is previously strongly acidified to pH<0.5 to stabilise the protonated species and favour their extraction into the organic phase. Thereafter, the analytes are converted to their methyl esters to enhance the volatility of the compounds and quantified using GC-ECD. This method is a lengthy and labour intensive procedure. It has been demonstrated that the sample is altered to some extent during the preparation of the methyl esters (dehalogenation during the acidic methylation) and undergoes thermal degradation in the GC injection port.

We have now developed a simple and sensitive LC-MS/MS method for the analysis of four I-HAAs in drinking water with minimal sample preparation. Since LC can be used to analyse aqueous samples, there is no need for extraction and derivatization steps, and the surface-active behaviour, the strong acidity, and the thermal degradation in the GC injection port are avoided and the sample is not altered. Nevertheless to reach a low detection limit, concentration of the sample is still needed, thus solid-phase extraction (SPE) has been tested as an extraction technique. For the mass spectrometric analysis, Table 1 lists the precursor → daughter ions monitored for each compound and Figure 1 shows the multiple reaction monitoring (MRM) results for the four I-HAAs. In this paper, the analytical method will be further described and results from treated waters will also be presented.

Table 1. Precursor and product ions, cone voltage and collision energy values optimised for the analysis of iodoacetic acids

Compound	Acronym	Precursor ions [m/z]	Product ions [m/z]	Cone voltage	Dwell time (ms)	Collision energy
Monoiodoacetic acid	MIAA	185.0	127.0	25	150	10
Monoiodoacetic acid-d_3	MIAA-d_3	187.0	127.0	25	150	10
Iodochloroacetic acid	IClAA	221.5	177.0 127.0	25 25	150 150	10
Iodobromoacetic acid	IBrAA	265.0	221.0 127.0	25 25	150 150	10 10
Diiodoacetic acid	DIAA	312.0 267.0	267.0 127.0	25 25	150 150	10 20

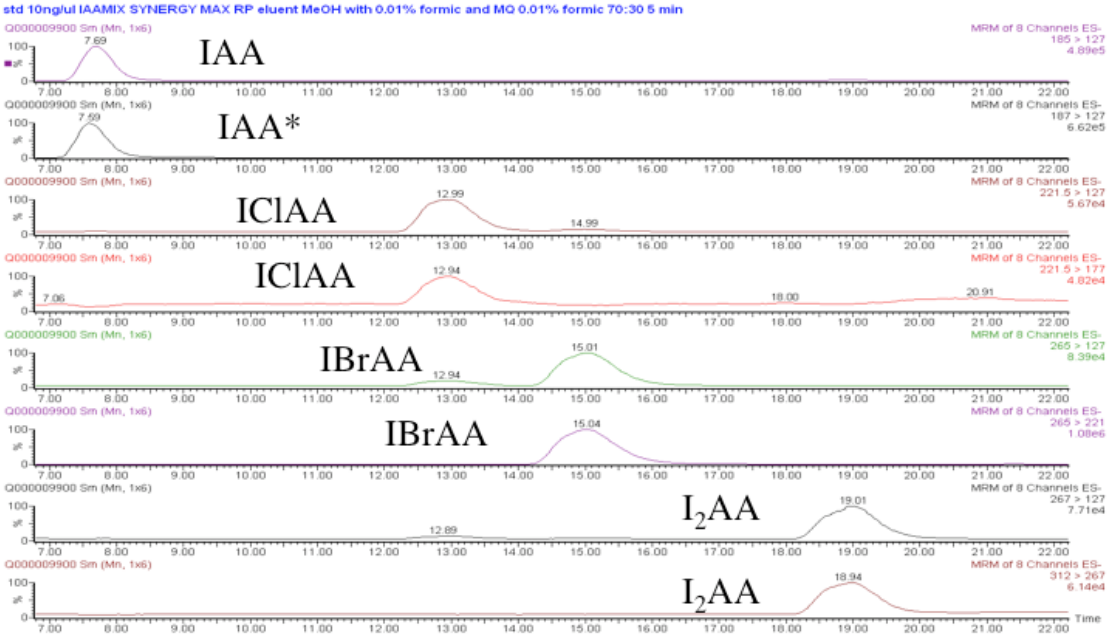

Figure 1 MRM measurements of four iodo-acetic acids