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Araştırma Makalesi / Research Article

A Dispersive Liquid-Liquid Micro Extraction-Gas Chromatography-Mass Spectrometric Method for The Determination of 4-Nonylphenol in Water Samples

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Abstract

In this study an environmentally-friendly, uncomplicated, and responsive method involving dispersive liquid-liquid microextraction (DLLME) was presented for the isolation and analysis of 4-nonylphenol in aquatic environments. The extraction process employed the undecanol–water dispersive liquid-liquid system to isolate 4-nonylphenol. Essential variables impacting the efficiency of microextraction, such as the quantities of 1-undecanol and acetonitrile, as well as the ionic strength of the aqueous solution, were fine-tuned. Furthermore, the chromatographic parameters of the Gas Chromatography-Mass Spectrometer (GC-MS) were optimized for precise analysis, and the analysis of 4-nonylphenol was conducted using a linear calibration curve spanning 2-1000 μg/L, achieving a rapid 6-minute retention time. The method exhibited a detection limit of 0.05 μg/L and a preconcentration factor of 188. Analyte recovery rates ranged from 96% to 103%, having a relative standard deviation below 3%.The applied procedure was effectively evaluated for its suitability in examining tap water and river water samples.

Keywords
4-Nonylphenol; GC-MS; Liquid-liquid micro extraction; Preconcentration

Su Örneklerinde 4-Nonylfenolün Tayini için Dispersif Sıvı-Sıvı Mikroekstraksiyon-Gaz Kromatografisi-Kütle Spektrometrik Bir Yöntem

Öz

Bu çalışmada çevre dostu, basit ve oldukça hassas bir teknik olan dağılma sıvı-sıvı mikroekstraksiyon (DLLME) yöntemi, sucul ortamlarda 4-nonylfenolün ayırma ve analizi için geliştirilmiştir. Ekstraksiyon işlemi, 1-undekanol-su dağılma sıvı-sıvı sistemi kullanılarak 4-nonylfenolün izolasyonunu içermiştir. 1-undekanol ve asetonitril miktarı ile sulu çözeltinin iyonik şiddeti gibi mikroekstraksiyon verimliliğini etkileyen temel değişkenler hassas bir şekilde ayarlanmıştır. Ayrıca, Gaz Kromatografisi-Kütle Spektrometresi (GC-MS) cihazının kromatografik parametreleri de hassas analiz için optimize edilmiş ve 4-nonylfenol analizi 2-1000 μg/L aralığında lineer kalibrasyon eğrisi kullanılarak gerçekleştirilmiştir, bu sayede hızlı bir 6 dakikalık alıkonma süresi elde edilmiştir. Yöntem, 0.05 μg/L tespit limiti ve 188 ön zenginleştirme faktörüne sahiptir. Analit geri kazanım oranları %96 ile %103 aralığındadır ve göreceli standart sapma %3'ün altındadır. Geliştirilen prosedür, musluk suyu ve nehir suyu örneklerinin incelenmesi için etkili bir şekilde değerlendirilmiştir.

Anahtar kelimeler
4-Nonilfenol; GC-MS; Sıvı-sıvı mikroektraksiyon; Ön zenginleştirme

1. Introduction

In many applications that provide comfort and convenience in our daily lives, unfortunately, numerous harmful chemical substances can pollute the environment. These harmful chemicals pose a serious threat to the living organisms in their respective environments (Deniz *et al.* 2018). The problem of exposure to harmful chemicals has been notable in emerging nations, and among these chemicals are alkylphenols (APs). Out of these chemicals, 4-n-nonylphenol is the more prevalent and extensively studied alkylphenol. 4-Nonylphenol

(4-NP) is a major degradation product of nonylphenol ethoxylates. It is widely used as a nonionic surfactant in various industrial and agricultural applications, pesticide formulations, lubricant additives, textile printing, dyeing auxiliaries, and various other consumer goods. Additionally, it stands out as the predominant component of the extensively studied anthropogenic pollutant known as nonylphenol (Fukamachi *et al.*2004, Abdulla Bin-Dohaish *et al.* 2012, Zheng *et al.* 2018, Erarpat *et al.* 2019, Xu *et al.* 2020, Weatherly *et al.* 2023). 4-Nonylphenol (4-NP) has been identified as a carcinogenic and teratogenic substance, and more recently, It has been considered a trigger for the beginning of a number of neuropsychiatric conditions in humans. (Fukamachi *et al.*2004, Jie *et al.* 2013, Xu *et al.* 2020). Multiple studies have indicated that 4-nonylphenol is frequently detected in a wide range of food items, including vegetables, fruits, crops, dairy products, beverages, in aquatic environments such as soil, ground water, river, tap water. It is believed that these contaminations may originate from packaging materials (Jie *et al.* 2013, Zheng *et al.* 2018, Xu *et al.* 2020).

Environmental water quality criteria for NPs have been set up by the US EPA as a consequence to the increased awareness of potential health hazards, suggesting thresholds of 6.6 µg/L in freshwater and 1.7 µg/L in saltwater. (Erarpat *et al.* 2019, Weatherly *et al.* 2023) . Due to both the adverse effects of 4-nonylphenol on the environment and human health and its easy release, several countries, including the USA, Canada, and China, have implemented strict regulations to control its usage. As a result, the detection and analysis of 4-nonylphenol have sparked significant interest among researchers.

NP, arising from the degradation of alkylphenol ethoxylates, constitutes around 80% of the alkylphenol ethoxylates' decomposition products. The expression "nonylphenol" encompasses a broad variety of isomeric substances characterized by the common formula $C_6H_4(OH)C_9H_{19}$. NP consists of a blend of para-, ortho-, and meta-isomers, with para-NP (4-NP) prevailing as the most prevalent with a molecular mass of 220.34 g/mol.

Various analytical techniques have been utilized to examine 4-NP in various sample matrices. Among these techniques are included High-Performance Liquid Chromatography (HPLC) (Zhou *et al.* 2011, Staniszewska *et al.* 2018), Gas Chromatography-Mass Spectrometry (GC-MS) (Chormey *et al.* 2023, Hailiang *et al.* 2023), and voltammetry (Zhang *et al.* 2018). Highly sensitive analytical methods should be chosen when analyzing analytes at low levels. On the other hand, regardless of the sensitivity of the analysis method, the matrix in which the analyte is present can hinder the accurate analysis of the analyte at very low levels. Therefore, in many analyses, different extraction or preconcentration methods are applied prior to analysis. Liquid-liquid extraction (LLE), solid phase extraction (SPE) are traditional extraction techniques employed for isolating analytes from complex sample solutions with diverse matrices (Anthemidis *et al.* 2009). Nonetheless, these approaches frequently consume a significant amount of time, and the solvents used in the extraction process can be toxic and have high vapor pressures (Soylak *et al.* 2011). In recent times, there has been notable interest in environmentally friendly methods aimed at reducing the use of toxic organic solvents. Liquid phase microextraction methods have been formulated involving a focus on the principles of green chemistry (Urucu *et al.* 2019). For this purpose, in the literature, various methods such as cloud point extraction (CPE) (Aydın Urucu *et al.* 2013; 2014), single drop microextraction (SDME) (Xiao *et al.* 2006), supramolecular solvent-based microextraction (SUSME) (Zhao *et al.* 2018), dispersive liquid-liquid microextraction (DLLME) (Fattahi *et al.* 2007), deep eutectic solvent-based microextraction (DESME) (Aracier *et al.* 2023), switchable solvent-based microextraction (SSME) (Aydın Urucu *et al.* 2021) and ionic liquid microextraction (ILME) (Altunay *et al.* 2019) have been employed for the extraction or preconcentration of numerous organic and inorganic analytes from different matrices.

In this study, the analysis of 4-nonylphenol in aqueous environments using GC-MS was performed with high sensitivity for the first time by employing the microextraction method with 1-undecanol. Optimum parameters were determined using undecanol-acetonitrile (ACN) as the extraction solvent mixture in dispersive liquid-liquid microextraction method to accurately analyze 4-NP in aqueous environment using GC-MS. The method was then applied to a real river water sample.

2. Material and Method

2.1 Material

4-nonylphenol (4NP) was purchased from Sigma, while 1-undecanol, acetonitrile (ACN), methanol (for GC), and sodium chloride (NaCl) were acquired from Merck.

2.2 Instrumentation

Gas chromatographic analysis were performed using an Agilent 5975C 7890 gas chromatographic system, and an HP 5973 mass employed for the identification and quantification of 4-nonylphenol in samples. Chromatographic experiments were conducted using an HP-5MS column having dimensions of 30m×250 µm i.d.×0.25 µm. A 1.0 µL sample volume was injected into the system using the splitless mode. High-purity helium served as the carrier gas, flowing at a rate of 1.0 mL min^{-1}. The column temperature program consisted of a single ramp from 110 °C (held for 1.0 min.) to 320 °C at a rate of 30 °C/min. (held for 3.0 min.), total run time is 11 minutes. The MS source and transfer line temperatures were set at 280 °C and 290 °C, respectively. For NP quantification, the selected ions were 107 and 220 (m/z). Compound identification was conducted using the Wiley 9N11 library on ChemStation and The Nist Mass Spectral Search Program (V2.0)

2.3 Sample

Samples of water, including both faucet water and river water, were gathered within Turkey. Each sample was then filtered using a membrane filter with a pore size of 0.45 µm. Subsequently, the filtered samples were stored in polyethylene bottles at 4 °C, away from light.

2.3 Extraction Procedure

Into a 15 mL conical falcon tube, 1 mL of a methanol solution containing 4NP at a concentration of 100 µg/L, along with 200 µL of 1-undecanol, was added. Additionally, the ionic strength was adjusted to 4% using a NaCl solution. Then, 0.2 mL of acetonitrile (ACN) was introduced, and the final volume was adjusted to 10 mL with distilled water. After 20 seconds mixing by vortex, the mixture was centrifuged at a speed of 6000 rpm for a duration of 10 minutes. Due to its lower density in compared to water, small droplets of 1-undecanol were observed to be floating on the surface of the aqueous solution. After the sample tube was cooled in an ice bath, the organic solvent solidified and adhered to the inner surface of the sample tube. The water phase was then carefully extracted using a pipette, while the organic phase was diluted by methanol to a final volume of 2 mL. Subsequently, to account for the possibility of the mixture containing traces of water, the mixture was evaporated with the nitrogen evaporating system until it reached the volume of the added 1-undecanol. After reconstitution with methanol (1 mL), the sample underwent filtration using a 0.45 µm filter and then introduced to GC-MS.

3. Results and Discussion

In this work, the DLLME (dispersive liquid liquid microextraction) technique combined with GC-MS was employed to detect 4-nonylphenol in water samples. Important parameters including the quantities of extraction solvents and the effect of salt were thoroughly investigated and optimized to achieve high enrichment factors.

3.1. Effect of 1-undecanol Amount

In the DLLME method, the choice of the extracting solvent plays a critical role in attaining elevated recovery rates and enrichment factors. The extracting solvent needs to exhibit specific characteristics, including minimal toxicity, limited water solubility, reduced volatility, a melting point near room temperature, and should not disrupt the analytical methods employed for the assessment of the substances. (Urucu *et al.* 2019). Therefore, 1-undecanol (m.p. ~14 °C) and 1-dodecanol (m.p. ~25.5

°C) were evaluated as potential extraction solvents. The use of 1-undecanol resulted in higher extraction efficiency compared to 1-dodecanol, leading to the selection of 1-undecanol as the preferred extraction solvent.

The impact of different volumes of 1-undecanol on the dispersive liquid-liquid microextraction (DLLME) of 4-NP was examined within the range of 50-250 µL, while maintaining the remaining analytical parameters constant. The findings indicated a swift augmentation in the analytical signal. within the range of approximately 50 to 100 µL of 1-undecanol, and then gradually increased within the range of 100-200 µL. However, beyond 200 µL, the analytical signal remained constant. Consequently, the enrichment factor decreased as the volume of 1-undecanol increased. The most favorable analytical response was achieved with a 200 µL quantity of 1-undecanol; consequently, this volume was selected for subsequent trials. (Figure 1).

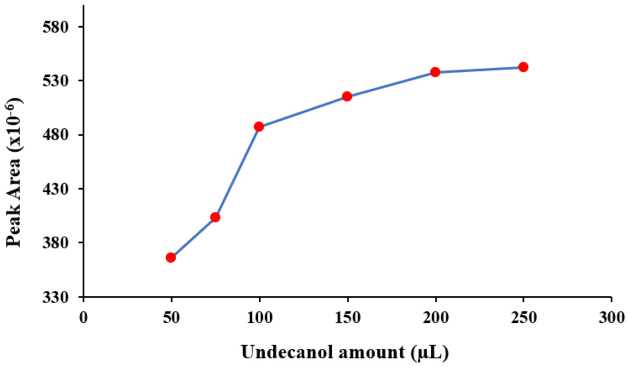


Figure 1. The effect of 1-undecanol amount on the extraction of 4NP.

3.2. Effect of Acetonitrile (ACN) Amount

Acetonitrile is an organic solvent that is miscible with water; therefore, it is commonly used to enhance the extraction efficiency when extracting organic compounds from aqueous environments using an organic solvent (Hu *et al.* 2021, Bakanov *et al.* 2023). In this study, to investigate the effect of acetonitrile on the extraction and enrichment efficiency, other parameters were kept constant while working with 50 - 500 µL of ACN. The extraction efficiency was observed to be low up to 200 µL and then showed a rapid increase between 200-300 µL, remaining constant thereafter (Figure 2). Therefore, the use of acetonitrile in the extraction process was found to enhance the extraction efficiency, and the optimum amount of ACN was determined to be 300 µL. Subsequent experiments were conducted using this amount.

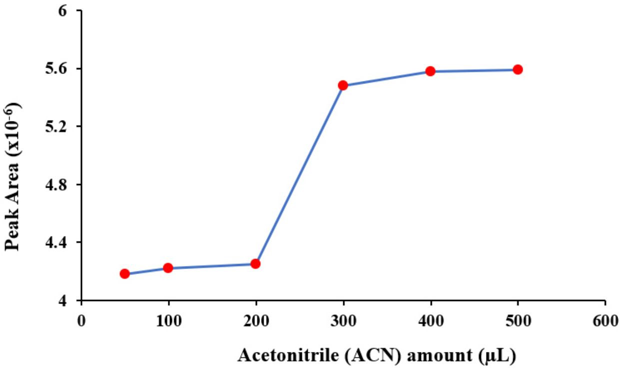


Figure 2. The effect of acetonitrile (ACN) amount on the extraction of 4NP.

3.3. Ionic strength of solutions

The ionic strength of aqueous solutions is determined by the concentration of dissolved ions and the ion charges in water, generally increasing as the ion concentration rises. Neutral salts are frequently employed to enhance the ionic potency of aqueous solutions. Ionic strength plays a significant role in the extraction of dispersed organic compounds using an organic solvent. As the ionic strength of the aqueous solution increases, the distribution of organic compounds in the aqueous phase decreases, resulting in an increased transfer to the organic phase (Xue *et al.* 2014). This effect, known as salting-out, can enhance the extraction efficiency by increasing the ionic strength of the aqueous solution with a neutral salt. In this study, the ionic strength of the aqueous solution was increased using a NaCl solution, and experiments were conducted with NaCl concentrations ranging from 1% to 5% to determine the optimal NaCl amount. As illustrated in Figure 3, the optimal NaCl concentration was found to be 4%."

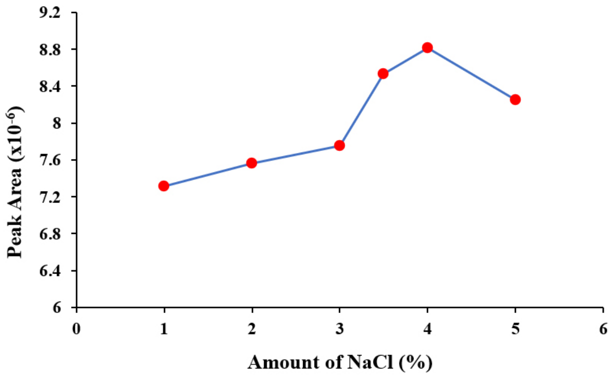


Figure 3. The effect of salt (NaCl) amount on the extraction of 4NP.

3.4. Influence of Sample Volume

The influence of sample volume on the extraction of 4NP was investigated across the range of 10 to 100 mL, employing model solutions prepared under optimum conditions. Complete retrieval of the analyte was accomplished for sample volumes reaching up to 75 mL. The preconcentration factor of 4NP was evaluated by computing the proportion between the maximum and minimum final sample volumes of 75 mL and 0.4 mL respectively, resulting in a factor of 188.

3.5. Analytical Parameters and Application to Real Samples

For quantitative gas chromatographic analysis, it is necessary to first observe the presence of 4NP using a specific chromatographic system and determine its retention time. In this study, under the chromatographic conditions provided in section 2.2, a peak corresponding to 4NP was observed in the chromatogram at a retention time of 6.13 minutes. Total ion chromatogram and library search reports for 4-nonylphenol were given in Figure 4.

On the other hand, Figure 5 displays the chromatogram and the obtained calibration curve for standard solutions prepared in the concentration range of 2-1000 µg/L for the quantitative analysis of 4NP. Based on the collected data, a linear calibration curve was established across a broad concentration range under the specified chromatographic conditions.

The GC-MS analysis of 4NP generated a calibration curve that exhibited linearity within the concentration range of 2-1000 µg/L, accompanied by a excellent correlation coefficient (R^2) of 0.9989. The calculated preconcentration factor, derived from the proportion of phase volumes, equated to 188. The method's limit of detection (LOD) was defined as 0.05 µg/L using the 3Sb/m approach (where Sb represents the standard deviation of the blank solution, with a sample size of n = 7, and m denotes the calibration curve slope). The relative standard deviations (RSD) obtained from seven replicates of 2 µg/L 4NP measurements were 2.8%. The precision of the suggested DLLME technique was evaluated employing the standard addition approach. Different quantities of 4-nonylphenol were added to river water and tap water samples, and the concentrations of 4-nonylphenol were subsequently determined using the developed extraction procedure. The results and recoveries are displayed in Table 1, indicating a strong agreement between the obtained results and the added values.

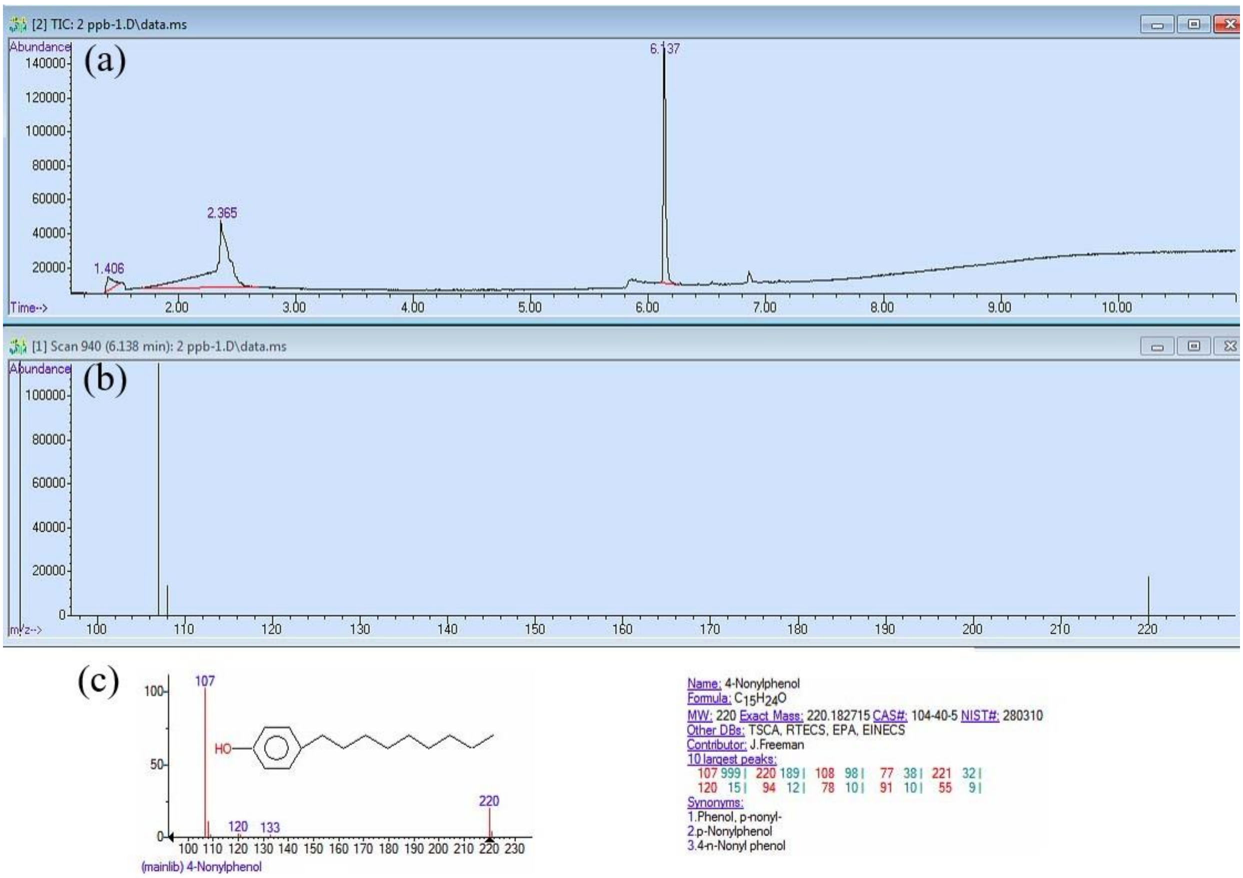
Table 1. Determination of 4-Nonylphenol in Water Samples

Sample	Added amount of 4NP (µg/L)	Detected concentration of 4NP (µg/L)	Recovery (%)
Faucet water	0	n.d.	n.d.
	2	1.92	96.40±0.5
	10	9.89	98.92±0.3
	20	19.85	99.27±0.1
River water	0	n.d.	n.d.
	2	1.93	96.60±0.6
	10	10.26	102.60±0.5
	20	20.24	101.17±0.1

4. Conclusion

In this study, a highly sensitive, simple, and environmentally friendly method is proposed for the dispersive liquid-liquid microextraction followed by GC-MS analysis of 4-nonylphenol, a concerning environmental contaminant in aqueous environments. The extraction process was carried out using 1-undecanol in the presence of acetonitrile, under a 4% NaCl environment. After the extraction process. GC-MS analysis of 4-

nonylphenol was completed in a short 6-minute retention time. The proposed procedure exhibits a low detection limit of 0.05 µg/L and excellent R.S.D. values of 2.8%. Furthermore, the technique was applied to actual samples, including faucet water and river water, and it exhibited recoveries of nearly 100% in the analyses. With an enrichment factor of 188, the method is believed to be a highly effective approach for the analysis of 4-nonylphenol in aqueous environments.



Name: 4-Nonylphenol
Formula: $C_{15}H_{24}O$
MW: 220 Exact Mass: 220.182715 CAS#: 104-40-5 NIST#: 280310
Other DBs: TSCA, RTECS, EPA, EINECS
Contributor: J.Freeman
10 largest peaks:
107 999 | 220 189 | 108 98 | 77 38 | 221 32 |
120 15 | 94 12 | 78 10 | 91 10 | 55 9 |
Synonyms:
1.Phenol, p-nonyl-
2.p-Nonylphenol
3.4-n-Nonyl phenol

Figure 4. Total Ion Chromatogram (a), mass spectrum (b) and Library Search Report (c) for 4-Nonylphenol.

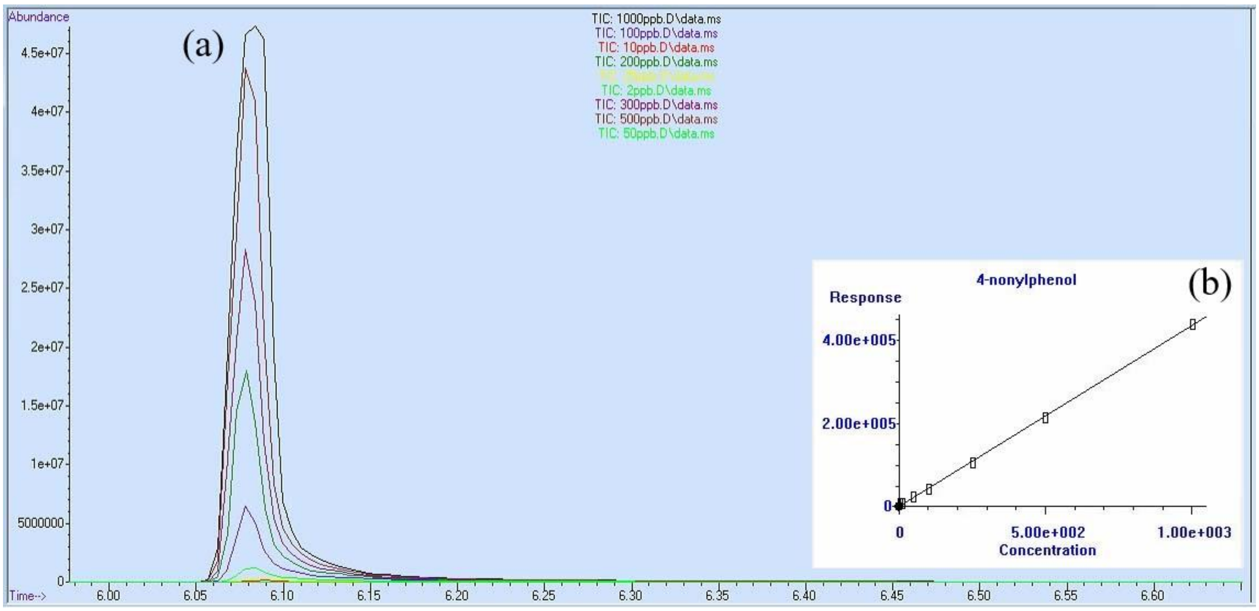


Figure 5. Chromatograms of Calibration Standards (a) and Calibration Curve (b) of 4-Nonylphenol.

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