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Original Research Article

Determination of trihalomethanes using gas chromatograph equipped with pulsed discharge electron capture detector (PDECD)

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ABSTRACT

Trihalomethanes (THMs) are the result of the reaction between chlorine and organic matter in the chlorination process of water. Measurement of this compound in water is necessary due to the possible risks to human health. In this study, direct aqueous injection (DAI) using a gas chromatograph equipped with a pulsed discharge electron capture detector (PDECD) was used to analyze the THMs. The results showed that there is a significant linear relationship between concentration and peak area up to a concentration of 300 µg/L for THMs (chloroform, bromodichloromethane, dibromochloromethane and, bromoform). The limit of detection (LOD) was obtained 4.2, 4.0, 4.3 and 5.3 µg/L. Without any preconcentration of samples, small quantities of LOD values indicate the proper sensitivity of the detector and the analysis method. As a result, instead of the common type of electron capture detector (using ^{63}Ni), pulsed discharge electron capture detector can be used.

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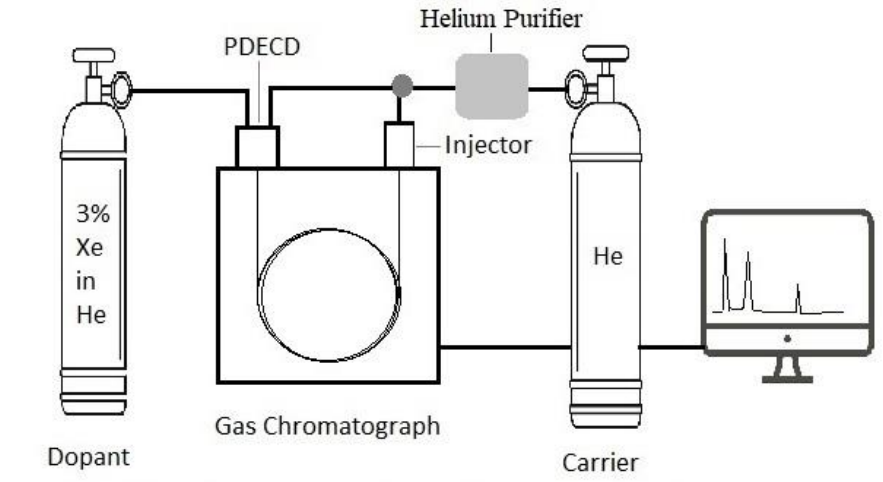
Graphical Abstract



Gas Chromatograph equipped with Pulsed Discharge Electron Capture Detector

Introduction

Water treatment using chlorine, in the presence of organic compounds, produces trihalomethanes (THMs). In THMs, three hydrogen atoms of methane (CH_4) have been substituted by halogen atoms. Although THMs can be considered very diverse, four substances are more important than others. Chloroform (trichloromethane-$CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform (tribromomethane-$CHBr_3$) are four major compounds that may be created in water treatment operations [1].

Humic substances (the main source of decomposition of plant debris)-main precursors for organic compounds in the chlorination process-form an important part of natural organic matter. These enter the aqueous media naturally. These are not completely eliminated in conventional water treatment processes. Furthermore, in swimming pools, organic matter from human activities also exists in the pool water. It has been proved that during the chlorination of water, these substances have been responsible for the formation of mutagenic and carcinogen organic halogenated compounds [2]. The effect of chloroform is also proved in the respiratory system and respiratory sensitivities in some studies. Today, there is no doubt about THMs risks. Other known complications of THMs are included liver and kidney damages, effects on the reproductive system, damage to the nervous and circulatory system [3, 4]. Formation of side organic matter in the chlorination of water has been considered more about human health and the problems made at treatment facilities after reports proved THMs formation in 1974. Since then, there were many types of research on determining its factors and finding methods of treatment to decrease their concentration.

In 1975, the United States environmental protection agency (EPA) put THMs in category A (which definitely cause cancer in humans), followed by the world health organization (WHO) emphasized the necessity to eliminate these compounds in drinking water [5]. Due to the undesirable effects of THMs on human health, the decline of formation and elimination of them have been considered in recent years. Iran, like the WHO, has set the guideline of THMs at 560 µg/L [5, 6]; however, in many countries they are lower than the WHO guideline. The EPA has announced it at 80 µg/L [7].

If the total THMs are more than the guideline, it is necessary to decide on the modification of the treatment methods or the processes for eliminating of these materials, therefore, accurate measurement of total THMs is important. In recent years, various articles have been published in this regard. According to the volatility of THMs, the main basis of the measurement methods is to determine the amount of them by using gas chromatography (GC). The commonly used techniques based on GC method include purge and trapping, liquid-phase micro-extraction, using the headspace technique at injection time and liquid-liquid extraction [8, 9]. Direct aqueous injection (DAI) of samples has also been used to measure volatile substances and chlorinated hydrocarbons [10]. In DAI method, there is no need for sample preparation, the analysis time is short and toxic and expensive organic solvents are not used for extraction. In fact, it is very ideal for many analytical chemists to inject a sample in gas chromatography without any sample preparation [11, 12].

The most common detectors for the detection and measurement of THMs are mass spectrometer and electron capture (ECD). Among these detectors, the ECD has been used in most studies, and even in more standard methods [12]. This detector has high sensitivity and low detection limit. However, there are some problems using ECD. The radioactive source of beta radiation (electron) and strict lab regulations, the impossibility of contamination cleaning and the small range of linear response can be considered as the negative aspects of using this detector [13].

The pulsed discharge helium ionization detector (PDHID) was also used in this research study [14]. Although this detector has been introduced for several years, it has not been used widely for unclear reasons. Moreover, few studies have been carried on its application. It is a non-radioactive and general-purpose detector that can easily act as a pulsed discharge helium ionization detector (PDHID), pulsed discharge photo ionization detector (PDPID), and pulsed discharge electron capture detector (PDECD). In fact, PDHID is a non-destructive detector (with 0.01 to 0.1 ionization percent) and very sensitive. The response of this detector to organic compounds is linear over five orders of magnitude with minimum detectable quantities (MDQs) in the low picogram range.

Pulsed discharge electron capture detector (PDECD) is the selectable detector for the identification and measurement of electronegative compounds such as chlorofluorocarbons (CFCs), chlorinated insecticides, and other halogenated compounds. The minimum amount detectable for

these types of compounds is within the range of femtogram (10^{-15} g). Response characteristics and sensitivity are comparable or better with the type of radioactive electron capture detector (^{63}Ni) [14, 15]. The dopant gas (3% xenon in helium) acts as a safe electron source. This gas is ionized by photons in the discharge zone, and the generated electrons, in the absence of an electron absorber, creates a constant steady current. When the electron absorbent materials like halogenated compounds enter the detector from the column, the electron capture process occurs, which reduces the detector current and the detector's response is shown as a peak [16]. Instead of ^{63}Ni as a radioactive substance with beta (electron) radiation, xenon gas is responsible for electron emission. As a result, the detector is non-radioactive, the electron is produced only when it is needed and the electron producing process is completely safe**.** This detector is compatible with DAI and its response is not affected by the presence of water.

In this paper, a fast sensitive method, based on DAI and the gas chromatograph equipped with PDECD, was used. This method is quick, cost effective, with high precision and low detection limit. Moreover, it does not need any sample preparation. Due to the volatility of the THMs and unnecessity for a preliminary process, the accuracy of the measurement will be increased. In fact, the ability of the PDECD to measure THMs is evaluated in combination with the DAI method.

Experimental

Materials and methods

The THMs standard solution of 2000 μg/mL (certified reference material with analytical purity) was purchased from Supelco Inc., Bellefonte, PA, USA, in which the concentration of four THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$) were equal. Additionally, deionized water was used for dilution. To measure the concentration of THMs, a gas chromatograph (YL-600, Younglin Instrument, Korea) equipped with PDECD (VICHI, Valco Instrument Co. Inc., USA) and column TRB-5 (30 m×0.53 mm×1.5 μm, Teknokroma, Spain) was used.

Preparation of THMs solution

Standard solutions with the required concentrations of THMs (10, 25, 50, 100, 150, 200, 300, 500, and 1000 μg/L) made from the dilution of a standard solution of 2000 μg/mL. To prepare the actual sample, the samples were taken from the output water treatment plant, the samples were placed in an incubator at 40 °C for 24 h in order to remove the THMs, and two samples of 50 and 100 μg/L with the equal concentrations of four THMs were prepared.

Measurement of THMs concentration

The helium as the carrier gas, with the flow of 6 mL/min, dopant gas (a mixture of 3% xenon in helium) with the flow rate of 3 mL/min and a one-meter column as the same type as the main column (as pre-column to protect the main column) were used. Two microliters of aqueous samples were injected using a split method with a ratio of one to five. The injector and the detector were set at 180 °C and 200 °C respectively. Furthermore, the oven temperature was set at 90 °C for 3 min and then increased 10 °C/min to 120 °C. Consequently, it remained at this temperature for 3 min. Each of the prepared concentrations was injected three times and the average area of each peak was used to calculate the calibrating curve and other calculations.

Results and Discussion

Figure 1 shows the chromatogram of standard THMs solution at the concentrations of 25 µg/L. As seen in Figure 1, the separation of the THMs ends in less than 7 min, and the THMs peaks have a good resolution.

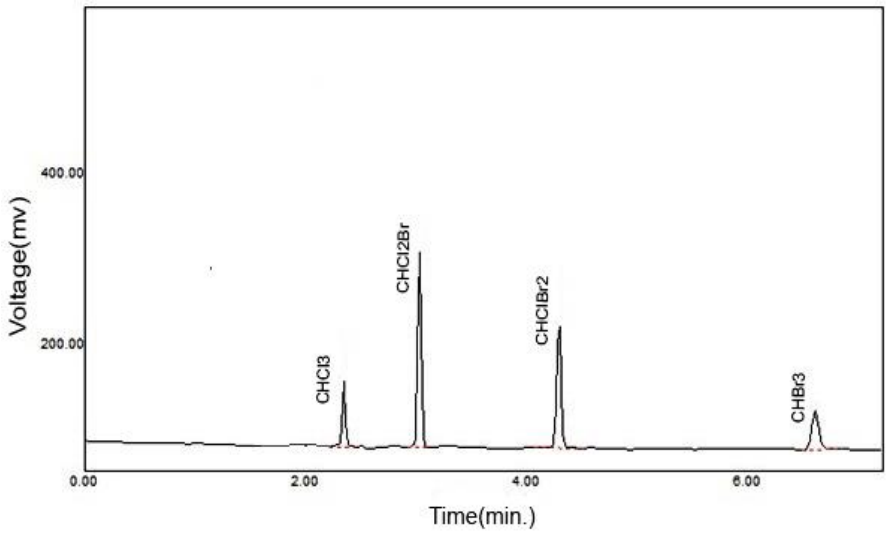


Figure 1. Chromatogram of standard THMs solution at the concentration of 25 µg/L using a PDECD

Figure 2 shows the THMs calibration curves for six concentrations of 10, 25, 50, 100, 200, and 300 µg/L. In this concentration range, the relationship between the area and concentration is linear. To find the range of linearity, the test was performed on samples up to 1000 µg/L using concentrations of 500 and 1,000 µg/L.

Table 1 demonstrates the coefficient of determination (R^2) values. R^2 measures the percent of the variation in the y variable (peak area) which might be attributed to variation in the x variable (concentration). R^2 is always between zero and one. The higher the R^2, the better the model fits the data. According to Table 1, by increasing the concentration, the linear response of the detector to the

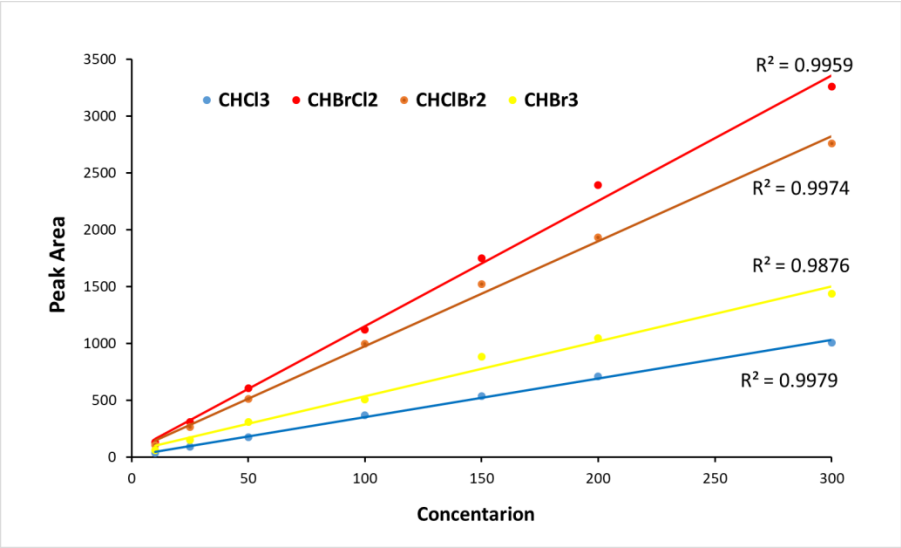


Figure 2. Concentration versus peak area of THMs for the concentration up to 300 µg/L

Table 1. R^2 values and calibration equation for different concentrations of THMs. Concentration (µg/L) versus peak area

	10 to 200 µg/L	10 to 300 µg/L	10 to 500 µg/L	10 to 1000 µg/L
$CHCl_3$	0.9997	0.9979	0.9883	0.9564
	y = 3.5678x - 0.4641	y = 3.3932x + 1.237	y = 2.9653x + 51.664	y = 6.4934x + 578.11
$CHBrCl_2$	0.9985	0.9959	0.9640	0.9486
	y = 11.785x + 0.4687	y = 11.031x + 5.037	y = 8.758x + 265.77	y = 5.3987x + 498.44
$CHBr_2Cl$	0.9987	0.9974	0.9634	0.9476
	y = 9.713x + 1.421	y = 9.2338x + 5.534	y = 7.2994x + 236.29	y = 2.552x + 323.89
$CHBr_3$	0.9982	0.9876	0.9650	0.903
	y = 5.81x + 1.109	y = 4.8291x + 5.244	y = 3.8989x + 138.13	y = 2.1817x + 159.74

concentration of THMs decreased. The best linear relationship for THMs was found with a concentration of up to 200 µg/L; however, according to Table 1, up to 300 µg/L concentration can be considered linear, covering the guideline defined for total THMs in most countries.

Up to 500 µg/L, the chloroform calibration curve can be considered linear, while for the other three compounds, it is not linear. Up to 1000 µg/L will be non-linear for all four THMs.

Figure 3 illustrates the calibrating curves with added two concentrations of 500 and 1,000 µg/L. The nonlinearity of peak surfaces area versus concentration is clear in high concentrations.

Calculated limit of detection (LOD) for the analysis of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ up to 300 µg/L was found to be 4.2, 4.0, 4.3 and, 5.3 µg/L, respectively. Despite the direct injection of the aqueous sample and the lack of any pre-concentration process, LOD values are small. If the limit of quantification (LOQ) to be almost three times more than LOD, then LOQ values will be 12.6, 12.0, 12.9, and 15.9 µg/L, respectively.

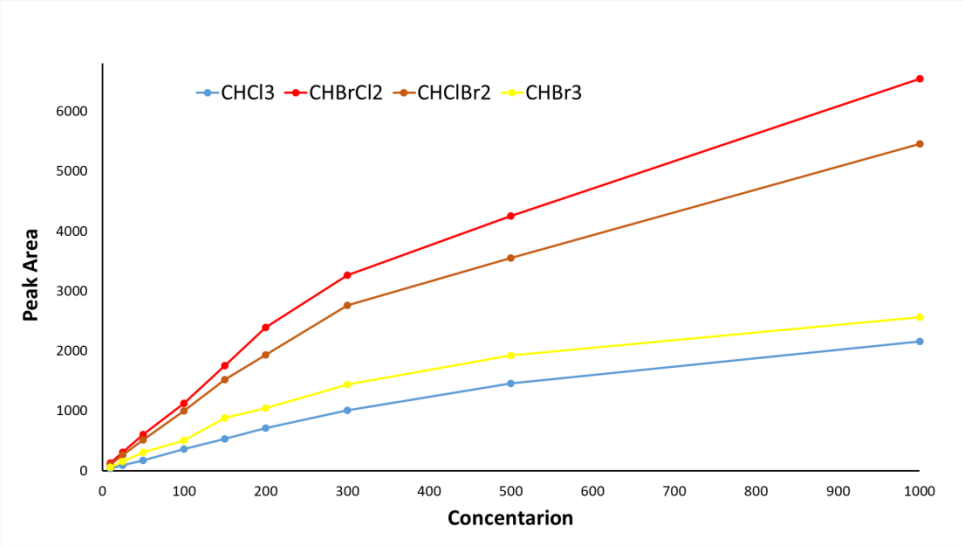


Figure 3. Concentration versus peak area of THM for concentration up to 1000 µg/L

The total LOD value for this range was 17.8 µg/L, which is far from the guideline by EPA (80 µg/L), indicating the proper efficiency of the PDECD detector by direct aqueous injection. Moreover, the total amount of LOQ is 54.4 µg/L, which is about 27 µg/L below the recommended guideline by EPA, which allows for accurate quantitative measurement of THMs with certainty.

Also, the water sample from the outlet water of the treatment plant was used for the preparation of two samples with the concentration of 50 and 100 µg/L for each of THMs (total 200 µg/L and 400 µg/L) after 24 h of incubation at 40 °C for the removal of all available THMs. The results of the tests are given in Table 2, calculated using the linear equation obtained from the calibration curve of Figure 2.

It is clear that the obtained results are very close to the real values, indicating the accuracy of the measurements. For the analysis of the THMs in a real sample, a sample of water was prepared after the treatment from the outlet water of the treatment plant. The results are shown in Table 3. $CHClBr_2$

and $CHBr_3$ were not observed in the sample, and the total concentration of chloroform and dichlorobromomethane were below the national standard of Iran.

Table 2. Concentration of THMs measured in two samples of 50 and 100 µg/L for each of the THMs using the outlet water of the treatment plant. Recovery percent is given in brackets

THMs	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total
50 µg/L	49.3 (98.6)	49.7 (97.4)	48.1 (96.2)	48.8 (97.6)	195.9 (97.6)
100 µg/L	98.3 (98.3)	97.7 (97.7)	99.5 (99.5)	96.6 (96.6)	392.1 (98.0)

Table 3. Concentration of THMs measured in the outlet water sample of the water treatment plant

THMs	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
Concentration (µg/L)	35.2	28.6	-	-

Conclusions

The direct injection is a quick method without any need for preliminary preparation of the sample. It can eliminate the errors that may occur in the sample preparation stage due to the volatility of the THMs or the problems in extraction method efficiency. Furthermore, the elimination of solvent extraction processes also prevents sample contamination and toxic and expensive organic solvents to be used for extraction. Moreover, by adding a pre-column, the problem of the column contamination can be eliminated, as the pre-column is easily interchangeable. The use of the pre-column in the usual THMs analysis, although increases the cost of the analysis due to the replacement of the pre-column after some analyzes, eliminating the sample preparation steps is a factor in the reduction of the cost and time. This leads to further analysis at a specified time. The linearity of the response to the concentration up to 300 µg/L for the THMs is above the EPA guideline. Despite the direct injection, the total LOD for THMs is small and it is much less than the EPA guideline. Use of the non-radioactive detector, the proper linear response range for PDECD, user-friendliness, the direct injection of a water sample, and the lower cost of maintenance compared to the radioactive detector, are the benefits of using PDECD. Finally, considering the advantages of this detector, it can easily be used as an alternative to the radioactive electron capture detector. Additionally, according to the EPA guideline of THMs (80 mg/L), the combined use of direct aqueous injection and the PDECD can provide the required sensitivity for accurate measurement while does not need the use of pre-concentration or liquid-liquid extraction.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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