Multiple Headspace Extraction for Benzene and Toluene Quantitative Analysis in Hot Oils

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A B S T R A C T

In this article, the concentration of some volatile organic compounds (VOCs) in the hot oil sample of the Pars petrochemical ethylbenzene unit is presented. Pars Petrochemical is one of the largest producers of ethylbenzene in the Middle East. The hot oil impurities that were analyzed were benzene and toluene (BT). The hot oil sample was taken in May 2023 at a special sampling station on the site. The presence of BT is related to its intensity in the hot oil sample. The Multiple Headspace Extraction (MHE) method was used for the extraction and quantitative analysis of BT followed by gas chromatography (GC) analysis. A GC with flame ionization detector (FID) instrument was used for the analysis of BT. This method offers advantages for the analysis of volatile pollutants because it eliminates the use of organic solvents and various sample purification steps that often lead to erroneous results. The MHE method is independent of standard concentration and could be used in a wide range of BT in Hot Oil without calibration for different ranges. Also, linearity, detection limits, and accuracy were looked into as part of the validation process. The limit of detection (LOD) and limit of quantification (LOQ), respectively, were between 0.05 - 0.56, and 0.17 - 1.9 mg/kg. Less than 13.95 percent (n= 15) was the relative standard deviation statistically. A quick and easy method for detecting BT in hot oil samples was used for the first time. This work will be a step forward for the detection of other aromatic and cyclic hydrocarbons in hot oil samples.

Doi: 10.5829/ijee.2024.15.04.03

INTRODUCTION

Hot oil is a general name for most heat transfer oils (liquids). It can contain minerals, synthetic aromatics, or other types of oils (1, 2). Heat transfer oil is mainly used for indirect heating of process fluid in industrial plants such as oil and petrochemical production. Therefore, they have a high boiling point and high heat capacity (3, 4). Many efforts have been made to develop oil-based fluids as a result of the need to do so in many industrial fields because they have preferred heat transfer properties at high temperatures (5, 6). Heat exchangers' potential for energy savings and compaction depends heavily on increased heat transfer (7). Heat transfer oils, which are used to reduce energy consumption with high efficiency and are known as hot oil, were developed by researchers to increase the rate of heat transfer (8, 9).

A properly designed and installed heat transfer fluid system is vulnerable to operational stress factors that can degrade its performance as well as shorten the life of the fluid and system components (10). Heat transfer fluids are an essential part of the operation of many high-temperature processes (11, 12). When the heat transfer fluid does not perform as expected, it can have detrimental effects on product quality, production rates, and equipment life, and increase troubleshooting costs (13). When fluid quality deteriorates due to use or contamination (age), problems may arise due to changes in fluid chemistry and physical properties (14). These can include an increased risk of corrosion, the potential for fouling, solids/sludge formation, pumping problems, and fluid dilution due to materials entering the heat transfer fluid. To resist the effects of fluid aging and possible system effects, it is important to identify hot oil impurities. Biphenyl-based oil is the most important type of synthetic hot oil which could decompose to produce benzene and toluene despite the high stability of good traditional oils (15, 16). Hot oil stability and status could

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be tracked by identifying these two compounds. This finding may help locate leakage in the heat exchanger if benzene and toluene (BT) have been used during the plant's operation.

Research done since 2010 Deepwater Horizon (DWH) disaster had a significant positive impact on analytical methods for the chemical analysis of petroleum, photochemical, biological, and petroleum transformation products, as well as their dispersants and biodegradation products (17). A deeper understanding of the molecular level of composition and complexity of oil changes is provided by advanced gas chromatography (GC) techniques like comprehensive two-dimensional GC, pyrolysis with mass spectrometry (MS), and tandem MS (18, 19). To address these issues, new techniques and tools must be created for their implementation. The headspace device is the most effective tool for measuring light volatile hydrocarbons in thermal oil, such as potential BT (20, 21). Because the majority of the compounds (more than 90%) have boiling points higher than 370 ºC and cannot be directly injected into GC device, either their heavy weight prevents them from producing peaks, or the given peak does not accurately reflect the value. Also, a part of the sample remains inside the liner and is not separated from the GC column in any way. In the headspace method, by heating the vial inside the device's oven, light and volatile compounds are converted into vapor and after some time they reach equilibrium with the liquid phase. According to the device's calibration, it will be possible to quantitatively measure light compounds after the specified equilibration period. The Multiple Headspace Extraction (MHE) methods can be applied to samples like thermal oil where it is challenging to directly prepare a calibration standard (22-24). It should be noted that thermal oil is heavy and viscous, making it impossible to guarantee complete solubility and the creation of a uniform solution when you dissolve something like BT. The standard and sample matrix are examined separately in MHE. The method's premise is that to remove all desired analytics (for instance, BT), Headspace extracts the test subject, such as thermal oil, in large quantities and one at a time. However, it has been demonstrated that this approach only requires a few iterations. Temperature and time of sample heating are the most important parameters in MHE and should be determined by trial and error or by similar headspace applications on literatures.

Ethylbenzene is produced in Pars Petrochemical Company (PPC), Asalouye, Bushehr, Iran, a unit using the circulating hot oil sample. Hot oil can contain BT during exchanger leakage brought on by unexpected factory repairs, which will increase hot oil's impurity level and significantly lower its production efficiency. This study's goal is to use a headspace device and GC device to measure the concentration of BT in hot oil samples. Additionally, standard and real samples were used to optimize the BT measurement conditions. It

should be noted that we have developed a new method that enables us to precisely identify the composition and component concentrations of mixtures made up of two or three volatile hydrocarbon media.

MATERIALS AND METHODS

Chemicals, reagents, and materials
Heat transfer oils (99.9%) are provided by the global producers. BT was supplied by Nouri Petrochemical Company (Iran); Styrene was supplied by Pars Petrochemical Company (Iran); Acetone (99.9%) was obtained from Merck (Germany). All chemicals purchased from companies in this study were used without further purification.

Chromatographic and headspace parameters
A headspace device connected to a chromatographic apparatus was used in modified ISO 11423 methods for the isolation, identification, and quantification of BT, as previously reported in the literature (25-29). Chromatography conditions and methods included a poly ethylene glycols capillary column (CP WAX 52CB, 30 m, 0.32 mm id, and 0.5 µm thickness) was used for BT analysis. The initial column temperature was 55°C (hold 10 minutes) raise to 220°C at a rate of 10 °C/min and then hold for 60.50 minutes (total time 87 minutes). The injector temperature was 220 °C, and Spilt Ratio was 50. The detector temperature was 240 °C with nitrogen as a carrier gas at 7 PSIG. The flame ionization detector (FID) was also used using synthetic air (300 ml/min), hydrogen (30 ml/min), and nitrogen makeup (25 ml/min); and FID data acquisition: 100 V. Headspace was Quma QHSS-42 and its parameter methods included a/ vial menu: first vial =1 / last vial =1 / repeat vial = 5 or 6; method menu: method 2 including temperature & press: oven=160 ºC, valve=165 ºC, tube=165 ºC, Aux 1&2=0 press=500; run parameter: run time=90, PC time=90 minutes, single P0 = yes, shake= No; injection purge = No change; misc. parameter menu: wait for RDY=yes, lock =yes, meth. seq. 0000, standby=Yes. The injection volume of the sample inside the headspace (sample loop) was determined to be 1.0 ml. The method was based on the extraction of analytics by the headspace, in which a small amount of oil sample containing analytics was placed in a glass vial (20 ml) sealed with a silicone/PTFE septum and the vial was heated. The heat vaporizes the BT, using up the vial's dead volume or headspace, shifting the equilibrium to the gas phase. Finally, the needle punctured the septum of the vial and collected a volume of the gas phase, and injected it into the chromatograph for analytical measurement. The needle remained at the vial during all extractions. Figure 1 shows a summary of sample extraction and analysis steps.
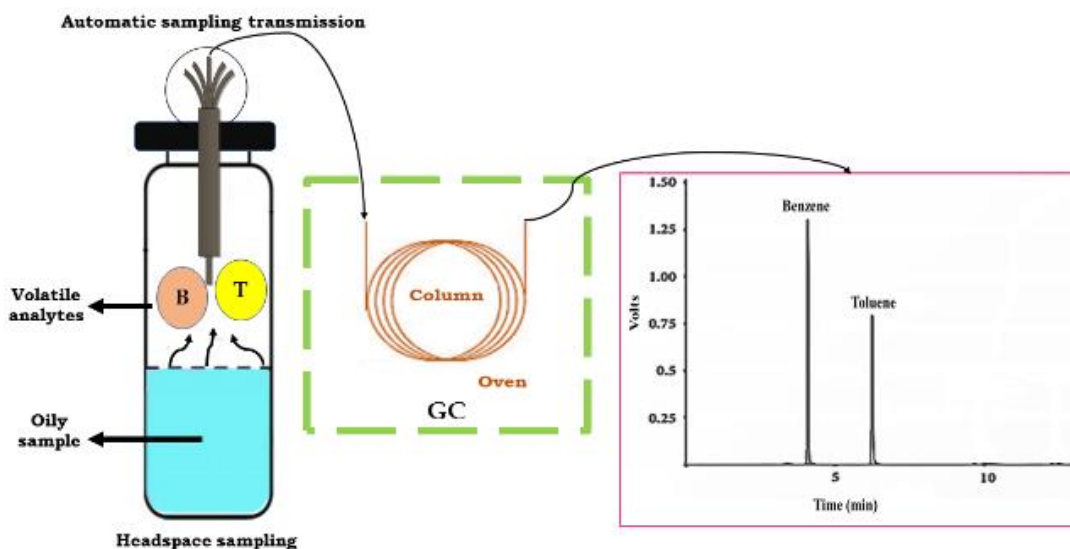
Figure 1. Automated sampling transfer and analysis by Gas Chromatography

Preparation of samples to confirm the test method

To decontaminate the materials, before use, all glassware was washed with acetone and then cleaned with ultrapure water. Then they were dried in the oven at 110 ℃ for 24 hours. Then it was placed in the oven at 400 ℃ for 1 hour. After that, to prevent moisture and dust, they were dried in a dryer for five hours before use and then stored in a protected state. A 1 ml of the sample was poured into the headspace vial and closed. This vial was placed inside the machine and analyzed 5 or 6 times. Device performance was monitored at times close to injection (approximately every 88 minutes). The area of peaks related to BT was recorded for each repetition and their concentration was calculated using the respective formulas. To establish a standard or require relevant data, a mixture of BT was made in a solvent without them (styrene). To achieve this, 1 ml of benzene and 1 ml of toluene were poured into a 10 ml flask and the volume was reached with solvent (styrene). The prepared mixture containing benzene and toluene each 10% by volume was obtained. A headspace vial was capped and 2 µl of internal standard mixture was added. During the standard sample analysis, the GC method and headspace were modified according to programs 1 and 2, respectively.

Program 1-GC:

Column Oven: 55 (hold 10 min) raise to 220 by 10 and then hold 30.50 (total time: 57 min).

Program 2- Headspace:

Temperature& Press: Oven=130, Valve=140, Tube=140-
Run Parameter: Run time=60 min, PC time=60 min, Single P0 = yes.

Samples are being prepared to verify the test technique

The smallest analytical concentration can be calculated with an acceptable degree of uncertainty using the limit of quantification (LOQ). The signal-to-noise ratio data for the standard injected into the chromatographic apparatus are output using the limit of detection (LOD) of a method, which is different from the instrument's smallest response (30). Several factors, including precision and accuracy, linearity, LOD and LOQ, method uncertainty, selectivity, and specificity; robustness; an international proficiency test between accredited laboratories; the use of chart control data; and the examination of t- and F-tests in terms of accuracy and precision, are tested to validate the method (31-34). Some of the key factors influencing the test method were looked into in this study. Each BT run and combination received five replicate samples each day for analysis. Over the course of three days, fifteen replicate samples for each BT run and combination were examined. For each of the three chosen concentrations, samples were prepared in the same manner each day. Previous studies have shown that the suggested method was used for the hot oil sample to perform reproducibility measurements (daily accuracy) and average accuracy (intraday accuracy) (35). To estimate the linearity of all values, a three-point external calibration curve with concentrations ranging from 0. 5 to 1.5 mg/kg was chosen. Also, three different days were used to determine repeatability (inter-day precision). On the chromatography output results, graphs and calculations were performed using Excel software.

RESULTS AND DISCUSSION

Preparation of device conditions and method

The extraction of BT from thermal oil becomes a difficult task that calls for techniques that can initially concentrate analytics because of its low solubility (36). To expedite and enhance performance, micro-extraction was used, and some extraction variables were looked into. The amount of extraction solvent (heat transfer oil, 1 ml), temperature, and extraction time were used to evaluate this method in the heat transfer oils standard. Since there is no documented method for measuring light compounds in thermal oil, the equilibrium time and temperature must be found experimentally and by trial and error. The main oil sample showed the presence of benzene and toluene in the initial Headspace tests, therefore, focusing on benzene, the temperature of 90 °C was chosen as the equilibrium temperature regarding boiling point of benzene to insure all of benzene remove to gas phase during equilibrium time. Then, one microliter of pure benzene was introduced into 3 sealed vials separately and the vials were heated in the oven of the headspace for 30, 60, and 90 minutes respectively. By comparing the peak area obtained from these three vials, the time of 60 minutes was determined to be more appropriate. One of the principles of MHE is to keep the extraction needle in the vial during extractions (37). There is a command in the headspace settings that should do this and is intended for this purpose. For this, Single Pen should be changed to Yes, which means one penetration during several injections. According to (Figure 2), the schematic shows the condition of the needle and vent required for MHE the time program for headspace shown in Table 1.

As can be seen from the injection program mentioned in Table 1, the time to pressurize the vial has increased from 10 seconds as default to 40 seconds to ensure complete vial pressurization. Also, before the needle exits the vial (time 1.11), the vent path is opened to empty the space inside the vial (above the liquid). In the case of multiple repetitions and the option Single Pen = Yes, the needle should not be removed from the vial, and in fact, the command related to time 1.40 should not be executed, but as mentioned, it is not clear whether this happens or not. Therefore, to reduce the risk of breaking or tilting the needle, the instruction to remove the needle is included in the program. In addition, when a program is executed several times, the needle must be removed from the vial at the last time, for which this order is necessary.
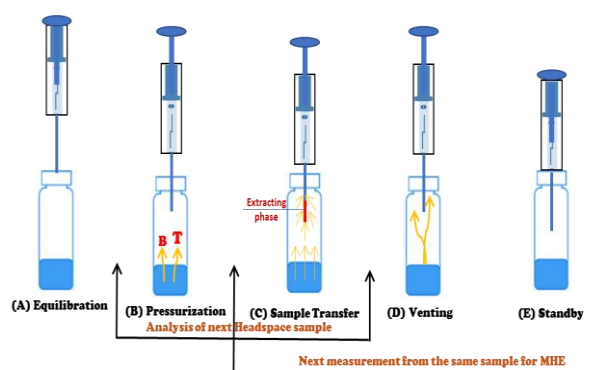

Figure 2. Schematic of needle and vent position for MHE

Analysis by MHE method

To start the test, first, 1 µl of benzene was injected into the vial for the standard, and it was extracted 3 times with holding time of 30 minutes. However, it was later determined that the time should be increased to 60 minutes. Some of the sample (1.4771 g) was extracted 3 times with a holding time of 90 minutes. The temperature of both was 90 degrees. It should be noted that the holding time for the MHE method and the working time of the Headspace device must be the same. That is, PC time=90min and Run time=90min should be set, while the method of GC device was also set in such a way that it ends a little before the Headspace operation time. For this purpose, the hold time for standard and sample injections in the GC method has been changed so that the total time is 28 and 88 minutes, respectively. The correlation of points (R^2) was less 0.99 for sample results and equilibrium time or temperature should be modified.

Also, during the above preliminary tests, it was determined that there is a large amount of toluene in the sample; it was decided to consider both peaks of benzene and toluene and determine their amount in thermal oil. To make a standard, 1 ml of BT was poured separately into a 10 flask and made up to volume with styrene. This mixture contains 10% volume/volume of benzene or toluene. As mentioned before in MHE, standard concentration is independence of sample and any other BT concentration could be used 2µl of the above standard was poured into the vial.

Then extracted at oven temperature 130 °C and holding times of 60 minutes. This temperature was chosen regarding toluene boiling point. The temperature of the oven for thermal oil increased to 160 °C. On the

Table 1. Time injection program schedule used for tests

No EVENT [0]	Press OFF [3]	Probe ON [5]	Press ON [6]	Press OFF [46]	Vent ON [47]	Vent OFF [57]	Start [58]
1 Valve On [59]	1 Valve Off [1.09]	Press On [1.10]	Vent ON [1.11]	Probe Off [1.40]	Vent Off [1.55]	Press Off [1.58]	

other hand, due to raising the temperature, the holding time was changed to 90 minutes so that a suitable number of repetitions can be performed in one shift. To make sure that 90 minutes is suitable, an almost equal amount of thermal oil (about 1 ml) was added to two separate vials and analyzed at a temperature of 160 °C and hold times of 90 and 120 minutes, and the peak areas of both were approximately equal and 90 minutes could be considered as final. In addition, if using the holding time of 120 minutes, according to the limitation of setting the performance time (Run time) in the headspace, the time of the GC method should be set to about 118 minutes.

A 1 ml of hot oil (1.487 g) was analyzed five times at a temperature of 160 °C and a run time of 90 minutes. Also, the valve and headspace line temperatures were 165 °C. Table 2 summarized the information of five repetitions of the above sample and standard. According to Table 2, the correlation coefficient of the points seems appropriate; it can be used to obtain the concentration of benzene/toluene in thermal oil. By referring to various references and applications, it was observed that apart from the original formula, some modified and optimized formulas were also used. A brief explanation of the formulas is given in the calculation section. Therefore, Table 3 stated the results on application number 5991-0974 approach, and without considering the first point for calculating the line and slope (38, 39). For the calculations used in Table 3, an Excel template has been prepared, which by entering the area of the sample and standard peaks, the concentration of the desired substance is calculated.

To compare the effect of the volume of oil used, 2 ml of the same oil was tested under previous conditions and repeated 5 times, the results of which are summarized in Table 4. Moreover, because the standards are the same, the data related to the standard are reported in Table 3 are used for calculations.

Focusing on benzene and comparing the results mentioned in Tables 3 and 4; it was observed that the results are very close to each other and the effect of

volume increase is somehow compensated by the increase in surface area.

Calculations
As mentioned earlier, the method is based on reducing the area of peaks in successive repetitions, which is logarithmic, and based on this, the general relationship is given by Equation 1. This implies that provided a constant is available, one extraction can yield the entire chromatographic area (40).

$$Ln\ A_i = -q(i-1) + \ln A_1 \qquad [1]$$

where q is the slope of the regression line of the points and can be defined as Equation 2.

$$Q = e^{-q} \qquad [2]$$

The constant was produced by the peak reduction's geometric progression from each extraction (41). Because it is assumed to follow a first-order reaction profile, the amount of analyte extracted by the BT is proportional to the initial amount in the sample and will decrease logarithmically with the number of extractions (42). Using Q and the peak area of the first iteration, the total peak area is calculated according to Equation 3.

$$\sum_{i=1}^{i\to\infty} Ai = \frac{A1}{1-Q} \qquad [3]$$

It is necessary to pay attention to the point that the first point usually has the highest error and the reason for this could be the difference of the extraction matrix compared to the subsequent extractions. For this reason, in some sources, amendments have been made to it. By examining different sources, the following three general methods have been observed:

Method 1: Use all the points that are used in the application 5965-0978. This method seems to be used when the regression line obtained from all points has a good correlation (43).

Method 2: Failure to consider the first point in calculating the regression line and using equation 4 to calculate the

Table 2. The results of the real and standard samples (correlation coefficients are calculated without considering the first point)

Run	PC time 90, Run time 90, Temp. 160				PC time 60, Run time 60, Temp. 130			
	Sample area (Benzene)	Ln area	Sample area (Toluene)	Ln area	Standard (Benzene) area	Ln area	Standard (Toluene) area	Ln area
1	93553	11.446	454618	13.027	757558	13.538	737808	13.511
2	84059	11.339	421316	12.951	480142	13.082	454375	13.027
3	75234	11.228	389686	12.873	361501	12.798	340841	12.739
4	67260	11.116	359666	12.792	272471	12.515	254147	12.446
5	57627	10.962	320686	12.678	200663	12.209	185058	12.128
	R^2	0.992	R^2	0.9905	R^2	0.999	R^2	0.999

Table 3. The results of MHE calculation for BT

	Slop	Intercept	Correlation (R^2)	Q	Total area	The ratio of the total area of the sample to the standard	Standard weight (mg)	Sample weight (mg)	Final concentration (ppm)
Benzene in oil	-0.1247	11.597	0.9928	0.88297	811832			0.00105	
Benzene in the standard mixture	-0.2901	13.6662	0.9996	0.78426	2664823	0.30465	0.176		51.1
Toluene in oil (Method 2)	-0.0899	13.1384	0.9905	0.91403	5355306			0.00105	
Toluene in the standard mixture (Method 2)	-0.2988	13.6309	0.9995	0.74169	2496825	2.14485	0.176		359.5

Table.4. Comparison of the effect of the volume of oil used

PC time 90, Run time 90, Temp. 160

Run	Sample area (Benzene)	Ln area (Benzene)	Sample area (Toluene)	Ln area (Toluene)
1	115666	11.658	529081	13.179
2	113150	11.636	530619	13.182
3	102593	11.539	495809	13.114
4	94983	11.461	474084	13.069
5	86840	11.372	446208	13.008
R^2	0.998	R^2	0.994	
Q	0.9166	Q	0.9451	
Total area (by 2nd Proc.)	1472125	Total area (by 2nd Proc.)	10195304	
Ratio of area	0.55243	Ratio of area	3.8258	
Sample amount (Kg)	0.00194	Sample amount (Kg)	0.00194	
Final concentration (mg/Kg)	**50.1**	Final concentration (mg/Kg)	**347.1**	

total area of the sample and standard according to the request of 5991-0974 (44).

$$\sum_{i=1}^{i \to \infty} Ai = A1 + \frac{A2}{1-Q} \qquad [4]$$

Method 3: Modifying the first point using the regression line equation and replacing the modified surface A* in the original relationship.

In the following, for the sake of simplification, only the results of benzene are considered, and the calculations for toluene are similar to the same. First, the levels' natural logarithm (ln) is obtained, and then the slope of the line and the width from the origin are obtained using

the number of analyzes and the calculated logarithms. There is some function in Excel, which could be used for that. RSQ function for R^2 slope for slope and EXP for Q calculation.

The R^2 factor, or the correlation coefficient of the used points, is not used in calculations, but it is necessary to control the suitability of the points on data stated in Table 2. The results are stated as follows for benzene in hot oil sample.

Slope=-0.12446, R^2 = 0.992793, Q=0.882972, and total area = 93553+ (84059/ (1-0.882972) = 811832.6

With the same method, the total area for benzene in the standard is also calculated. Using the above data and Equation 5, the weight of benzene in the oil sample can be calculated.

$$Wi = \frac{\sum Ai}{\sum Aex} . Wex \qquad [5]$$

where in W_i = weight of benzene in oil, W_{ex} = weight of benzene in the standard, $\sum A_i$= total area of benzene in the oil sample, and $\sum An_{ex}$ = total area of benzene in the standard. The calculated weight of benzene is as follows:

$$W_{Benzene} = \frac{\left[\frac{811832.6}{2664823}\right] \times 0.176}{0.00105} = 51.1 \, mg/Kg$$

Method validation

The validation analysis was carried out over the course of three days using the standards and sample repetitions as described. Based on prior research (45, 46), a LOD/LOQ calculation was made. According to the formula LOD= 3.3 (S_y/S), the standard deviation and the calibration curve's slope of the output curve from the calculation, respectively, were used to determine the LOD (31, 47-49). Additionally, the calibration curve's slope and the standard deviation of the output were used to calculate the LOQ, which was calculated using the formula: LOQ= 10(S_y/ S) (31, 47, 50, 51). Displays statistical calculations for each combination across various samples,

Table 5. Determination of LOD/LOQ of BT by headspace GC-FID analysis

Compound	Hot oil standard						
	Retention time(min)	Linear range (mg/kg)	Intercept	Slope	R^2	LOD (mg/kg)	LOQ (mg/kg)
Benzene	4.161± 0.01	0.50 to 1.50	-0.2567	0.5529	0.995	0.56	1.9
Toluene	6.374± 0.01	0.50 to 1.50	-0.0011	0.5243	0.999	0.05	0.17

with an RSD of less than 20%, these results also satisfy US EPA quality control requirements (52, 53). The presented method's recovery and precision were comparable to those described in the literature (35, 54). The proposed method and analytical performance characteristics are stated in Table 5. The LOD/LOQ were evaluated in standard water containing BT. In the studied range, all BT obtained coefficients of determination (R^2) greater than 0.995, which indicates linearity and satisfaction.

Comparison of the results reported here with those of other studies was carried out quantitatively and the main volatiles of BT from hot oil were identified. Analytical methods developed for volatile compounds in hot oil were quantitative and presented data as relative values, such as comparing levels of internal standards or total extracted volatiles (55, 56). Hence, the quantitative method reported here for volatile compounds in hot oil may fill a void and fulfill the need for a method for determining volatile compounds in hot oil in other classes and types of hot oil. The final method for the analysis of BT in hot oil was done for the first time, and perhaps this method can be used for other cyclic hydrocarbon pollutants in hot oil in the researchers' work, which needs further study and investigation, which will be determined in future research.

CONCLUSION

One of the most worrisome problems facing the petrochemical industry at present is the extraction of aromatic hydrocarbons from all refinery streams. The findings of this research on the oil sample containing cyclic hydrocarbons support the effectiveness of the new technique that we have developed to manage its conditions. It should be noted that we have developed a new method that enables us to accurately calculate component concentrations for mixtures containing at least two volatile hydrocarbons. It takes less than two hours. The new express control technique we have created has no counterparts anywhere in the world. For the first time, this paper develops a technique for the quantitative determination of BT volatile hydrocarbons based on the MHE method in liquid matrices of hot oil samples. Headspace has several benefits over traditional extraction methods and liquid-liquid and solid extraction techniques due to the risky nature of BT for sample preparation. The

hot oil sample can be easily measured and analyzed, among other things, without the need for a solvent. This is the first time in which a solvent-free extraction method that provides a reliable quantification for the analysis of hot oil has been developed. Additionally, regardless of species, this methodology enables the possibility to be used in all hot oil samples. On the other hand, to screen BT in hot oil tests and enable the determination of all analytics in various concentrations, a fundamental quantitative expository GC-FID strategy was developed and approved. The performance characteristic of BT, including LOD and LOQ, were deemed to have at best satisfactory performance characteristics.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT
Mohammad Reza Ghavidel: Formal analysis, Investigation, Writing - review & editing, Methodology, Data curation, Validation. **Mohammad Heydari:** Investigation, Writing - original draft, Methodology.

DECLARATION OF COMPETING INTEREST
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY
The datasets generated and/or analyzed during the current study are available from the corresponding authors on reasonable request.

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Persian Abstract

چکیده

در این مقاله غلظت برخی از ترکیبات آلی فرار (VOCs) در نمونه روغن داغ واحد اتیل بنزن پتروشیمی پارس ارائه شده است. پتروشیمی پارس یکی از
بزرگترین تولیدکنندگان اتیل بنزن در خاورمیانه است. ناخالصی‌های روغن داغ که مورد تجزیه و تحلیل قرار گرفتند، بنزن و تولوئن (BT) بودند. نمونه‌گیری از
روغن داغ در ماه می ۲۰۲۳ در یک ایستگاه نمونه‌برداری ویژه در سایت انجام شد. وجود BT به شدت آن در نمونه روغن داغ مربوط می‌شود. روش استخراج
چندگانه فضای سر (MHE) برای استخراج و تجزیه و تحلیل کمی BT به دنبال تکنیک‌های کروماتوگرافی گازی استفاده شد. برای تجزیه و تحلیل BT از
ابزار GC/FID استفاده شد. این روش مزایایی را برای تجزیه و تحلیل آلاینده‌های فرار ارائه می‌دهد زیرا استفاده از حلال‌های آلی و مراحل مختلف تصفیه نمونه
را که اغلب منجر به نتایج اشتباه می‌شود حذف می‌کند. روش MHE مستقل از غلظت استاندارد است و می‌تواند در طیف گسترده‌ای از BT در روغن داغ بدون
کالیبراسیون برای محدوده‌های مختلف استفاده شود. همچنین، خطی بودن، محدودیت‌های تشخیص و دقت به عنوان بخشی از فرآیند اعتبارسنجی مورد بررسی
قرار گرفت. LOD و LOQ به ترتیب بین ۵۶/۰− ۰۵/۰ و ۹/۱ − ۱۷/۰ mg/kg بود. کمتر از ۱۳/۹۵ درصد (۱۵=n) از نظر آماری انحراف معیار نسبی بود.
روشی سریع و آسان برای تشخیص BT در نمونه‌های روغن داغ برای اولین بار مورد استفاده قرار گرفت. این کار گامی رو به جلو برای تشخیص سایر
هیدروکربن‌های حلقوی در نمونه‌های روغن داغ خواهد بود.