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Abstract

Petroleum hydrocarbons are among the major environmental contaminants released into aquatic systems through petroleum refining operations, industrial activities and wastewater discharge processes. Accurate determination of these compounds requires efficient extraction procedures and reliable analytical techniques, as the extraction step greatly influences hydrocarbon recovery and analytical sensitivity. In the present study, the extraction performance of selected organic solvents, namely chloroform, *n*-hexane and carbon tetrachloride, was comparatively evaluated for petroleum hydrocarbon analysis in natural and industrial wastewater samples using gas chromatography-mass spectrometry (GC-MS). Natural and wastewater samples were collected from different locations associated with the Fergana Oil Refinery, Uzbekistan, including observation boreholes, wastewater discharge points, wastewater collection basins and treated wastewater outlets. Prior to extraction and chromatographic analysis, the physico-chemical properties of the collected samples were investigated to assess variations in water quality and contamination characteristics. GC-MS analysis enabled the successful identification of petroleum hydrocarbon compounds distributed across different molecular fractions. Comparative assessment of the extraction solvents demonstrated significant differences in extraction efficiency and chromatographic performance. Among the investigated solvents, chloroform exhibited superior extraction capability, providing broader chromatographic coverage and higher hydrocarbon recovery compared with *n*-hexane and carbon tetrachloride. Statistical analysis further confirmed significant variations among the extraction solvents ($p < 0.05$). The wastewater samples showed substantially higher petroleum hydrocarbon concentrations than groundwater samples, reflecting the greater impact of petroleum refining and wastewater discharge activities on industrial water systems. The developed analytical method demonstrated satisfactory analytical performance with acceptable precision, reproducibility and recovery characteristics. The findings indicate that optimization of extraction conditions significantly influences petroleum hydrocarbon determination and may contribute to improved environmental monitoring and contamination assessment of petroleum-affected water systems.Unlike previous laboratory-based solvent comparison studies, the present work evaluates extraction solvent performance using real groundwater and refinery wastewater matrices from the Fergana Oil Refinery, providing practical guidance for petroleum hydrocarbon monitoring under site-specific environmental conditions.

Keywords

Petroleum hydrocarbons; Gas chromatography-mass spectrometry; Extraction solvents; Wastewater analysis; Hydrocarbon profiling; Environmental monitoring

1. INTRODUCTION

Petroleum hydrocarbons are among the most widespread environmental contaminants released into aquatic systems through industrial activities, petroleum refining operations, accidental spills, transportation processes, and urban runoff. Rapid industrial development and increasing consumption of petroleum products have significantly increased the release of hydrocarbon contaminants into natural environments, particularly surface water and groundwater systems. Petroleum-derived compounds are characterized by their persistence and complex chemical composition, which may lead to long-term environmental contamination and ecological disturbances (Varjani and Upasani, 2017). The contamination of aquatic environments by petroleum products represents a significant environmental issue since these compounds can accumulate in sediments and living organisms, resulting in adverse impacts on ecosystem stability and human health (Abdel-Shafy and Mansour, 2016). Recent environmental monitoring studies have further demonstrated widespread petroleum hydrocarbon contamination in aquatic systems and highlighted its occurrence in surface waters, sediments, and aquatic organisms, emphasizing the need for continuous monitoring and risk assessment (Chokor et al., 2026; Wayar et al., 2026).

Petroleum products comprise highly complex mixtures containing aliphatic, aromatic, alicyclic, and polycyclic hydrocarbons with different physicochemical properties and environmental behaviours. Among these compounds, polycyclic aromatic hydrocarbons (PAHs) are of particular concern since several members of this group have demonstrated mutagenic, carcinogenic, and toxic properties (Speight, 2014; Chen et al., 2019). Petroleum contamination in water systems can alter several physicochemical characteristics, including taste, odor, turbidity, and dissolved oxygen concentration. Additionally, hydrocarbon films formed on water surfaces can interfere with gas exchange between the atmosphere and aquatic systems, consequently affecting biological activity and aquatic biodiversity (Nollet and De Gelder, 2019). Therefore, monitoring petroleum-derived contaminants in environmental waters has become increasingly important for environmental assessment and pollution control strategies.

The determination of petroleum hydrocarbons in environmental samples remains analytically challenging due to the complex nature of petroleum mixtures and the presence of matrix interferences. Environmental water samples commonly contain organic and inorganic constituents that may interfere with hydrocarbon analysis, particularly when contaminants are present at low concentrations. Consequently, accurate determination of petroleum products requires efficient analytical methods capable of separating and identifying target compounds with high sensitivity and selectivity (Khan et al., 2023). Analytical reliability is strongly influenced by sample preparation procedures because inefficient extraction may reduce analyte recovery and produce inaccurate quantitative results.

Various analytical methods have been developed for petroleum hydrocarbon determination in environmental samples, including gravimetric analysis, infrared spectroscopy, ultraviolet-visible spectrophotometry, fluorimetric methods, and chromatographic techniques (EPA Method 8015D, 2018). Gravimetric methods are commonly employed for highly contaminated samples; however, they often suffer from relatively poor sensitivity and limited selectivity. Spectroscopic methods provide rapid analysis but may be affected by matrix interferences and overlapping signals originating from different compounds. Among currently available analytical techniques, gas chromatography coupled with mass spectrometry (GC-MS) has become one of the most reliable and widely used methods because of its high sensitivity, selectivity, and capability to identify individual hydrocarbon compounds within complex environmental matrices (EPA Method 8270E, 2018; Castillo et al., 1999; Reddy and Quinn, 1999). GC-MS additionally enables characterization of hydrocarbon profiles over broad concentration ranges and provides detailed compositional information useful for pollution source identification and environmental monitoring studies (Skoog et al., 2018; Boczkaj et al., 2016; Chen et al., 2019).

Sample preparation remains one of the most critical stages in petroleum hydrocarbon analysis. Extraction procedures directly affect analyte recovery, selectivity, sensitivity, and analytical reproducibility. The selection of an appropriate extraction solvent is therefore essential because solvent characteristics such as polarity, volatility and hydrocarbon affinity influence extraction performance (Poole, 2020). Various organic solvents, including chloroform, hexane, carbon tetrachloride, petroleum ether, and other low-polarity solvents, have been widely employed for extracting petroleum compounds from aqueous matrices (Delgado et al., 2012; Saari et al., 2007). However, differences in solvent properties may substantially affect hydrocarbon recovery and extraction efficiency, and comparative studies have shown substantial variability

in hydrocarbon extraction performance depending on solvent characteristics and matrix composition (Saari et al., 2007; Esmaeili and Saremnia, 2018). Recent studies have emphasized improving extraction performance while simultaneously considering environmental sustainability and analytical reliability (Płotka-Wasylka et al., 2021).

Although various organic solvents have previously been evaluated for petroleum hydrocarbon extraction, most comparative studies have been conducted using simplified laboratory matrices or specific contaminated soils, while relatively few investigations have assessed solvent performance in complex refinery-affected groundwater and industrial wastewater under actual environmental conditions. The Fergana Oil Refinery represents one of the major petroleum-processing facilities in Central Asia, where petroleum-related contamination of groundwater and wastewater requires reliable analytical approaches for environmental monitoring. In this study, the novelty lies not in the comparison of extraction solvents alone, but in the integrated evaluation of chloroform, *n*-hexane, and carbon tetrachloride for petroleum hydrocarbon recovery from real refinery-associated groundwater and wastewater samples collected from different operational locations within the Fergana refinery system. The study further combines comparative extraction efficiency with GC-MS-based hydrocarbon profiling to evaluate solvent performance under environmentally relevant matrix conditions. The findings provide practical information for selecting suitable extraction procedures for petroleum hydrocarbon monitoring in refinery-impacted aquatic environments.

2. MATERIALS AND METHODS

2.1 Materials

Analytical-grade chloroform ($CHCl_3$, ≥99.8%), *n*-hexane (C_6H_{14}, ≥99%), carbon tetrachloride (CCl_4, ≥99.5%), hydrochloric acid (HCl, 37%), sulfuric acid (H_2SO_4, 98%), activated carbon, and aluminum oxide (Al_2O_3) were used throughout the study. Standard hydrocarbon compounds including *n*-octane (C_8H_{18}), *n*-decane ($C_{10}H_{22}$), eicosane ($C_{20}H_{42}$) and tetracontane ($C_{40}H_{82}$) with purity ≥95% were obtained from certified reference standards (LGC Labor GmbH, Germany). Ultrapure water (18.2 MΩ·cm) was used for solution preparation and cleaning procedures.

2.2 Sample Collection and Preservation

Natural and wastewater samples were collected from different locations associated with the Fergana Oil Refinery, Fergana, Uzbekistan, including observation boreholes, wastewater discharge points, wastewater collection basins, and treated wastewater outlets. The sampling strategy was designed to represent different environmental compartments influenced by refinery activities, including groundwater, untreated industrial wastewater, wastewater collection systems, and treated wastewater prior to discharge. Three independent samples (n = 3) were collected from each sampling location to ensure analytical reproducibility and to account for variability among environmental matrices. The selected sampling locations represented areas with varying levels of potential petroleum hydrocarbon contamination associated with refinery operations and wastewater handling processes. Potential contamination pathways in the study area include petroleum refining operations, wastewater transport and storage systems, industrial discharge activities, and infiltration of petroleum-derived contaminants into the surrounding groundwater.

The samples were collected in pre-cleaned amber glass bottles (1 L capacity) according to standard water sampling procedures. Immediately after collection, samples were preserved by acidification using concentrated sulfuric acid until the pH reached approximately 2.0 to minimize hydrocarbon degradation during storage. Samples were transported to the laboratory under refrigerated conditions (4 ± 1 °C) and analyzed within 24 h. Prior to extraction procedures, pH, total hardness, and mineral content were measured using standard water quality analytical methods (O‘z O‘U 0791:2019; USEPA Method 3510B).

2.3 Extraction Procedure

Petroleum hydrocarbons were extracted using three selected organic solvents: chloroform, *n*-hexane, and carbon tetrachloride. Carbon tetrachloride was included solely for comparative evaluation because it has historically been employed as an extraction solvent for petroleum hydrocarbon analysis in environmental studies and standard analytical methods. Its inclusion enabled comparison of extraction performance with chloroform and *n*-hexane under identical experimental conditions. However, because of its well-documented toxicity, environmental hazards, and regulatory restrictions in many countries, carbon tetrachloride was evaluated only for comparative analytical purposes and should not be considered a

recommended solvent for routine environmental monitoring. A 500 mL aliquot of each water sample was transferred into a separating funnel and adjusted to pH 2-3 using hydrochloric acid (37%). Subsequently, 50 mL of the extraction solvent was added, and the mixture was agitated using a magnetic stirrer at 300 rpm for 10 min to facilitate the transfer of petroleum hydrocarbons into the organic phase. After phase separation for approximately 15 min, the organic layer was collected. A second extraction step was performed by adding an additional 20 mL of the same solvent to the remaining aqueous phase to improve extraction efficiency. Both organic extracts were combined and purified through a column packed with activated aluminum oxide to remove residual moisture and polar impurities. The purified extracts were collected in pre-weighed glass vials and stored at 4 °C prior to GC-MS analysis (USEPA Method 3510B, 1994; Poole, 2020; O'z O'U 0791:2019).

2.4 Gas Chromatography-Mass Spectrometry Analysis

Hydrocarbon identification was performed using a gas chromatograph coupled with a mass spectrometer (GC-MS system) (EPA Method 8270E, 2018; Skoog et al., 2018; NIST Mass Spectral Library). Chromatographic separation was conducted using a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 □m). Helium was used as the carrier gas at a constant flow rate of 1.0 mL min^{-1}. The injection volume was 1 □L in split mode (split ratio 10:1). The injector temperature was maintained at 280 ºC. The GC oven temperature was initially maintained at 50 ºC for 2 min, then programmed to increase at a rate of 10 ºC min^{-1} up to 200 ºC, followed by a slower increase of 5 ºC min^{-1} to 300 ºC, where it was finally held for 10 min to ensure complete elution of hydrocarbon components. Mass spectrometric detection was performed using electron ionization mode at 70 eV with a scan range of *m/z* 40-550. Compound identification was performed by comparing the acquired mass spectra with the NIST Mass Spectral Library together with chromatographic retention behaviour. Hydrocarbon standards (*n*-octane, *n*-decane, *n*-eicosane, and *n*-tetracontane) were used to confirm the retention times of the corresponding calibrated compounds. Other petroleum hydrocarbons, including aromatic compounds, were identified based on mass spectral similarity and retention behaviour and are therefore reported as tentatively identified compounds.

2.5 Calibration and Quantitative Determination

Instrument calibration was performed using certified hydrocarbon standards consisting of *n*-octane, *n*-decane, *n*-eicosane, and *n*-tetracontane. Calibration curves were generated using five concentration levels ranging from 0.05-50 mg L^{-1} by plotting chromatographic peak area against analyte concentration using linear regression analysis (EPA Method 8270E, 2018; ISO/IEC 17025:2017; Skoog et al., 2018). Quantitative determination was limited to petroleum hydrocarbon fractions represented by these calibration standards. Aromatic hydrocarbons, including toluene, ethylbenzene, naphthalene, and phenanthrene, were identified qualitatively based on their retention times and mass spectral matching with the NIST Mass Spectral Library and were not individually quantified using external calibration standards.

Analytical performance was evaluated in terms of calibration linearity, recovery, and precision following USEPA Method 8270E and ISO/IEC 17025 guidelines. Recovery experiments were conducted using fortified water samples prior to extraction, while analytical precision was assessed from triplicate analyses and expressed as relative standard deviation (RSD). The objective of the present study was to comparatively evaluate the extraction performance of selected organic solvents under identical analytical conditions rather than to develop and validate a new standardized analytical method. Therefore, the analytical evaluation focused on calibration performance, recovery, and precision to ensure reliable comparison of extraction efficiencies among the investigated solvents.

2.6 Statistical Analysis

All experiments were conducted in triplicate and results are presented as mean ± standard deviation (SD). Statistical analysis was performed using one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison test at a significance level of $p < 0.05$ to evaluate differences among extraction solvents.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characteristics of Water Samples

The physico-chemical properties of water samples collected from locations associated with the Fergana Oil Refinery were investigated prior to extraction and chromatographic analysis. Parameters including pH, total hardness and total mineral content were evaluated because these characteristics may

influence hydrocarbon behaviour, extraction efficiency and analytical response during sample preparation and GC-MS analysis. The measured values for the investigated samples are summarized in Table-1.

The pH values of the collected water samples ranged from 6.98 to 8.12, indicating that the investigated waters varied from slightly acidic to weakly alkaline conditions. Observation boreholes exhibited pH values within commonly accepted environmental ranges, while wastewater samples collected from industrial discharge points showed relatively higher mineral content and hardness values. The wastewater collection basin and wastewater discharge point exhibited elevated total hardness values of approximately 29.20-29.60 mg-eq·dm^{-3} and mineral contents ranging between 4.28-4.62 g·dm^{-3}, which were substantially higher than those observed for groundwater samples.

The increased mineral concentrations in industrial wastewater samples may be associated with petroleum refining activities and the discharge of dissolved inorganic constituents into surrounding water systems. Similar observations have been reported in petroleum refinery wastewater systems where elevated dissolved solids and mineral content were associated with industrial activities (Esmaeili and Saremnia, 2018). High concentrations of dissolved salts and suspended materials can influence the partitioning behaviour of hydrocarbons during liquid-liquid extraction processes. Increased ionic strength may alter hydrocarbon solubility and affect interactions between analytes and extraction solvents, potentially influencing extraction recovery (Nollet and De Gelder, 2019).

In contrast, groundwater samples obtained from observation boreholes demonstrated lower mineral content (0.62-0.78 g dm^{-3}) and reduced hardness values compared with wastewater samples. These characteristics suggest relatively lower anthropogenic influence and reduced contamination levels. Variations in water composition among sampling sites indicate that matrix complexity differs substantially across the investigated samples and may affect extraction behaviour during petroleum hydrocarbon analysis.

The observed differences among sampling locations further justify the necessity of evaluating extraction solvents under actual environmental conditions rather than under simplified laboratory systems. Environmental matrices containing varying concentrations of dissolved ions and organic constituents can influence extraction selectivity and chromatographic response. Therefore, understanding the initial physicochemical characteristics of the water samples provides important information for interpreting extraction performance and hydrocarbon distribution behaviour during subsequent analytical procedures.

Table 1: Physicochemical characteristics of water samples collected from the Fergana Oil Refinery area.

Sampling location	Sample type	pH	Total hardness (mg·eq dm^{-3})	Mineral content (g·dm^{-3})
Observation well No. 121	Groundwater	6.98 ± 0.03	6.40 ± 0.21	0.62 ± 0.02
Observation well No. 014	Groundwater	7.12 ± 0.04	7.10 ± 0.18	0.78 ± 0.03
Wastewater treatment outlet	Treated wastewater	7.54 ± 0.05	12.50 ± 0.27	2.46 ± 0.05
Wastewater discharge point	Industrial wastewater	7.88 ± 0.02	29.20 ± 0.34	4.28 ± 0.08
Wastewater collection basin	Industrial wastewater	8.12 ± 0.04	29.60 ± 0.29	4.62 ± 0.06

Values are expressed as mean ± SD (n = 3)

3.2 Solvent Quality Assessment and Chromatographic Characteristics

The purity of extraction solvents represents an important factor affecting the reliability and accuracy of petroleum hydrocarbon determination because impurities present in extraction media may generate interfering peaks during chromatographic analysis. Prior to extraction experiments, chromatographic analyses of the selected organic solvents were performed to evaluate solvent quality and identify possible background interference. Representative chromatograms of chloroform, *n*-hexane and carbon tetrachloride are shown in Figure 1(a-c).

The obtained chromatographic profiles demonstrated differences in baseline characteristics and background signal distributions among the investigated solvents. The chromatogram of chloroform (**Figure 1a**) exhibited a relatively stable baseline with fewer secondary peaks and low background noise, indicating minimal chromatographic interference. Similarly, carbon tetrachloride (**Figure 1c**) showed a simple

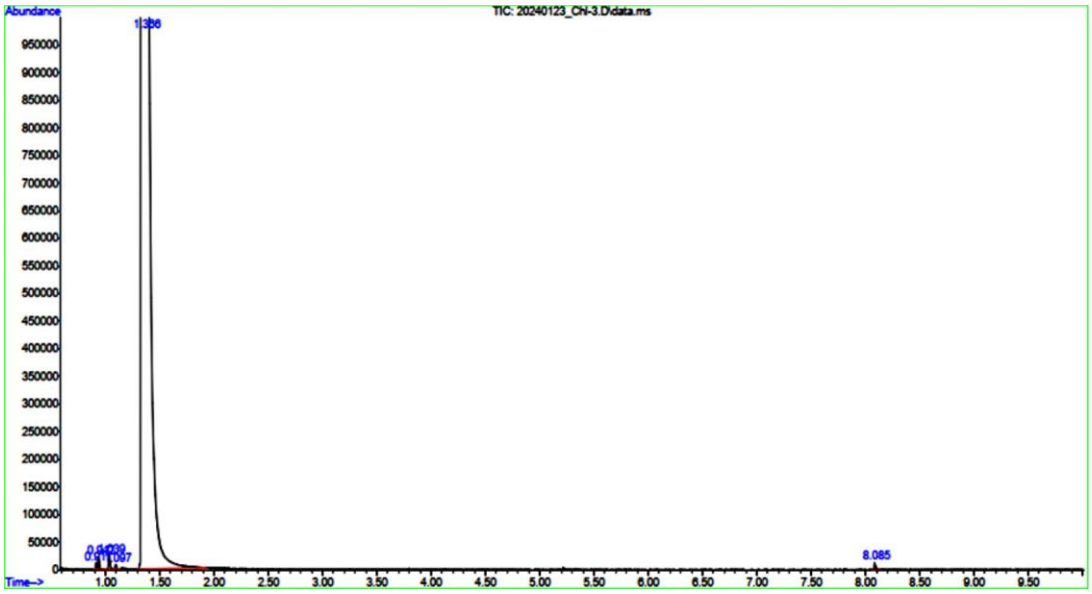
chromatographic pattern with limited background contributions and comparatively fewer minor peaks. In contrast, the chromatogram of *n*-hexane (**Figure 1b**) displayed additional low-intensity peaks at different retention times, suggesting the presence of trace impurities that may arise from manufacturing processes, storage conditions, or residual contaminants.

The observed differences in chromatographic profiles indicate that solvent composition may influence analytical sensitivity and hydrocarbon detection. Impurities present in extraction solvents can interfere with qualitative and quantitative analyses, particularly when target compounds occur at relatively low concentrations. Background peaks generated by solvent contaminants may overlap with hydrocarbon signals, resulting in inaccurate compound identification and reduced analytical precision. Similar observations have been reported in previous studies where solvent purity significantly affected chromatographic sensitivity and reproducibility during hydrocarbon analysis (Poole, 2020).

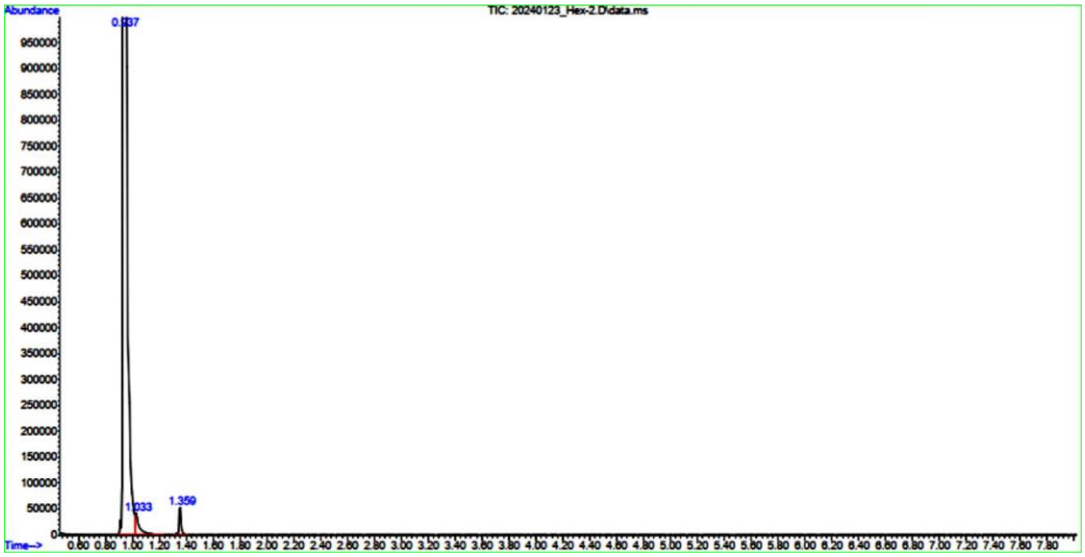
To minimize analytical interference, purification procedures were applied before extraction experiments. Selected solvents were treated using activated aluminum oxide and activated carbon to remove residual contaminants and polar impurities. Following purification, chromatographic analysis indicated improved baseline stability and reduced background interference. The purification process enhanced chromatographic reliability and improved the quality of subsequent petroleum hydrocarbon analysis.

Differences in solvent purity may also affect extraction performance because contaminants present within the extraction medium can alter solvent-analyte interactions and compete with target compounds during extraction processes. Therefore, preliminary evaluation of solvent quality represents an essential step in ensuring reliable analytical performance. The obtained findings indicate that chromatographic assessment of extraction solvents before sample analysis contributes to reducing analytical uncertainty and provides confidence that chromatographic signals detected in environmental samples primarily originate from petroleum derived compounds rather than solvent-related artifacts.

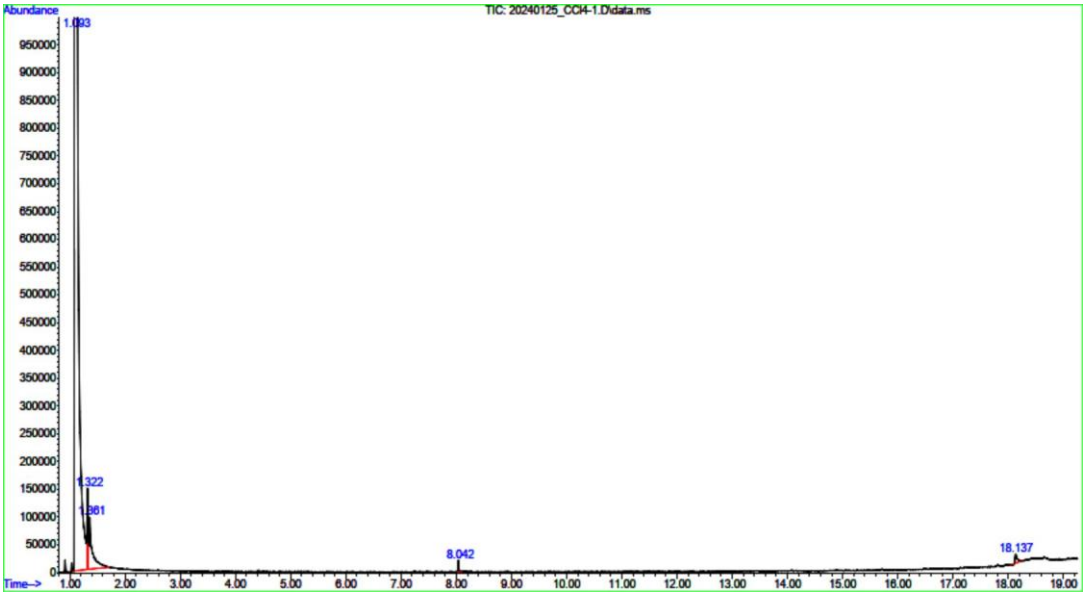
Fig. 1: GC chromatograms of selected extraction solvents: (a) chloroform, (b) *n*-hexane, and (c) carbon tetrachloride used for petroleum hydrocarbon extraction



(a)



(b)



(c)

3.3 GC-MS Analysis of Standard Hydrocarbon Compounds

To evaluate analytical reliability and assess instrument performance, chromatographic analyses of certified hydrocarbon standards were conducted prior to environmental sample analysis. Standard compounds including *n*-octane (C_8H_{18}), *n*-decane ($C_{10}H_{22}$) ($C_{10}H_{22}$), *n*-eicosane ($C_{20}H_{42}$) and *n*-tetracontane ($C_{40}H_{82}$) were selected since they represent hydrocarbon fractions commonly present in petroleum-derived products with different molecular weights and physicochemical properties. Representative chromatograms of the analyzed standards are presented in **Figure 2(a-d)**.

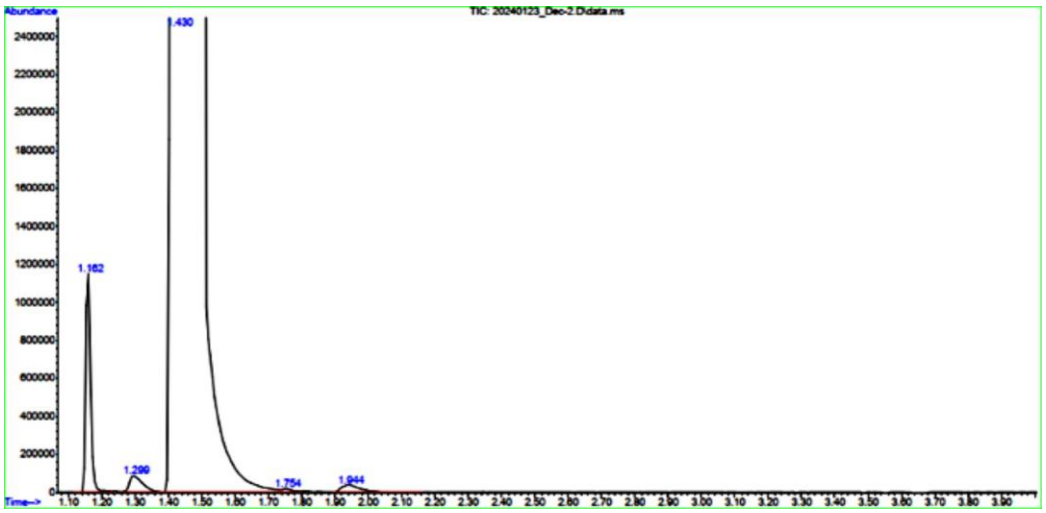
The chromatographic profiles of the investigated standards demonstrated well-defined and symmetrical peaks, indicating satisfactory chromatographic separation and stable instrumental performance. Distinct differences in retention behaviour were observed among the investigated compounds. Lower molecular weight hydrocarbons, such as n-octane (**Figure 2a**) and *n*-decane (**Figure 2b**), exhibited shorter retention times due to their higher volatility and lower boiling points. In contrast, heavier hydrocarbon compounds such as *n*-eicosane (**Figure 2c**) and *n*-tetracontane (**Figure 2d**) showed longer retention times because of stronger interactions with the stationary phase of the chromatographic column and reduced volatility.

The chromatographic results further demonstrated a progressive increase in retention time with increasing molecular weight, confirming expected chromatographic behaviour for hydrocarbon compounds analyzed using GC-MS. Similar retention characteristics have been reported in previous studies involving petroleum hydrocarbon profiling, where hydrocarbon separation primarily depends on molecular structure and boiling point distribution (EPA Method 8270E, 2018).

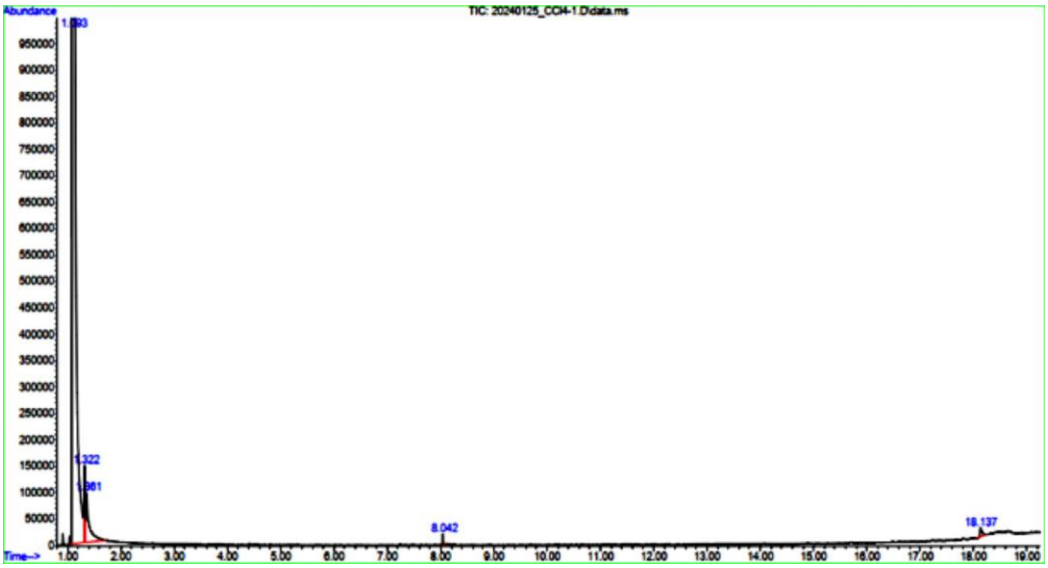
The generated calibration curves demonstrated satisfactory linear relationships between analyte concentration and chromatographic peak area over the investigated concentration range (0.05-50 mg L^{-1}). Linear regression analysis yielded coefficients of determination (R^2) greater than 0.99 for all calibration standards, indicating excellent linearity and confirming the suitability of the GC-MS system for quantitative petroleum hydrocarbon determination within the investigated concentration range. The high linearity values demonstrate a stable and reproducible instrumental response, while the analytical performance was further supported by acceptable recovery (85-105%) and precision (RSD < 5%) obtained during method evaluation. These results indicate that the developed analytical procedure is suitable for the comparative assessment of extraction solvent performance and petroleum hydrocarbon determination in refinery-associated groundwater and wastewater samples.

The use of standard compounds covering a broad molecular range improved the reliability of hydrocarbon characterization because petroleum products generally consist of mixtures containing compounds with different molecular structures and boiling characteristics. Furthermore, retention time matching and comparison of mass spectral fragmentation patterns with NIST library data facilitated reliable identification of hydrocarbons in environmental samples. The chromatographic behaviour of the investigated standards confirms that the developed GC-MS method provided adequate sensitivity, reproducibility and analytical performance for petroleum hydrocarbon profiling and quantitative determination in the environmental water samples.

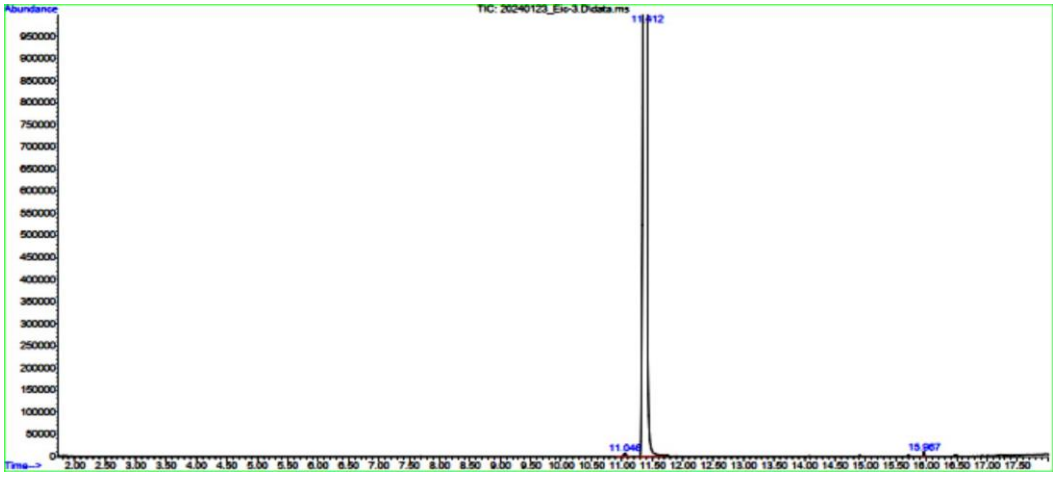
Fig. 2: GC chromatograms of hydrocarbon standards used for calibration and analytical validation: (a) *n*-octane, (b) *n*-decane, (c) *n*-eicosane and (d) *n*-tetracontane.



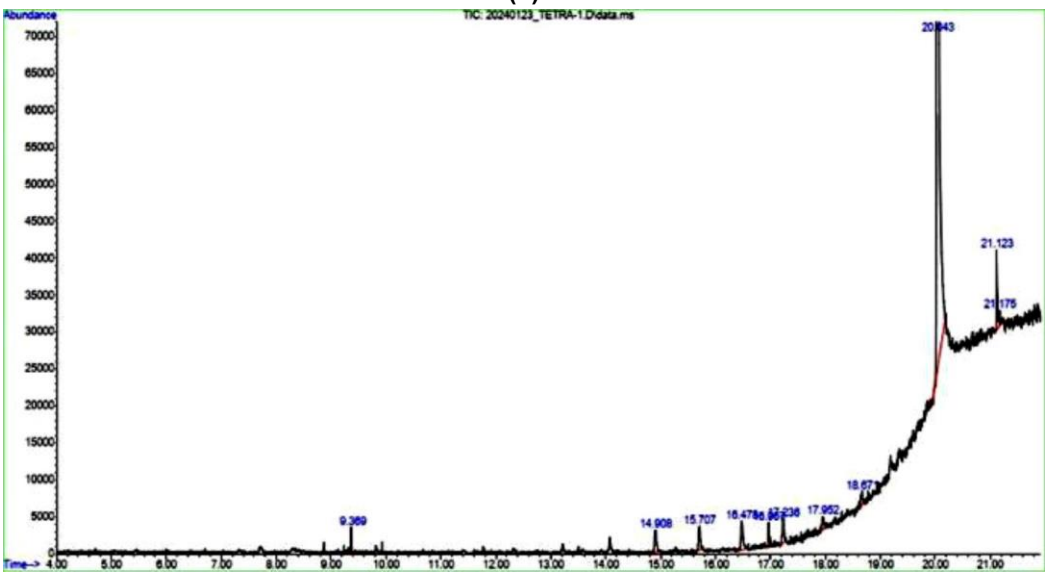
(a)



(b)



(c)



(d)

3.4 Comparative Evaluation of Solvent Extraction Performance

The extraction efficiency of petroleum hydrocarbons is strongly influenced by the physicochemical properties of extraction solvents because solvent polarity and molecular interactions determine the partitioning behaviour of hydrocarbons between aqueous and organic phases. To evaluate extraction performance, three selected organic solvents, namely chloroform, *n*-hexane and carbon tetrachloride, were applied for petroleum hydrocarbon extraction from collected water samples. Comparative extraction results obtained using selected solvents are summarized in Table-2

The results demonstrated noticeable differences among the extraction solvents in terms of hydrocarbon recovery and chromatographic response. Chloroform consistently produced higher extraction values than the other investigated solvents across most sampling locations. In wastewater samples collected from industrial discharge points and wastewater basins, petroleum hydrocarbon concentrations extracted using chloroform reached 14.80 and 15.20 mg/dm^3, respectively, whereas extraction with *n*-hexane produced values of 12.54 and 14.60 mg/dm^3 and carbon tetrachloride yielded comparatively lower values of 8.80 and 8.50 mg/dm^3.

Groundwater samples from observation boreholes also exhibited similar trends. For observation well No. 121, the measured hydrocarbon concentrations were 0.68 mg/dm^3 for chloroform extraction, 0.52 mg/dm^3 for *n*-hexane extraction and 0.38 mg/dm^3 for carbon tetrachloride extraction. Similar extraction behaviour was observed for observation well No. 014 and treated wastewater samples. These findings indicate that the extraction capability of the investigated solvents varied considerably depending on the solvent characteristics and sample matrix composition.

The superior extraction behaviour observed for chloroform may be attributed to its intermediate polarity and stronger interaction with a wider range of hydrocarbon compounds. Petroleum products generally contain hydrocarbons with varying chemical characteristics, including aliphatic, aromatic, and cyclic structures. Solvents with suitable polarity characteristics may improve solubility and facilitate more effective transfer of hydrocarbon compounds from the aqueous phase into the organic phase. Previous studies have reported that solvent polarity significantly influences extraction recovery and selectivity during hydrocarbon determination in environmental samples (Poole, 2020).

The higher extraction efficiency of chloroform compared with carbon tetrachloride may also be associated with differences in analyte-solvent interactions and partition coefficients. Although carbon tetrachloride has historically been used in hydrocarbon analysis because of its non-polar nature, lower extraction performance observed in this study suggests reduced effectiveness for recovering hydrocarbons from complex environmental matrices. In contrast, n-hexane showed intermediate performance, which may be attributed to its strong affinity for non-polar compounds while demonstrating reduced efficiency toward relatively complex hydrocarbon mixtures.

Furthermore, wastewater samples exhibited significantly higher petroleum hydrocarbon concentrations than groundwater samples, indicating stronger contamination associated with petroleum refining activities. The elevated hydrocarbon concentrations observed in wastewater collection basins and industrial discharge points suggest continuous anthropogenic contributions from refining operations. Similar observations have been reported in environmental monitoring studies where industrial wastewater exhibited substantially greater hydrocarbon contamination than groundwater systems (Abdel-Shafy and Mansour, 2016).

Although chloroform demonstrated comparatively higher extraction performance, the use of chlorinated solvents, including chloroform and carbon tetrachloride, requires careful consideration due to their potential health hazards and environmental impacts. In particular, carbon tetrachloride is subject to strict regulatory restrictions owing to its toxicity and ozone-depleting properties. Therefore, its inclusion in the present study was intended only for comparative analytical evaluation and should not be interpreted as a recommendation for routine analytical applications. Selection of extraction solvents should balance analytical efficiency with laboratory safety, environmental sustainability, and current regulatory requirements. Future studies should explore safer and greener extraction solvents that provide comparable analytical performance while minimizing environmental and occupational risks. The present investigation extends previous solvent comparison studies by demonstrating extraction performance under actual refinery-affected environmental conditions rather than controlled laboratory systems. The observed differences among groundwater, treated wastewater, and industrial wastewater matrices indicate that sample composition substantially influences extraction behaviour, emphasizing the importance of validating analytical procedures using representative environmental samples.

Table 2: Comparative extraction performance of selected organic solvents for petroleum hydrocarbon determination in environmental water samples

Sampling location	Chloroform (mg dm^{-3})	*n*-Hexane (mg·eq dm^{-3})	Carbon tetrachloride (mg dm^{-3})
Observation well No. 121	0.68 ± 0.03	0.52 ± 0.02	0.38 ± 0.01
Observation well No. 014	0.84 ± 0.04	0.65 ± 0.03	0.49 ± 0.02

Wastewater treatment outlet	5.42 ± 0.17	4.63 ± 0.15	3.21 ± 0.11
Wastewater discharge point	14.80 ± 0.43	12.54 ± 0.39	8.80 ± 0.27
Wastewater collection basin	15.20 ± 0.48	14.60 ± 0.42	8.50 ± 0.23

Values are expressed as mean ± SD (n = 3)

3.5 Hydrocarbon Identification and Chromatographic Profile Analysis

The chromatographic profiles obtained after GC-MS analysis revealed the presence of complex mixtures of petroleum-derived compounds in both natural and wastewater samples. Hydrocarbon identification was performed through comparison of retention times and mass spectral fragmentation patterns with the NIST Mass Spectral Library database. Representative chromatograms of environmental samples extracted using selected organic solvents are presented in **Figure 3(a-c)**, while the identified compounds and their corresponding retention characteristics are summarized in **Table-3**.

The obtained chromatograms exhibited multiple peaks distributed across broad retention time regions, indicating the occurrence of hydrocarbon compounds with varying molecular structures and physicochemical properties. Differences in chromatographic behaviour among detected compounds may be attributed to variations in molecular weight, boiling characteristics and interactions with the stationary phase of the chromatographic column. Lower molecular weight compounds generally appeared at shorter retention times due to their relatively higher volatility, whereas heavier hydrocarbon fractions demonstrated longer retention times because of stronger interactions with the stationary phase and reduced volatility.

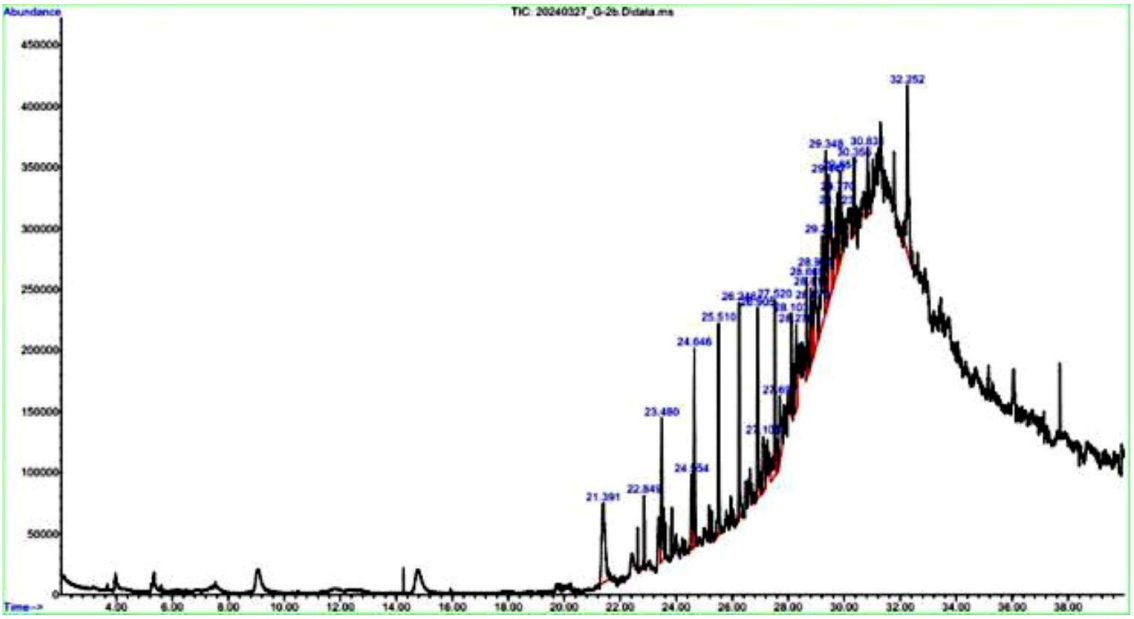
The chromatographic profiles also demonstrated noticeable differences among investigated environmental samples. Wastewater samples collected from industrial discharge locations showed greater peak abundance and signal intensity compared with groundwater samples collected from observation wells. The larger number of peaks observed in wastewater samples indicates greater hydrocarbon diversity and higher contamination levels associated with petroleum refining activities. Moreover, wastewater discharge samples exhibited relatively broad chromatographic regions containing multiple overlapping peaks, suggesting the presence of mixed hydrocarbon fractions originating from industrial processes.

Differences in chromatographic peak distributions were also observed among extraction solvents. Samples extracted using chloroform (**Figure 3c**) exhibited a greater number of resolved peaks and higher signal intensities compared with samples extracted using n-hexane and carbon tetrachloride (**Figure 3a-b**). The broader chromatographic coverage observed for chloroform suggests improved extraction of hydrocarbons possessing different physicochemical characteristics. In contrast, carbon tetrachloride extracts demonstrated comparatively fewer detectable peaks, indicating lower extraction capability toward certain hydrocarbon fractions under the investigated experimental conditions.

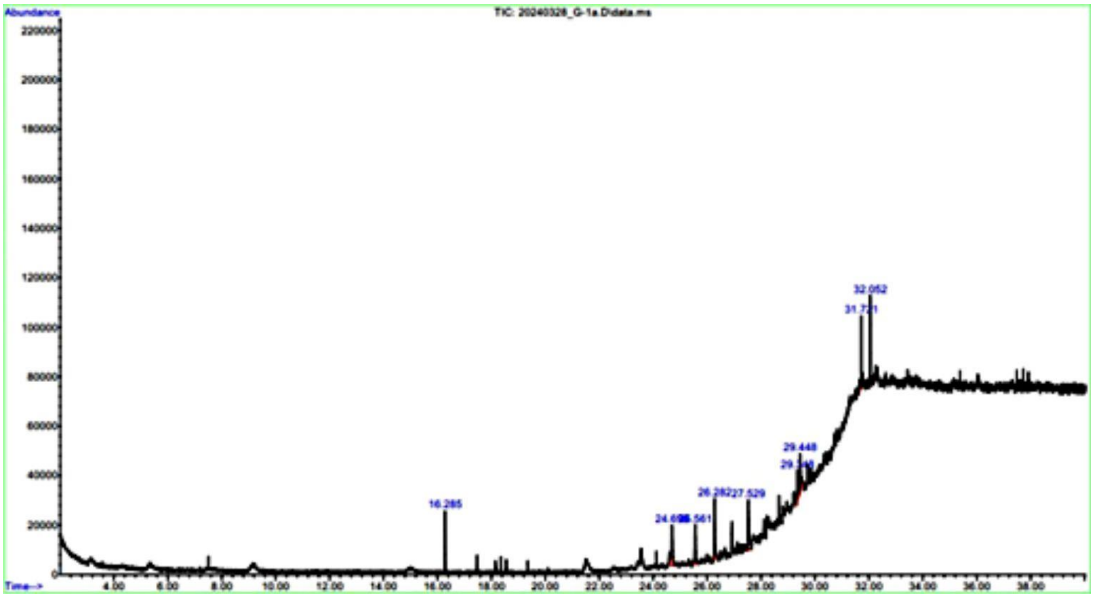
The detected chromatographic profiles suggest that petroleum contamination within the investigated water systems consists of chemically diverse hydrocarbon mixtures rather than isolated compounds. Characterization of these chromatographic patterns provides valuable information regarding contaminant distribution and potential pollution sources. Furthermore, evaluation of hydrocarbon profiles contributes to a better understanding of extraction behaviour and supports the subsequent quantitative determination of petroleum hydrocarbons in environmental samples.

The compounds listed in Table 3 represent qualitative identification based on GC-MS analysis and comparison with the NIST Mass Spectral Library. Their presence was confirmed by characteristic mass spectra and retention behaviour; however, individual quantitative concentrations were not determined because certified calibration standards for these compounds were not included in the present study.

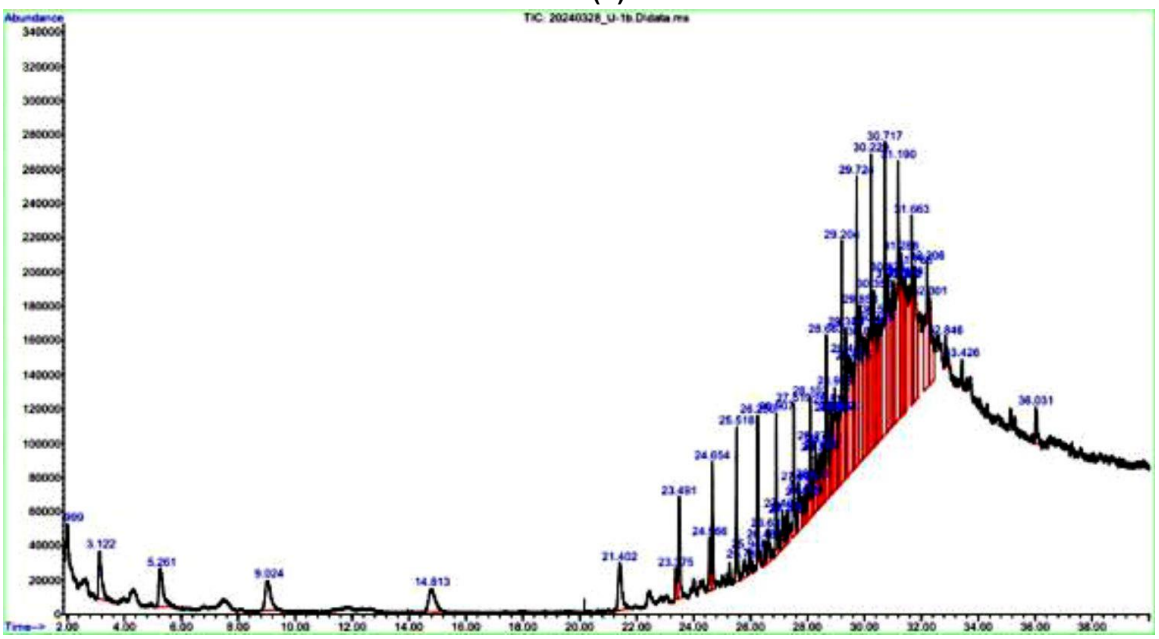
Fig. 3: Representative GC-MS chromatograms of environmental samples extracted using selected solvents: (a) sample extracted using n-hexane, (b) sample extracted using carbon tetrachloride, and (c) wastewater sample extracted using chloroform from the factory discharge point.


Abundance
TIC: 20240327_G-2b.D\data.ms
Time-->
32.252
29.348
30.833
24.046
25.510
23.480
21.391
22.849

(a)


Abundance
TIC: 20240328_G-1a.D\data.ms
Time-->
32.052
31.721
29.448
16.285
26.282
27.529

(b)


Abundance
TIC: 20240328_U-1b.D\data.ms
Time-->
30.717
30.221
29.720
29.204
25.518
24.054
23.491
3.122
5.261
9.024
14.813
21.402
36.031

(c)

Table 3: Petroleum hydrocarbons detected by GC-MS. Compounds calibrated with certified reference standards are reported as confirmed, whereas the remaining compounds were tentatively identified by comparison with the NIST Mass Spectral Library and chromatographic retention behaviour.

Compound	Molecular formula	Molecular weight (g mol^{-1})	Retention time (min)	Hydrocarbon class
n-Octane	C_8H_{18}	114.23	4.92	Aliphatic hydrocarbon
n-Decane	$C_{10}H_{22}$	142.29	6.74	Aliphatic hydrocarbon
n-Dodecane	$C_{12}H_{26}$	170.34	10.43	Aliphatic hydrocarbon
n-Tetradecane	$C_{14}H_{30}$	198.39	14.28	Aliphatic hydrocarbon
n-Hexadecane	$C_{16}H_{34}$	226.44	18.73	Aliphatic hydrocarbon
n-Eicosane	$C_{20}H_{42}$	282.55	24.91	Long-chain hydrocarbon
Toluene	C_7H_8	92.14	3.82	Aromatic hydrocarbon
Ethylbenzene	C_8H_{10}	106.17	5.21	Aromatic hydrocarbon
Naphthalene	$C_{10}H_8$	128.17	12.47	Polycyclic aromatic hydrocarbon
Phenanthrene	$C_{14}H_{10}$	178.23	21.38	Polycyclic aromatic hydrocarbon

Compound identification was based on comparison with the NIST Mass Spectral Library and chromatographic retention behaviour. Confirmation using certified reference standards was available only for the calibrated hydrocarbon standards included in this study.

3.6 Quantitative Determination of Petroleum Hydrocarbons

Quantitative determination of petroleum hydrocarbons in environmental samples was performed using calibration curves generated from certified hydrocarbon standards analyzed under identical GC-MS conditions. The reported quantitative values therefore represent petroleum hydrocarbon concentrations determined using the calibrated hydrocarbon standards, whereas aromatic hydrocarbons identified by GC-MS were used for qualitative compositional profiling only and were not individually quantified. Quantification was based on chromatographic peak area measurements, and hydrocarbon concentrations were calculated using the corresponding calibration equations. The measured concentrations of petroleum hydrocarbons in the investigated water samples are summarized in **Table 4.** The analytical results demonstrated considerable differences in petroleum hydrocarbon concentrations among the investigated sampling locations. Wastewater samples collected from petroleum refining and discharge areas exhibited substantially higher hydrocarbon concentrations than groundwater samples from observation boreholes. The highest concentrations were observed in wastewater collection basins and industrial discharge locations, while relatively lower concentrations were detected in groundwater systems.

The observed concentration differences indicate that petroleum refining activities represent an important source of hydrocarbon contamination within the investigated area. Wastewater generated during industrial processing generally contains residual oils, petroleum fractions, and other hydrocarbon-derived compounds that can accumulate within surrounding environmental systems. In contrast, groundwater samples are expected to experience lower direct anthropogenic influence because of natural filtration processes occurring during subsurface transport. Similar trends have been reported in environmental investigations where industrial wastewater exhibited greater hydrocarbon contamination levels compared with groundwater systems (Abdel-Shafy and Mansour, 2016). The quantitative results also demonstrated that extraction solvent selection substantially influenced the measured hydrocarbon concentrations. Chloroform extraction consistently generated higher concentration values compared with *n*-hexane and carbon tetrachloride extraction. The higher quantitative responses observed for chloroform suggest more efficient transfer of hydrocarbon compounds from the aqueous phase into the extraction medium. Enhanced extraction efficiency may be attributed to improved solvent-analyte interactions and broader extraction capability toward hydrocarbon compounds with different molecular characteristics.

Method validation results indicated acceptable analytical performance for the developed extraction and GC-MS procedure. Calibration curves demonstrated excellent linearity across the investigated concentration range with coefficient of determination (R^2) values greater than 0.99. Recovery studies performed using spiked water samples produced recovery percentages ranging from approximately 85-105%, indicating satisfactory analytical accuracy and extraction reproducibility. Relative standard deviation (RSD) values below 5% further confirmed good precision of the analytical procedure.

The developed GC-MS method demonstrated satisfactory analytical performance based on linear calibration, acceptable recovery (85-105%), and good precision, with RSD values below 5%. These validation parameters indicate that the method is suitable for comparative evaluation of extraction solvent performance and petroleum hydrocarbon determination in the investigated environmental water samples.

Comparison of the measured concentrations with environmental water quality standards suggests that several wastewater samples exceeded recommended hydrocarbon concentration limits. Elevated concentrations in industrial discharge locations indicate potential contamination risks and highlight the necessity for continuous monitoring and appropriate treatment procedures before wastewater discharge into surrounding environments.

The measured petroleum hydrocarbon concentrations were substantially higher in untreated refinery wastewater and wastewater collection basins than in groundwater samples, indicating a greater degree of contamination associated with petroleum refining activities. Although the present study did not perform a formal regulatory compliance assessment using country-specific discharge standards, the elevated hydrocarbon concentrations observed in industrial wastewater highlight the need for continuous environmental monitoring and effective wastewater treatment to minimize the release of petroleum-derived contaminants into surrounding aquatic environments. These findings are consistent with previous studies reporting increased petroleum hydrocarbon contamination in refinery wastewater and its potential environmental impacts

The obtained quantitative findings demonstrate that the developed analytical procedure provides reliable determination of petroleum hydrocarbons in environmental water samples and supports the application of GC-MS for environmental contamination assessment. Furthermore, the results indicate that extraction conditions play a significant role in quantitative performance and should be carefully optimized to ensure accurate environmental monitoring.

The primary objective of the present study was to compare extraction solvent performance under identical analytical conditions rather than to establish a new standardized analytical method. Therefore, emphasis was placed on comparative extraction efficiency, analytical precision, and recovery of petroleum hydrocarbons from refinery-associated environmental samples.

Table 4: Quantitative determination of petroleum hydrocarbons in environmental water samples using GC-MS analysis

Sampling location	Petroleum hydrocarbon concentration (mg dm^{-3})	Recovery (%)	RSD (%)
Observation well No. 121	0.68 ± 0.03	89.5 ± 1.8	3.4
Observation well No. 014	0.84 ± 0.04	91.2 ± 2.1	3.8
Wastewater treatment outlet	5.42 ± 0.17	93.4 ± 2.3	3.1
Wastewater discharge point	14.80 ± 0.43	96.8 ± 2.5	2.9
Wastewater collection basin	15.20 ± 0.48	97.3 ± 2.7	3.2

3.7 Extraction Efficiency Analysis

Statistical analysis was performed to determine whether the observed differences in petroleum hydrocarbon extraction among chloroform, *n*-hexane, and carbon tetrachloride were statistically significant. All extraction experiments were conducted in triplicate, and the results are expressed as mean ± standard deviation (SD). One-way analysis of variance (ANOVA) followed by Tukey's post hoc test was employed at a significance level of $p < 0.05$ to compare extraction efficiencies among the investigated solvents. The statistical results are summarized in **Table 5.**

Table 5: Statistical evaluation of extraction performance of selected organic solvents for petroleum hydrocarbon determination

Extraction solvent	Recovery (%)	RSD (%)	Extraction efficiency (%)	*p*-value
Chloroform	96.8 ± 2.5	2.9	95.2 ± 2.4	<0.05
n-Hexane	87.5 ± 2.3	3.8	84.7 ± 2.6	<0.05
Carbon tetrachloride	78.3 ± 2.7	4.5	76.4 ± 2.9	<0.05

Values are expressed as mean ± SD (n = 3). Statistical analysis was performed using one-way ANOVA followed by Tukey's post hoc test at a significance level of $p < 0.05$.

The obtained statistical analysis indicated significant differences among the extraction solvents ($p < 0.05$), confirming that the choice of solvent significantly affected petroleum hydrocarbon recovery from environmental water samples. Chloroform demonstrated the highest average extraction efficiency among the investigated solvents, followed by *n*-hexane and carbon tetrachloride. The mean extraction efficiencies were observed to range between approximately 92-98% for chloroform, 80-89% for *n*-hexane, and 70-82% for carbon tetrachloride. The relatively low standard deviation values obtained for all investigated solvents indicate satisfactory analytical reproducibility and consistency of the extraction procedure. Relative standard deviation (RSD) values below 5% further confirm good precision of the developed analytical method. Low variability among replicate measurements suggests that the analytical procedure was sufficiently stable and reproducible under the selected experimental conditions. The higher extraction efficiency observed for chloroform may be associated with favourable solvent-analyte interactions and its ability to dissolve a broader range of petroleum-derived compounds. Petroleum hydrocarbons consist of chemically diverse fractions containing compounds with different molecular weights and polarities. Therefore, solvents possessing suitable physicochemical characteristics may facilitate improved partitioning of hydrocarbons from aqueous matrices into the organic phase. Similar observations have been reported in liquid-liquid extraction studies where solvent properties significantly affected extraction performance and hydrocarbon recovery (Poole, 2020). The recovery study conducted using spiked water samples further demonstrated acceptable analytical performance. Recovery percentages for standard hydrocarbon compounds ranged between 85-105%, indicating that the developed analytical procedure provided satisfactory accuracy and minimal analyte loss during extraction and purification procedures. The recovery values obtained in this study fall within commonly accepted analytical criteria for environmental monitoring methods and indicate reliable analytical performance. Additionally, matrix effects appeared to influence extraction behaviour among environmental samples. Wastewater samples containing elevated dissolved solids and organic constituents exhibited slightly larger variations in recovery compared with groundwater samples. The increased complexity of wastewater matrices may alter analyte partitioning behaviour and influence extraction efficiency. Nevertheless, the observed variability remained within acceptable analytical limits. The statistical findings provide quantitative support for the differences observed among extraction solvents and strengthen the interpretation of chromatographic results. Unlike qualitative observations alone, statistical analysis confirms that the superior performance of chloroform was not associated with random variation but reflected significant differences in extraction behaviour. However, despite demonstrating higher analytical performance, the use of chlorinated solvents should also be evaluated considering environmental sustainability and laboratory safety aspects. Thus, the statistical evaluation confirms that extraction efficiency is strongly dependent on solvent selection and that optimization of extraction procedures plays an important role in improving analytical reliability for petroleum hydrocarbon determination in environmental samples.

4 CONCLUSIONS

The present study comparatively evaluated the performance of chloroform, *n*-hexane, and carbon tetrachloride for the extraction and GC-MS determination of petroleum hydrocarbons in groundwater and refinery wastewater samples collected from the Fergana Oil Refinery region, Uzbekistan. The novelty of this work lies in the comparative evaluation of extraction solvent performance using real refinery-affected groundwater and wastewater matrices collected from different operational locations, combined with GC-MS-based hydrocarbon profiling under actual environmental conditions. This approach provides practical analytical information for petroleum hydrocarbon monitoring in refinery-impacted aquatic environments. Significant differences in extraction efficiency and chromatographic performance were observed among the

investigated solvents. Chloroform demonstrated superior extraction capability, providing broader chromatographic coverage, higher hydrocarbon recovery, and improved analytical sensitivity compared with the other solvents. GC-MS analysis successfully identified petroleum-derived hydrocarbons distributed across different molecular fractions in both natural and industrial wastewater samples. Wastewater samples collected from refinery discharge points and collection basins exhibited substantially higher hydrocarbon concentrations than groundwater samples, indicating the strong influence of petroleum refining activities on environmental water quality. The analytical procedure demonstrated satisfactory linearity, recovery, and precision for the comparative evaluation of extraction solvents. These validation parameters support the use of the method for comparing solvent extraction performance in refinery-associated groundwater and wastewater samples under identical experimental conditions. Statistical analysis further confirmed significant differences among the extraction solvents ($p < 0.05$), highlighting the importance of optimizing extraction conditions for reliable hydrocarbon determination in complex environmental matrices. The obtained results demonstrate that solvent selection plays a critical role in petroleum hydrocarbon analysis and that GC-MS combined with optimized extraction procedures provides an effective approach for monitoring petroleum contamination in aquatic systems. Although chloroform exhibited the highest extraction efficiency under the investigated conditions, its application should be considered alongside environmental and occupational safety aspects. Therefore, future studies should focus on developing environmentally sustainable extraction strategies that maintain analytical performance while improving laboratory safety and green analytical applicability.

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