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Determination of haloacetic acids in water using solid-phase extraction/microchip capillary electrophoresis with capacitively coupled contactless conductivity detection

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Research Article

Determination of haloacetic acids in water using solid-phase extraction/microchip capillary electrophoresis with capacitively coupled contactless conductivity detection

Haloacetic acids (HAAs) were determined by a fast and simple analysis method based on microchip electrophoresis and capacitively coupled contactless conductivity detection (C^4D). Two chlorinated acetic acids, dichloroacetic acid (DCAA) and TCA were detected in swimming pool water. Different BGEs were tested, and sodium carbonate was selected as BGE for the separation and detection in the reported experiments. Additionally, pH values and concentrations of carbonate buffer were optimized. The response times for the two analytes were less than 3 min; the lowest detected concentrations for TCA and DCAA after extraction and cleanup were 38 and 62 μg/L and the RSDs for the migration times were 1.9 and 2.2%. TCA and DCAA were identified swimming pool water samples at concentrations ranging from 391 to 1058 μg/L. In combination with a SPE-based concentration and cleanup procedure, this miniaturized system shows the potential for development as an on-site monitoring method for chlorinated acetic acids found in swimming pool water or other suspected water systems.

Keywords:
Capacitively coupled contactless conductivity detection / Haloacetic acids / Microchip CE / Swimming pool water DOI 10.1002/elps.200900496

1 Introduction

Haloacetic acids (HAAs) are well known as a group of disinfection byproducts formed during the water chlorination process to control infectious microbial contaminants [1, 2]. Chloroacetic acids are directly formed from dissolved humic matter by oxidation of natural waters with chlorine [3]. HAAs are highly water soluble and are toxic to humans, plants and algae, *e.g.* TCA has been used as an herbicide [4]. They are of concern to public health because of their suspected carcinogenicity and mutagenicity as well as developmental, reproductive and hepatic toxicity [5]. To improve public health protection, the US Environmental Protection Agency (EPA) has regulated five HAAs, known as HAA5; monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), TCA, monobromoacetic acid and dibromoacetic acid with a maximum contaminant level of 60 μg/L for the combined concentration of HAA5 in the drinking water (http://www.epa.gov/EPA-WATER/1998/March/Day-31/w8215.htm). Of these compounds, TCA is most commonly found in swimming pool water, often at concentrations exceeding 1 mg/L [6].

Many approaches have been developed for the determination of HAAs in water. GC with electron-capture detection, coupled with liquid–liquid extraction or SPE has been widely used for the determination of HAAs in a variety of samples [7–12]. This method, however, requires derivatization resulting in potential problems of interference and recovery as well as being time consuming. A few researchers have proposed alternative techniques to address these issues, such as ion chromatography [13], LC [14], CE [15, 16] and ESI-MS [17]. Although methods such as ESI-MS provide excellent sensitivity and selectivity, their use for screening applications is limited by their high cost and time requirements.

Microfluidic-based analytical approaches have significantly improved during the past decade. Microfluidic electrophoresis separation has been coupled with various detection strategies including LIF [18] and surface-enhanced Raman scattering [19]. Although these detection techniques are sensitive, the development of alternative detection techniques, which are compatible with miniaturization and full on-chip integration, remains an active area of investigation. Electrochemical detection methods have shown merit in this area due to their portability, low cost and ease

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Abbreviations: **C^4D,** contactless conductivity detection; **DCAA,** dichloroacetic acid; **HAA,** haloacetic acid; **MCAA,** monochloroacetic acid

of miniaturization [20, 21]. One limitation for most reported applications of amperometric, potentiometric and conductimetric detection, however, is that the electrodes are required to be in direct contact with liquid solution, resulting in unexpected electrochemical reactions and fouling of the electrode surfaces. Since the initial applications of contactless conductivity detection (C^4D) with CE reported by da Silva and Zemann independently in 1998 [22, 23], C^4D has drawn more attention for use in both CE and microchip CE. Several groups including Wang's [24, 25] and Hauser's [26, 27] have reported significant progress in the use of C^4D with the PMMA and glass microchips for determining a variety of analytes. C^4D offers various advantages for microchip separations, including the elimination of electrode surface fouling, effective isolation from high separation voltages, simplified detector design and electrode alignment. Although glass and PMMA have been widely used for construction of microchips, these devices are relatively difficult to fabricate under ordinary lab conditions. In addition, the thinner cover plates (100 μm) used to improve the sensitivity may be difficult to fabricate [28]. Recently, we reported a facile electrode alignment to form a PDMS microchip with C^4D system [29, 30]. The electrodes were easy to build in the PDMS substrate with the desirable dielectric thickness (*e.g.* 50 μm).

Although commercial CE systems have been used to measure HAAs [16], CE chip-based assays for the detection of HAAs have not been previously reported. The effects of BGEs, pH and concentration of carbonate on the separation and response are herein discussed. An SPE with a highly crosslinked styrene–divinylbenzene sorbent has been applied to detect low levels of chlorinated acetic acids typically found in swimming pool waters. The present microchip system combines the distinct advantages of C^4D with CE microchips that can be easily produced in the lab. The resulting microchip-based monitoring of haloactic acids is advantageous in terms of speed, portability, efficiency, cost, sample size and simplicity compared with the conventional methods.

2 Materials and methods

2.1 Chemicals and apparatus

SU-8 2035 photoresist was purchased from Micro Chem (Newton, MA, USA), and Sylgard 184 silicone elastomer and curing agent were obtained from Dow Corning (Midland, MI, USA). Aqueous solutions were prepared using analytical grade reagents and 18 MΩ/cm resistance water (NANOpure Diamond, Barnstead, Dubuque, IA, USA). MCAA, DCAA and TCA (PESTANAL® analytical standard grade) were purchased from Fluka through Sigma-Aldrich (Milwaukee, WI, USA). Methanol, acetate, chlorate, sulfate, phosphate, EDTA, tartate, citrate, borate and sulfuric acid were also purchased from Sigma-Aldrich. The stock solutions of the HAAs were prepared in methanol. Buffers were prepared and pH values adjusted with HCl or NaOH. Concentrations were reported with respect to the polyatomic anions. All chemicals were used without further purification. SPE resin Poly RP (bead size 10 μm, pore size 100 Å) was purchased from Sepax Technologies (Newark, DE, USA). The water samples were collected from local swimming pools (one indoor and two outdoor pools). The pH measurements were performed with a combined glass electrode and a digital pH meter (Orion 420A, Thermo, Waltham, MA, USA). A home-made high-voltage power supply was used for separation and injection in all the

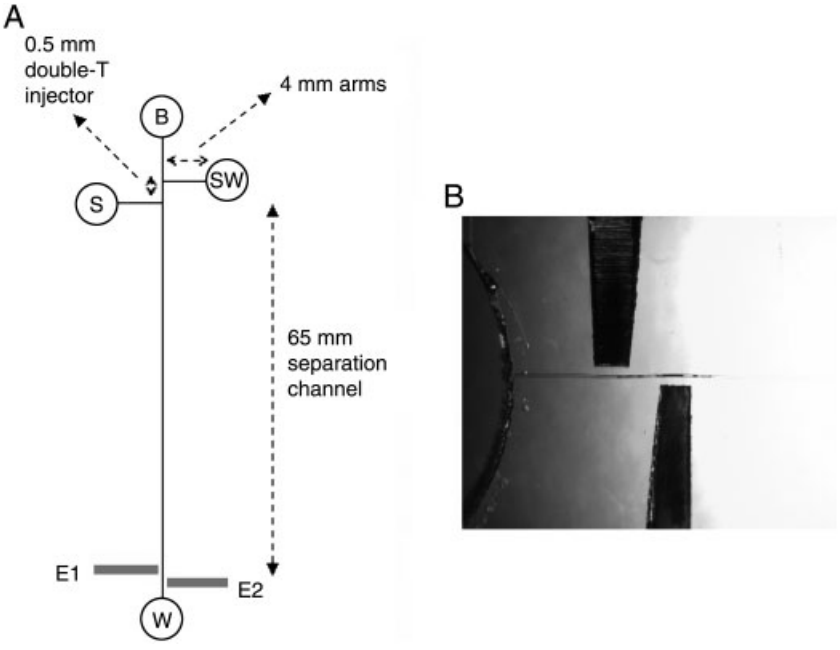

Figure 1. Schematic diagram of the microchip (A) and detailed view of electrode alignment (B). Channel width: 50 μm, channel depth: 50 μm, double T arms: 4 mm long, solution reservoirs: 5 mm diameter. S, sample reservoir; SW, sample waste reservoir; B, BGE reservoir; W, waste reservoir; E1, input electrode and E2, output electrode.

experiments. Injection and separation were controlled using a BAS ChromGraph Interface DA-5 (BASi, West Lafayette, IN, USA). Conductivity detection was performed by using TraceDec contactless conductivity detector (Innovative Sensor Technologies GmbH, Strasshof, Austria). Because the standard TraceDec cell was not used, the electrical leads from the TraceDec adaptor were attached to the two aluminum electrodes (Fig. 1) using small nonserrated alligator clips. The data acquisition was performed using BAS ChromGraph Control software. The electrodes were fabricated from 10 μm thick, 0.5 mm wide and 15 mm long aluminum foil strips. The two electrodes were imbedded into PDMS and arranged in an anti-parallel orientation on each side of channel, longitudinally displaced along the channel by 0.5 mm and spaced 0.05 mm from the channel wall and in the same vertical plane as the channel. All electrode placements were made with the assistance of a stereo microscope. The electrodes were placed a distance of 2 mm from the end of separation channel which was 65 mm between the double T injector and the detection electrodes (Fig. 1).

2.2 Fabrication of the microchips and electrophoresis procedures

PDMS microchips were fabricated according to a previously described procedure [20]. A microchip with a 65 mm long separation channel was used for all experiments (Fig. 1). The standard amount of buffer dispensed into each reservoir (buffer, sample and wastes) was 50 μL. Electrical connections to the microfluidic devices were made using platinum electrodes placed into the reservoirs at the ends of the channel. During the sample injection, potentials of −100 and +450 V were applied at the sample and the sample waste reservoirs, respectively, whereas buffer reservoirs were floating. During the separation step, the potential of +1200 V was applied between the buffer and the buffer waste reservoirs, whereas the potentials applied to the sample and sample waste reservoir were floating. The buffer waste reservoir (W, see Fig. 1) was the cathode. For this separation, the negatively charged analytes were electrophoretically moving toward the anode at the buffer reservoir and being carried toward the cathode by the EOF.

2.3 Sample preparation

Swimming pool water samples (50 mL) were acidified by adding 2 mL concentrated sulfuric acid. The acidified samples were then passed through an SPE cartridge (250 mL PolyRP resin) at a flow rate of 1.5 mL/min which had been previously conditioned using methanol, 1 M H_2SO_4 and deionized water. The acidified pool water was passed through the SPE cartridge followed by 0.5 mL deionized water and eluted with 1 mL sodium carbonate (10 mM, pH 10) at a flow rate of 0.5 mL/min. Quantitative analysis of the HAAs present in the swimming pool water was carried out using a standard addition method. Separate samples were extracted and analyzed after addition of standard spikes that resulted in final concentration increases of 500 and 1000 μg/L. Determinations were made for prespiked concentrations using abscissa intercepts of linear regressions.

3 Results and discussion

3.1 Effect of BGEs

The choice of electrolyte is important for the success of both CE separations and conductivity detection. The choice of electrolyte and its concentration influences electromigration dispersion which in turn causes peak broadening and deformed peak shapes, resulting in decreased separation efficiency [31]. The mobility of the electrolyte should be as similar as possible to the mobility of the analytes of interest in order to decrease the electromigration dispersion. The C^4D signal is also influenced by the conductance of the electrolyte co-ion and counter-ion plus the analyte ion. The difference in the conductance between the electrolyte co-ion and the analyte ion determines the response of the analyte. According to the theoretical approach reported by Katzmayr *et al.* [32], a larger value for the C^4D response is expected with an increase in the difference in mobilities between the analyte ion and the electrolyte co-ion. Due to these competing influences in signal optimization, eight different electrolytes were studied for the separation of the three chlorinated acetic acids (Fig. 2). In the presence of acetate and borate, the signals of the analytes (TCA, DCAA and

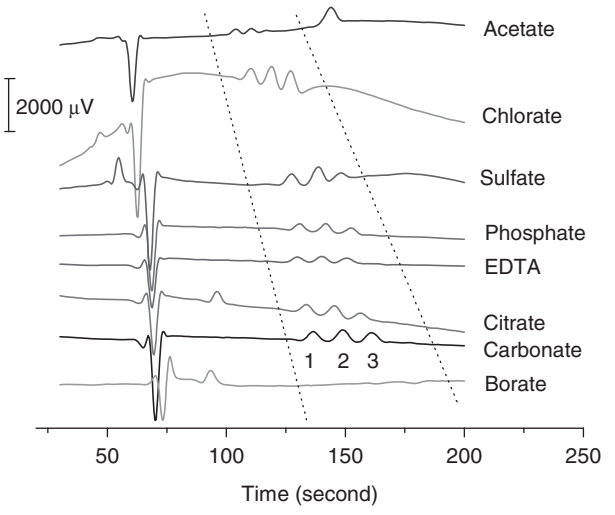

Figure 2. Effect of BGEs on the separation and response of analytes. Peak definition: 1, TCA (41.3 μg/L); 2, DCAA (53.7 μg/L) and 3, MCAA (49.7 μg/L). Conditions: all electrolytes, pH 10; separation potential, +1200 V; injection potential, −100 V/+450 V; injection time, 7 s; excitation voltage applied, 80 V and frequency, 300 kHz.

MCAA) were relatively low. This result was most likely due to the similarity in mobility of acetate and borate to the chlorinated acetates. In contrast, although both chlorate and sulfate electrolytes resulted in good separation and response of the analytes, they showed an unstable baseline, possibly due to their low buffer capacities. Multi-carboxyl electrolytes (EDTA and citrate) performed better than the previously described electrolytes but still showed small signals or drifting baselines. Although the use of different buffer systems resulted in significant differences in signal intensities and elution times for the analytes (TCA, DCAA and MCAA), their relative order migration remained the same indicating that the EOF was not inverted (Fig. 2, dashed lines). Among the eight electrolytes, carbonate and phosphate were the best carrier electrolytes for both separation and detection. Each of these electrolytes provided a stable baseline, symmetrical peaks and relatively large signals for the analytes. This result may be due in part to the difference in mobilities between electrolyte co-ion and analyte ion. Because carbonate is the predominant contributor to the relatively hard water found throughout the southwest United States, sodium carbonate was selected for the separation and detection of HAAs in this experiment.

3.2 Effect of pH and the concentration of carbonate

The pH and concentration of electrolyte not only influences the potential which is proportional to the EOF coefficient, but also influences the conductance of the solution. Both of these variables need to be optimized for separation and detection of analytes. For this experimental configuration, the cathode direction of the EOF formed by the SiOH groups on the oxidized surface of the PDMS is in the opposite direction to that of the anionic analyte mobility. The relatively large EOF mobility, however, resulted in the movement of analytes toward the cathode. The tendency of the analytes to move toward the anode allowed them to stay in the separation channel for a longer time increasing their separation. Figure 3 shows the effect of pH on the separation and response of analytes. At the higher pH value, both separation and response for these analytes were better than at lower pH. This is possibly the case because the bicarbonate form [HCO_3^-] co-ion predominates at pH 8, decreasing the difference in conductance between the co-ion and the analyte ion.

Figure 4 shows the effect of the BGE concentration on the separation and response of the chlorinated acetic acids. With respect to signal optimization, the signal of the analytes for contactless conductivity detectors is determined by the difference in conductance between sample zone and BGE.

For higher concentrations of BGE, greater variations in the signal intensities are expected resulting in smaller values for the *S*/*N*. The relative peak heights of the analytes were lower at BGE concentrations above 10 mM. Although it is not obvious from the amplification shown for these electropherograms in Fig. 4, the *S*/*N* values decreased with

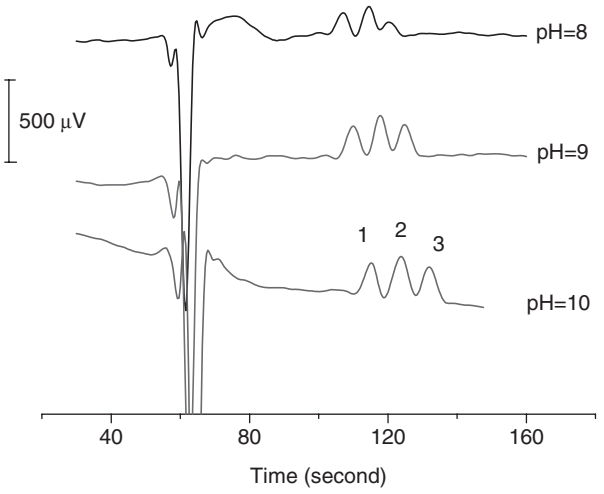

Figure 3. Effect of the pH on the separation and response of the analytes. Other conditions were the same as in Fig. 2.

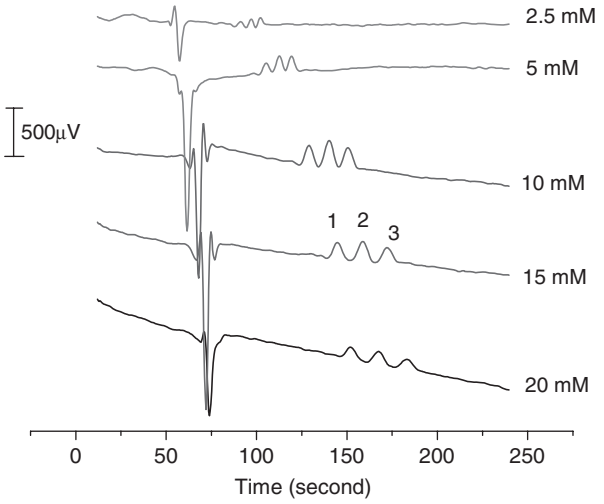

Figure 4. Effect of the sodium carbonate concentration on the separation and response of the analytes. Other conditions were the same as in Fig. 2.

increasing concentrations of BGE. Additionally, higher concentrations of BGE resulted in better separation of the analytes. This was likely due to the decrease of EOF at the larger ionic strengths. To optimize separation and *S*/*N*, 10 mM carbonate at pH 10 was selected as running electrolyte.

3.3 Analytical performance of microchip CE-C^4D for standards in deionized water

The calibration for the microchip CE-C^4D method was carried out for each compound in deionized water over a concentration range between about 3.9 and 133.3 mg/L (slightly different for each compound). Calibration plots showed a linear response between peak height and concentration. In detail, MCAA exhibited correlation coefficient of 0.997 over a

concentration range of 3.9–124.0 mg/L; DCAA displayed a correlation coefficient of 0.990 from 4.0 to 128.0 mg/L and TCA showed a correlation coefficient 0.970 from 4.2 to 133.3 mg/L. Estimated from the S/N characteristics ($S/N > 3$), detection limits in deionized water without concentration of HAAs were in the range between 2.1 and 2.7 mg/L. The RSDs for the migration times and the peak heights were 1.8–2.3% and 2.8–3.9% for three analytes ($n = 9$), respectively. The high degree of reproducibility in signal response was likely due to the absence of unwanted surface fouling associated with the contactless electrodes. Although relatively fast, simple and reproducible, the microchip system showed detection limits that were about an order of magnitude higher than for conventional CE systems equipped with CCD [16]. The chip also showed long-term stability and could be used for up to a week without any significant changes in operation. The overall precision of migration time and peak height of three compounds within a given set of experiments performed over a 7-day period was similarly stable (RSD of migration time $< 3.0\%$ and RSD of peak height $< 5.2\%$, $n = 49$).

3.4 Detection of HAAs in swimming pool water

The concentration of HAAs often found in swimming pool water is in the high parts *per* billion or low parts *per* million levels. A variety of sample cleanup and preconcentration processes, such as SPE and microwave evaporation [33, 34], have been adopted to remove the interferences and meet the limit of detection for various analytical techniques. It has been previously suggested in the literature that detection of HAAs in potable water by CE would require SPE prior to analysis [35]. We observed that dissolved solids present in the local (Las Vegas, NV, USA) tap water and additional components in pool water resulted in poor analytical characteristics in the electropherograms (*e.g.* drifting baselines, poor separation and nonsymmetrical peaks). For this study, highly cross-linked styrene divinylbenzene (PolyRP) was used for sample concentration and cleanup. Because the sample pH of the acidified pool water was lower than the pK_a of the chloroacetic acids (pK_a, TCA = 0.77, pK_a, DCAA = 1.25 and pK_a, MCAA = 2.87), these compounds were retained on the sorbent resin. After the retained HAAs were removed from the resin, they were analyzed without further treatment.

Figure 5 shows the electropherograms of tap water (typically used to fill the local swimming pools) which was spiked with TCA (383 μg/L), DCAA (620 μg/L) and MCAA (513 μg/L) prior to cleanup and concentration; outdoor swimming pool water after concentration and cleanup without standard spikes and tap water spiked with TCA (38 μg/L), DCAA (62 μg/L) and MCAA (62 μg/L) prior to cleanup and concentration (inset). Peaks for TCA, DCAA and MCAA were observed in the spiked tap water. Peaks for TCA and DCAA were observed in tap water at concentration levels as low as 38 and 62 μg/L but MCAA was not detected at levels below about 500 μg/L (Fig. 5 inset).

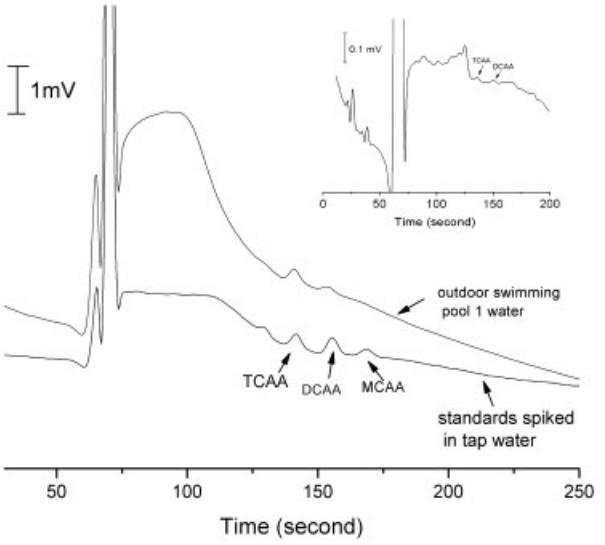

Figure 5. Swimming pool water and spiked tap water. Standards TCA (383 μg/L); DCAA (620 μg/L) and MCAA (513 μg/L) were spiked into tap water, extracted and analyzed. Unspiked outdoor swimming pool water was extracted and analyzed. Inset; standards TCA (38 μg/L); DCAA (62 μg/L) and MCAA (62 μg/L) were spiked into tap water, extracted and analyzed. Other conditions were the same as in Fig. 2.

Table 1. HAAS neasured in swimming pool water

Sample[a)]	TCA (μg/L) ± SD	DCAA (μg/L) ± SD	MCAA (μg/L) ± SD
Indoor swimming pool	ND	582 ± 72	ND
Outdoor swimming pool 1	697 ± 38	391 ± 47	ND
Outdoor swimming pool 2	1058 ± 83	509 ± 57	ND

a) Samples were extracted from 50 mL as described in Section 2 and values were determined by standard addition method. ND, not detected; values are averages, SD ($n = 3$).

Table 1 lists the concentrations of TCA and DCAA measured in one indoor swimming pool and two outdoor swimming pools using a standard addition method. DCAA was detected in all three pools, whereas TCA was measured in two pools and MCAA was not observed in any of the pools. TCA and DCAA were measured after extraction from tap water at concentrations below those measured in the three pools (except for the indoor pool where TCA was not detected). Because the lowest concentration of MCAA that could be detected in spiked extracted tap water was about 500 μg/L, concentrations in the swimming pool water that were lower than this would not be detected.

4 Concluding remarks

The HAAs TCA, DCAA and MCAA were measured using microchip CE with C^4D. This system was characterized and

optimized with respect to type of electrolyte, as well as concentration and pH for the bicarbonate buffer system. By coupling this analytical technique with SPE, TCA and DCAA could be detected in outdoor swimming pool water at concentration ranges above 100 μg/L which are typically found in residential pools [6]. Analysis of water from three local swimming pools showed the presence of TCA and DCAA at concentrations ranging from 400 to 1000 μg/L. The relative speed and simplicity of this technique show some advantages as compared with conventional laboratory-based analysis systems such as CE [16], GC and LC [14]. The combination of the low cost and simple construction of PDMS microchips with the contactless conductivity detector system also shows the potential for creating an on-site and disposable ''lab-on-a-chip'' system for screening of selected HAAs in swimming pool water.

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The authors have declared no conflict of interest.

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