Iranian Journal of Analytical Chemistry
Volume 12, Spring 1, March 2025 (109-122) Original Research Article
مجله ایرانی شیمی تجزیه
دوره ۱۲، شماره ۱، فروردین ۱۴۰۴ (۱۰۹-۱۲۲)

A analysis technique of trihalomethanes by GC-FID device

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Received: 9 October 2025 **Accepted:** 6 December 2025
DOI: 10.30473/IJAC.2025.76092.1327

Abstract

In water chlorination for removing pathogens, trihalomethanes (THMs) are among the significant carcinogenic by-products of drinking water chlorination. The conventional measurement means for these compounds is a GC device with an ECD detector (GC-ECD) or GC/MS. A GC-ECD or a GC/MS is utilized for analyzing THMs at the microgram per liter scale. Purchasing an ECD detector is not easy or cost-effective. This article introduces a new concentration method using the headspace technique in a GC-FID device for measuring the concentration of THMs. In this method, four compounds, chloroform ($CHCl_3$), di-bromochloromethane ($CHClBr_2$), bromodichloromethane ($CHCl_2Br$) and bromoform ($CHBr_3$), are plotted on a 5-point calibration chart after being measured on a microgram per liter scale. This method, designed in a laboratory, can be used to measure concentrations, and analyze data in the laboratories of water and wastewater, environment, petroleum and petrochemistry, etc. High accuracy of the method (µg/L) is the main feature of this method. Here, the design method and advantages of this method are presented with diagrams and tables.

Keywords
Measurement accuracy; Preconcentration method; Water distribution network; Headspace technique; Electron Capture Detector (GC-ECD).

1. INTRODUCTION

The use of precise instrumentation and techniques is vital in many industries and research activities [1-4]. One such area is the water industry, where the analysis and identification of numerous substances in drinking water at ppm and even ppb levels is essential. Among these substances, the measurement and identification of trihalomethanes are of particular importance [5,6].

In this article, four main trihalomethanes (THMs) compounds, including chloroform ($CHCl_3$), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform ($CHBr_3$), which are formed in the water chlorination process, are investigated. These compounds are identified in the text and diagrams with numbers 1 to 4 and with their corresponding scientific abbreviations (as their structures in **Fig. 1**). The common method for measuring THMs in water distribution networks is to apply a gas chromatography device equipped with an ECD detector. Due to the presence of radioactive nickel-63 in this detector and its import restrictions, its use is difficult in many laboratories in the country. In this study, a new method based on the headspace technique in a GC-FID device is introduced to measure these four compounds at µg/L. First, a brief review of the history of THMs monitoring in the Iranian water network is presented, and then the necessity and challenges of the methods available in the country's laboratories are explained. Next, while explaining the limitations of the current methods, the proposed method is introduced, and the results are analyzed with figures and tables. Finally, a general conclusion of the research is presented.

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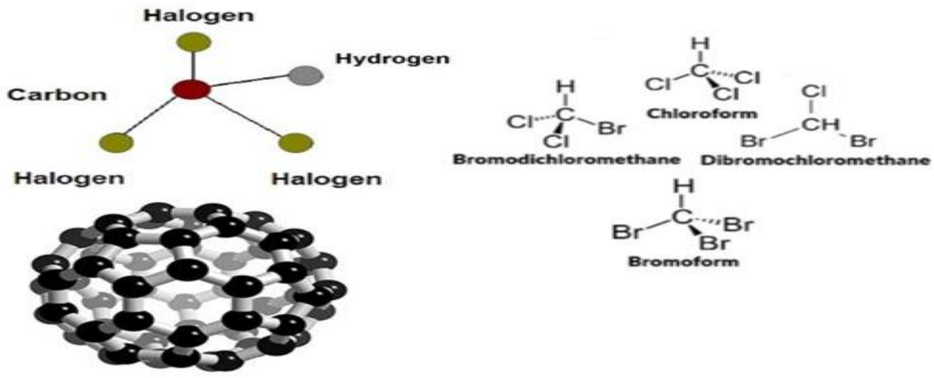


Fig.1. A molecular structural of trihalomethanes [7, 8].

1.1. Preconcentrationof THMs in Iranian water distribution networks and used analysis devices

THMs include four compounds $CHCl_3$, BDCM, DBCM, and $CHBr_3$, and are among the most important byproducts of chlorinated disinfection in water. Due to carcinogenic risks, the US Environmental Protection Agency reduced the total THMs limit to 100 µg/L in 1979 and to 80 µg/L in 1998 [9]. Common methods for measuring these compounds are mainly based on GC-ECD or GC-MS [10,11].

Several studies have also been conducted in Iran. In the study of [12], THMs concentrations in southern cities of the country were reported to be higher than the permissible limit. Moreover, in [13] was demonstrated that the amount of THMs in the water distribution network of Ahvaz is significantly higher in summer than in other seasons. In the study of [14], the seasonal difference and the difference between old and new networks in the city of Maragheh were also investigated. In northern Iran, strong seasonal changes of THMs and HAA5 have also been reported [15].

Factors affecting the formation of THMs include the concentration of primary organic matter, pH, temperature, residual chlorine and bromine concentration [14, 16]. Despite the high sensitivity of GC-ECD, its use is associated with safety and import limitations due to the presence of a radioactive source of Ni-63 [17–21]. This has increased the need for alternative methods.

By reducing the electron flow in the ECD, organic compounds such as $CHCl_3$, $CHClBr_2$, $CHCl_2Br$, and $CHBr_3$ are detected [22, 23]. In this process, an inert, dry carrier gas transports the sample from the column to the ECD, where electrons are generated by nitrogen or a methane/argon mixture [24, 25]. To determine the concentration, a standard mixture with low amounts of organic compounds is first measured, and then the sample results are compared with a calibration curve. In this study, although the main detector of interest is the ECD, due to practical limitations, the sample was preconcentrated with the Hedaspace HS-20 method, and measured with a GC-FID at the µg/L level.

ECD detector, by measuring the ion current intensity, has very high sensitivity and very low detection limit. In contrast, FID is a destructive detector but has good sensitivity, wide line width, low noise, simple operating conditions, and small size. Furthermore, FID is one of the most common detectors for organic compounds [26, 27]. Due to these advantages, GC-FID is of great importance in many laboratory applications, including water and fatty acid samples [28,29].While FID is capable of measuring a wide range of organic compounds, ECD only detects a subset of analytes, but the much higher selectivity and sensitivity of ECD makes it in some cases several hundred times more sensitive than FID, and detects much lower concentrations [30–32].In this context, although GC-FID is inherently insensitive to halogenated compounds, its combination with the headspace method can increase the response, and reduce matrix errors. Therefore, it is necessary to develop a reliable and low-cost GC-FID-based method for the measurement of THMs at the µg/L scale. In the present study, a headspace–GC-FID method is introduced, and its characteristics including accuracy, calibration, retention time, validation, limit of detection, and limit of qualification are presented.

2. RESEARCH METHOD

In this method, calibration levels of 5, 10, 20, 50, and 100 µg/L of mixed THMs (each level containing the four compounds: chloroform, BDCM, DBCM, and bromoform) were prepared and analyzed using headspace extraction coupled to a GC-FID system. A Shimadzu GC-2030 equipped with a BPX-5 capillary column (30 m × 0.25 mm × 0.5 µm) and a Shimadzu HS-20 autosampler was used. The injector operated in split mode (1:50) with a carrier gas velocity of 1 mL/min, and the FID detector temperature was set at 250 °C (H_2: 30 mL/min, air: 50 mL/min). Carbon tetrachloride (CCl_4) was employed as the internal standard at a constant concentration of 50 µg/L. Quality control procedures were performed according to ISO/IEC 17025, including midpoint calibration verification.

For headspace sampling, 15.0 mL of each aqueous standard or sample was transferred into 20-mL amber crimp vials fitted with PTFE/silicone low-bleed septa and sealed with aluminum caps. Vials were incubated at 60 °C for 30 min with continuous orbital agitation at 500 rpm, ensuring equilibrium before sampling. A 1.0-mL headspace loop was automatically withdrawn after incubation. The transfer line and HS syringe were maintained at 80 °C to prevent condensation. All steps, from preparation to sealing, were performed rapidly to minimize volatilization losses.

The primary THM stock standard (Techlab-France, initial concentration 200 ppm) was diluted with HPLC-grade methanol to obtain a 1000 µg/mL stock. Working solutions for calibration (5–100 µg/L) were freshly prepared by serial dilution with deionized water. Three replicate vials were analyzed at each level. Stock and working standards were stored in amber glass at 4 °C, protected from light, and monitored weekly for stability. Calibration curves for each THM were constructed and evaluated individually. The temperature and time settings for a 35-minute GC cycle in HS-20 were as shown in **Table 1**.

Table 1. Temperature and time program of headspace.

Type	Value	Type	Value
Oven temperature	60	Pressure equilibrium time	0.1
Sample line temperature	150	Load time	0.5
Transfer line temperature	150	Load equilibrium time	0.1
Sampling level	-	Needle flush time	5
Multi injective count	1	Injection time	0.1
Pressurize gas pressure	50	Pressurize time	0.5
GC cycle time	35	Equilibrium time	5

The units of t, T and P are minute, °C and kpa, respectively.

In this method, CCl_4 was used as the internal standard. The selection of CCl_4 as the internal standard for the Headspace-GC-FID method was for the sake of chemical stability. CCl_4 is chemically very stable, it is well transported in the vapor phase, and its retention time in GC-FID is such that it does not overlap with any of the four THM compounds. Likewise, its structure (halogenated tetrahydride) is close to THMs in terms of volatility, and has a similar behavior in Headspace technique.

Stability investigation results in Headspace technique: the stability of CCl_4 was investigated experimentally through three steps (i) measurement of its response after 10, 20 and 30 minutes of incubation, (ii) investigation of the repeatability of successive injections, and (iii) no decrease in signal observed in 5 successive repetitions. The results showed that CCl_4 is stable under Headspace extraction conditions.

Calculation of relative response factor (RRF): the RRF values for all four compounds based on their respective equations showed that the response variations with respect to IS were less than 5%.

The matrix effect control was carried out: (i) using deionized water as the standard matrix, (ii) using IS to eliminate injection variations and extraction fluctuations, and (iii) keeping temperature and headspace time constant for all experiments. Despite these controls, the matrix effect remained within acceptable limits.

The following three steps were presented in the new Headspace-GC-FID preconcentration method as follows:

1. Presenting the calculation of LOD and LOQ based on 3σ/m and 10σ/m (σ: standard deviation of the blank signal, m: slope of the calibration curve).
2. Illustrating magnified chromatograms for low concentrations to show that peaks at the 5µg/L level are separated from the baseline. 3. Explaining that headspace technique increases the Signal/Noise compared to direct injection.

In this way, the conditions that enable our method to achieve low detection limits were reported clearly and quantitatively. Finally, in the sample preconcentration method by headspace and FID detector, THM was analyzed at the level of µg/L, and the calibration curves yielded favorable results.

2. DISCUSSION AND RESULTS

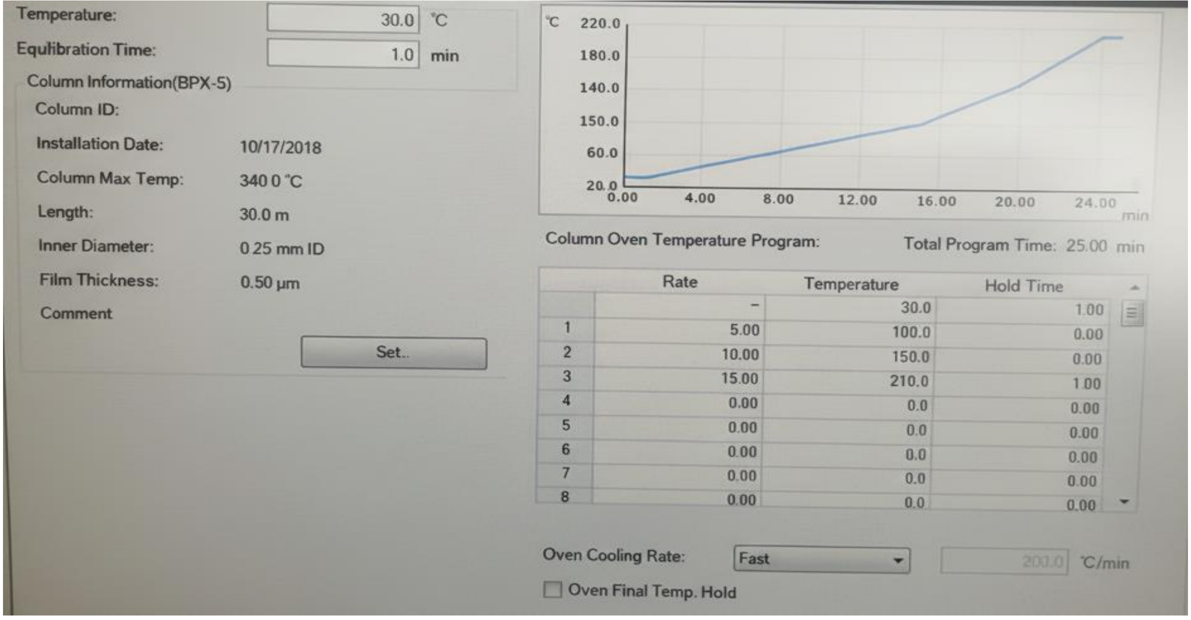
The important steps for a laboratory measurement method are method of sampling and sample preparation, instrument analysis conditions and method standardization [28]. This section describes the importance of GC method development and validation in water analysis.In this analysis, validation characteristics such as recovery, precision/validation, LOD, LOQ, area under the curve and retention time are presented as important parameters in tables and graphs.

Before these conditions, the samples and standard solutions were stored in a refrigerator at 2–4°C and brought to an ambient temperature of 25°C before

DOI: 10.30473/IJAC.2025.76092.1327

use. In each of the headspace vials, 15 mL of the sample or standard solution was poured up to the mark line. The upper space of headspace vials was left empty and sealed with a septum for the vial cap and placed in the device.

A PlainTest chlorimeter (England) was used to determine the residual chlorine level and as such a Hack device to determine the turbidity of the samples. The standard method 6232:1 was used as a template. Various affecting parameters such as temperature, pH, residual chlorine and turbidity are measured the same as the standard methods for water and wastewater in Iranian laboratories. The oven setting conditions are according to the temperature program in **Fig.2**.



Temperature: 30.0 °C

Equlibration Time: 1.0 min

Column Information(BPX-5)

Column ID:

Installation Date: 10/17/2018

Column Max Temp: 340.0 °C

Length: 30.0 m

Inner Diameter: 0.25 mm ID

Film Thickness: 0.50 µm

Comment

Column Oven Temperature Program:

Total Program Time: 25.00 min

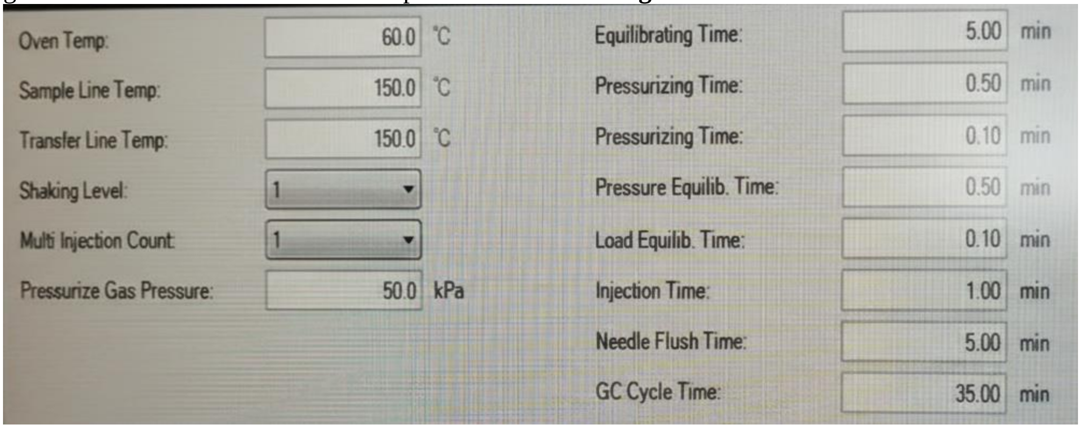
	Rate	Temperature	Hold Time
	-	30.0	1.00
1	5.00	100.0	0.00
2	10.00	150.0	0.00
3	15.00	210.0	1.00
4	0.00	0.0	0.00
5	0.00	0.0	0.00
6	0.00	0.0	0.00
7	0.00	0.0	0.00
8	0.00	0.0	0.00

Oven Cooling Rate: Fast 200.0 °C/min

☐ Oven Final Temp. Hold

Fig.2. Oven temperature program versus time for THMs.

According to Fig.2 above, the maximum temperature of the BPX-5 column with a length of 30 m, an internal diameter of 0.25 mm and a membrane thickness of 0.50 microns is 340°C, with an equilibrium time of 1 minute at 30°C. The changes in the hold time with respect to temperature for the entire program time of 25 minutes are given in this Fig.2. At a hold time of 1 minute, the peak resolution no longer changes, meaning that after 24 minutes at 220°C, the figure becomes a flat line.The headspace setting conditions are according to the computer program in **Fig.3**.



Oven Temp: 60.0 °C

Sample Line Temp: 150.0 °C

Transfer Line Temp: 150.0 °C

Shaking Level: 1

Multi Injection Count: 1

Pressurize Gas Pressure: 50.0 kPa

Equilibrating Time: 5.00 min

Pressurizing Time: 0.50 min

Pressurizing Time: 0.10 min

Pressure Equilib. Time: 0.50 min

Load Equilib. Time: 0.10 min

Injection Time: 1.00 min

Needle Flush Time: 5.00 min

GC Cycle Time: 35.00 min

Fig.3. Headspace computer program settings for THMs.

In Fig. 3, the parameters are displayed in two rows that depend on time and temperature. At 60°C the sample line temperature, transfer line temperature, and gas pressure are given. At 50 kPa, the sample line and transfer line temperatures are both 150°C. The equilibration time and pressurization time, pressurization equilibrium time, load time, load equilibrium time, injection time, and needle flush time are shown for a GC cycle time of 35 min. Sampling was performed when equilibration was complete to obtain a regular peak, which is more dependent on the sample size and temperature. In

DOI: 10.30473/IJAC.2025.76092.1327

addition, the GC-230-FID device used, and the peripheral equipment are given in **Fig. 4** below. The FID detector settings are at 220°C.

Fig. 4. The images of GC-2030-FID with HS-20 headspace. A Shimadzu HS-20 headspace was used to extract the samples, and a GC-2030-FID device from Shimadzu Japan was used to analyze THMs.

Four main compounds of THMs include $CHCl_3$, $CHClBr_2$, $CHCl_2Br$, and $CHBr_3$. These 4 compounds are indicated in the text and diagrams with the numbers 1 to 4, and with the abbreviations and scientific symbols chloroform, DBCM, BDCM, and bromoform, respectively.

To investigate the LOD and LOQ values, eight replicates of THM solutions were prepared in micrograms per liter. After using the calibration curve, it was determined that the standard deviation decreases with increasing concentration. Recovery and accuracy were performed with eight replicates for each THM by adding THM to water at a concentration of 20 ppb, and the results are presented in **Table 2**. In the regression equations, the linearity of the method (y = ax + b) was proven for all four compounds with high R² values ($R^2 > 0.995$). This value indicated a very good linearity of the method response in the concentration range of 5–100 µg/L. Moreover, the complete calibration data including mean measured concentrations, standard deviations (SD), and RSD% were provided in Table 2.

Table 2. Recovery and precision results for THM compounds (with 8 repeats).

Compound	Value Added (µg/L)	Repeat								%R	%RSD
		١	2	3	4	5	6	7	8	95.8	2.5
Chloroform	20	18.9	18.7	19.2	19.3	19.4	19.1	19.7	19.8		
DBCM	20	20.1	20.3	20.4	20.5	20.5	20.2	20.2	20.3	98.85	1.6
BDCM	20	18.9	19.6	18.9	19.1	19.1	19.2	19.2	20.5	98.80	2.7
Bromoform	20	17.9	18.9	19.3	19.4	19.5	19.8	19.9	19.4	94.95	2.8

%RSD = (SD/mean) × 100; %Bias= (Expected – Measured)/Expected × 100;
%Recovery= %R= 100 – %Bias; Recovery calculated from eight repeats.

Many high-boiling point substances may cause problems in the absorption of the analyte in the injection section or in the initial section of gas chromatography and liquid chromatography columns. This can subsequently cause negative and positive errors in the “retention time” of the analyte [26, 33].

In **Table 3**, the LOD was calculated with 7 replicates at an accuracy of 5 ppb. According to Table3, the LOD and LOQ of THMs were

DOI: 10.30473/IJAC.2025.76092.1327

4.8 and 14.42 respectively. In **Table 4**, the compounds and the retention times (from 1 to 4) for THMs are given, with the lowest and highest retention times corresponding to chloroform and bromoform, respectively.

In the new Headspace-GC-FID preconcentration method for measuring THMs in the microgram per liter range, the increased sensitivity was not due to the inherent sensitivity of the FID to halogenated compounds. Instead, this sensitivity was due to headspace preconcentration and optimization of extraction conditions including incubation temperature, equilibration time, and sample volume. These steps resulted in the effective concentration of THMs in the vapor phase being significantly higher than the actual sample concentration and the FID response, reaching a detectable level.

Table 3. The determination of LOD, LOQ and standard deviation against concentration in THMs.

Compound	Conc. (ppb)	Repeat							STDEV	LOD	LOQ
		1	2	3	4	5	6	7			
Chloroform	5	5.4	4.9	4.6	5.5	5.4	4.5	4.6	0.4061014	1.215304195	3.645912584
DBCM	5	4.6	5.5	5.4	4.7	5.3	4.6	5.4	0.3852179	1.15653804	3.46696141
BDCM	5	4.9	5.5	4.6	5.6	5.5	4.5	4.8	0.4309458	1.29283741	3.87851223
Bromoform	5	4.8	4.4	5.3	4.9	5.6	5.4	5.2	0.3807887	1.14265966	3.42797898
SUM									4.806161375	14.41648413	

Table 4. Retention times of THM compounds.

Component name	Retention time
Chloroform	2.029
BDCM	2.256
DBCM	2.931
Bromoform	4.434

The retention time pattern is quite consistent with the typical behavior of THMs in nonpolar columns. The increase in retention time is associated with the increase in halogen (bromine with higher molar weight). All analytical techniques of chromatography with different detectors such as (RI, FID, ECD, ELSD, etc.) require long analytical procedures. LOQ for sample must be done by calibration curves [34]. For accurate LOQ, calibration of the GC-FID system with calibration standards for each analyte is essential [35]. In fact, the good stability of GC-FID facilitates the calibration curve and the linear range improves the accuracy of operation. **Figs.5** and **6** illustrate the variations of the calibration curves of BDCM and DBCM, respectively.

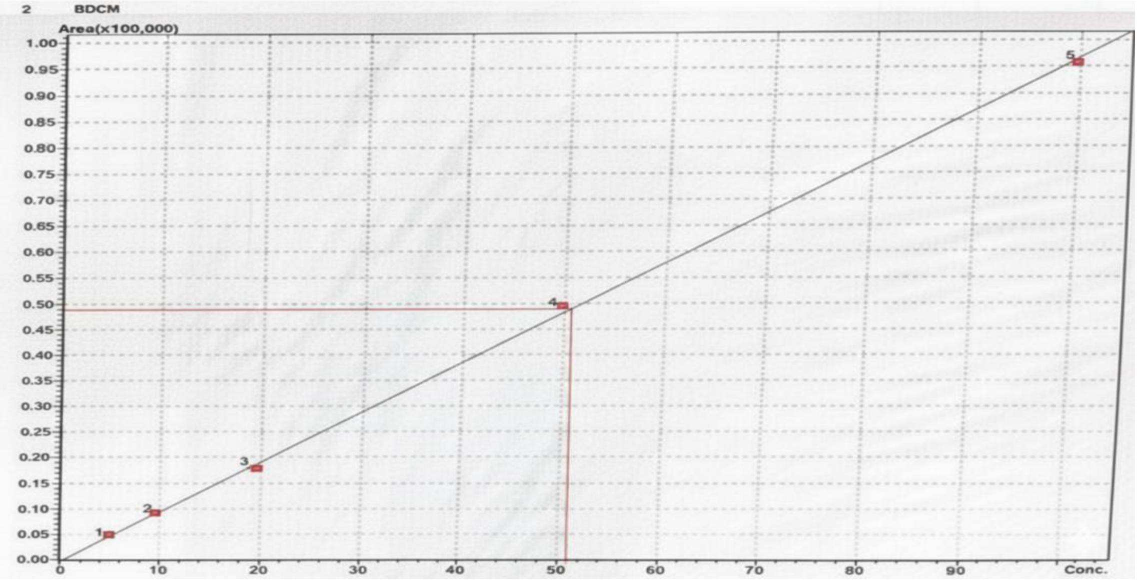


Fig.5. Calibration curve of BDCMby new preconcentration method based on Headspace-GC-FID.

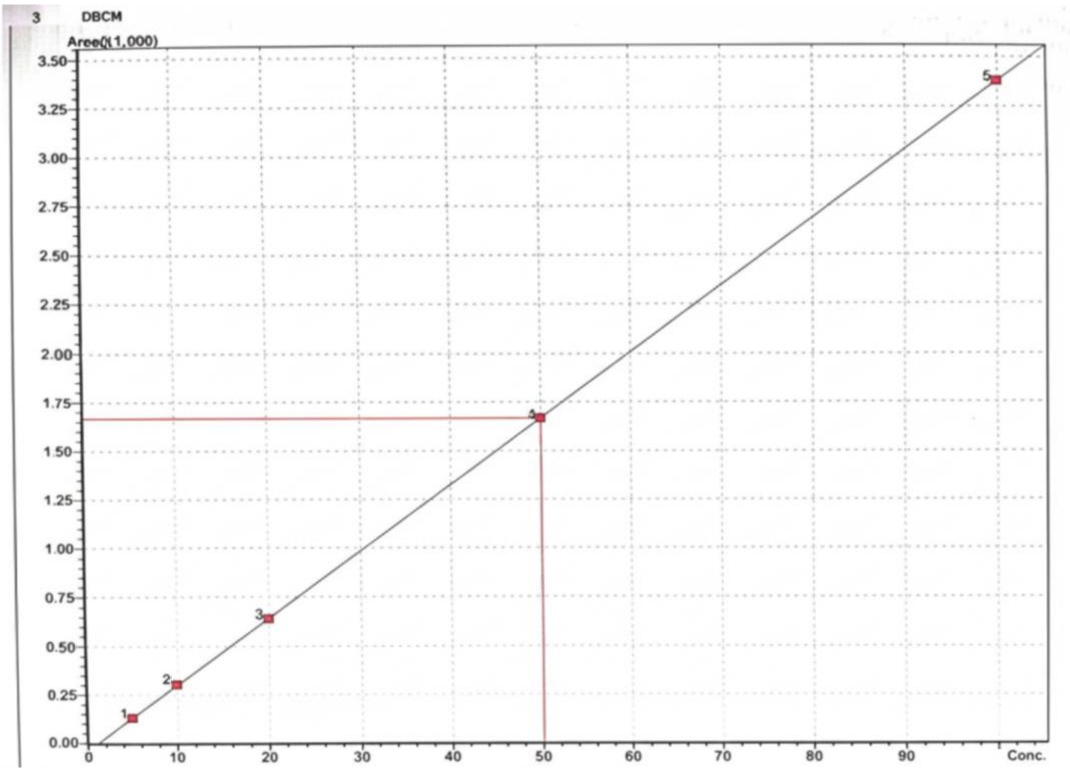


Fig.6. Calibration curve of DBCMby new preconcentration method based on Headspace-GC-FID.

Fig.7 illustrates the calibration curve of bromoform. The bromoform calibration plot shows the linear relationship between concentration and GC-FID detector response for bromoform, and completes the method linearity assessment section. The chloroform calibration curve was most similar to the BDCM calibration curve and was omitted due to space limitations, and instead, comparative curves were presented for comparing the concentrations of 4 compounds of THM on the calibration curve.

FID had very low sensitivity to chloroform, but it had most sensitive to BDCM, with the lowest bromine content among the three brominated compounds. Therefore, its signal intensity decreased less than DBCM and bromoform, and its response behavior was closer to chloroform. When comparing the slope of the calibration curve based on the physical nature of the compounds, it was observed that the more the number of bromine atoms, the weaker the FID signal, and the lower the slope of the calibration curve. Therefore, the slope hierarchy was as follows: Chloroform>BDCM>DBCM>Bromoform.

Additionally, due to the close linear behavior for both chloroform and BDCM, a high R^2 value (> 0.995) of stable linearity was observed in the range of 5–100 µg/L. In small gap between response factors compared to the other two compounds, BDCM had the most similar combustion pattern to chloroform due to its two chlorine atoms.

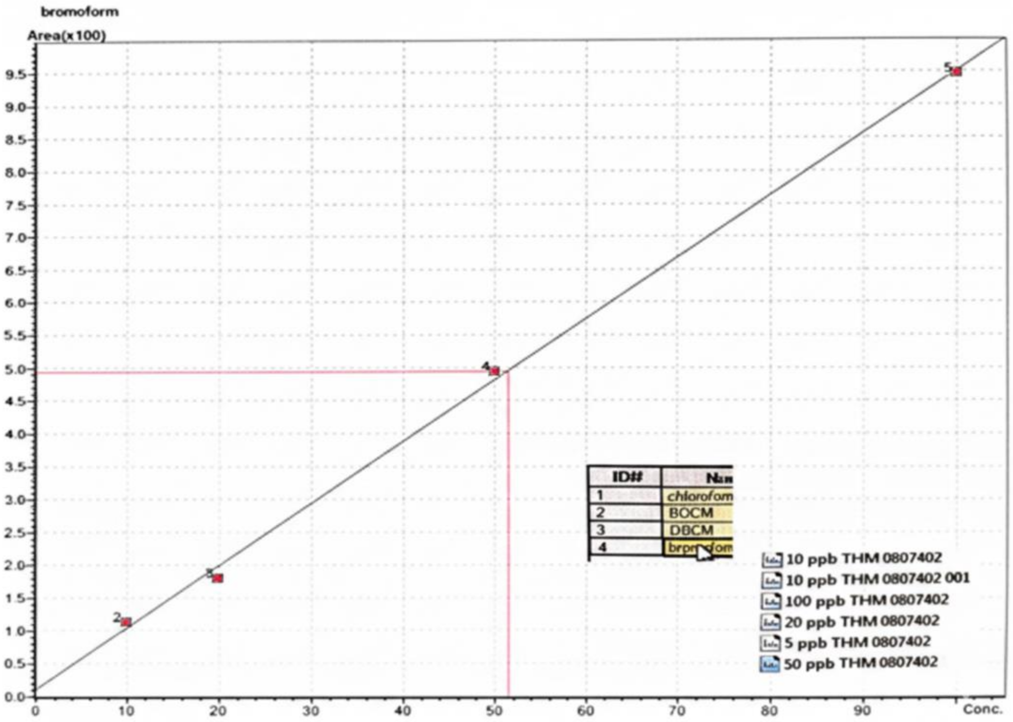


Fig.7. Calibration curve of bromoform by new preconcentration method based on Headspace-GC-FID.

Fig. 8 illustrates the chromatograms of the four compounds chloroform, BDCM, DBCM, and bromoform over a time period of 0–20 min and a signal intensity range of 0–3500 µV. According to this figure, each compound appears at a distinct and unique retention time, allowing for complete separation and selective identification of the species. The peak of the first compound, chloroform, appears at the shortest retention time (about 2.0 min) and usually has one of the highest signal intensities among the four compounds. Moreover, chloroform usually creates a relatively stronger response due to its lower molecular weight and better combustion behavior in the FID.

The compound BDCM, which appears at a retention time of about 2.2–2.3 min, also reveals a relatively high intensity peak, and is most similar to chloroform in terms of peak height. The order of increasing retention time is also consistent with the increasing degree of halogenation, increasing from chloroform to BDCM, then DBCM, and finally bromoform. Furthermore, the DBCM and bromoform peaks, with less intense than chloroform and BDCM, can be clearly identified and quantified due to their appropriate time resolution and lack of overlap. The range created for the x and y axes can allow for direct comparison of the intensity of the responses and complete resolution of the peaks.

In Fig. 8, the peaks of chromatogram of THM standard mixture (5–50 µg/L) analyzed by HS-GC-FID using a BPX5 (30 m × 0.25 mm × 0.5 µm) capillary column correspond to chloroform (Rt ≈ 2.06 min), BDCM (Rt ≈ 2.39 min), DBCM (Rt ≈ 2.93 min), and bromoform (Rt ≈ 4.48 min). Peak intensity increases proportionally with concentration in the 5–50 µg/L range. The figure shows clear separation of all THM species with symmetric peak shapes and acceptable baseline stability.

As Fig.8, all four THM species were efficiently separated under the applied HS-GC-FID conditions. Chloroform exhibited the earliest retention time (Rt ≈ 2.06 min), followed by BDCM (Rt ≈ 2.39 min), DBCM (Rt ≈ 2.93 min) and bromoform (Rt ≈ 4.48 min). The chromatographic peaks display good resolution, proper symmetry, and stable baseline behavior.

The peak height and area increased proportionally with concentration, confirming linear detector response in the examined range. Additionally, no interfering peaks were observed in the retention window of the target analytes, demonstrating method selectivity and suitability for the quantification of THMs in drinking water.

In general, it is observed that chloroform and BDCM exhibits the highest peak height due to the stronger FID response, while DBCM and bromoform have lower intensity, which is consistent with the increase in the number of bromine atoms, and the decrease in ionization efficiency in the FID.

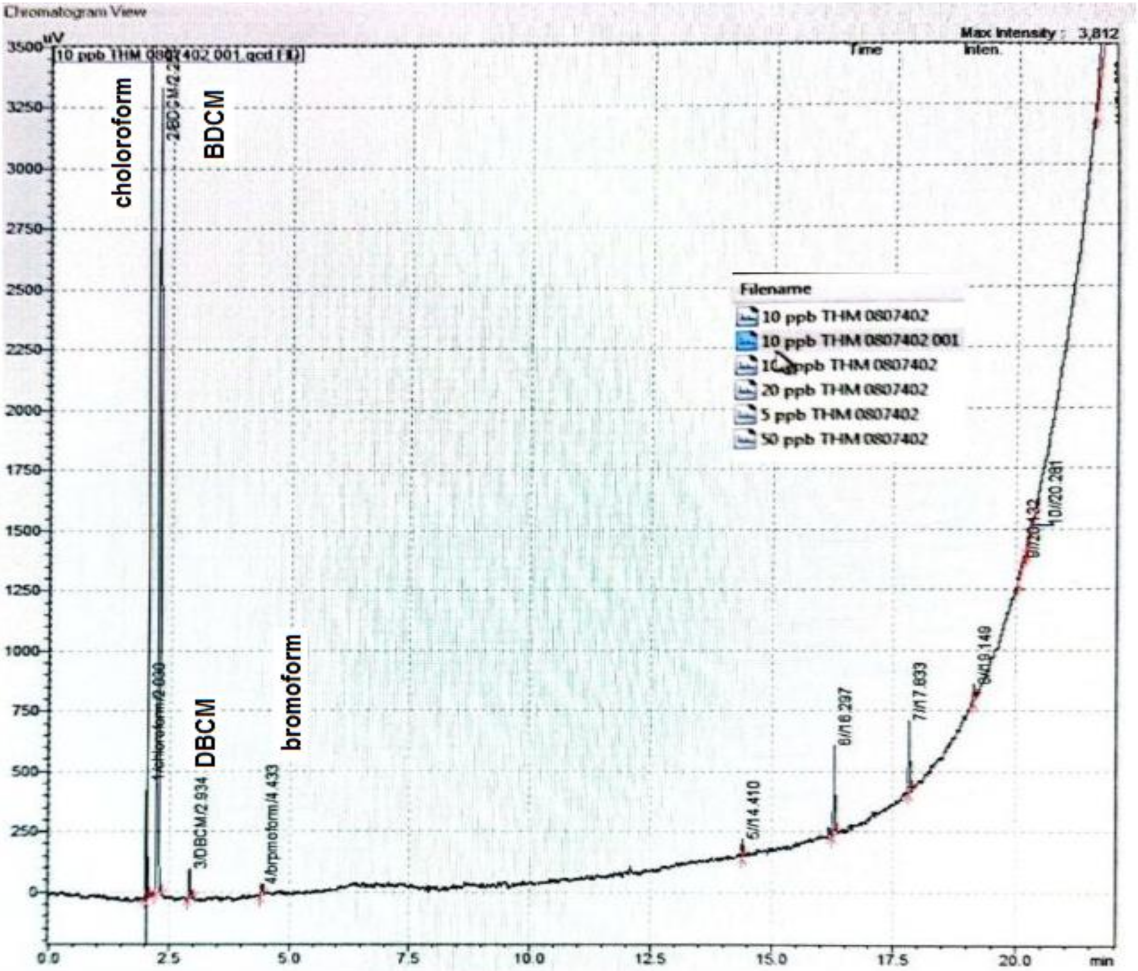


Fig.8. Chromatogram curves for four THM compounds of BDCM, DBCM, bromoform and chloroform, with the y-axis showing signal intensity (0–3500 µV) and the x-axis showing retention time (0–22 min)by new preconcentration method based on Headspace-GC-FID.

Fig. 9displays the chromatograms of four THM compounds, including chloroform, BDCM, DBCM, and bromoform, over a time period of 0 to 5.75 minutes and a signal intensity range of 0 to 2.75 µV. This plot has a higher magnification of the small signal numbers compared to the original plot to allow for a more accurate assessment of peak separation, baseline, and noise levels.

All four compounds are visible on this short time scale, with the largest peak appearing at approximately 2.25 minutes. As expected, this peak is associated with one of the two compounds, chloroform or BDCM, which creates a higher response than DBCM and bromoform in FID devices. This compressed time period indicates that the chromatographic separation is performed with good efficiency, and that the maximum peaks are detectable without overlap.

Moreover, a horizontal reference line is drawn in Fig. 9 to represent the baseline or reference level of signal intensity. The presence of this line allows for a visual comparison between the actual peak heights and the background noise. The significant difference between the peak heights and this reference line is a confirmation of the acceptable signal-to-noise ratio, and the ability to detect compounds even at low levels.

The scaled representation in Fig. 9 clearly illustrates that, despite the lower response of the FID device for compounds with low concentrations, all peaks of the four compounds are still separable, detectable, and distinguishable from the baseline. Such a plot is a confirmation of the resolution accuracy and stable quality of the baseline in the proposed method. This plot, with appropriate magnification, highlights the difference between the peak intensities and the baseline, and indicates that the proposed method has the necessary stability and resolution even at low signal levels.

DOI: 10.30473/IJAC.2025.76092.1327

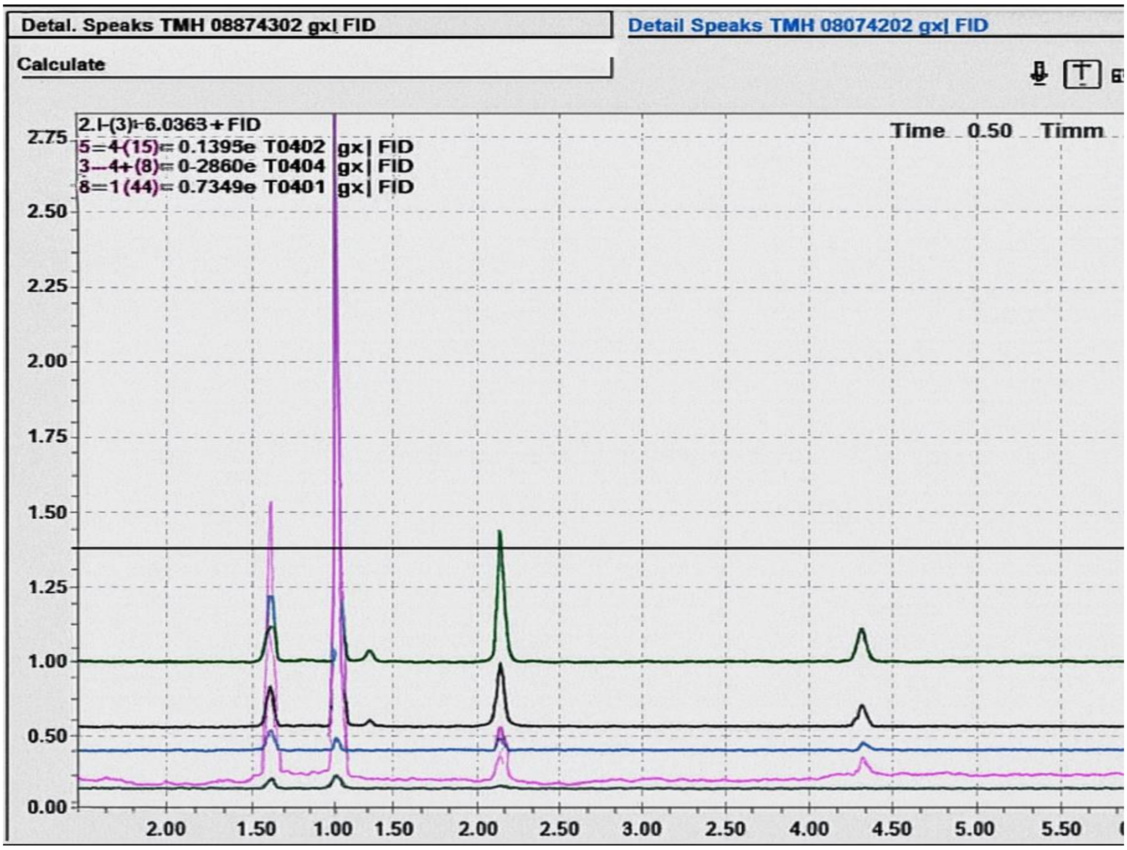


Fig.9. Comparison of picks in the calibration curves of BDCM, DBCM, bromoform and chloroform by new preconcentration method based on Headspace-GC-FID.

3.1. Comparison of proposed method with reference method

Since GC-ECD was not available at the time of the experiments or parallel runs were not possible, the following steps were carried out in the new method to address this concern:

1. Providing scientific justification for direct non-comparability: the proposed method is based on a headspace preconcentration step, while GC-ECD typically uses direct injection, so it was not possible to directly compare the raw signal values (peak area) between the two instruments.
2. Indirect comparison based on literature data: compared to commonly reported GC-ECD methods, the proposed method is therefore not intended to completely replace GC-ECD, but rather to provide an acceptable method for laboratories that do not have access to ECD.
3. Comparison based on performance characteristics in analyzing volatile compounds: in a direct comparison between two methods for analyzing volatile compounds with a gas chromatography device, the reference method uses an electron absorption detector (GC-ECD), and the proposed method combines static headspace (HS) preconcentration with flame ionization detector (GC-FID).

The GC-ECD method has very high sensitivity, and is easily able to detect concentrations in the ppb range and even lower. The setup of GC-ECD and its maintenance costs are high, it requires special and expensive calibration standards, and it offers very good selectivity. In contrast, the proposed method using FID, which is inherently less sensitive than ECD, is at a medium to high level in terms of sensitivity, but by using headspace preconcentration, it has succeeded in reaching the detection limit in the ppb range. The biggest advantage of this new method is its very low setup cost, complete elimination of the need for special and expensive standards, and acceptable selectivity for routine and everyday laboratory applications.

Therefore, the proposed Headspace-GC-FID preconcentration method, while maintaining sufficient sensitivity for ppb level measurement, is economically and practically much simpler, cheaper, and more accessible than the reference GC-ECD method, and is considered a more suitable option for routine analyses.

4. CONCLUSION

For extraction of samples the Shimadzu HS-20 headspace and for analysis of THMs the GC-2030-FID were applied. In this method, M-501-PAK calibration with a standard length of 1 mL was used for THM mixture with a concentration of 200 ppm. Solutions of 5 ppb, 10 ppb, 20 ppb, 50 ppb and 100 ppb were prepared using the above standard model and diy distilled water. Samples and standard solutions were extracted in a similar manner to the HS-20 headspace device and analyzed by Shimadzu GC-2030 device. After the method was validated, THM was analyzed in the drinking water distribution network of Shiraz city, and at all points, the THM level was found to be lower than the reported value or LOQ (14.42 ppb, according to Table 2). The quality control of these cases was carried out in accord with the 17025 standard and acceptable results were obtained. In addition, by sampling from the water network and the water storage tanks of Shiraz and analyzing by the new innovative method, the calibration curves were checked at the midpoints of the curve. According to Table 1, a deviation was observed less than 10% and the method was conducted in daily tests at the laboratory.

Acknowledgments

The authors thank all experts at the laboratory of water and waste company (in Shiraz city) for their technical support.

Conflicts of interest

There are no conflicts of interest to declare.

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DOI: 10.30473/IJAC.2025.76092.1327

یک تکنیک برای آنالیز تری‌هالومتان‌ها با دستگاه GC-FID

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تاریخ دریافت: ۱۷ مهر ماه ۱۴۰۴ **تاریخ پذیرش:** ۱۵ آذرماه ۱۴۰۴

چکیده

در فرآیند کلرزنی آب برای حذف پاتوژن‌ها، تری‌هالومتان‌ها (THMها) از مهم‌ترین محصولات جانبی سرطان‌زای فرآیند کلرزنی آب آشامیدنی بهشمار می‌روند. روش متداول اندازه‌گیری این ترکیبات، استفاده از دستگاه کروماتوگرافی گازی مجهز به آشکارساز جذب الکترونی (GC-ECD) یا کروماتوگرافی گازی–طیف‌سنج جرمی (GC/MS) است. این دستگاه‌ها برای آنالیز تری‌هالومتان‌ها در مقیاس میکروگرم بر لیتر بهکار می‌روند. خرید آشکارساز ECD به‌راحتی امکان‌پذیر و مقرون‌به‌صرفه نیست. این مقاله یک روش جدید تغلیظ بر پایه تکنیک هداسپیس (Headspace) را در دستگاه کروماتوگرافی گازی با آشکارساز یونیزاسیون شعله‌ای (GC-FID) برای اندازه‌گیری غلظت تری‌هالومتان‌ها معرفی می‌کند. در این روش، چهار ترکیب کلروفرم ($CHCl_3$)، دی‌برموکلرومتان ($CHClBr_2$)، برمودی‌کلرومتان ($CHCl_2Br$) و برموفرم ($CHBr_3$) پس از اندازه‌گیری در مقیاس میکروگرم بر لیتر، روی یک نمودار کالیبراسیون ۵ نقطه‌ای رسم می‌شوند. این روش که به‌صورت آزمایشگاهی طراحی شده است، قابلیت استفاده در آزمایشگاه‌های آب و فاضلاب، محیط زیست، نفت و پتروشیمی و سایر صنایع مرتبط را دارد. دقت بالای روش (در حد µg/L) مهم‌ترین ویژگی آن بهشمار می‌رود. در این مقاله، جزئیات روش طراحی‌شده به همراه مزایای آن و با استفاده از نمودارها و جداول ارائه شده است.

کلید واژه ها

دقت اندازه‌گیری، روش پیش‌تغلیظ، شبکه توزیع آب، تکنیک هداسپیس، آشکارساز جذب الکترونی (GC-ECD).

DOI: 10.30473/IJAC.2025.76092.1327