**A novel hydrogen fluoride assisted – glass surface etching based liquid phase microextraction
for the determination of 4-*n*-nonylphenol in water by gas chromatography-mass spectrometry
with matrix matching strategy**

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Abstract

A novel extraction method named hydrogen fluoride assisted – glass surface etching based liquid phase microextraction (HF-GSE-LPME) was proposed to determine 4-*n*-nonylphenol at trace levels by gas chromatography-mass spectrometry (GC-MS). After the evaluation of system analytical performance for the HF-GSE-LPME-GC-MS system, limit of detection (LOD) and limit of quantification (LOQ) values were calculated as 7.1 and 23.8 ng/g, respectively. Enhancement in detection power of the method was determined as 22 folds when LOD values of the GC-MS and HF-GSE-LPME-GC-MS systems were compared with each other. Applicability and accuracy of the established method was checked by performing spiking experiments. Matrix matching calibration strategy was applied to boost the accuracy of quantification in both matrices, and the percent recovery results obtained for bottled drinking water and dam lake water samples were in the range of 98 – 107% and 90 – 117%, respectively.

Keywords: Hydrogen fluoride; Glass etching; 4-*n*-nonylphenol; Gas chromatography-mass spectrometry; Water samples.

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Introduction

Endocrine disruptor compounds (EDCs) are emerging contaminants that are of great environmental concern because of their ability to change the natural function of the endocrine system ^{1,2}. In addition to naturally occurring EDCs, chemists have synthesized a large number of EDCs that are harmful to animal and human health ². Biological activities of organisms are damaged by EDCs that mimic or block hormones ³. Consequently, EDCs cause serious health problems such as cancer, obesity, diabetes, developmental, thyroidal and reproductive disorders even at low concentrations ^{4,5}.

Nonylphenols (NPs) toxic compounds known as the most common EDCs are well-known environmental pollutants that are categorized among the 13 priority hazardous substances according to the European Union ⁶. These compounds are mainly released into the environment by the degradation of nonylphenol ethoxylates, a subgroup of alkylphenol ethoxylates ^{7,8}. In spite of all these negative effects, NPs have a broad usage area such as detergents, wetting and dispersing agents, agricultural and industrial products, emulsifiers, plastics, dentistry, food packing, textile, cosmetics and pesticides ^{6,7,9}. 4-*n*-nonylphenol (4-*n*-NP) has been reported at different concentrations in various matrices such as drinking water, surface waters and sediments, wastewater and soil ^{10–12}. These concentrations were 53 ng/g ¹³, 10.30–84.00 ng/L ¹⁴, 6–135 ng/L ¹⁵, 0.16–37 µg/L ¹⁶ and 17.4–1533.1 ng/L ¹⁷ for sediment, drinking water, river water, wastewater and lake water, respectively. The daily intake of 4-*n*-NP was reported as 7.5 µg for adults, and studies in the literature shows that 4-*n*-NP concentration can be found at different levels in environmental samples ¹⁸. For these reasons, a sensitive analytical method should be developed to detect 4-*n*-NP at parts per billion (ppb) levels.

Modern chromatographic and hyphenated instrumental methods have been utilized for the determination of 4-*n*-NP. Some of these methods are gas chromatography-mass spectrometry (GC-MS) ^{12,19}, high performance liquid chromatography (HPLC) ^{20,21}, liquid chromatography-mass spectrometry (LC-MS) ^{22,23} and liquid chromatography-tandem mass spectrometry (LC-MS/MS) ^{24,25}. In general, thermally stable and volatile compounds are determined by GC systems ²⁶. When GC is combined with a mass spectrometer, the GC-MS system provides selectivity or specificity by creating different fragmentation products of the analyte(s) ²⁷.

In quantitative determinations, complex matrices affects sensitivity and accuracy of an analytical method, especially at low concentration of the analyte(s) ²⁸. Several methods have been developed to decrease interference effects arising from heavy matrices and preconcentrate the analyte. Traditional extraction methods such as liquid phase extraction and solid phase extraction are not compatible with green analytical chemistry because of their high chemical consumption ²⁹. Nowadays, solid and liquid phase microextraction methods have been employed to isolate and preconcentrate analyte(s) from complex matrices, and these methods are preferred because they are simple, environmentally friendly, rapid and highly efficient, compared to the traditional extraction methods ^{30,31}. There are several preconcentration methods such as dispersive liquid-liquid microextraction (DLLME) ³², cloud point extraction (CPE) ³³, single drop microextraction (SDME) ³⁴, switchable solvent based liquid phase microextraction (SPS-LPME) ³⁵, hollow-fiber liquid phase microextraction (HF-LPME) ³⁶ and solid phase microextraction (SPME) ³⁷, used to preconcentrate organic pollutants in water samples. SPME methods employ polymer coated fibers that are used as adsorbent for analyte(s), but these fibers are expensive, fragile and unstable. For these reason, application of this method has been limited to real samples ³⁸. In order to overcome these problems, etched surface-based methods have been developed. Here, a surface is etched with hydrofluoric acid (HF) or hydrochloric acid to form microporous surfaces and an extraction solvent is coated on the etched surface. After that, a bulk sample solution is passed through and analyte molecules are preconcentrated on the etched surface ³⁹⁻⁴¹. Silicate glasses are materials easily etched by HF or other HF containing aqueous solutions at room temperature ⁴². The overall reaction of HF assisted glass surface etching is given as ^{42,43};

The glass surfaces etched by HF have micropores and broad surface structure. Therefore, these surfaces offer a favorable surface to coat extraction solvents and preconcentrate target analyte(s). It is assumed that there are adhesion forces between extraction solvent and etched glass. Adhesion is known to be the molecular attraction exerted between the dissimilar particles and/or surfaces of bodies in contact. Several possible interactions (molecular interactions, strong intermolecular forces, weak intermolecular interactions and strong chemical bonds) are possible to form adhesion. Pores, voids and

roughness surfaces generate an effective adhesion by increasing adherence adhesive materials to surface⁴⁴. Van der Waals forces in addition to the specific chemical interactions ensure to form adhesion forces in liquids⁴⁵.

In this study, a new liquid phase microextraction method named hydrogen fluoride assisted-glass surface etching based-liquid phase microextraction (HF-GSE-LPME) was developed for the determination of 4-*n*-nonylphenol by GC-MS. A glass tube with etched inner surface was used to extract and preconcentrate the analyte from aqueous solution. The developed method was successfully applied to bottled drinking water and dam lake water samples to test the accuracy and applicability of the method.

Materials and method

Chemicals

4-*n*-nonylphenol (99.9%, purity) was purchased from Dr. Ehrenstorfer GmbH (Augsburg – Germany). Cyclohexane and hydrofluoric acid were purchased from Sigma Aldrich (USA). Chloroform, dichloromethane, ethyl acetate, methanol, ethanol and isopropyl alcohol were obtained from Merck (Darmstadt – Germany), while acetone was purchased from Isolab Chemicals (Eschau – Germany). Helium gas was purchased from Seral Gaz (İstanbul – Turkey). Deionized water taken from an Elga Flex 3 Water Purification System (resistivity of 18.2 Ω .cm) was used for all sample/standard preparation and cleaning processes.

GC-MS conditions

An Agilent HP6890 series GC system was used for chromatographic elution, and the system was connected to an HP5973 series MS detector that was used to identify 4-*n*-NP. Mobile phase and its flow rate, temperature program, column, sample injection mode and volume, electron impact ionization source temperature/energy, MS quadrupole temperature and transfer line connecting GC

and MS systems are summarized in Table 1. The mass fragment ions (mass to charge ratio, m/z) used to quantify/qualify 4-*n*-NP were m/z 107/220.

Samples

A standard stock solution (1000 mg/kg) of 4-*n*-NP in acetone, and a series of standard solutions in 0.10% acetone were gravimetrically prepared. Drinking water samples bottled in polyethylene terephthalate (exposed to sunlight) were collected from Davutpaşa Campus – Yıldız Technical University, and mixed together to constitute a composite sample. Dam lake water sample was taken from Altınapa located in Konya, Turkey. These water samples were filtrated through 0.45 μ m filters and stored in a refrigerator at 4.0 °C. The drinking and dam lake water samples were diluted ten times, and acetone was added into the samples to fix acetone content to 0.10%. After blank analysis, the samples were spiked to desired concentrations, extracted and preconcentrated by the developed method and the extracts sent to the GC-MS system.

Extraction method

A glass tube was filled with hydrofluoric acid by an injector, and the inner surface of the glass tube was etched for a period 7.5 min. The etched glass tube was washed with deionized water, and cyclohexane (approximately 1.5 mL) was loaded into the etched glass tube and held for 3.5 min to penetrate the etched surface. Then, excess cyclohexane was removed from the inner surface of the glass tube. The standard/sample solution (12.0 mL) was successively filled into and discharged from the etched glass tube coated with cyclohexane three times, and the final solution emptied into a waste container. After this step, 100 μ L of acetone was passed over the etched glass surface two times to elute the adsorbed analyte. Finally, approximately 70 μ L of the eluent was transferred into an insert vial and sent to GC-MS system measurement. The extraction protocol is graphically represented in Figure 1.

Glass tube designs

The eight different glass tubes given in Figure 2 were designed using soda-lime-silica glass to enhance extraction yield of the analyte and ease the applicability of the proposed extraction method. These glass tubes were produced at the Glassblowing Unit of the Central Laboratory in Yıldız Technical University.

Surface morphology of etched glass tube

Glass surface morphology before and after the etching process by HF were examined by scanning electron microscope (SEM). The etched glass (Figure 3, B) had microporous structure while a smooth surface was observed for the non-etched glass (Figure 3, A). When the microporous structure was scaled up, horizontal lines were explicitly seen (Figure 3, C). These lines create a suitable surface to hold organic solvents.

Results and discussion

Effective parameters of the HF-GSE-LPME method were optimized by a univariate approach to enhance the signal to noise ratio of 4-*n*-NP.

Type of glass tube and etching period

In this optimization step, different glass tube designs were investigated to evaluate their effects on extraction efficiency of the analyte. The best result with low standard deviation was obtained for Design 2 (Figure 4). In addition, the sample and eluent solutions were loaded more easily into Design 2 glass tube than the other designs. Hence, the optimum design was chosen as Design 2.

HF was loaded into the selected glass tube by an injector and different periods between 2.5 and 10 min were tested to examine the effect of etching period on analyte preconcentration. The results obtained in this optimization are given in Figure 5, and the 7.5 min etching period gave the highest peak area when compared to the other periods. The optimum etching period was set as 7.5 min for the subsequent experiments.

Type of extraction solvent and coating period

One of the most important parameters in this method is extraction solvent type, since preconcentration factor directly relates to extraction capability of an extraction solvent for an analyte. Moreover, the extraction solvent should cover and stay on the etched surface ⁴⁰. Therefore, four different solvents (chloroform, dichloromethane, ethyl acetate and cyclohexane) were tested to find the most efficient extraction solvent. The highest results were attained with cyclohexane (Figure 6), and it was selected as optimum extraction solvent type.

Coating period is another important parameter for efficient extraction of the analyte because it determines the total etched surface that would be covered with the extraction solvent. Hence, coating periods were tested in the range of 1.0 – 10.0 min to determine maximum load capacity of the extraction solvent onto the etched glass tube surface. The glass tube was completely filled with the extraction solvent and allowed to stand for the different tested periods. Approximately 2.0 mL of cyclohexane was required to completely fill the glass tube. As can be seen in Figure S1 (Electronic Supplementary Information, ESI), peak area values increased by about 2 folds from 1.0 min to 3.5 min, and decreased at the higher coating periods. Hence, 3.5 min coating for extraction solvent was used in the following experiments.

Type and amount of eluent

The analyte molecules were extracted from the aqueous sample into the extraction solvent coated onto the etched surface, and then released from the glass tube by an eluent. An appropriate eluent is therefore required to collect the analyte from the etched surface. For this reason, methanol, ethanol, isopropyl alcohol and acetone were tested as potential eluents. The highest signals were recorded for acetone as presented in Figure S2, therefore, it was selected as optimum eluent type.

In the proposed extraction process, another important parameter was eluent volume because preconcentration factor is inversely proportional to eluent volume ⁴⁰. For this purpose, 100, 200 and

300 μ L volumes of acetone were tested in order to obtain lower detection limit. The highest peak area values were obtained for 100 μ L of acetone, which was about three times higher than the 200 μ L volume (Figure S3). Volumes lower than 100 μ L were tested but the amount of eluent obtained from the glass tube was insufficient to be analyzed by GC-MS. A significant portion of the eluent was dispersed and remained on the tube surface. Hence, 100 μ L volume was selected for subsequent experiments.

Sample volume

High sample volumes produce high preconcentration factors and vice versa ⁴⁶, hence; 8.0, 10.0 and 12.0 mL of sample volumes were investigated to increase the preconcentration factor for the analyte. In this optimization, a linear increment with increasing sample volume was observed according to the peak area values given in Figure S4. However, volumes higher than 12.0 mL could not be tested because the effective volume of the syringe used was approximately 13 mL. Therefore, the optimum sample volume was selected as 12 mL.

Sample and eluent load cycles

Interaction between sample and the etched surface was investigated to monitor its influence on extraction yield. Sample load cycle was tested in the range of 1 and 4 times. There was an increment in peak areas up to 3 times, but peak areas decreased at 4 times sample load cycle. Here, 3 times sample load cycle (Figure S5) was chosen as the optimum one for the proposed method.

The final optimization experiment was done for eluent load cycle by testing cycles between one and three times. In this microextraction method, the eluent should penetrate into the etched surface to desorb the analyte of interest. One cycle was not sufficient to collect the analyte, but two cycles (Figure S6) gave the highest results. Therefore, two eluent load cycle was chosen as the optimum one. All optimum conditions found are summarized in Table 2.

Analytical figures of merit

Analytical performance of the GC-MS system was evaluated under the optimum chromatographic conditions. Aqueous standard solutions (0.10% acetone) prepared between 0.50 and 30.0 mg/kg were directly sent to the GC-MS system and the limit of detection (LOD) and limit of quantification (LOQ) were calculated as 0.16 and 0.53 mg/kg, respectively.

Aqueous standard solutions (0.10% acetone) prepared between 25.0 and 1000.0 ng/g were extracted by the proposed extraction process explained in Section 2.4. After the extraction process, approximately 70 μ L of eluent solution was taken into an insert vial and sent to the GC-MS system. LOD and LOQ values for the HF-GSE-LPME-GC-MS system were found to be 7.1 ng/g and 23.8 ng/g, respectively. When the LOD values of HF-GSE-LPME-GC-MS and GC-MS systems were divided each other, enhancement in detection power (EDP) of GC-MS system was calculated as 22 folds. Additionally, LOD, LOQ, dynamic range, relative standard deviation of the lowest concentration in the dynamic range, correlation coefficient and EDP for both systems are given in Table 3.

Recovery studies

Applicability and accuracy of the developed method were checked by carrying out spiking experiments. Drinking water and dam lake water were selected for this purpose, and were analyzed. 4-*n*-NP was not detected in these samples under the optimum chromatographic and extraction conditions. After blank analysis, different concentrations between 100.0 and 500.0 ng/g of 4-*n*-NP were spiked to the drinking water and dam lake water samples. The spiked sample solutions were then extracted by the optimized HF-GSE-LPME method. The percent recovery results for drinking water and dam lake water samples were calculated between 59 and 137% via external calibration method. According to these results, it can be deduced that positive and negative interference affected recovery of the analyte from dam lake water and drinking water matrices, respectively. To eliminate these matrix effects, matrix matching calibration strategy was employed to improve accuracy of the recovery

results. Clean matrix (undetected analyte signal) of each sample was used to prepared calibration standard solutions between 100 and 500 ng/g, and the developed calibration plots were used to quantify the spiked samples. The percent recovery results calculated for the samples by matrix matching calibration ranged from 90 to 117% as given in Table 4.

Conclusion

This study proposed a simple, effective and low cost HF-GSE-LPME method for the extraction and preconcentration of 4-*n*-NP from bottled drinking water and dam lake water samples before GC-MS determination. Under the optimum chromatographic and extraction conditions, approximately 22 folds improvement in detection power was recorded for the analyte. After blank analyses, recovery experiments were carried out in bottled drinking water and dam lake water matrices, but there were negative/positive interence effects for the interest of analyte. Matrix matching calibration strategy was employed to eliminate matrix effects, and improved recovery results were obtained. This study demonstrated that the proposed method can be used to extract and preconcentrate other organic and inorganic contaminants from environmental samples.

Declaration of interest: There are no conflicts to declare

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Tables

Table 1 GC-MS system parameters.

Parameter	Value
Mobile phase and its flow rate	Helium, 2.8 mL/min
Temperature program	Initial temperature was 70 °C; increased to 240 °C (30 °C/min); increased to 280 °C (60 °C/min; increased to 300 °C (30 °C/min)
Column	HP-5MS, 5% phenyl methyl siloxane column with dimensions of 30 m x 250 µm inner diameter x 0.25 µm film thickness
Sample injection mode and volume	Spitless mode, 1.0 µL
Electron impact ionization source temperature, ionization energy	230 °C, 70 eV
MS quadrupole temperature	150 °C
Transfer line	280 °C

Table 2 Optimum conditions for HF-GSE-LPME process.

Parameter	Optimum Condition
Glass Type	Number 2
Etching period	7.5 min
Type/coating period of extraction solvent	Cyclohexane / 3.5 min
Type/volume of eluent	Acetone / 100 μ L
Sample volume/load cycle	12.0 mL / 3 times
Eluent load cycle	2 times

Table 3 Analytical performance of GC-MS and HF-GSE-LPME-GC-MS.

System	LOD ^a , ng/g	LOQ ^b , ng/g	Dynamic range, ng/g	Correlation coefficient	EDP ^c
GC-MS ^d	158.5	528.3	489.8 – 14678.8	0.9995	22.2
HF-GSE-LPME-GC-MS ^e	7.1	23.8	24.2 – 999.9	0.9991	

^aLOD: Limit of detection.

^bLOQ: Limit of quantification.

^cEDP: Enhancement in detection power.

^dGC-MS: Gas chromatography-mass spectrometry

^eHF-GSE-LPME-GC-MS: Hydrogen fluoride assisted – glass surface etching based liquid phase microextraction – gas chromatography-mass spectrometry.

Table 4 Recovery results for spiked drinking water and dam lake water samples.

Sample	Concentration, ng/g	External Calibration		Matrix Matching Calibration	
		%Recovery	±SD*	%Recovery	±SD*
Drinking Water	107.5	59.0	0.9	101.0	1.5
	267.7	70.6	7.0	106.5	10.6
	358.2	67.1	2.1	97.9	3.0
	539.9	69.2	5.6	98.4	7.9
Dam Lake Water	101.7	129.4	11.3	116.2	10.1
	280.7	136.3	11.5	107.6	9.1
	527.4	129.9	4.2	90.6	2.9

*Uncertainties (±): standard deviation for $n = 3$.

Figure Captions

Figure 1 The extraction procedure for HF-GSE-LPME method.

Figure 2 Glass tube designs.

Figure 3 SEM images of non-etched glass (A: 2 μm) and the glass etched with HF (B: 100 μm and C: 1 μm).

Figure 4 Optimization of glass type (Constant parameters; etching period: 5 min, standard concentration/volume/load cycle: 2.0 mg/kg/8.0 mL/1 time, type/coating period of extraction solvent: cyclohexane/1.0 min, type/volume of eluent: methanol/0.50 mL, eluent load cycle: 3 times).

Figure 5 Optimization of etching period (Constant parameters; glass type: 2, standard concentration/volume/load cycle: 0.5 mg/kg/8.0 mL/1 time, type/coating period of extraction solvent: cyclohexane/1.0 min, type/volume of eluent: acetone/0.50 mL, eluent load cycle: 3 times).

Figure 6 Extraction solvent type optimization (Constant parameters; glass type: 2, etching period: 7.5 min, standard concentration/volume/load cycle: 2.0 mg/kg/ 8.0 mL/1 time, coating period of extraction solvent: 1.0 min, type/volume of eluent: methanol/0.50 mL, eluent load cycle: 3 times).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6