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Detection of Polycyclic Aromatic Hydrocarbons in Water and Beverages Using Membrane-Assisted Solvent Extraction Coupled with Large Volume Injection GC-MS

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Abstract

The present investigation aimed to enhance the identification of polycyclic aromatic hydrocarbons in water and beverages by employing large-volume injection (LVI) in conjunction with membrane-assisted solvent extraction for gas chromatography-mass spectrometry analyses. High-purity solvents and isotope-labeled standards were used to calibrate and create polycyclic aromatic hydrocarbon (PAH) standards. Water samples from polluted rivers in India and commercially available beverages were collected and preserved under controlled conditions. Microwave-assisted solvent extraction (MASE) was optimized by adjusting temperature and pH for efficient extraction. The extracts were analyzed using gas chromatography-mass spectrometry (GC-MS) with a large-volume injection system for sensitive PAH detection. MASE-LVI-GC-MS efficiently determined 16 PAHs in aqueous samples by optimizing extraction parameters like shaking speed, temperature, and solvent composition. Recovery percentages were above 65 %, and a relative standard deviation of 6 % guaranteed repeatability to 18 % during five consecutive extractions. It was shown that great sensitivity was achieved by reaching detection limits within the range of nanograms per litre. In conclusion, membrane-assisted solvent extraction combined with large-volume injection and GC-MS efficiently detects PAHs in various water and beverage samples, achieving nanogram-per-liter sensitivity. It offers uniform extraction, rapid analysis, and reduced solvent use across diverse matrices.

Keywords: Gas chromatography-mass spectrometry (GC-MS); Isotope-labelled standards; Large volume injection (LVI); Membrane-assisted solvent extraction (MASE); Polycyclic aromatic hydrocarbons (PAHs); Relative standard deviation (RSD).

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are pollutants that may be produced when carbonaceous materials are not entirely consumed or when they undergo pyrolysis at elevated temperatures [1-5]. PAHs stand out as a significant group of persistent organic pollutants commonly encountered in the environment. Most - (PAHs) detected in environmental settings

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originate from incomplete combustion processes involving petroleum-derived products, oil spills, and various industrial activities, as expected. Certain substances, particularly those that are less dense, can dissolve in water. Consequently, these substances may also be present in rivers and underground water sources. PAHs primarily enter the human body by inhalation of airborne particles and ingestion of food products, with drinking water also contributing to a lesser extent. PAHs are dangerous, although only a certain group of these chemicals have been demonstrated to have cancer-causing and mutation-causing features [6-10].

According to the WHO, one of the top 10 risks to human health is indoor air pollution caused by -(PAHs), which are released when solid fuels like coal and biomass (which includes wood, animal dung, and crops) are burned [11]. This kind of pollution has been associated with more than 1.5 million deaths prematurely globally due to pneumonia, chronic asthma, and cancer of the lungs throughout the 2000s. The examination of PAHs has great importance, and their surveillance is crucial for improving health and environmental protection [12-16]. The European Union suggested analyzing the content of 15 additional polycyclic aromatic hydrocarbon molecules, which have been designated as priority chemicals in food items. The European water framework directive (WFD) 2008/105/EC governs the occurrence of many PAHs by establishing regulations aimed at mitigating contamination of surface water [17].

This compilation identifies a group of priority substances posing substantial risks to aquatic ecosystems. Liquid samples containing PAHs are commonly assessed using traditional techniques like solid-phase extraction coupled and liquid-liquid extraction with chromatography [18-23]. Nonetheless, these methods necessitate considerable organic solvent usage. Alternatively, solvent-free techniques like solid-phase microextraction [24] and stir-bar sorptive extraction are viable alternatives [25-31]. Another effective method for reducing solvent consumption is membrane extraction [32-34].

This technique utilizes a membrane to segregate the specimen (donor) from the chemical solvent (acceptor), hence avoiding their mixture. The primary advantages are the use of a minimum amount of solvent, cost-effectiveness, the possibility to remove matrix components, and the lack of emulsion formation, which is a major problem in classical liquid-liquid extraction. The article discusses the integration of membrane-assisted extraction of solvent (MASE) with large-volume injection (LVI). The first exposition of this methodology was presented by Hauser and Popp [35]. Substances of organic origin within a liquid sample can traverse a solid barrier impervious to water and access an organic liquid phase. The effectiveness of this method has been shown with a variety of compounds, such as Flame retardants, organophosphorus insecticides, chlorobenzenes, triazines, and polychlorinated biphenyls (PCBs) [36-43]. This study focused on enhancing the efficiency of membrane-assisted extraction with solvents to precisely quantify the concentrations of the 16 EPA PAHs in beverages and water.

2. Materials and Methods

2.1. *Materials and reagents*

High-purity solvents (≥ 99.5 %), including heptane, dichloromethane, methanol, and others,

were used throughout the experiments. A 1:1 acetone-benzene mixture was also employed. All reagents, including a 2000 mg/L 16-PAH standard mixture (Sigma-Aldrich, USA), were used for calibration. Isotope-labeled standards (fluorene-d10, chrysene-d12, anthracene-d10) were sourced from Thermo Fisher. The PAH mixture was diluted to 100 mg/L with acetone, and labelled isotopes were prepared in ethanol (1000 mg/L), with final dilutions to 1 mg/L in methanol and ethyl acetate.

2.2. *Samples*

Samples of water were systematically obtained from the river's surface in India, particularly in an area adjacent to operational industrial sites recognized for their role in environmental pollution. The sampling process was meticulously scheduled to obtain representative samples of probable contaminants from industrial runoff. To maintain sample integrity and avert damage from light exposure, the water samples were promptly stored at 4 °C in amber bottles, specifically intended to protect sensitive chemical components from photodegradation. In addition to the water samples, a variety of commercially available beverages, including apple juice, red wine, and different types of milk-skim milk (0.3 % fat), semi-skimmed milk (1.5 % fat), and whole milk (3.5 % fat) were obtained from a local retail establishment. The beverages were stored under identical conditions at 4 °C in a dark location to prevent any changes in their chemical composition or quality before analysis. This regulated storage technique was utilized to maintain the physicochemical characteristics of the water and beverage samples to facilitate subsequent experimental assessment.

2.3. *Microwave-assisted solvent extraction (MASE)*

Samples of water contaminated with pollutants were introduced into 15 mL headspace vials as part of the Microwave-Assisted Solvent Extraction (MASE) procedure utilizing the ETHOS X system (Milestone Srl, Sorisole, Italy). Polypropylene membrane bags (4 cm in length, 6 mm internal diameter, 0.03 mm wall thickness) were hung within the vials and sealed using Teflon rings. To mitigate any memory effects, the membrane bags were conditioned overnight, followed by triple extraction with ethyl acetate to recycle the bags and avert contamination. Samples were agitated at 50 °C with a shaking speed of 700 rpm for 60 min, as established during preliminary testing to optimize analyte recovery. The solvent-to-sample ratio was meticulously tuned to augment recovery efficiency, with methanol used to promote solubility. Critical parameters including temperature, pH, agitation speed, and salting-out effects were methodically assessed to optimize the extraction process. After extraction, organic extracts were injected into the gas chromatograph utilizing a 1000 µL syringe without additional processing, and extraction yields were evaluated by injecting equimolar quantities of analytes into 400 µL of organic solvent through large-volume injection (LVI).

2.4. *Gas chromatography-mass spectrometry with large-volume injection*

The analysis utilized a modular MPS 2 sample system (Gerstel, Germany) in conjunction with an Agilent HP 6890 Series Gas Chromatograph (Agilent Technologies, USA), which was equipped with an HP 5973 mass-selective detector. A capillary HP5-MS column (30 m × 0.25 mm, 0.25 μm film thickness) was employed, utilizing helium as the carrier gas at a flow rate of 1.0 mL/min. The gas chromatography oven temperature was initially set to 50°C with a 2-minute hold, thereafter, increasing to 290 °C at a rate of 10 °C/min, followed by a final 5-min hold. The mass-selective detector functioned in electron impact ionization mode at 70 eV, utilizing full-scan mode throughout a mass range of 35 to 410 m/z, while quantification was performed through single ion monitoring, concentrating on selected highlighted ions, with supplementary ions employed for validation. An extensive injection system combined with MPS 2 employed 1000 μL syringes, improving sensitivity and detection thresholds, which were determined at ng/L levels according to signal-to-noise ratios. The injection system included temperature programmability, head pressure venting control, and a cooled injection system liner to preserve optimal analytical conditions, hence providing reliable and reproducible findings for the target analytes.

3. Results and Discussion

3.1. *Optimization of MASE*

In the optimization of microwave-assisted solvent extraction (MASE), various factors influencing the efficacy of the extraction procedure were examined, including solvent selection, solvent quantity, extraction duration, and the composition of the acceptor and donor solution. Following MASE, extraction efficiencies were evaluated by comparing GC responses obtained from injecting 100 μL of the solutions derived from MASE with those from conventional methods.

3.1.1. *Assessment of extraction solvent*

Recent investigations reveal that the extraction efficiency of PAHs differs considerably among solvents. The current findings demonstrate that cyclohexane attains exceptionally high normalized response percentages (85 % to 100 %) for both lighter and heavier PAHs (Fig. 1), including naphthalene and benzo[a]pyrene, corroborating the results published by Khan *et al.* in contaminated soils [44]. Conversely, Boateng *et al.* highlighted the inadequacy of hexane in precisely quantifying hazardous compounds, specifically indicating that hexane demonstrates markedly reduced extraction efficiencies (20 % to 40 %) for heavier PAHs, including dibenzo [a,h]anthracene [45]. Tao *et al*. [46] acknowledged the essential importance of method validation in guaranteeing precise PAH analyses. The choice of a suitable extraction solvent is crucial for environmental monitoring and public health evaluations, as ineffective extraction techniques may lead to the underreporting of PAH concentrations [46].

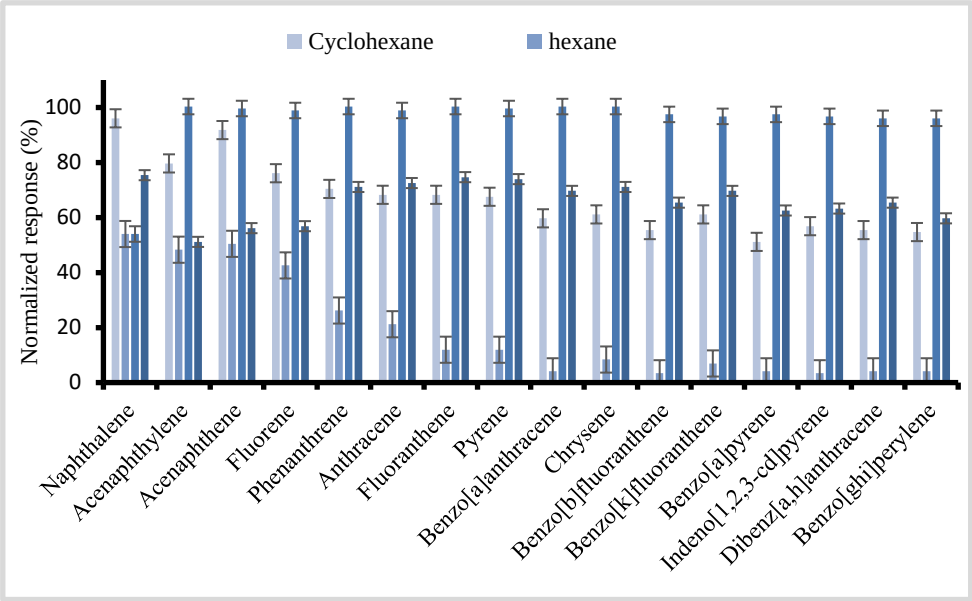

Fig. 1. Analyzing different solvents as recipients in MASE, normalization against the most effective extraction solvents for every analyte (n = 3).

3.1.2. *Analysing the constituents of the contributor resolution*

The salting-out effect was evaluated by including sodium chloride at different concentrations (0 % to 30 %) into a 5 g/L solution of target analytes, agitated for one hour at 45 °C and 750 rpm; however, no notable enhancement in extraction efficiency was detected, as demonstrated in Fig. 2a-c. This conclusion contradicts earlier research by Eskandari *et al.* revealed increased extraction yields utilizing the salting-out effect in the analysis of PAHs [47]. The results of the present investigation demonstrate that pH modifications utilizing 10 % (w/v) NaOH and 6 % HCl are generally recognized to improve extraction efficiency. Sun *et al*. [48] did not produce significant advantages, indicating intricate interactions within beverage matrices. Bian *et al*. [49] examined the efficacy of liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) methods to remove PAHs, specifically highlighting that methanol enhanced chemical enrichment by diminishing glass adsorption of PAHs.

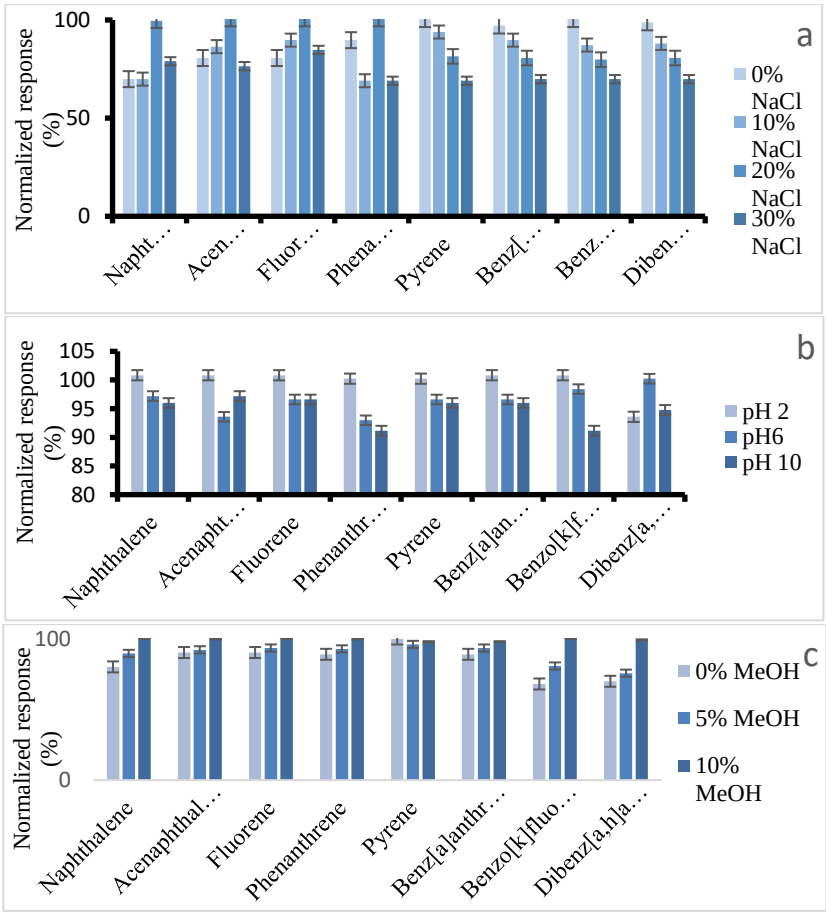

Fig. 2. Extraction impact of donor composition: extraction of acenaphthene, benzo[a]anthracene, phenanthrene, pyrene, fluorene, dibenz[a, h]anthracene, naphthalene, benzo[k]fluoranthene (n = 3) was influenced by the salt content (a), pH variations (b), and methanol addition (c).

3.1.3. *Extraction conditions: Shaking speed, temperature, and time*

The identification and examination of PAHs in water and drinks are significantly enhanced by the utilization of sophisticated methodologies, including MASE paired with large-volume injection gas chromatography-mass spectrometry (LVI-GC-MS) (Fig. 3a). Liu *et al.* [50] assessed that augmenting shaking speed during MASE markedly enhances extraction efficiency. Furthermore, the essential operational parameter of shaking speed has been corroborated by Bose *et al.* [51] observed the influence of diverse settings on PAH recovery. Ramírez *et al.* [52] emphasize the significance of sophisticated extraction techniques in enhancing PAH monitoring in aquatic environments, highlighting its implications for environmental monitoring.

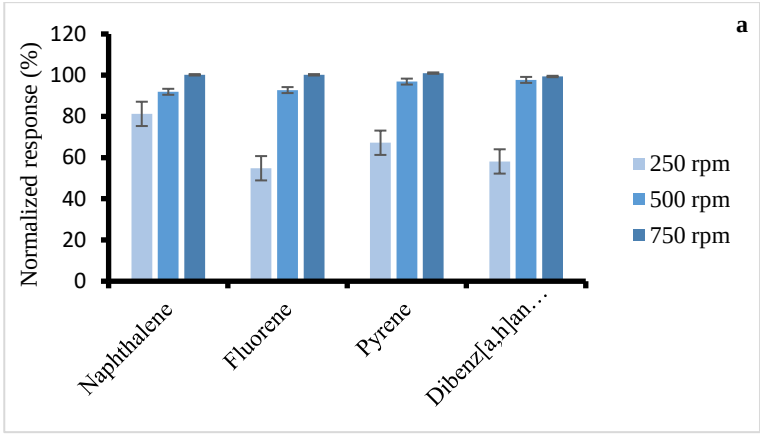

Fig. 3(a). Extraction parameters for the compounds dibenzo, pyrene, fluorene, and naphthalene[a, h] anthracene: Shaking rate.

The evaluation of the impact of temperature on the extraction efficiency of PAHs reveals that increasing the temperature from 40 °C to 60 °C significantly enhances extraction yields for various compounds, including naphthalene, fluorene, pyrene, and dibenzo[a,h]anthracene (Fig. 3b). The results demonstrate that naphthalene, fluorene, and pyrene achieved peak extraction efficiencies of 90 % at 60 °C, consistent with findings from Putra *et al*. [53] highlighted that higher temperatures improve the solubility of PAHs in solvents, leading to a nearly 30% increase in extraction yield when the temperature was raised from 30 °C to 50 °C. Additionally, Shang *et al.* [54] showed that microwave-assisted extraction (MAE) significantly improved extraction efficiencies, with yields exceeding 95 % for naphthalene and fluorene at 60 °C, indicating the importance of thermal energy in disrupting matrix interactions and enhancing volatility. Furton *et al*. [55] supported this by demonstrating that supercritical fluid extraction (SFE) of PAHs achieved optimal yields at elevated temperatures, reporting extraction efficiencies of 85 % for dibenzo[a,h]anthracene at 60 °C, aligning with our nearly 100 % efficiency for the same compound.

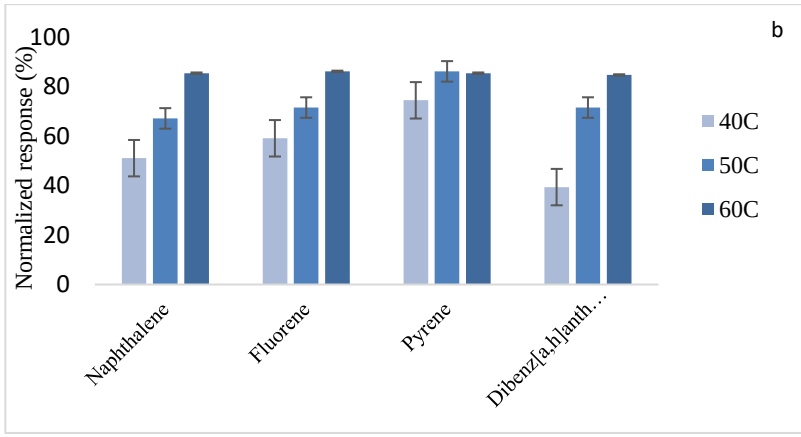

Fig. 3(b). Extraction parameters for the compounds dibenzo, pyrene, fluorene, and naphthalene[a, h] anthracene: Temperature.

The findings regarding the optimal extraction times for dibenzo, pyrene, fluorene, and naphthalene [a,h] anthracene align well with existing literature on PAHs (Fig. 3c). This study reveals that naphthalene and fluorene reach approximately 80 % extraction efficiency within 20 min, peaking near 100 % by 40 min, which is consistent with Schäffer *et al*. [56] noted similar rapid extraction rates for lighter PAHs. In contrast, pyrene and dibenzo[a,h]anthracene exhibit slower extraction kinetics, achieving optimal efficiency around 60 minutes, corroborating findings from Choo *et al.* [57] highlighted the prolonged extraction times needed for heavier PAHs due to larger molecular sizes and stronger hydrophobic interactions. Zhao *et al*. [58] further supported these observations, indicating that lighter PAHs could be efficiently extracted in shorter time frames using solid phase microextraction, while Gao *et al*. [59] emphasized the role of solvent polarity and temperature in optimizing extraction conditions. Additionally, Amin *et al*. [60] reinforced the importance of minimizing extraction time while maximizing yield for PAH recovery, which resonates with this study's conclusion that naphthalene and fluorene can be effectively extracted within 30-40 min.

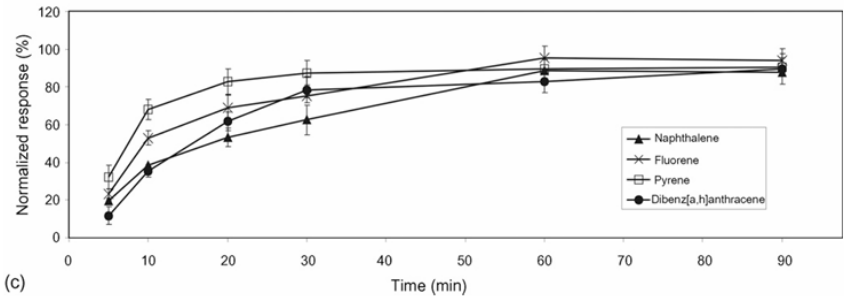

Fig. 3(c). Extraction parameters for the compounds dibenzo, pyrene, fluorene, and naphthalene[a, h] anthracene: Extraction time.

3.2. *Validation*

The entirely computerized MASE technique for assessing PAHs has demonstrated outstanding efficiency, attaining extraction efficiencies of 65 % with ethyl acetate as the solvent. This method employed a 60-min extraction duration at a temperature of 50 °C with agitation maintained at 750 rpm (Table 1). Losacco *et al.* [61] conducted a comparative study that confirmed the accuracy of the MASE approach, with within-day and inter-day repeatability values between 6 % and 18 % and 11 % and 18 %, respectively. The detection limits for PAHs in this investigation ranged from 3 to 40 ng/L, indicating a high sensitivity appropriate for trace analysis. Moreover, calibration curves demonstrated robust linearity (R^2 values ranging from 0.992 to 0.998), corroborated by ANOVA results ($P < 0.05$) and lack-of-fit tests, which validated the suitability of the regression models utilized. The findings validate those presented by Martins *et al.* [62], thereby enhancing the credibility of the MASE approach for PAH analysis in environmental monitoring. These findings highlight the increasing requirement for effective analytical methods to evaluate the effects of environmental pollution.

Table 1. The evaluated substances competitive edge.

Compound	Linearity (R)a	Regression curves [a, b] [Y=(a ± Sa) X]	ANOVA lack of fit P-value	Extraction efficiency (%, n=5)	Within-day repeatability (RSD, %, n=5)	Inter-day repeatability (RSD, %, n=10)	LOD (ng/L)	LOQ (ng/L)
Naphthalene	0.995	Y= (0.098 ± 0.002) X	0.8658	83	18	12	13	48
Acenaphthene	0.992	Y= (0.88 ± 0.03) X	0.4800	87	9	18	27	90
Anthracene	0.997	Y= (1.49 ± 0.05) X	0.4578	75	8	12	20	67
Fluorene	0.998	Y= (1.89 ± 0.05) X	0.7499	92	6	14	10	33
Pyrene	0.995	Y= (1.72 ± 0.06) X	0.4800	87	10	17	15	50
Phenanthrene	0.997	Y= (1.77 ± 0.05) X	0.4758	91	8	14	3	10
Chrysene	0.994	Y= (1.09 ± 0.04) X	0.8002	70	12	11	9	30
Benzo[a]anthracene	0.994	Y= (1.24 ± 0.05) X	0.7951	84	8	13	9	30
Benzo[a]pyrene	0.995	Y= (0.94 ± 0.03) X	0.5562	67	9	14	40	133
Fluoranthene	0.996	Y= (1.83 ± 0.06) X	0.5039	91	10	16	9	30
Benzo[b]fluoranthene	0.996	Y= (1.18 ± 0.06) X	0.4198	82	9	10	13	43

a. Range of 0.05–100 ng/L with 8 levels duplicated.
b. X stands for compound concentration, Y indicates the ratio of the compound signal to the internal standard signal, 'an' indicates the slope, and 'S' indicates the slope's standard error.

3.3. *Matrix effects and application to real samples*

The current study evaluated extraction strategies for PAHs in diverse matrices, including pure water and beverages including milk, juice, and red wine, exhibiting good extraction efficiency and methodological robustness. Fang *et al.* [63] validated the efficacy of SPME across several matrices; however, Wang *et al.* [64] observed negligible matrix effects in alcoholic drinks using liquid-liquid extraction (LLE).

3.3.1 *River water samples*

The observed amounts of PAHs in this study (0.01 to 0.64 g/L) correspond with other research, underscoring the variability and environmental issues associated with PAHs in freshwater ecosystems (Table 2). Khalil *et al*. [65] observed comparable PAH concentrations in river waters from developing countries, suggesting anthropogenic contributions. The analytical methodologies employed produced trueness values ranging from 72 % to 114 %, aligning with the findings of Chuang *et al*. [66] validated their reliability for environmental monitoring. Zonkpoedjre *et al*. [67] underscored the ecological hazards associated with low PAH concentrations, highlighting the necessity for regular monitoring.

Table 2. Outcomes from the analysis of the river water sample and the accuracy of the process

Compound	Conc. sample (µg/L ± SD, n = 5)	Trueness (% ± SD, n = 5)
Naphthalene	0.64 ± 0.07	73 ± 7
Fluorene	0.11 ± 0.01	99 ± 3
Acenaphthene	0.04 ± 0.005	86 ± 6
Anthracene	0.06 ± 0.008	101 ± 2
Pyrene	0.18 ± 0.13	103 ± 6
Benzo[b]fluoranthene	0.22 ± 0.06	87 ± 2
Benzo[a]pyrene	0.31 ± 0.09	82 ± 1
Fluoranthene	0.20 ± 0.05	106 ± 6
Acenaphthylene	0.01 ± 0.004	90 ± 6

3.3.2. *Wine and juice samples*

The extraction effectiveness of the MASE approach has been evaluated in multiple studies concerning diverse food matrices, demonstrating a range of recovery rates that underscore both the advantages and drawbacks of this technology (Table 3). In a study by Yan *et al*. [68], the MASE approach attained recoveries of 80 % to 130 % for PAHs in fruit juices, demonstrating performance comparable to the present findings for apple juice, which exhibited recoveries between 75 % and 136 %. Studies by Marques *et al*. [69], on red wine samples indicated recoveries ranging from 71 % to 126 %, aligning with the findings of the current investigation and demonstrating that MASE effectively extracts pollutants from complex matrices such as red wine [69]. In contrast, Tavengwa *et al*. [70] revealed that although MASE achieved good recoveries for specific compounds, such as fluorene (99 % ± 4 % at 0.33 g/L), it was ineffective for others, such as naphthalene, which was undetectable in both apple juice and red wine samples [70]. This contrasts with the findings of Lee *et al*. [71] demonstrated that naphthalene was efficiently recovered (88 % ± 16 %) at elevated concentrations, highlighting the influence of concentration on extraction efficiency.

Table 3. Results of the spiked apple juice and red wine samples (trueness ± SD; %, n = 3).

Compound	Apple juice Spiking level		Red wine Spiking level	
	0.33 g/L	1 g/L	0.33 g/L	1 g/L
Naphthalene	-	88 ± 16	-	-
Fluorene	99 ± 4	101 ± 2	103 ± 4	120 ± 13
Acenaphthylene	124 ± 10	136 ± 5	118 ± 16	116 ± 9
Anthracene	105 ± 4	102 ± 1	109 ± 6	112 ± 8
Fluoranthene	79 ± 3	76 ± 1	74 ± 3	82 ± 10
Pyrene	75 ± 5	74 ± 3	71 ± 9	81 ± 3
Benzo[a]anthracene	113 ± 7	105 ± 2	116 ± 2	109 ± 4
Benzo[b]fluoranthene	102 ± 7	93 ± 4	109 ± 8	87 ± 16
Acenaphthene	100 ± 10	120 ± 4	104 ± 16	126 ± 8
Phenanthrene	94 ± 5	96 ± 1	92 ± 5	110 ± 3

3.3.3. *Milk samples*

The assessment of the Modified Accelerated Solvent Extraction (MASE) technique for identifying PAHs in milk samples demonstrates significant heterogeneity in efficacy contingent upon fat content (Table 4, Fig. 4). Zhang *et al.* [72] found analogous findings, investigating PAHs in dairy products and demonstrating that elevated fat concentrations substantially influenced both recovery rates and detection limits. The study demonstrated that the trueness of naphthalene in whole milk was significantly elevated, supporting the findings of the current research, which indicated that trueness improved with increased fat content. Assaf et al. [73] found that fluorene showed enhanced recovery in high-fat dairy products, underscoring the significance of matrix effects in PAH detection. Conversely, the study by Xing *et al.* [74] indicated that specific PAHs, such as benzo[a]pyrene, exhibited significantly diminished trueness with increasing fat content, aligning with the findings presented here, where trueness decreased from 113 % to 67 %. A study by Matei *et al*. [75] further indicated that the limits of detection (LOD) for pyrene were elevated in full-fat milk relative to skim milk, highlighting the significance of fat content in the assessment of analytical techniques for PAHs.

Table 4. Trueness and detection limits by MASE procedure of 10 g/L spiked milk samples with different fat content.

Compound	0.3 % fat		1.5 % fat		3.5 % fat	
	Trueness (%)	LOD (ng/L)	Trueness (%)	LOD (ng/L)	Trueness (%)	LOD (ng/L)
Naphthalene	114	19	122	50	131	85
Fluorene	92	21	99	28	101	116
Acenaphthylene	129	17	125	33	125	40
Phenanthrene	100	20	101	51	83	134
Fluoranthene	88	20	109	54	90	125
Pyrene	96	113	105	241	93	243
Benzo[a]anthracene	99	285	103	965	75	1670
Benzo[b]fluoranthene	69	59	65	568	31	1831
Benzo[a]pyrene	113	309	109	2020	67	5871
Anthracene	104	32	108	77	106	199

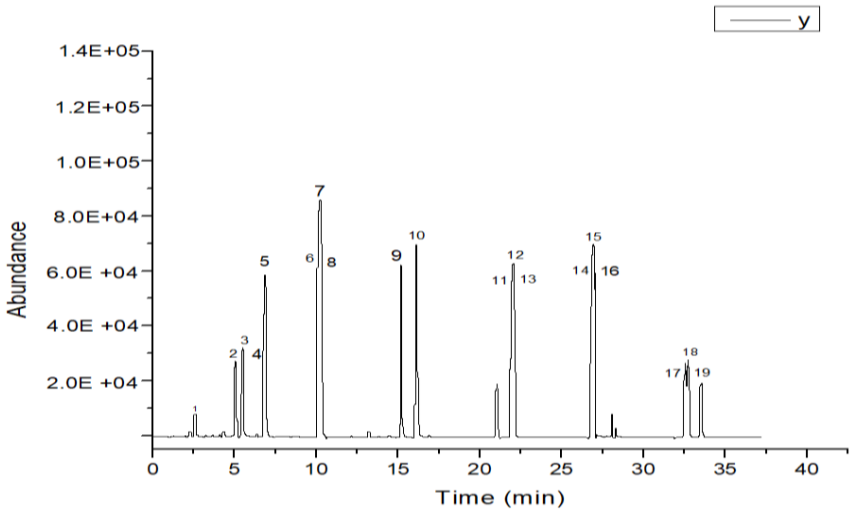

Fig. 4. Chromatographic analysis of an apple juice sample spiked to g/L. Extraction conditions: 60 min extraction time, 50 °C, 750 rpm. pyrene, anthracene-d10, benzo[b]fluoranthene, phenanthrene, fluorene-d10, dibenz [a,h] anthracene, anthracene, indenol[1,2,3-cd]pyrene, fluoranthene, fluorene, benzo[ghi]perylene, chrysene-d12, naphthalene, chrysene, acenaphthene, benzo[k]fluoranthene, benzo[a]anthracene, benzo[a]pyrene, acenaphthylene.

4. Conclusion

In conclusion, the study demonstrates that MASE combined with large-volume injection gas chromatography-mass spectrometry (LVI-GC-MS) is a reliable and effective method for detecting PAHs in water and various beverages. The method achieved high extraction efficiencies of over 65 % and showed consistent precision and sensitivity, with detection limits ranging from 3 to 40 ng/L. The technique performed well across different matrices, including juice, red wine, and milk, although matrix effects, particularly fat content in milk, influenced trueness and detection limits. Compared to other microextraction methods, MASE-LVI-GC-MS provided comparable or better sensitivity. These findings suggest that MASE-LVI-GC-MS is a robust approach for PAHs analysis, enhancing environmental monitoring and public health protection by enabling accurate detection in diverse samples.

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