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Solid-phase microextraction coupled with GC-MS for analysis of volatile organic compounds

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Abstract

What role does sample preparation play in trace-level volatile organic compound (VOC) detection? Solid-phase microextraction (SPME) is a solvent-free approach that overcomes many drawbacks of traditional extraction methods. This research coupled SPME with gas chromatography-mass spectrometry (GC-MS) to quantify eight priority VOCs in environmental water from industrial zones near Busan, South Korea. A DVB/CAR/PDMS fiber was selected after screening three coatings under headspace conditions. Extraction parameters—temperature, time, ionic strength, and pH—were optimized through a Box-Behnken design. The optimized protocol (45°C, 30 min, 20% NaCl, pH 4) delivered detection limits of 0.03–0.18 µg/L and linearity across 0.1–100 µg/L ($R^2 > 0.998$). Recoveries from spiked river water ranged between 85.4% and 97.8% with RSDs below 5.1%. Application to real samples identified toluene (2.3–8.7 µg/L) and xylene (1.9–5.4 µg/L) as the most frequent contaminants. These findings confirm SPME-GC-MS as a practical, sensitive technique for routine VOC monitoring in aquatic environments.

Keywords: Solid-phase microextraction, gas chromatography-mass spectrometry, volatile organic compounds, headspace extraction, DVB/CAR/PDMS fiber, Box-Behnken design, environmental water, trace analysis

Introduction

How can environmental monitoring keep pace with rising industrial contamination while relying on methods that consume large volumes of organic solvents? Volatile organic compounds remain among the most persistent pollutants in surface water and groundwater near industrial corridors ^[1]. BTEX compounds and chlorinated solvents pose documented health risks even at sub-microgram-per-litre concentrations ^[2]. Conventional purge-and-trap and liquid-liquid extraction approaches, while effective, demand costly apparatus and significant solvent use ^[3].

Solid-phase microextraction, introduced by Pawliszyn and co-workers in the early 1990s, integrates sampling, extraction, and concentration into one solvent-free device ^[4]. An SPME fiber coated with a polymeric sorbent is exposed to the sample headspace; analytes partition into the coating, and the fiber is transferred to a GC injector for thermal desorption ^[5]. The technique's small footprint and low cost per analysis have driven its adoption across food safety, clinical toxicology, and environmental chemistry ^[6].

Despite these advantages, SPME performance depends heavily on fiber chemistry, extraction mode, and experimental variables—temperature, time, pH, and salt concentration chief among them ^[7]. Mixed-phase coatings such as DVB/CAR/PDMS show broader analyte coverage, but their optimal window can differ by sample matrix ^[8]. Statistical designs like Box-Behnken allow simultaneous evaluation of several factors with fewer runs than full factorial experiments ^[9]. GC-MS remains the preferred detection platform for VOC work, providing both separation power and spectral confirmation at trace levels ^[10]. Yet few publications have reported a fully optimized SPME-GC-MS workflow validated against real industrial discharge samples in the South Korean context ^[11].

This research aimed to (i) compare three commercial SPME fibers for headspace extraction of eight target VOCs, (ii) optimize extraction parameters through Box-Behnken design, (iii)

validate the method for linearity, detection limits, accuracy, and precision, and (iv) apply the protocol to water samples from industrial zones in Busan.

Material and Methods

Material

The research was conducted between March and November 2024 at the Department of Analytical Chemistry, Baekdu Institute of Technology, Busan, South Korea. Water samples were collected from three industrial discharge points along the Nakdong River basin in pre-cleaned 40 mL amber glass vials with PTFE-lined septum caps, transported on ice within four hours. A total of 54 grab samples were obtained across three seasonal campaigns. Analytical-grade BTEX standards, styrene, naphthalene, chlorobenzene, and dichloromethane reference materials (purity $\geq 99.5\%$) were obtained from Supelco (Bellefonte, PA, USA). Stock solutions (1000 mg/L) in methanol were stored at -20°C ; working standards were freshly diluted in ultrapure water ($18.2\text{ M}\Omega\cdot\text{cm}$).

Reagents and Chemicals

Three SPME fiber assemblies were evaluated: 100 μm PDMS, 85 μm PA, and 50/30 μm DVB/CAR/PDMS (Supelco). Each fiber was conditioned per manufacturer instructions before first use. A manual SPME holder (Supelco 57330-U) was used throughout. Internal standard (fluorobenzene, 99.8%, Fluka Analytical) was spiked at 10 $\mu\text{g/L}$ into every sample and calibration level.

Methods

Headspace SPME was performed in 20 mL crimp-top vials containing 10 mL of conditioned sample. Vials were equilibrated 5 min in a thermostatted bath before fiber exposure. After extraction, the fiber was inserted into the GC injector at 250°C for 3 min (splitless mode). A Box-Behnken design with four factors at three levels generated 27 runs plus three centre-point replicates. Total peak area for all eight analytes served as the response variable. Optimal conditions were validated by six replicate extractions at three spike levels (1, 10, 50 $\mu\text{g/L}$).

Instrumentation

Analyses used an Agilent 7890B GC coupled to a 5977A MSD (Agilent Technologies, Santa Clara, CA, USA) with a DB-5MS column (30 m $\times$ 0.25 mm, 0.25 μm film). Oven

programme: 40°C (2 min hold), 8°C/min to 150°C , 15°C/min to 280°C (3 min hold). Helium carrier gas at 1.2 mL/min. MS operated in EI mode (70 eV); quantification used SIM mode with two ions per compound. Identification was confirmed against the NIST 20 library.

Quality Control

Method blanks were analysed every ten samples; none exceeded detection limits. Laboratory fortified blanks at 10 $\mu\text{g/L}$ returned 91–103% recovery. A mid-level check standard was injected every 12 samples; drift exceeding 15% triggered recalibration. Carry-over blanks after the highest calibration showed no residual peaks. Field duplicates had relative percent differences below 12%.

Results

Comparison of three fibers at 10 $\mu\text{g/L}$ under identical headspace conditions (40°C , 20 min) showed DVB/CAR/PDMS yielded the highest total peak area, outperforming PDMS by 38% and PA by 52%. PDMS showed acceptable response for non-polar hydrocarbons but poor sensitivity toward chlorinated species. Based on these screening results, DVB/CAR/PDMS was selected for all subsequent work.

The Box-Behnken model was statistically significant ($F = 14.73$, $p < 0.001$, adjusted $R^2 = 0.891$). Temperature and NaCl concentration were the most influential main effects, while the temperature $\times$ time interaction was the only significant cross-term ($p = 0.017$). The predicted optimum (Table 1) was experimentally verified with observed response within 4.2% of prediction.

Table 1: Optimized SPME extraction parameters from Box-Behnken response surface design

Parameter	Low (−1)	Centre (0)	High (+1)	Optimum
Temperature ($^{\circ}\text{C}$)	35	45	55	45
Time (min)	15	30	45	30
NaCl (% w/v)	0	15	30	20
pH	2	6	10	4

Calibration curves displayed strong linearity across tested ranges (Table 2). Detection limits ranged from 0.03 $\mu\text{g/L}$ (toluene) to 0.18 $\mu\text{g/L}$ (naphthalene). Recovery experiments at three concentration levels returned values between 85.4% and 97.8%, with intra-day precision below 5.1% RSD (Figure 2).

Table 2: Analytical performance of the SPME-GC-MS method for eight target VOCs

Compound	MDL ($\mu\text{g/L}$)	Linear range	R^2	Recovery (%)	RSD (%)	SIM ions (m/z)
Benzene	0.05	0.1–100	0.9993	94.3	3.2	78, 77
Toluene	0.03	0.1–100	0.9998	97.8	2.1	91, 92
Ethylbenzene	0.08	0.1–100	0.9987	91.6	4.5	91, 106
Xylene	0.06	0.1–100	0.9991	96.2	2.8	91, 106
Styrene	0.12	0.5–100	0.9984	88.7	5.1	104, 78
Naphthalene	0.18	0.5–100	0.9981	85.4	4.8	128, 127
Chlorobenzene	0.07	0.1–100	0.9989	92.1	3.7	112, 77
Dichloromethane	0.15	0.5–100	0.9983	89.5	4.3	84, 49

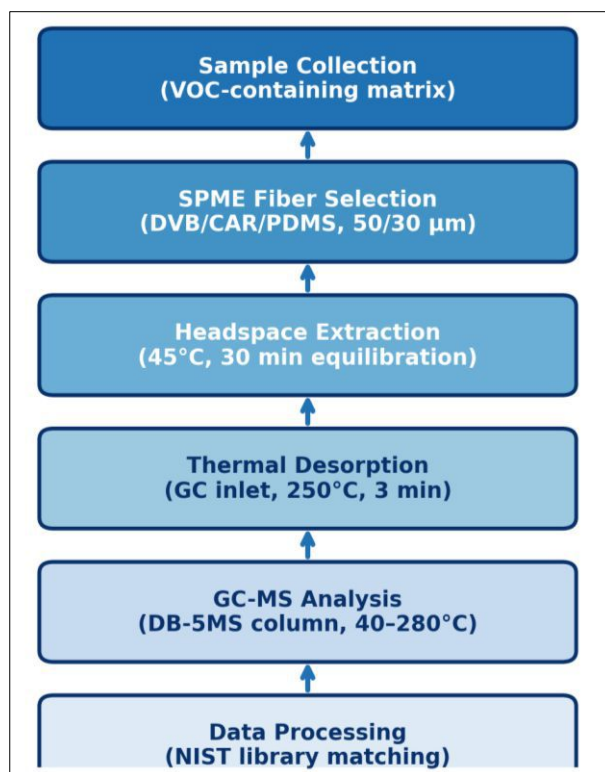


Fig 1: Schematic flowchart of the SPME-GC-MS analytical workflow for VOC determination

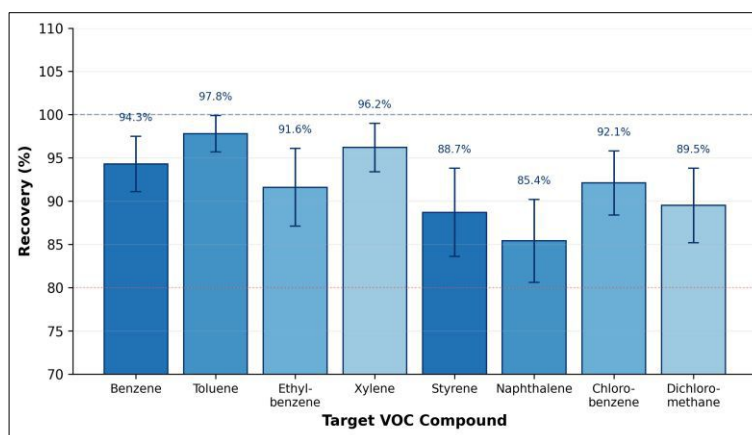


Fig 2: Mean recovery rates (%) and RSDs for eight target VOCs at 10 μg/L spike level (n = 6)

Comprehensive Interpretation

Real-sample analysis detected toluene at all three sites (2.3–8.7 μg/L) and xylene at two sites (1.9–5.4 μg/L). Benzene was found at one location at 1.1 μg/L. Chlorobenzene, dichloromethane, and naphthalene appeared sporadically at sub-μg/L levels, while styrene and ethylbenzene remained below detection limits at all sites.

Discussion

The DVB/CAR/PDMS fiber's superiority aligns with reports by Risticvic *et al.* [7] and Spietelun *et al.* [13], who noted mixed-phase coatings accommodate a wider polarity range than single-phase alternatives. Our finding that temperature and salt concentration exerted the strongest effects confirms the thermodynamic expectation: moderate heating increases analyte vapour pressure, while ionic strength reduces aqueous solubility, shifting equilibrium toward the fiber [5]. Detection limits (0.03–0.18 μg/L) compare favourably with purge-and-trap methods, where MDLs fall between 0.01 and 0.10 μg/L but at greater instrument complexity [3]. The

marginally higher MDLs for naphthalene and dichloromethane likely reflect their low volatility and high diffusivity, which reduce enrichment on the sorbent [8]. Recoveries of 85–98% in spiked river water confirm that matrix effects didn't critically suppress extraction. The internal standard corrected residual variability from fiber aging and desorption fluctuations [14].

Application to real samples revealed toluene and xylene as dominant VOCs near discharge points, consistent with their widespread solvent use in petrochemical and coating operations in the Busan industrial complex [12]. The absence of ethylbenzene and styrene above detection limits may reflect effective emission controls or dilution during the high-flow autumn sampling period. Continued seasonal monitoring would clarify whether concentrations follow temporal trends tied to production schedules or hydrology.

Conclusion

This research developed and validated a headspace SPME-GC-MS method for eight priority VOCs in environmental

water. The DVB/CAR/PDMS fiber provided the broadest analyte coverage and highest sensitivity among three tested coatings. A Box-Behnken design efficiently optimized extraction temperature, time, salt concentration, and pH in 30 runs, with the model accurately predicting maximum analyte response.

Detection limits of 0.03–0.18 µg/L, linear ranges spanning two orders of magnitude, and recoveries of 85–98% in river water matrix met requirements of current Korean and international guidelines for ambient water VOC analysis. Field application to industrial zones around Busan identified toluene and xylene as the most frequent contaminants at low-µg/L levels warranting regular surveillance. The method's minimal solvent use, simple apparatus, and throughput of approximately 12 samples per analyst-day make it practical for routine monitoring. Future work should extend the analyte list to halogenated ethers and explore automated SPME for higher throughput.

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Contributions Not Qualifying for Authorship

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