

## THE DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF HALOACETIC ACIDS COMPOUNDS (HAAs) IN DRINKING WATER

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*Keyword: Haloacetic acids; Solid phase extraction; Water analysis*

### Abstract

The occurrence of disinfection by product (DBPs) in drinking water has been an issue of major concern during the last century due to their adverse health effect. The development and optimization of analytical methods for the determination of DBPs especially haloacetic acids (HAAs) in water are key points in order to estimate human exposure to treated water. This paper focuses on the development of method for the analysis of HAAs for routine analysis of these compounds in Malaysian drinking water. A solid phase extraction technique with final analysis by gas chromatography - electron capture detector system (SPE-GC-ECD) was successfully developed for the purpose. At optimal conditions, the mean recoveries of 95 % with relative standard deviation (RSD) below 4 % were attained. Precision and accuracy were determined at a concentration level of 20 to 60  $\mu\text{g/l}$ . Limits of detection ranged from 0.011  $\mu\text{g/l}$  to 0.193  $\mu\text{g/l}$  for all nine HAAs. A study was carried out to assess the level of HAAs in Semenyih Catchment (SC) and the Semenyih River Water Treatment Plant (SRWTP). For all the nine HAAs targeted, only five components i.e MCAA, DCAA, TCAA, DBAA and BCAA were detected in different concentration of the raw and treated waters. None of HAA component was detected in water from Semenyih dam (SS1). Concentration of HAAs present in Semenyih river basin (SC) increased from SS 2 (the most upstream point) until SS 9 (downstream of the river at the intake point) due to discharges from agro-based, sewage, earthworks and land-clearing and manufacturing industries. However higher concentrations of HAAs were detected in the treated water of the SRWTP as expected due to the chlorination process.

Keywords: Haloacetic acids; solid phase extraction; liquid-liquid extraction; drinking water

### Abstrak

Kewujudan hasil sampingan disinfeksi (DBPs) dalam air minum merupakan satu isu yang penting semenjak abad lepas disebabkan oleh kesannya ke atas kesihatan. Perkembangan dan pengoptimuman kaedah analisis bagi penentuan sebatian DBP ini terutamanya asid haloasetik (HAAs) dalam air adalah merupakan perkara pokok bagi menilai pendedahan manusia terhadap sebatian ini dalam air minum. Kertas ini menfokus kepada perkembangan satu kaedah analisis HAA bagi penentuan rutin di dalam air minum Malaysia. Satu kaedah pengekstrakan fasa pepejal diikuti oleh penentuan akhir dengan kromatografi gas yang dilengkapi dengan pengesanan pemerangkapan elektron (SPE-GC-ECD) telah berjaya dikembangkan bagi tujuan ini. Pada keadaan optimumnya kaedah ini mempunyai peratus perolehan semula melebihi 95% dengan nilai sisihan piawai relatif kurang daripada 4%. Kepresisan dan kejituan telah dikaji pada aras kepekatan 20 hingga 60  $\mu\text{g/l}$ . Had pengesanan bagi semua sembilan HAA berjulat antara 0.011  $\mu\text{g/l}$  hingga 0.193  $\mu\text{g/l}$ . Kaedah ini telah digunakan dalam satu kajian mengenai aras HAAs di lembangan Sg. Semenyih (SC) dan di loji rawatan air Sg. Semenyih (SRWTP). Daripada sembilan sebatian HAA yang disasarkan, hanya lima sebatian sahaja iaitu MCAA, DCAA, TCAA, DBAA dan BCAA dapat dikesan dalam pelbagai aras kepekatan di dalam air mentah dan air terawat. Tiada HAA dikesan di dalam air daripada Empangan Semenyih (SS1). Aras HAA di lembangan Sg. Semenyih didapati bertambah dari hulunya (SS2) hingga ke titik pengambilan air mentah (SS9). Ini mungkin disebabkan perkembangan dalam penggunaan tanah dan kesan daripada pembangunan industri, kawasan pelupusan sampah dan buangan

daripada kawasan penempatan. Aras yang jauh lebih tinggi didapati dalam air di SRWTP disebabkan oleh proses penklorinan yang digunakan di loji tersebut. Walau bagaimanapun aras HAA yang didapati dalam kajian ini masih lagi di bawah had yang dibenarkan di dalam air minum.

## Introduction

Chlorination of public water supplies began in the early 1900s and quickly led to a massive reduction in waterborne diseases. Chlorination is a widely used method of disinfections because it is extremely efficient and cost effective. Most municipal water supply system in Malaysia use chlorination for water disinfections [1, 2]. Although, chlorination worked well, it was discovered that the use of chlorine posed potential health risks due to the formation of carcinogenic halo-organic compounds, as disinfections by-products (DBPs).

Haloacetic acids (HAAs) are one of important groups of DBPs in chlorination process of drinking water. Similar to Trihalomethane (THM), HAAs are formed by the reactions between chlorine and the natural organic matter. HAAs constitute the fraction of non-volatile halo-organic DBPs compounds. There are nine HAAs compounds that contain chlorine or bromine including monochloro-, dichloro-, trichloro-, monobromo-, dibromo-,tribromo-, bromochloro-, chlorodibromo-, bromodichloroacetic acids. The presence of HAAs in the environment poses health risk because, even at very low concentrations, many of these materials are carcinogenic and mutagenic [3].

Current method of HAAs analysis of involved liquid-liquid extraction (LLE) technique followed by analysis with gas chromatography with electron capture detector (GC-ECD) [4]. Solid Phase Extraction (SPE) technique has been suggested as an alternative method to overcome some problems inherent to LLE technique namely requirement of large amount of organic solvents and time consuming. The SPE technique is technically a simpler, faster and safer extracting technique. Initially, the results showed that a quaternary ammonium strong anion exchanger (SAX) sorbent was the most suitable for HAAs analysis. Method validation is necessary to evaluate to what extent the SPE technique is suitable for routine analysis of HAAs in drinking water as compare to the established LLE method.

Method validation is a process for establishing that performance characteristics of the analytical method are suitable for the intended application. Method validation is also a process of verifying a method if it is fit for purpose. This included process of establishing performance and limitations of the method, the extent to which analyte can be determined in terms of precision and accuracy in the presence of interferences [5, 6]. The aim of this work is to validate the procedure based on SPE technique for the extraction and analysis of HAAs in drinking water. The validated method was used to monitor HAAs in water within the Sungai Semenyih catchment (SSC) area and the Semenyih River Water Treatment Plant (SRWTP).

## Experimental

### *Reagents and materials*

The nine HAAs were obtained as solutions in methyl tertiary-butyl ether (MTBE) from Supelco in both their free acid form and as methyl esters. The internal standard used was 1,2,3-trichloropropane, purchased from Supelco and the surrogate standard used was 2-bromobutanoic from Aldrich. MTBE and methanol were obtained from J.T. Baker. Sodium sulfate, sodium bicarbonate, hydrochloric acid and ammonium chloride, all ACS grade, were obtained from Fisher Scientific. The deionised water used for preparing standard solutions was purified by Arium 611DI system from Sartorius AG.

### *Solid Phase Extraction (SPE) Technique*

#### *Preparation of standard solution*

Intermediate standard solution of HAAs mixture at concentration of 100 µg/ml was prepared by diluting 1.0 ml stock standard (1000 µg/ml) to 10 ml in a volumetric flask with MTBE. A series of working calibration standard solutions in concentration level of 20 to 60 µg/l were prepared appropriately using deionised water. 10 µl of a spiking surrogate standard (2-bromobutanoic) at 10 µg/ml was spiked in a series of calibration solutions prior to sample extraction.

#### *Analytical procedure*

A commercial quaternary ammonium strong anion exchanger cartridge (ISOLUTE® SAX) was used as SPE sorbent. Disposable 3 ml SPE cartridges with 500 mg sorbent were employed. Cartridges were activated and conditioned prior to use using 10 ml methanol, followed by 10 ml deionised water. Once activated, 100

ml of sample solution was passed through the SPE cartridge without a vacuum system. A clean up step was made using 10 ml of deionised water to remove possible contaminants sample in sorbent. Then the HAAs retained were eluted with 5 ml of 10% H<sub>2</sub>SO<sub>4</sub>/MeOH solution. Finally, the collected extracts were methylated with MTBE at 50°C for 2 hour to produce ester derivatives. After methylation, 7 ml of NaSO<sub>4</sub> solution was added to increase the extraction efficiency. The extracted samples were then neutralized with 1 ml NaHCO<sub>3</sub> saturated solution. Final samples were placed in amber vials prior to GC analysis

#### *Liquid-Liquid Extraction (LLE) Technique*

##### *Preparation of standard solution*

Similar standard solutions were also prepared for LLE technique. The preparation procedure is similar to the one mentioned in SPE technique above.

##### *Analytical procedure*

LLE procedure for the determination of HAAs in drinking water was described by EPA Method 552.3 [4]. Briefly, 40 ml of sample were adjusted to pH 0.5 with H<sub>2</sub>SO<sub>4</sub>, followed by addition of NaSO<sub>4</sub>. Then, 4 ml MTBE and internal standard were used as the organic phase and 2 ml 10% H<sub>2</sub>SO<sub>4</sub>/ MeOH was added into the sample prior to heating for 2 hour at 50°C. Finally, the extracted samples were treated similarly as in SPE process for neutralization before analysis by GC.

##### *Gas chromatographic system and conditions*

The experiments were performed with Perkin Elmer series NCI 900 gas Chromatograph equipped with electron capture detector (ECD). A straight split/splitless mode injection was used in the experiment. Compounds were separated using a DB 5.625 capillary column, 30 m x 0.25 mm i.d, with 0.25 µm film thickness. The injector and detector temperature were set at 210°C and 290°C, respectively. Nitrogen was used as the carrier gas at flow rate column of 5.0 ml/min. The GC oven temperature was started from initial temperature of 40°C, holds for 5 min, then increased at 10°C/min to 150°C, hold for 5 min, and finally increased at a rate 20°C/min to 200°C and hold for 10 min. The total run time was 33.5 min. A volume of 2.0 µl sample were injected into the GC using the 10 µl syringe. A calibration curve was plotted between GC peak areas versus concentration of each analyte (standards) to determine the linear range.

## **Result And Discussion**

HAAs are anionic species at the typical pH of water samples. This means that a strong anionic exchanger (SAX) can be used as SPE sorbent to preconcentrate the species. For this reason, a commercial quaternary ammonium strong anion exchanger cartridge (ISOLUTE<sup>®</sup> SAX) was used as sorbent in this study. Of the currently approved methods, only EPA Method 552.1 [7] provides method performance data for HAAs but even then is only for six components of HAAs instead of nine components. Since this EPA method has low analyte recovery, it is therefore not suitable for use on many drinking water samples. Considering the weakness of the EPA Method 552.1 and potential application of SPE extraction technique, some modifications have been studied to improve this method for water samples namely the sample pH, amount of reagents and condition of GC-ECD. These steps have been described earlier in the experimental section. The improved method was then validated. The validation parameters studied include linearity, accuracy, precision, method detection limit (MDL), limit of quantification (LOQ), and measurement of uncertainty.

##### *Linearity Range*

The concentrations of HAAs in the SPE and LLE techniques were calculated using a five-point calibration at concentrations of standard solutions in the range of 20 to 60 µg/l using three replicate injections at the method optimum condition. A linear curve fit was obtained using the linear least squares regression procedure. The calibration curves for both techniques have shown a good linearity with correlation coefficient of 0.99 or better as shown in Table 1 and 2.

##### *Accuracy and Precision*

Accuracy is often calculated as recovery percentage of the analysis and determinate at known level of spiking. The accuracy was determined by spiking known amounts of analyte to sample across the specified range of the analytical procedure to obtain 20, 40 and 60 µg/l concentrations. Precision can be expressed in terms of relative standard deviation (RSD). It is assessed using three different spiked concentrations and seven replicates for each concentration. The results of each HAAs are also shown in Table 1. As can be seen from the recovery results of SPE method stated in Table 1, the HAAs were recovered in the range of

64 % to 112% for spiking level between 20 µg/l to 60 µg/l. The percentage of relative standard deviation (%RSD) was well below 4.0 % for the stated spiked concentration.

Table 1. Mean Recovery and RSD of each HAAs Using SPE-GC-ECD.

Component	Corr. coeff. ( $r^2$ )	20 µg/l		40 µg/l		60 µg/l	
		(%R)	RSD (%)	(%R)	RSD (%)	(%R)	RSD (%)
Monochloroacetic acid	0.9953	64.3	3.3	66.6	2.3	69.3	1.4
Dichloroacetic acid	0.9972	90.1	2.2	93.6	2.1	86.0	0.9
Trichloroacetic acid	0.9928	91.0	1.4	91.3	1.5	78.9	3.5
Monobromoacetic acid	0.9989	74.7	2.0	86.9	1.2	75.7	3.8
Dibromoacetic acid	0.9797	96.6	3.2	108.4	0.9	96.3	1.4
Tribromoacetic acid	0.9862	86.6	3.2	113.9	1.9	111.6	1.5
Bromochloroacetic acid	0.9906	85.4	2.6	102.7	1.3	95.7	1.4
Chlorodibromoacetic acid	0.9980	103.4	4.7	101.6	0.8	109.0	1.8
Bromodichloroacetic acid	0.9873	105.4	5.0	112.0	1.4	100.7	1.7

Similar analyses were used to recover HAAs from spiked drinking water samples using LLE method. The water sample was then extracted according to standard procedure at optimum condition. As can be seen from the recovery results stated in Table 2, the HAAs were recovered in the range of 78 to 118 % for spiking level between 20 µg/l to 60 µg/l. The percentage of relative standard deviation (%RSD) ranging from 0.5 to 4.0 was obtained for the above stated spiked concentration.

Table 2. Mean Recovery and RSD of each HAAs Using LLE-GC-ECD

Component	Corr. coeff. ( $r^2$ )	20 µg/l		40 µg/l		60 µg/l	
		(%R)	RSD (%)	(%R)	RSD (%)	(%R)	RSD (%)
Monochloroacetic acid	0.9963	79.2	3.7	78.5	2.6	80.1	3.4
Dichloroacetic acid	0.9979	84.0	2.7	97.3	1.6	80.3	0.5
Trichloroacetic acid	0.9944	103.6	2.6	93.9	1.7	94.6	1.2
Monobromoacetic acid	0.9953	80.4	2.9	88.3	3.0	85.4	1.7
Dibromoacetic acid	0.9889	116.0	2.4	104.0	2.3	115.3	2.0
Tribromoacetic acid	0.9971	93.3	2.6	95.7	2.4	102.4	3.6
Bromochloroacetic acid	0.9905	94.0	3.1	97.9	1.8	118.1	3.2
Chlorodibromoacetic acid	0.9892	85.6	4.0	86.4	2.8	84.6	3.0
Bromodichloroacetic acid	0.9868	92.4	2.0	95.3	1.8	98.9	1.4

#### *Method Detection Limit (MDL) and Limit of Quantification (LOQ)*

MDL is the lowest concentration of an analyte in sample that can be detected but not necessarily quantified, under the stated conditions of the test. LOQ, also known as the limit of reporting, is the lowest concentration of an analyte that can be determined with acceptable precision and accuracy under the stated conditions of test [2]. MDL value is calculated from standard deviation of the replicate studies results multiplied by appropriate Student's t value for 99% confidence interval. For this case MDL does not account for variation in sample composition and only achieve under ideal condition. Quantitation limit is 3.33 times MDL. Table 3 shows the values of MDL and LOQ of each HAAs by using SPE and LLE extraction method.

#### *Measurement uncertainty for test result*

Measurement uncertainty is a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonable be attributed to the measured [2]. The parameter may be, for example, a standard deviation or the width of a confidence interval. It is understood that the result of the measurement is the best estimate of the value of the measured and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards contribute to the dispersion. Upon consideration of the complete procedure from sample preparation to instrumental determination, the expanded uncertainty for all HAAs under study was found to be not more than 2.522 and 2.318 µg/l for SPE and LLE method, respectively.

Table 3. MDL and LOQ for each HAAs using SPE and LLE methods

Component	Samples No.	SPE		LLE	
		MDL (µg/l)	LOQ (µg/l)	MDL (µg/l)	LOQ (µg/l)
Monochloroacetic acid	7	0.1532	0.5102	0.009	0.028
Dichloroacetic acid	7	0.0161	0.0536	0.122	0.405
Trichloroacetic acid	7	0.0112	0.0373	0.061	0.202
Monobromoacetic acid	7	0.0263	0.0876	0.004	0.015
Dibromoacetic acid	7	0.0533	0.1774	0.064	0.212
Tribromoacetic acid	7	0.0926	0.3084	0.068	0.226
Bromochloroacetic acid	7	0.0422	0.1405	0.053	0.177
Chlorodibromoacetic acid	7	0.1934	0.6440	0.04	0.134
Bromodichloroacetic acid	7	0.0857	0.2854	0.05	0.165

*Applications to the analysis of water samples*

The optimized and validated SPE-GC-ECD analytical method was applied for the determination of the formation potential of the HAAs in water within the Sungai Semenyih catchment (SSC) area and the Semenyih River Water Treatment Plant (SRWTP). For all the nine HAAs targetted, only five components namely monochloroacetic acid (MCAA), [dichloroacetic acid \(DCAA\)](#), trichloroacetic acid (TCAA) dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA) were detected in different concentrations in the raw water and treated waters (Tables 4 and 5). None of HAAs component was detected in dam water (SS1) indicating the absence of the polluting sources.

Table 4: Mean concentrations of HAAs (in µg/L ) within the Sungai Semenyih catchment area.

Component	Occurrence (%)	Station Numbers								
		SS 1	SS 2	SS 3	SS 4	SS 5	SS 6	SS 7	SS 8	SS 9
Monochloroacetic acid	12	-	-	-	-	0.1	-	-	0.1	-
Dichloroacetic acid	48	-	0.1	0.7	0.5	3.3	1.0	2.9	3.0	1.8
Trichloroacetic acid	25	-	0.1	0.4	2.6	1.9	0.7	1.6	1.0	0.6
Monobromoacetic acid	-	-	-	-	-	-	-	-	-	-
Dibromoacetic acid	15	-	-	0.1	0.5	0.7	0.1	0.5	0.5	0.4
Tribromoacetic acid	-	-	-	-	-	-	-	-	-	-
Bromochloroacetic acid	1	-	-	-	0.1	1.0	0.1	1.0	1.4	0.5
Chlorodibromoacetic acid	-	-	-	-	-	-	-	-	-	-
Bromodichloroacetic acid	-	-	-	-	-	-	-	-	-	-

As shown in Table 4, analysis of water samples within the Sungai Semenyih catchment area showed the presence of HAAs started from Sungai Saringgit (SS2) and increased downstream up to the raw water intake point (SS9). Although all the water samples were not chlorinated, the presence of HAAs even at very low levels of 0.1 to 2.6 µg/L indicate other sources of these compounds. The antropogenic inputs could be from industrial discharges, agricultural activities or the landfill. The high levels of HAAs at Sungai Rinching (SS 5) and Sungai Beranang (SS 7) were indicative of impacts of sewage discharges and palm oil mill effluent discharges around the SS5 and the discharge of leachate from the landfill near the SS7.

The impact of chlorination to the production of HAAs were clearly shown by the increased level of HAAs in the treated water. As shown in Table 5, there was a sharp increase in the total concentration of HAAs in treated water (10µg/L) as compared to raw water (1.5µg/L), settled water (2.0µg/L) and filtered water (2.1µg/L). This findings were in line with the reported levels of trihalomethanes (THMs) in treated water in Malaysia which were ascribed as due to the chlorination process at the plant [8, 9]. However the levels of HAAs detected here were still very much lower than the MCL which were 50µg/L and 100µg/L for dichloroacetic acid and trichloroacetic acid, respectively.

Table 5 Mean concentrations of HAAs (in µg/L ) within the Semenyih River Water Treatment Plant

Component	Occurrence (%)	Types of water				MCL (µg/L)
		Raw water	Settled water	Filtered water	Treated water	
Monochloroacetic acid	20	-	-	-	0.9	-
Dichloroacetic acid	95	0.7	1.1	1.2	5.0	50
Trichloroacetic acid	83	0.5	0.6	0.6	3.7	100
Monobromoacetic acid	-	-	-	-	-	-
Dibromoacetic acid	3	0.1	0.1	0.1	0.1	-
Tribromoacetic acid	-	-	-	-	-	-
Bromochloroacetic acid	10	0.2	0.2	0.2	0.3	-
Chlorodibromoacetic acid	-	-	-	-	-	-
Bromodichloroacetic acid	-	-	-	-	-	-

### Conclusion

A simple, rapid and selective SPE-GC-ECD analysis method for the determination of all nine chlorinated and brominated HAAs in drinking water has been developed. The method has provided good linearity for certain level of concentration of HAAs. Limits of detection ranged from 0.011 µg/l to 0.193 µg/l for all HAAs were achievable. Validation of the SPE-GC-ECD developed method has shown the superiority of the technique in addition to ability to overcome problems inherent to LLE extraction technique. Analysis of water within the Sungai Semenyih catchment area shows a low level of HAAs. However inflated concentrations of HAAs were found in the treated water. This can be ascribed as due to the impact of chlorination performed by the water treatment plant as disinfection process.

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