The use of trichloroacetic acid imprinted polymer coated quartz crystal microbalance as a screening method for determination of haloacetic acids in drinking water

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Abstract

An alternative screening method for haloacetic acids (HAAs) disinfection by-products in drinking water is described. The method is based on the use of piezoelectric quartz crystal microbalance (QCM) transducing system, where the electrode is coated with a trichloroacetic acid-molecularly imprinted polymer (TCAA-MIP). This MIP comprises a crosslinked poly(ethylene glycol dimethacrylate-co-4-vinylpyridine). The coated QCM is able to specifically detect the analytes in water samples in terms of the mass change in relation to acid–base interactions of the analytes with the MIP. The TCAA-MIP coated QCM showed high specificity for the determination of TCAA in aqueous solutions containing inorganic anions, but its sensitivity reduced in water samples containing hydrochloric acid due to a mass loss at the sensor surface. Cross-reactivity studies with HAA analogs (dichloro-, monochloro-, tribromo-, dibromo-, and monobromo-acetic acids) and non-structurally related TCAA molecules (acetic acid and malonic acid) indicated that recognition of the structurally related TCAA compounds by the TCAA-MIP-based QCM is due to a carboxylic acid functional group, and probably involves a combination of both size and shape selectivity. The total response time of sensor is in the order of 10 min. The achieved limits of detection for HAAs (20–50 \text{gl}^{-1}) are at present higher than the actual concentrations found in real-life samples, but below the guidelines for the maximum permissible levels (60 \text{gl}^{-1} for mixed HAAs). Recovery studies with drinking water samples spiked with TCAA or spiked with mixtures of HAAs revealed the reproducibility and precision of the method. The present work has demonstrated that the proposed assay can be a fast, reliable and inexpensive screening method for HAA contaminants in water samples, but further refinement is required to improve the limits of detection.

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Keywords: Haloacetic acids; Disinfection by-products; Molecularly imprinted polymer; Quartz crystal microbalance

1. Introduction

Chlorination, the most widely used disinfection process for drinking water, produces two classes of disinfection by-products (DBPs); trihalomethanes and haloacetic acids [1,2]. After trihalomethanes, haloacetic acids (HAAs) which include the following nine compounds: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBA), dibromoacetic acid (DBAA), tribromoacetic acid (TBA), bromochloroacetic acid (BCAA), dichlorobromoacetic acid (DCBAA), and dibromochloroacetic acid (DBCAA), represent the second most abundant DBP species in chlorinated drinking water. HAA disinfection by-products are usually present in water as a complex mixture, with a large proportion of DCAA and TCAA [3]. They are of great concern to public health, owing to their potential carcinogenic [4] and mutagenic effects [5]. Several previous DBP studies have focused mainly on the ingestion route of exposure to THMs, and todate THMs are monitored regularly in drinking water [6–8], whilst the presence of HAAs in water was rather disregarded. Evidence for the widespread occurrence of HAAs in environmental waters around the world is increasing [9–10]. Additionally, it is now clear that levels of THMs are not consid- ered to be a good indicator of the levels of HAAs [11]. Recently, however, potential health risks to humans from long term exposure to particular HAAs has led to increased efforts to monitor...
and reduce their concentration in drinking waters [12]. Since determination of HAAs is quite a new environmental concern, few references are available dealing with development of liquid chromatographic methods for their analysis. The standard methods for determination of HAAs (such as ion chromatography, GC–EC, GC–MS) are time consuming, complicated and costly for routine analysis of drinking water. A fast, simple and inexpensive analysis method is needed in order to complement these established sophisticated analytical techniques. The primary aim of the current study is to investigate the development of such a technique, with a view to eventually developing an on-line rapid screening method.

Electrochemical detection has been recognized as a useful method for organic analysis. However, this technique cannot be used for monitoring HAA concentrations directly in water [13,14]. Although several non-crosslinked conducting polymers, such as poly(pyrrole) [15] or poly(vinyl chloride) incorporating the selective molecule such as polyoximation macrocycles [16], have been used as a tool for the detection of organic ions in electrochemical analysis systems, none of these have shown sufficient specificity for the analytes. Recently, a conductometric sensor specific to the group of haloacetic acids (HAAs) has been developed by our research group [17]. The detection system of this sensor was based on molecular recognition of the analytes by a polymer prepared by a molecular-imprinting polymerisation technique with a transduction of polyvinyl chloride membrane support. Molecules of any size and shape can be imprinted in a polymer matrix, provided they are able to diffuse into the matrix at an appropriate rate. The imprinted molecules are then washed out, and the imprinted polymer is crosslinked to give a stable polymer with enhanced physical properties, which retains the non-covalent recognition for the imprinted molecule. The selective recognition is therefore maintained and provides a basis for a specific detection technique.

During the last decade, the introduction of polymer selectivity by the molecular imprinting technique has been made mostly with crosslinked polymers rather than non-crosslinked polymers. The reason is that the former polymers give greater stability and certainty of recognition. The most commonly used crosslinking monomer, ethylene glycol dimethacrylate (EDMA), has potential for molecular-imprinted polymer synthesis of organic compounds since it gives high molecular recognition of the polymer with good stability of the layer. However the EDMA polymer is hydrophobic and inert, and it is not therefore attractive to polar molecules of the analytes. Crosslinking polymerization of EDMA monomer with 4-vinyl pyridine (VPD) functional monomer is capable of generating an electrically conducting polymer [23] that would be advantageous, since the VPD monomer will not only form the recognition site in MIP matrix but also make EDMA crosslink to be electrically active. This increases the attraction capability of the MIP produced, and perhaps improves the mechanical properties and processibility of the layer on electrode, due to the increased polarity of polymer. In addition to this, trichloroacetic acid (TCAA), which was chosen as the print molecule for this work, can be used as a doping agent.

By making use of the molecular-imprinting polymerisation technique, with appropriate modulation of the polymer composition, the recognition material engineered should be able to detect TCAA and structurally similar compounds directly in drinking water. The current study was designed to show that by using the TCAA-imprinted polymer coated quartz crystal microbalance (TCAA-MIP-QCM), it would be possible to specifically detect the group of HAAs in water, using mass-sensitive measurements. In this study, we have successfully synthesized TCAA-imprinted polymer of crosslinked poly(VPD-co-EDMA) as a spin-coated film at gold electrode surfaces, and evaluated its interaction with six commonly occurring HAAs, i.e., TCAA, DCAA, MCAA, TBAA, DBAA and MBAA, on QCM-based assay protocol. Since piezoelectric QCM, which is a well-known mass detection method, offers simplicity and low cost for chemical analysis, this assay method was chosen for the current study. Unspecific conductivity effects would be minimized by a dual QCM electrode comprising of multi-electrode structures on a single piezo-crystal with larger electrode diameters in contact with the liquid phase and two time smaller electrodes facing the gas-phase, according to techniques previously described in the literatures [24,25].

2. Experimental

2.1. Chemicals and materials

Ethylene glycol dimethacrylate (EDMA), 4-vinylpyridine (VPD) and malonic acid were obtained from Aldrich Chemical Company (Milwaukee, WI, USA). 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from Janssen Chimica (Geel, Belgium). Trichloroacetic acid (TCAA) was purchased from Merck K.G. (Darmstadt, Germany). Dichloroacetic acid (DCAA), monochloroacetic acid (MCAA), dibromoacetic acid (DBAA), monobromoacetic acid (MBAA) and tribromoacetic acid (TBAA) were obtained from Fluka Chemie AG (Buchs, Switzerland). All chemicals for preparing buffer solution were analytical grade and were obtained from Merck (Darmstadt, Germany). All solvents were analytical grades and dried with molecular sieves prior to use.

2.2. Immobilisation of polymer on QCM electrode

To prepare the QCM electrode, a dual QCM-pattern designed as described in a previous study [24] was sequentially screen-printed on each side of 10 MHz AT-cut quartz disc (15 mm diameter), using the gold screen-printing technique. The electrode facing the aqueous phase had a diameter of 4.5 mm with 2.5 mm electrode on the gas-phase side. The thickness of the gold electrode layer on each side of the quartz crystal after sintering was determined by scratching with a needle and measuring depth of the scratches using an AFM (Digital Instruments Inc., Santa Barbara, CA) with a Nanotec Electrinica WSxM scanning probe microscopy software version 3.0 Beta 8.1, which this was found to be about 180 nm.

The procedure for immobilisation of MIP on electrodes was as follows: 14 mg of TCAA (0.08 mmol), 34 mg of VPD (0.32 mmol), 200 mg of EDMA (1.0 mmol) and 9 mg of AIBN (0.05 mmol) were dissolved in 1 ml of acetonitrile. Then, the
solution was purged with a stream of nitrogen gas for 1 min and pre-polymerisation was carried out at 65 °C for 1 min in a water-bath. The non-imprinted polymer (NIP) was prepared in the same manner as the MIP, but in the absence of the TCAA template. A crystal was spin-coated with 10 μl of the MIP solution onto the center of the surface of the analytical electrode with a rotation speed of 3000 rpm, following by spin-coating of 10 μl of the NIP solution at the reference electrode. Subsequently, the blank quartz was placed in a chamber flushed with nitrogen gas for 1 min. Polymerisation was carried out at 70 °C for 18 h in a hot-air oven. After the immobilizing process, the electrode was washed with five portions of 100 ml de-ionised water to remove the template molecules. For removing the templates absorbed in the recognition sites, a washing process in deionized water needed for at least 3 h. Finally, the electrode was dried in air for overnight. The thickness of the MIP coated films was inspected using an AFM method that was similar to the method employed for measuring of the gold layer onto electrodes.

3.3. Fabrication of the sensor device

The QCM constructed with a coated TCAA-MIP and a coated corresponding NIP gold electrode was mounted in a flow-cell with a volume of 250 μl and placed in a thermostat at 25 °C. A home-built oscillator circuit and a self-programmed frequency read-out were used with a processing software. The oscillator frequency was measured by means of an HP 53131A frequency counter. The response of the oscillator circuit were checked by means of a HP 8572C network analyser (Hewlett Packard, Germany) to obtain data relating to acoustic damping and frequency shifts. The sensor experiments were performed using a flow system with a flow rate of 2 ml/min. Before making a measurement, the sensor was stabilized by running 200 ml de-ionised water through the cell for 3 h. One hundred milliliters of a series of standard solutions of TCAA and analogs were run through the cell separately. The frequency of both TCAA-MIP-QCM and the corresponding NIP-based QCM was recorded as parallel until a stable frequency was obtained. The water samples were analysed under the same condition as that used for the standard solutions. For the sample measurement using the sensor, the response of sensor exposed to a solution of the analyte was reported as frequency shift response ($-\Delta F$) which was the difference value of frequency shift of MIP electrode and frequency shift of NIP electrode. All measurements were performed in triplicate.

3. Results and discussion

3.1. Performance of the TCAA-MIP-QCM

Piezoelectric quartz crystal microbalance is well known as a remarkably sensitive mass detection method. Recently the use of MIPs coated onto piezoelectric QCM sensing system has attracted increase attention [19,20]. Normally, the integration of MIP into a piezoelectric QCM sensor requires thin or ultra-thin MIP films (nanometres) on the transducer surface. This can be achieved in several ways; in situ electro-polymerisation; surface coating (direct or spin coating) [26]; physical entrapment of MIP particles into gel [27]; or chemical coupling of the MIP [28]. For this work the spin-coating method was used for immobilising MIP onto the QCM electrode.
Fig. 2. The effect of imprinted layer height on frequency shift of the TCAA-imprinted coated QCM exposed to TCAA at concentration level of 100 μg l⁻¹.

The TCAA-imprinted polymer matrix from crosslinked poly(VPD-co-EDMA) have been produced by copolymerisation of VPD functional monomer and EDMA crosslinker in the presence of TCAA template in acetonitrile at the optimised TCAA/VPD/EDMA mole ratio (1:4:12). This polymer constitution did not only give high molecular recognition, i.e. the frequency shift response to 100 mg l⁻¹ of TCAA was the highest comparing to that of the other TCAA/VPD/EDMA mole ratios; 1:2:12, 1:6:12, 1:8:12, 1:4:10, 1:4:15 and 1:4:18, but also provided a film on gold electrode surfaces with good stability in terms of adhesion. The low relative standard deviation (2.4%, n = 4) indicates good and reproducible coating. Viscosity, conductivity and pressure fluctuations were compensated for measurements with a coated NIP gold electrode as the reference electrode. The recorded Δf before and after MIP immobilization was found to be 0.0196 ± 0.0004 Hz, which corresponds to about 800 nm according to the Sauerbrey equation [29]:

$$\Delta f = \frac{f_0^2}{2N\rho q} \Delta m$$

where $f_0$ is the fundamental frequency of the crystal, N the modulus of quartz (167 kHz cm), $\rho_q$ the quartz density (2.648 g cm⁻³), and $A$ is the piezoelectrically active. The film thickness obtained by the QCM was in good agreement with that measured by the AFM method (Fig. 1).

A preliminary evaluation of the various layer heights for bulk effects in TCAA-imprinted polymer of crosslinked poly(VPD-co-EDMA) prepared at 1:4:12 TCAA/VPD/EDMA molar ratio was performed by QCM measurement. The frequency shift of the different heights of imprinted layer in the range 0–40 kHz (or 0–1580 nm as measured by an AFM method), showed a different frequency shift of the imprinted layer to 100 mg l⁻¹ (ppm) TCAA solution, as seen in Fig. 2. The frequency shift of sensor greatly increased at initial layer-heights of the MIP and started to level off after 20 kHz layer-height. The compensated sensor response with a 800 nm-thickness (or 20 kHz-height) of the MIP layer for 100 mg l⁻¹ TCAA solution is about 800 Hz. A measurement of noise of 6 Hz allows a detection limit for TCAA of about 54 μg l⁻¹ (ppb), with a signal-to-noise ratio of 3:1. A steady response with the sensor was found within 20 min.

The effect of swelling of the MIP film on the sensor response was also investigated. The results revealed that the frequency response obtained using a 24-h-hydrated polymer (9.965 Hz) is similar to the frequency response using from the dry polymer (9.967 Hz) when measured in air after evaporation of water. In general, EDMA generates an imprinted polymer that is compact, inert and highly stable with respect to rigidity of polymer structure. The negligible change in signal response of the sensor after hydration of the MIP suggests that the imprinted structure produced by the EDMA-based polymer is very stable.

Several buffer solutions (pH 1, 4 and 7 buffers) were tested as background solutions for the QCM measurements. The frequency changes of the MIP-based QCM for 10 mg l⁻¹ TCAA concentration were 482, 105, 210 and 374 Hz, respectively, when measured in de-ionised water, 0.2 M HCl–KCl buffer pH 1, 0.2 M phosphate buffer pH 4 and 0.2 M phosphate buffer pH 7 running solution. Hence, de-ionised water was employed as background solution for studying the interaction of TCAA-MIP-QCM with HAAs in water samples, since it afforded the highest sensor response.

Fig. 3. Signal response of the QCM sensor with (a) NIP- and (b) MIP-coated electrode to TCAA at concentration level of 1 mg l⁻¹.

3.2. The efficiency of TCAA-MIP coated QCM

3.2.1. Recognition of the template by the TCAA-MIP-QCM

The signal response of the QCM sensor with MIP and non-imprinted polymer-coatings when exposed to a solution of TCAA at a concentration of 1 mg l⁻¹ is presented in Fig. 3. The TCAA solution causes a decrease in the frequency shift of the MIP sensor, and this effect is completely reversible after washing with pure water. In contrast, the effect of the TCAA solution on the frequency signal of the NIP-based sensor is very slight. These results indicate that TCAA-imprinted polymer coated onto QCM electrode affords a highly specific and significantly strong signal response to the template in water. The mass change of the MIP film when exposed to TCAA solution is presumably due to the change in the mass of the polymer as tem-
anions at concentrations below 0.1 mM.

Fig. 4. Effect of different concentration of TCAA (0–200 mg l$^{-1}$) of TCAA at the imprinted sites is possible in de-ionised water. The main force of binding between the MIP and TCAA in water solution might be expected to derive from acid–base interaction between the carboxylate anion and vinylpyridinium cation of the MIP. In addition the results demonstrated that dissociation between the carboxylate anion and vinylpyridinium cation of the MIP to 0.1 mM KCl, K$_2$HPO$_4$ or KH$_2$PO$_4$ in water solution containing inorganic substances (as individual) at a concentration of 0.1 mM were measured under the optimized conditions. The polymer gave positive frequency shifts with 0.1 mM HCl ($\Delta f = +40$). In contrast, frequency shifts of the MIP to 0.1 mM KCl, K$_2$HPO$_4$ or KH$_2$PO$_4$ in water solution were negligible ($\leq 10$Hz). The positive frequency shift towards HCl of the MIP-based QCM electrode can be explained by a mass loss effect on the sensor surface due to the lighter ion protons [30]. These results demonstrated that TCAA-imprinted crosslinked poly(VPD-co-EDMA) coated QCM is very sensitive towards the inorganic acid, hydrochloric acid, and this is likely to limit the application of this sensor for the assay of HAAs in water samples containing hydrochloric acid. However the sensor is not affected by Na, K cation and Cl, HPO$_4$ and H$_2$PO$_4$ anions at concentrations below 0.1 mM.

As can be seen from Fig. 4, the TCAA-MIP-QCM gives frequency shift responses corresponding to the increasing repeated concentrations of TCAA in water. The response of the TCAA-MIP-QCM reaches a plateau at the higher concentration (>100 mg l$^{-1}$) of TCAA, suggesting a saturation of recognition sites in the imprinted polymer with the template molecules. The adsorption behaviour of the MIP film fabricated in the sensor can be fitted to the Langmuir isotherm. Accordingly, Scatchard analysis was used to estimate the binding parameters of the polymers. The Scatchard equation is as follows:

$$Q(TCAA) = \frac{Q_{max}}{K_D + [TCAA]} - \frac{Q_{max}}{K_D},$$

where $Q$ is the amount of TCAA bound to the polymer, $Q_{max}$ the apparent maximum number of binding sites, $K_D$ the equilibrium dissociation constant, and $[TCAA]$ represents the equilibrium concentration of TCAA. $K_D$ and $Q_{max}$ were determined from the slope of the straight line and the intercept of the Scatchard plot, and the binding constant ($K_D$) value was obtained from the reciprocal of the $K_D$ value. Plot of $Q/TCAA$ versus $Q$ (see Fig. 4, top right) yielded a straight line with a dissociation constant value ($K_D$) of 0.094 mM ($K_D = 10.60$ mM$^{-1}$) and the $Q_{max}$ value of 18.9 nmol.

The recognition range of the TCAA-MIP-QCM was examined using five structurally related TCAA compounds such as DCAA, MCAA, TBAA, DBAA and MBAA and two non-related TCAA compounds (non-haloacetic acids) such as acetic acid and malonic acid as the substrates. For this purpose, the $K_D$ and $Q_{max}$ of TCAA-MIP-QCM responding for analogs were determined. The results are collected in Table 1. The results revealed that five HAA analogs have high capability of locating in the TCAA-imprinted cavity compare to both non-haloacetic acids (acetic acid and malonic acid), but their degree of fitting is lower than that of the TCAA template.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_D$ (mM$^{-1}$)</th>
<th>$Q_{max}$ (nmol)</th>
<th>%CR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCAA</td>
<td>10.6</td>
<td>18.9</td>
<td>100</td>
</tr>
<tr>
<td>DCAA</td>
<td>7.0</td>
<td>14.1</td>
<td>80</td>
</tr>
<tr>
<td>MCAA</td>
<td>4.0</td>
<td>13.2</td>
<td>66</td>
</tr>
<tr>
<td>TBAA</td>
<td>6.4</td>
<td>13.8</td>
<td>84</td>
</tr>
<tr>
<td>DBAA</td>
<td>5.1</td>
<td>14.1</td>
<td>84</td>
</tr>
<tr>
<td>MBAA</td>
<td>4.3</td>
<td>13.2</td>
<td>83</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2.5</td>
<td>10.6</td>
<td>18</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>2.2</td>
<td>12.6</td>
<td>20</td>
</tr>
</tbody>
</table>

Substrates

$\%CR$ is the ratio of the frequency shift measured at EC$_{50}$ for analog to that of TCAA. EC$_{50}$ is the analyte concentration for which HAA binding to MIP is inhibited by 50%.

$Q_{max}$ of TCAA. $Q_{max}$ of TCAA was determined from the slope of the straight line and the intercept of the Scatchard plot, and the binding constant ($K_D$) value was obtained from the reciprocal of the $K_D$ value. Plot of $Q/TCAA$ versus $Q$ (see Fig. 4, top right) yielded a straight line with a dissociation constant value ($K_D$) of 0.094 mM ($K_D = 10.60$ mM$^{-1}$) and the $Q_{max}$ value of 18.9 nmol.

The recognition range of the TCAA-MIP-QCM was examined using five structurally related TCAA compounds such as DCAA, MCAA, TBAA, DBAA and MBAA and two non-related TCAA compounds (non-haloacetic acids) such as acetic acid and malonic acid as the substrates. For this purpose, the $K_D$ and $Q_{max}$ of TCAA-MIP-QCM responding for analogs were determined. The results are collected in Table 1. The results revealed that five HAA analogs have high capability of locating in the TCAA-imprinted cavity compare to both non-haloacetic acids (acetic acid and malonic acid), but their degree of fitting is lower than that of the TCAA template.

The specificity of the TCAA-MIP-QCM for each analog was evaluated by measuring the cross-reactivity (CR) (i.e. is the ratio of the frequency shift measured at EC$_{50}$ for analog to that of TCAA). The results are shown in Table 1. As can be seen, CR value of the template was higher than that of other five HAA analogs. Also, there is some cross-reactivity in the TCAA-MIP-QCM with the non-haloacetic acids, malonic acid and acetic acid, but much lower degree than that obtained with HAA analogs. The selectivity profile of the TCAA-MIP-QCM for HAA and non-haloacetic acids was in order as TCAA > DCAA > TBAA > DBAA > MBAA > MCAA > malonic acid > acetic acid. From the selectivity profile obtained, it seems that the tri- or di-substituted HAA cross-react more than the mono-substituted HAAs, while the cross-reactivity of chloro-HAA and bromo-HAA analogs with the same degree of halogen substitution is not different. Thus, the recognition of the analogs of HAA by the TCAA-MIP-QCM is due to a carboxylic group, and that this involves a combination of both size and shape selectivity. It appears that TCAA-MIP-QCM gives %CR value higher than 80% for four out of six HAAs (e.g.
Six HAAs such as MBAA, DBAA, MBAA, DCAA, TBAA, DBAA and MBAA, and CR value between 70% and 60% for one out of six HAAs (e.g. MCAA) and CR value about 20% for non-haloacetic acids, malonic acid and acetic acid. This result suggests that there could be a possibility of inter-anionic competitions for recapture in TCAA binding sites. The mechanism for determination trace HAAs of the TCAA-MIP-QCM electrode may involve in the cooperation and competition of favorable structures of polymer–salt complexes formed between TCAA-MIP and six HAAs anions [31]. It is possible that HAAs have similar capability of attaining charge balance in the polyion salts and/or similar supramolecular arrangement within the complex as TCAA, but that TCAA has preference over the HAAs in terms of re-binding.

3.2.2. Analytical characteristics of the TCAA-MIP-QCM in the QCM-based assay of HAAs. Analytical characteristics of the TCAA-MIP-QCM in the QCM-based assay of HAAs were examined with a HAA concentration ranging from 0.1 to 100 mg l\(^{-1}\) in de-ionised water (n = 3). The calibration curves constructed from the frequency shift parameter (−ΔF) dependency provided reasonable results for analysis of TCAA and other five HAAs analogs (see Fig. 5). There was a linear relationship between frequency shift responses of the sensor against the logarithm of concentrations (log C) of TCAA and analogs (individually) and the mixture of total six HAAs, \( R^2 \) value = 0.98 with the equation shown for each analyte in Table 2. The measured EC\(_{50}\) value is 4.5 mg l\(^{-1}\) for TCAA and about 20 mg l\(^{-1}\) for the other five HAAs (see Table 2), calculated as the analyte concentration for which HAA binding to MIP is inhibited by 50%. The limits of detection (LOD) according to 3 \( S_b \)/m criterion, where \( S_b \) is the linear calibration and \( m \) estimated as the standard deviation of the signal response for HAAs, were measured EC\(_{50}\) value is 4.5 mg l\(^{-1}\) for TCAA and about 20 mg l\(^{-1}\) for the other five HAAs (see the precise value for each compound in Table 3). Detection limits of TCAA and DCAA were in the mid to low \( \mu \)g l\(^{-1}\) range. The WHO has a guideline value for DCAA (50 \( \mu \)g l\(^{-1}\)) and TCAA (200 \( \mu \)g l\(^{-1}\)) [32], i.e. water samples must not contain these HAAs at concentration above these values. TCAA-MIP-QCM can therefore detect and measure DCAA or TCAA at concentrations below the maximum permitted concentrations. Moreover, the LOD values obtained for TCAA or DBAA analyses were lower than those in the literature using conductivity or amperometry methods (with incorporation of liquid chromatography analysis system) [16], see Table 3. The LOD values for MCAA or DBAA analyses were also lower than those in previous reports using HPLC–UV methods [16]. When compared with the membrane sensor, using a TCAA-imprinted polymer-deposited polyvinyl chloride membrane of a previous study [17], detection limits of HAAs with the QCM sensor were not improved (see Table 3).

For a mixture of HAAs in water samples, the proposed method can be used only for assay of total HAA. The US

<table>
<thead>
<tr>
<th>Compound</th>
<th>Equation</th>
<th>( R^2 )</th>
<th>LOD (mg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCRA</td>
<td>(-ΔF = −326.47 \log(C) + 102.4)</td>
<td>0.984</td>
<td>4.5</td>
</tr>
<tr>
<td>DCRA</td>
<td>(-ΔF = −318.72 \log(C) + 109.8)</td>
<td>0.990</td>
<td>15</td>
</tr>
<tr>
<td>MCAA</td>
<td>(-ΔF = 289.75 \log(C) + 148.7)</td>
<td>0.997</td>
<td>19</td>
</tr>
<tr>
<td>TBAA</td>
<td>(-ΔF = −312.83 \log(C) + 119.6)</td>
<td>0.986</td>
<td>20</td>
</tr>
<tr>
<td>DBAA</td>
<td>(-ΔF = −316.47 \log(C) + 140.6)</td>
<td>0.992</td>
<td>23</td>
</tr>
<tr>
<td>MBAA</td>
<td>(-ΔF = −292.7 \log(C) + 144.5)</td>
<td>0.996</td>
<td>25</td>
</tr>
<tr>
<td>Six HAAs</td>
<td>(-ΔF = −569.40 \log(C) + 321.7)</td>
<td>0.996</td>
<td>4.5</td>
</tr>
</tbody>
</table>

* Refers to TCAA, DCRA, MCAA, TBAA, DBAA and MBAA altogether.

![Fig. 5](image-url) The calibration plot of frequency shift parameter (−ΔF) vs. added HAAs for the TCAA-MIP-QCM in the QCM-based assay of HAAs. Each point represents the average of three independent measurements.

Table 2: Analytical characteristics of the TCAA-MIP-QCM in the QCM-based assay when the QCM-based assay is conducted for a HAA(s) concentration ranging from 0.1 to 100 mg l\(^{-1}\) in de-ionised water.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>QCM</th>
<th>Membrane</th>
<th>UV</th>
<th>Conductivity</th>
<th>Amperometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCRA</td>
<td>50.0</td>
<td>1.0</td>
<td>5.10</td>
<td>80.0</td>
<td>10.0</td>
</tr>
<tr>
<td>DCRA</td>
<td>60.0</td>
<td>4.2</td>
<td>8.0</td>
<td>16.0</td>
<td>10.0</td>
</tr>
<tr>
<td>MCAA</td>
<td>35.0</td>
<td>4.2</td>
<td>70.0</td>
<td>8.0</td>
<td>1.00</td>
</tr>
<tr>
<td>TBAA</td>
<td>20.0</td>
<td>0.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DBAA</td>
<td>20.0</td>
<td>0.5</td>
<td>90.0</td>
<td>30.0</td>
<td>10.0</td>
</tr>
<tr>
<td>MBAA</td>
<td>30.0</td>
<td>5.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* An on-line method.

<p>| | | | | | |</p>
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</thead>
</table>

* Cited from Ref. [17].

* Cited from Ref. [16].

* Used in conjunction with liquid chromatography.
Environmental Protection Agency (USEPA) has set a maximum contaminant level of 60 g l$^{-1}$ for the five commonly occurring acids namely TCAA, DCAA, MCAA, DBAA and MBAA in the Stage 1 of the disinfection by-product regulation [33]. The specificity and selectivity apparent with the six HAAs indicates the possibility of using the TCAA-MIP-QCM as an analysis tool for measuring concentrations of HAA mixtures in drinking water samples. The stability of the TCAA-MIP-QCM is good, in that its analytical performance is unaffected after being stored for more than 1 month at room temperature. The advantages of the method developed in this work are the ease of the automation of the sensor system, the low cost per unit of sensor device as well as the potential to manufacturer the sensor on an industrial scale.

### 3.3. Analysis of drinking water samples

The QCM-based assay has been applied to the group analysis of HAAs in real-life samples. Two brands of commercial bottled water obtained either from a supermarket or local supplier and a municipal tap water with home filtration system were subjected to analysis by this method. Measurement of HAAs by the LLE-GC-ECD method is recommended by the USEPA [34], and assay of samples by this method revealed only TCAA in the samples at concentration levels of 0.8, 1.0 and 1.1 mg l$^{-1}$ each. A calibration curve was prepared by dissolving TCAA in de-ionised water to attain the solutions having TCAA (or total six HAAs) concentration between 0.01 and 50 mg l$^{-1}$ for the five commonly occurring acids namely TCAA, DCAA, MCAA, TBAA, DBAA and MBAA altogether.

<table>
<thead>
<tr>
<th>Compound/spiked concentration</th>
<th>Measured, µg l$^{-1}$ after adding HAAs (%) recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottled water from supermarket</td>
<td>Bottled water from local supplier</td>
</tr>
<tr>
<td>TCAA 0.1 mg l$^{-1}$</td>
<td>103 ± 0.9</td>
</tr>
<tr>
<td>TCAA 10 mg l$^{-1}$</td>
<td>102 ± 1.4</td>
</tr>
<tr>
<td>Total six HAAs 0.12 mg l$^{-1}$ (0.02 mg l$^{-1}$ each)</td>
<td>102 ± 2.6</td>
</tr>
<tr>
<td>Total six HAAs 12 mg l$^{-1}$ (2 mg l$^{-1}$ each)</td>
<td>101 ± 1.4</td>
</tr>
</tbody>
</table>

$^a$ Expected concentrations are amounts added plus the amounts already present in the water sample (mean ± R.S.D, n = 3).

$^b$ With home filtration system.

$^c$ Total six HAAs refers to TCAA, DCAA, MCAA, TBAA, DBAA and MBAA altogether.

### 4. Conclusions

It has been shown that TCAA-MIP-QCM can specially detect the group of HAAs in drinking water, using mass-sensitive measurements. The selectivity of the QCM to HAA analogs is satisfactory. Also, the analytical dynamic range for six HAAs (trichloro-, dichloro-, monochloro-, tribromo-, dibromo-, and monobromo-acetic acids) is large. The limits of detection of HAAs are at present higher than concentrations commonly found in actual drinking water samples, but are well below the maximum permissible levels of HAAs (60 µg l$^{-1}$) in water sample. However, further refinement will undoubtedly improve the limit of detection. It can therefore be concluded that the assay with TCAA-MIP-QCM can be used as a screening method of drinking waters contaminated with HAAs. The proposed method offers fast and cheap measurements.

### Acknowledgements

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### References

[34] USEPA, Method 552.3, Environmental Monitoring and System Laboratory, Cincinnati, OH, 2003.