Simultaneous determination of bromate, chlorite and haloacetic acids by two-dimensional matrix elimination ion chromatography with coupled conventional and capillary columns

Hui Boon Teh [a], Sam Fong Yau Li [a,b,c,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[b] NUS Environmental Research Institute, 5A Engineering Drive 1, T-Lab Building, Singapore 117411, Singapore
[c] Shenzhen Engineering Laboratory for Eco-efficient Polysilicate Materials, School of Environment and Energy, Peking University Shenzhen Graduate School, University Town, Xili, Nanshan District, Shenzhen 518055, PR China

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ABSTRACT

A new, highly sensitive and reliable two-dimensional matrix elimination ion chromatography (IC) method was developed for simultaneous detection of bromate, chlorite and five haloacetic acids. This method combined the conventional IC in first dimension with capillary IC in the second dimension coupled with suppressed conductivity detection. The first dimension utilizes a high capacity column to partially resolve matrix from target analytes. By optimizing the cut window, the target analytes were selectively cut and trapped in a trap column through the use of a six-port valve, while the separated matrix were diverted to waste. The trapped target analytes were delivered on to the capillary column for further separation and detection. Temperature programming was used to improve selectivity in second dimension column to obtain complete resolution of the target analytes. Compared to the performance of one-dimensional IC, the two-dimensional approach resulted in a significant increase in sensitivity for all target analytes with limit of detection ranging from 0.30 to 0.64 μg/L and provided more reliable analysis due to second column confirmation. Good linearity was obtained for all the target analytes with correlation coefficients >0.998. The proposed method was successfully applied to the determination of oxyhalides and haloacetic acids in various matrices with recoveries ranging from 90 to 116% and RSD less than 6.1%. The method allows direct injection of samples and the use of columns with different selectivity, thus significantly reduces the level of false positive results. The method is fully automated and simple, making it practical for routine monitoring of water quality. The satisfactory results also demonstrated that the two-dimensional matrix elimination method coupled with capillary IC is a promising approach for detection of trace substances in complex matrices.

1. Introduction

Water disinfection is the process of removing or killing of pathogenic microorganisms. It has helped to reduce significantly the incidences of water-borne diseases such as poliomyelitis and cholera. The most common disinfectants used in water disinfection are chlorine, chlorine dioxide and chloramines. Ozone is another type of disinfectant that is effective in treating chlorine resistant organisms. However, during the disinfection process, disinfection by-products (DBPs) are formed due to the reaction of disinfectants with natural organic and inorganic matter in the source water [1–5]. These DBPs take many forms, over 600 kinds of DBPs have been reported to date for the major disinfectants used as well as their combinations [5–7]. Based on the outcomes from toxicological studies, exposure to these compounds has been associated with a number of health problems.

Haloacetic acids (HAAs) are one of the most prevalent group of DBPs in chlorinated water [8]. They are highly soluble in water as anions (pK_a range from ∼0.7 to 2.8) and majority of them are suspected to be carcinogenic agents and potential health threats, such as spontaneous abortions and birth defects [9–11]. The U.S. Environmental Protection Agency (US EPA) has regulated the five commonly occurring HAAs (HAA5: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA)) under the

* Corresponding author at: Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore. Tel.: +65 65162681.
E-mail address: chmlifys@nus.edu.sg (S.F.Y. Li).

Disinfectants and Disinfection Byproducts (D/DBP) Rule with a maximum contamination level (MCL) of 60 µg/L in drinking water [12]. Among the five HAAs, DCAA and TCAA are proven to be animal carcinogenic even at low concentration [13]. Therefore, World Health Organization (WHO) has established guidelines for chlorinated HAAs (MCAA: 20 µg/L; DCAA: 50 µg/L; TCAA: 200 µg/L), but not for brominated HAAs [14].

The standard methods recommended by the US EPA for determination of HAAs in water is gas chromatography with electron capture detection (GC–ECD) [15–18]. Many gas chromatography with mass spectroscopy (GC–MS) methods have also been reported [19,20]. These methods provide high recoveries and low detection limits, but the transfer, extraction and derivatization of samples make the methods complex, time-consuming, labor-intensive and require the use of toxic organic solvents. Several alternative separation methods have been reported for the determination of HAAs, such as capillary electrophoresis (CE) [21,22], ion-chromatography (IC) [23–27] and liquid-chromatography (LC) with UV detection [28,29] or with mass spectrometry (MS) [30–32]. Although these methods provide shorter analysis time and do not require derivatization compared to GC-based methods, off-line preconcentration of samples and large injection volume are needed to comply with the minimum reporting levels required by the regulatory agencies. The high-field asymmetric waveform ion mobility spectrometry (FAIMS) methods also can provide very low detection limits with little sample preparation, but the instrument is not widely used in laboratories [33,34]. Therefore, highly sensitive new strategies without the need of off-line preconcentration and derivatization are desirable to increase simplicity and economize analysis time in HAAs determination.

Along with HAAs, many studies have investigated the formation and presence of oxyhalide through drinking water ozonation [4,35,36]. In particular, bromate is one of the most important inorganic oxyhalide byproduct whose concentration in drinking water has to be controlled. Bromate (BrO_3^-) is primarily generated from ozone or hypochlorite disinfection when bromide ions are present in the water, or when chlorinated water is exposed to sunlight [4,37]. The International Agency for Research on Cancer (IARC) has classified bromate as a Group 2B substance (the agent is possibly carcinogenic to humans), thus there is a need to determine its concentration level in drinking water. The WHO specified a guideline of 10 µg/L for bromate in drinking water with cancer risks of 10^{-5} for 2 µg/L of bromate [38]. The US EPA also promulgated a MCL of 10 µg/L for bromate in drinking water under the D/DBP Rule [12]. Besides bromate, chlorite is another oxyhalide byproduct which is also regulated by agencies. Chlorite (ClO_2^-) is formed when chlorine dioxide is used as disinfectant [39]. Although not so toxic compared to bromate, chlorite are reported to have nervous system effects on fetuses, infants or young children [12]. Therefore, the WHO specified a guideline of 0.7 mg/L and US EPA promulgated a MCL of 1 mg/L for chlorite in drinking water [12,14].

Due to their potential health risk to humans, numerous standard methods have been developed for the analysis of oxyhalide, especially for bromate, by US EPA and International Organization for Standardization with many of these methods focused primarily on using IC combined with conductivity detection or postcolumn reaction (PCR) followed by UV/vis detection [40–47]. EPA Method 300.1 was published as an update to Method 300.0 in which the detection limit of bromate was further reduced from 20 µg/L to 1.4 µg/L by using a higher capacity column. EPA Method 317 and 326, using conductivity detection and PCR, offer excellent detection limit for bromate, however removal of chlorite is required prior to analysis and some of the reagents are possible carcinogens. Recently, Method 302 was established using two-dimensional IC to provide a more robust solution for drinking waters with high concentrations of anions compared to PCR. Method 321.8 is a highly sensitive

method for determination of bromate using IC-ICP-MS, however sample pretreatment is required to remove HAAs. There are many other MS-based techniques have been reported for the trace analysis of oxyhalides in drinking water [48–50]. Although sub-ppb level detection limits and multi-component analysis could be achieved with the methods, they each add considerable complexicity and significant cost to the analysis.

Oxyhalides and HAAs are among the most common DBPs found in drinking water in the µg/L level, but also found in environmental waters such as surface water and groundwater [51]. The determination of trace of these compounds in samples that contained high levels of common anions, such as chloride, sulfate and carbonate, is the main challenge. The presence of high levels of matrix ions can co-elute with the analytes of interest making analysis with direct injection of sample not possible. In addition, the matrix ions can overload the separator column causing analyte peak distortion or broadening. As such, sample pretreatment step is required to improve method sensitivity. Alternatively, sample dilution can be used to lower the matrix ion concentration but it will also lower the analyte concentration, which makes trace analysis difficult. Another approach for high matrix concentration samples is heart-cut column-switching whereby a switching valve is used to divert majority of matrix ions to waste followed by further detection of the analyte peaks. In line with this, various instrumental configurations have been used for applications such as determination of perchlorate [52,53] and bromate [47] in drinking water. These methods provide excellent detection limits but only targeted single analyte analysis.

Since bromate, chlorite and HAA5 are the important regulated DBPs, it is a great advantage if a method can be used to detect all of these compounds simultaneously. Suppressed IC technique is widely used for the separation and determination of ionic solutes in water in general with the advantages of low-cost, low background, simple operation and construction. However, due to presence of mg/L matrix in sample and frequent co-elution with each other, plus their low concentration and the non-specific nature of suppressed conductivity, to establish a single routine and reliable IC method is a significant challenge. In IC, one of the great achievements in recent years is the introduction of capillary scale IC. The scaling down from conventional analytical IC columns (2 mm and 4 mm i.d.) to capillary columns (0.4 mm i.d.) provides several benefits in term of speed, time, sensitivity and cost of ownership. While many applications of IC have been described, relatively few capillary IC applications exist. In this study, we demonstrate the application of an inline matrix elimination two-dimensional IC (2D-IC) method for the determination of bromate, chlorite and HAA5 in various water samples with suppressed conductivity detection. The approach combined the conventional IC with capillary scale IC and used independent temperature control of each column to manipulate the overall selectivity of the system. To our best knowledge, this is the first two-dimensional method reported to date to incorporate regulated oxyhalides and HAAs in a single separation and detection run. This 2D-IC system coupling conventional IC with capillary IC provides the method with superior sensitivity and the use of different chemistry columns minimizes the possibility for false positive. The approach also offers a possibility for routine analysis of these compounds by IC with advantages of simultaneous, fully automated and higher throughput alternative to individual standard methods.

2. Experimental

2.1. Chemicals

Analytical grade MCAA, MBAA, DCAA, DBAA and TCAA, as well as the potassium salts of bromate, chlorate (ClO_3^-),