# SPECTROPHOTOMETRIC DETERMINATION OF FOUR NAPHTHALENE SULFONATES IN SEAWATER AFTER THEIR MOLECULARLY IMPRINTED STIR BAR SORPTIVE EXTRACTION

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## ABSTRACT

A novel 1- naphthalene sulfonic acid (1-NS) molecularly imprinted polymer (MIP)-coated stir bar for sorptive extraction of four naphthalene sulfonates (NSs) from seawater samples was prepared. 1-NS was applied as template molecule. The extraction conditions, including pH, the absorption and desorption times, stirring speed, amount of NaCl and temperature were optimized and the optimum conditions were established as: the absorption and desorption times were fixed respectively at 10 and 15 min, stirring speed was 600 rpm, pH was adjusted to 4.1, amount of NaCl was 1 mol $L^{-1}$ and extraction process was performed at a temperature of 45 $^0$C. The linear ranges were 5-250 µg $L^{-1}$ for 3, 6-NDS-1-OH (1-naphthol-3,6-disulfonic acid), 2-NS (2-naphthalene sulfonate) and 1-NS and 10-250 µg $L^{-1}$ for 5-$NH_2$-1-NS (5-Amino-1-naphthalenesulfonic acid). The detection limits were within the range of 1.20- 2.97 µg $L^{-1}$. Under the optimum conditions, with the enrichment factor of the NSs were 27, 10, 14 and 7 fold for 2-NS, 1-NS, 3, 6- NDS-1-OH and 5-$NH_2$-1-NS respectively. The RSDs was within 1–9.4%. The method is very suitable for the determination of naphthalene sulfonates (NSs) in seawater samples.

**Keywords:** Naphthalene sulfonates, molecularly imprinted polymer coated stir bar (MIPSB), Seawater, Chabahar Bay.

## INTRODUCTION

Naphthalene sulfonates (NSs) are aromatic compounds including H-acid with low biodegradability, high polarity and high toxicity [1, 2]. Naphthalene sulfonates are frequently used as solubilizing and dispersing agents in a wide range of industrial product formulations including optical brighteners, pesticides, tanning agents, azo dyes, ion exchange resins, pharmaceuticals and plasticizers [2-4]. The presence of at least one sulfonated group $SO_3^-$ makes these compounds very resistant towards oxidative attack, highly water soluble and mobile. Hence, after production and application in different industrial sectors, naphthalene sulfonates easily enter environmental waters and do not significantly sorb onto sediments or soil [2]. NSs have been found in wastewater effluents, surface waters, landfill leachates, and even in tap and drinking water and these pollutants are not easily eliminated from water with conventional methods [4, 5]. All these properties make them potentially hazardous for aquatic environment such as surface and ground waters. The presence of these compounds in the environment can be due to their use in the chemical industry [1, 5]. For these reasons, NSs have been investigated for some time and several analytical methods such as reversed phase liquid chromatography [1], capillary zone electrophoresis [4], spectrophotometry [5], high performance liquid chromatography/mass spectrometry (HPLC-MS) [6] and gas chromatography/mass spectrometry (GS-MS) [7] have been developed to determine them in environmental water.

Therefore, pre-concentration and detection of toxic NSs is of intense current interest in toxicological research and environmental cleanup and the developments of new methods for quantifying trace amounts of NSs in aquatic environment are required. This is mainly due to their low concentrations in the water sample or the severe matrix interferences in real samples such as seawater. Employing extraction before analytical analysis, can overcome these disadvantages, because it can pre-concentrate the analytes and also eliminate the interfering elements at the same time.

Molecularly imprinted polymers (MIPs) are a chemical technique involving covalent and/or non-covalent bond formations between templates and monomers having interacting functional groups. The template creates a specifically imprinted groove in the polymeric network during the course of polymerization. Finally, eluting template molecules away from the polymer leaves several grooves with a permanent memory to the recognition of the target molecule (template) [9-11]. Recently, this method involved as new selective sorbents for solid-phase extraction (SPE) of organic and inorganic compounds in complex matrices due to its stability, ease of preparation, low cost and specific recognition for the template molecules [12-14].

For NSs extraction, Ion-pair solid-phase extraction (ion-pair SPE), molecularly imprinted polymers (MIP), anion-exchange, polymeric and organic carbon solid phases are used [1, 5, 9]. Solid- phase microextraction (SPME) has been widely applied for the analysis of environmental and biological samples that coupled with gas chromatography (GC) and high-performance liquid chromatography (HPLC). This technique typically use conventional chromatographic stationary phases coated on fibers to extraction analytes [15, 16]. In 2001 were introduced the simplest way of combining SPME technology with MIPs that the method involved packing a capillary with the MIP particles for in-tube SPME by Mullet et al [17]. Therefore, this method requires the use of extra instrumentation and has other important drawbacks such as the lack of compatibility between the solvent needed to desorb template (analytes) from the MIP and the mobile phase applied [13, 17].

A sorptive extraction procedure to use a polydimethylsiloxane (PDMS) sorbent as the coating was first introduced in 1999 with Baltussen et al. derived from SPME and called stir bar sorptive extraction (SBSE) [18]. The method utilizes glass stir bars coated by PDMS for extract nonpolar compound from water sample. SBSE is based on the same principles as those of SPME. Nevertheless, this possesses a better recovery for its larger volume and surface area and sample capacity [18-20]. Since only the PDMS is available as sorbent on commercial stir bar and shows better affinities to nonpolar and weakly polar compounds, attempts have been made for applying other coatings especially for more polar analytes [13, 20-21].

In this paper, a novel NSs molecularly imprinted polymer -coated stir bar (MIPSB) was prepared for extraction of NSs from seawater. The extraction conditions were optimized and a method for determination NSs by MIP-coated stir bar coupled with UV spectrophotometry was developed. Spiked sample analysis was performed for the evaluation of MIP-coated stir bar sorptive extraction. MIP was synthesized using a combination of 4-vinylpyridine (VP) as the functional monomer, ethylene glycol dimethacrylate (EDMA) as the cross-linker and 2, 2'- azobisisobutyronitrile (AIBN) as the initiator and 1-naphthalene sulfonic acid as the template molecule.

## EXPERIMENTAL

### Reagents and materials

VP, EDMA, sodium 2-naphthalene sulfonate (2-NS), 1-naphthol-3,6-disulfonic acid disodium salt (3,6-NDS-1-OH), 5-Amino-1-naphthalenesulfonic acid (5-$NH_2$-1-NS) AIBN and 1- naphthalene sulfonic acid dehydrate (1-NS) used for the polymer syntheses were purchased from Sigma-Aldrich (St. Louis, MO, USA). All salts, acids and organic solvents were of analytical grade and were obtained from Merck KGaA (Germany) and used as received. Naphthalene, phenol (ph), 4- nitrophenol (4-NP), 2- chlorophenol (2-CP) and 4- chlorophenol (4-CP) were obtained from Fluka AG, Switzerland and used to check the selectivity of MIPSB. A stock solution of NSs (500 mg.$L^{-1}$) was separately obtained by dissolving the proper amount of each NSs in water in a 50 mL flask and diluting to the mark. Work solutions were prepared daily with suitable dilution of this solution. The 2- NS was solubilized in 70:30 (V/V) water/ methanol. The stir bar (15 mm × 2 mm i.d.) was prepared by putting an iron bar into a glass tube. Then the two ends of the glass tube were sealed by heat.

Figure 1 shows the structurally related four naphthalene sulfonates used in his paper.

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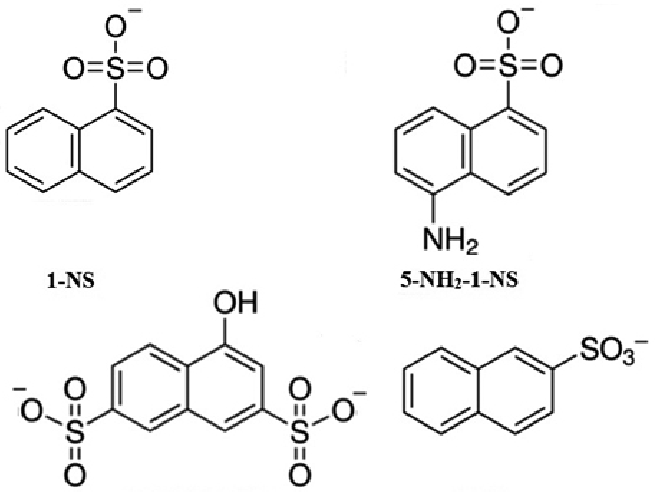

**Figure 1.** Chemical structure of the four naphthalene sulfonates used in this paper.

**Apparatus**

Spectrophotometry was carried out on a photonix Ar model 2015 UV–Vis spectrophotometer (Iran) at the wavelength of 210 nm. The IR spectra of NIP, leached and unleached 1-Ns imprinted polymers particles and stir bar were characterized by a Shimadzu model 680 (Japan) infrared spectrometer.

**Pretreatment of the stir bar**

The bare glass bar was sequentially cleaned by distilled water, for make its surface active for silanization and subsequent polymerization, it was treated with 1.0 mol $L^{-1}$ NaOH for 8 h, redistilled water for 1 h, 1.0 mol $L^{-1}$ HCl for 1 h and rinsed again with water and dried for 1 h in an oven (150 $^{0}$C). Double bonds were created on the glass surface of the bar by procedures reported previously with putting it for 3h in a 25% (V/V) 3- (methacryloxy) propyltrimethoxy silane solution in acetone at room temperature. Finally, the stir bar was washed with methanol and dried with a stream of nitrogen [13].

**Preparation of MIPSB**

The MIPSB was prepared by the procedure for the coating of the stir bar with MIP is illustrated in one of our previous reports [13]. MAA (0.34 mL), EDMA (2.93 mL) and AIBN (166.66 g) were added to 13.33 mL of methanol/water (4:1, V/V) in a 25- mL flask.

Then, the pretreated stir bar was injected into the reaction mixture and deoxygenized with a nitrogen stream for 5 min. The solution was ultrasonicated for 10 min and sealed and then kept at 60 $^{0}$C for 8 h in a water bath. After the polymerization, the MIPSB was removed from the bath and rinsed with 0.5 mol $L^{-1}$ HCl in order to remove the template from it [1, 13]. A blank stir bar coated with non-imprinted polymer (NIP) was prepared under the same way in the absence of the template (1-NS) [1, 13]. There are hydrogen bonding or ionic interactions between templates and the functional monomers.

As shown in Figure 2, the MIP coating was covalently attached to the stir bar surface via the double bonds. Double bonds were created on the glass surface of the bar using 3- (methacryloxy) propyltrimethoxysilane as a coupler prior to MIP synthesis. Upon radical formation, initiated thermally, the polymerization reaction was carried out.

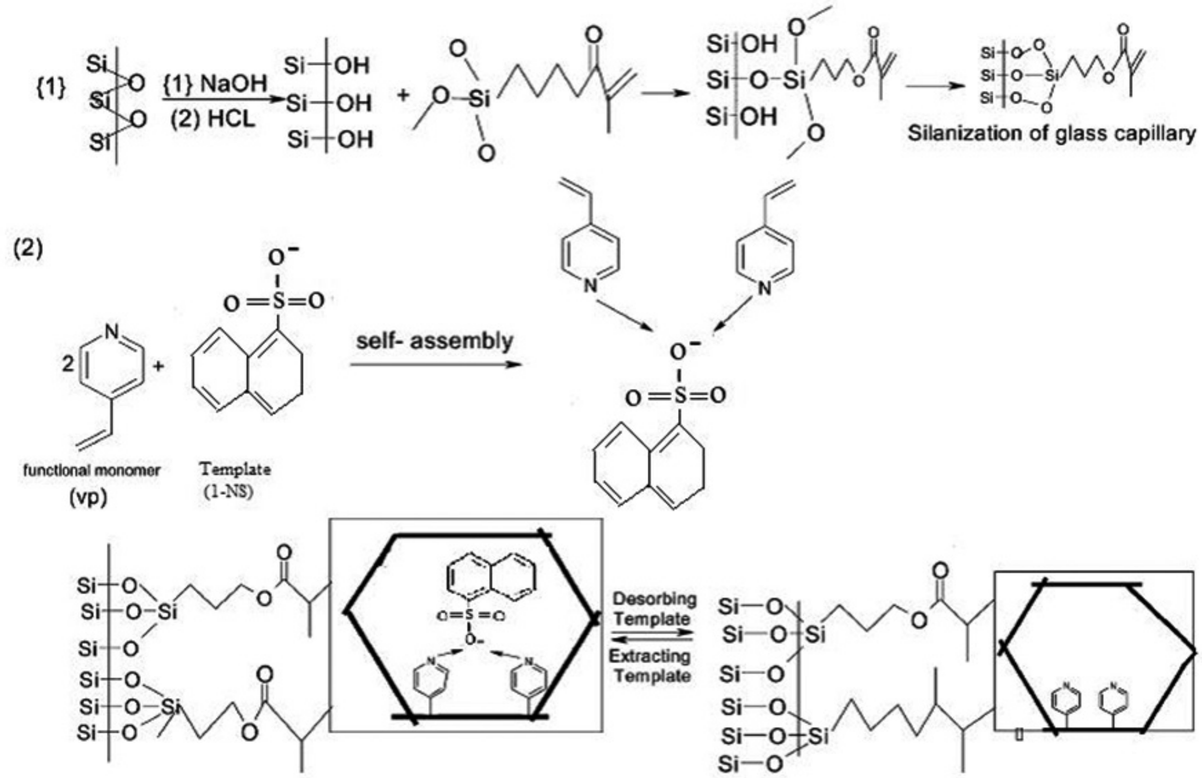

**Figure 2.** Schematic diagram of the preparation of MIPSB using 1-NS as the target molecule. (1) Silanization of stir bar and (2) coating of 1- naphthalene sulfonic acid MIP-coated stir bar.

**MIPSB procedure**

10 mL of aqueous solution containing four NSs was added into a 10-mL round bottom flask and the pH was adjusted to 4.1 by drop wise addition of either 1 mol $L^{-1}$ of sodium hydroxide or hydrochloric acid in concentration of 1 mol/L. Then 0.59 g of NaCl was added and The MIPSB was immersed in the solution, and stirred at 600 rpm for 10 min at room temperature. After extraction was completed, the MIPSB was removed from the solution, gently dried with tissue paper, and immersed in 5 mL of acetonitrile in a glass vial and stirred at 600 rpm for 15 min at 45 $^{0}$C. Finally, the eluent was then directly introduced into UV–Vis spectrophotometer for detection.

## RESULTS AND DISCUSSION

### Infrared spectra

The IR spectra of NIP, leached and unleached 1-Ns imprinted polymers particles and stir bar were characterized by using KBr pellet method (Figure 3). As is obvious, in the region of 1638-1648 cm$^{-1}$, no absorption band is present which shows the absence of vinyl groups in the polymer materials. Lack of absorption in this range confirms the complete polymerization of VP [13]. Meanwhile, there is distinct difference between the IR spectra of the NIP, leached and unleached polymer.

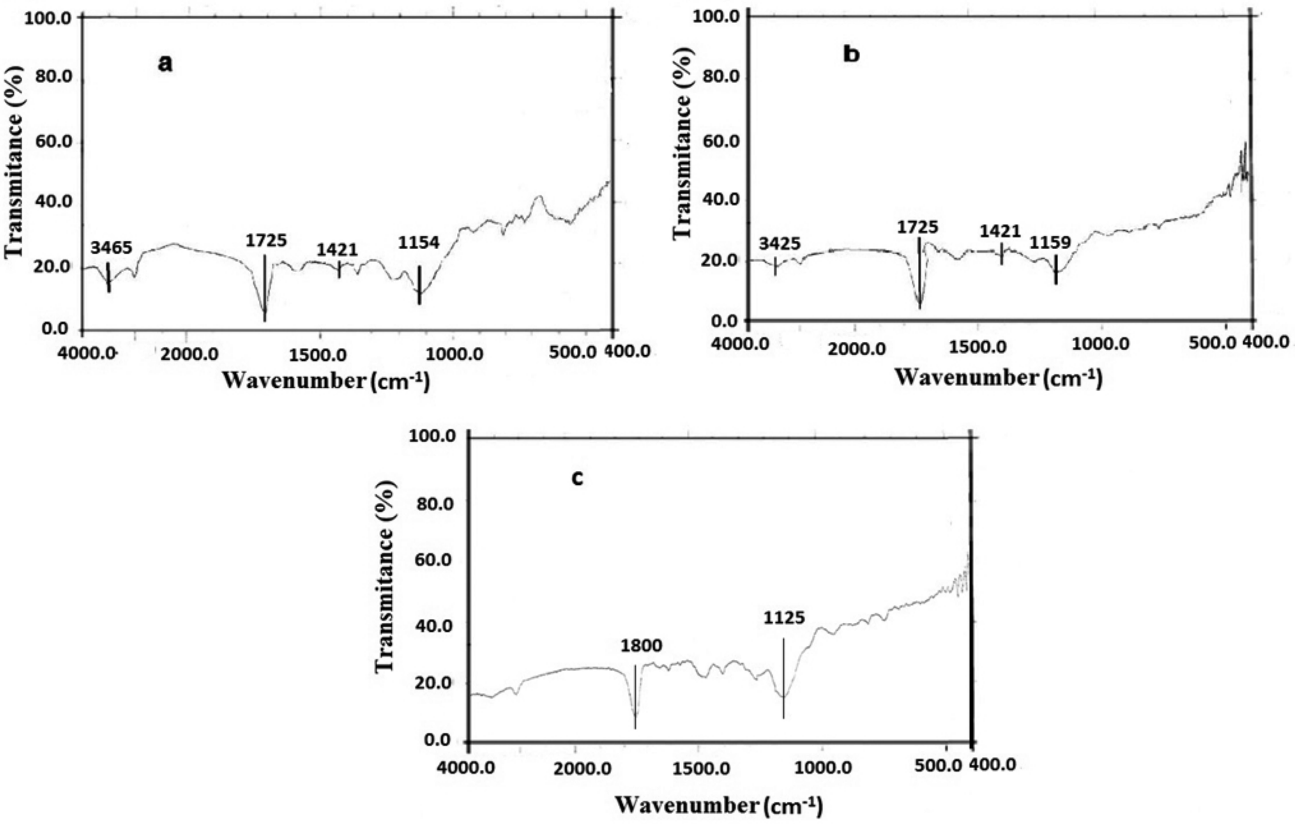

**Figure 3.** Infrared spectra of leached (a) and unleached (b)1- NS imprinted polymer material and (c) non-imprinted polymer.

### Optimization of MIPSB for NSs extraction

In order to optimize the MIPSB extraction operating conditions for four NSs analysis, numerous parameters that could influence on the MIPSB extraction were studied in 500 µg L$^{-1}$ of a standard of NSs in water sample.

### Selection of the optimum pH

The effect of pH on the absorption of NSs from water samples on the prepared stir bar was investigated in detail. Sample solutions were adjusted to a pH range of 2.0 – 8.5 and subjected to the general procedure. The retained NSs was stripped off from the stir bar and determined by UV–Vis spectrophotometer. Figure 4 is the effect of pH on the extraction of NSs by MIPSB. As could be seen, the adsorption percentage was increased with the increase of pH from 2.0 to 4.1 and the recovery was at the highest point at a pH of 4.1. Thus, the pH of 4.1 was selected for the extraction of NSs by MIPSB in the further experiments. The compounds were strongly retained on the MIP when the sample was prepared in acidified water. This observation is presumably a reflection of the fact that electrostatic interactions between the analytes and the pyridyl group residues in the polymer would be expected to have higher affinity at the lower pH value. It is possible that, at the very low pH, the enhanced hydrophobic effect in sorption (the hydrophobic of proton-solfonate ion pair is higher than anionized sulfonate) compensates for the impeded electrostatic interaction to MIPSB (pKa of the analytes studied are between 0.17 and 2.68). At the very high pH the hydroxide ion could effectively compete for the organic cationic group, thereby lowering sorption of anionized sulfonate.

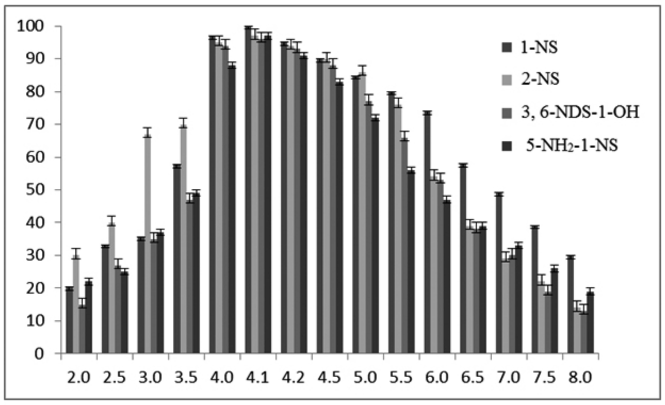

**Figure 4.** Effect of pH on extraction efficiency of NSs.

### Choice of the elution solvents

Five-milliliter volumes of different elution solvents such as methanol/ acetonitrile (50/50), acetonitrile, methanol/ $H_2O$ (50/50), methanol, methanol/ $H_2O$ (4:1) 20% NaOH 1 mol/L, methanol/ $H_2O$ (4:1), methanol/ $H_2O$ (4:1) 10% NaOH 1 mol/L, HCl (0.5 mol/L), methanol/ acetic acid (1:1) and methanol/ acetic acid (4:1) were selected to optimize extraction solvent by using 500 µg L$^{-1}$ NSs standard solution. The highest extraction amount was achieved in acetonitrile. That's probably because acetonitrile is a polar aprotic solvent with relatively high dielectric constant which can easily elute highly polar NSs.

**Effect of adsorption and desorption time**

The adsorption (extraction) and desorption time were optimized. The adsorption time was varied from 5 min to 15 min. Results indicated that the extraction equilibrium reached at 10 min.

Desorption time was also investigated from 5 to 20 min. The results showed that the percent recovery of NSs increases as desorption time increases and reaches a maximum at 15 min. The percent extraction of NSs increases as the adsorption time increases and reaches a maximum at 10 min. So 10 min and 15 min were selected for extraction and desorption procedures.

**Effect of stirring rate**

Effect of stirring rate was also studied. The increasing of stirring rate could enhance the extraction amounts. The experimental results indicated that the extraction efficiency increases by increasing the stirring rate up to 600 rpm and then remains constant. SBSE is an extraction technique which is based on equilibrium. This equilibrium can be achieved faster by high speed stirring. Therefore at a predetermined time, increasing the speed leads to an increment in extraction. After reaching the equilibrium point, any increase in the speed of agitation has no more effect on the amount of the analyte extracted, so the signal will be independent of agitation from this point. Consequently, 600 rpm was selected as optimum stirring speed.

**Effect of temperature**

The extraction efficiency increased with an increase in temperature and became constant after 45 °C. This might be due to the breaking of adsorptive forces between the active sites of the imprinted polymer and analytes (NSs).

**Effect of NaCl**

The ionic strength on the extraction efficiency was investigated by adding different amounts of sodium chloride (NaCl) ranging from 0.25 to 1.25 mol /L. Results showed that the extraction equilibrium reached at 1 mol /L. So, following research were carried out by saturation of the samples by NaCl.

**Analytical performance**

**Linearity, limit of detection and enrichment factor**

Under the optimum conditions, the calibration curve was linear over a concentration range of 5-500 µg L$^{-1}$ for 1-NS, 2-NS and 3,6-NDS-1-OH and 10-500 µg L$^{-1}$ for 5-NH$_2$-1-NS. The least square equation over the dynamic linear range is presented in table 1. The percent extraction (E%) of NSs was obtained from the following equation:

$E\%=100\ (C_B/C_A)$

Where $C_A$ and $C_B$ are the concentrations of four NSs in solution before and after extraction.

Under the optimal experimental conditions, the limits of detection (LODs) obtained from 3S$_d$ (blank) /m were found to be in the range of 1.27 (1-NS)- 1.25 (2-NS)- 1.20 (3,6-NDS-1-OH)- 2.97 (5-NH$_2$-1-NS) µg L$^{-1}$; where S$_d$ is the standard deviation of 5 consecutive measurements of the blank and m is the slope of the calibration curve. As shown in Table 1, the enrichment factors (defined as the ratio of calibration curve slopes after and before MIPSB extraction) were obtained 27 fold for 3,6-NDS-1-OH, 10 fold for 2-NS, 14-fold for 1-NS and 7-fold for 5-NH$_2$-1-NS respectively (Table 1). In table 2 this work compared with other extraction methods reported in the literatures for NSs determination.

**Table 1**. Analytical figure of merit for MIPSB coupled with UV for the detection of NSs.

| Analyte | Linearity Range (µg/L) | Equation of calibration curve[a] | determination coefficient (R$^2$) | Limit of detection (µg/L) | Enrichment factor |
|---|---|---|---|---|---|
| 3, 6- NDS- 1- OH | 5- 500 | A = 1.6193 C-0.0019 | 0.9974 | 1.20 | 27 |
| 2- NS | 5- 500 | A = 1.5606 C-0.0056 | 0.9942 | 1.25 | 10 |
| 1- NS | 5- 500 | A = 1.864 C-0.0055 | 0.9952 | 1.27 | 14 |
| 5-NH$_2$-1-NS | 10- 500 | A = 0.2018 C-0.0004 | 0.9944 | 2.97 | 7 |

Where C and A are the concentrations of NSs, ion and UV response, respectively.

**Sensitivity**

In order to further investigate the recognition ability of MIPSB over NIPSB to the target molecule, the same NSs solutions containing all analytes were extracted using both MIPSB and NIPSB (Figure 5). The percent extraction of MIP-coated stir bar were investigated with NSs standard solutions. The NIP-coated stir bar was used for comparison. As shown in Fig. 5, the percent extraction of MIP-coating was much higher than that of NIP-coating and enhancement of sensitivity of MIPSB is obvious.

**Table 2.** Comparison of the published methods for NSs determination with the proposed method in this article.

| Method | NS determind | Detection method | LOD (µg L$^{-1}$) | Linear range (µg L$^{-1}$) | Ref |
|---|---|---|---|---|---|
| SPE | 1-NS, 2-NS, 2, 7- NDS, 1-NS-4- OH, 1-NS-2- NH$_2$, 1, 5- NDS-2-NH$_2$, 1, 5- NDS and 3, 6-NDS- 1- OH | HPLC | NM* | 5- 100 | 1 |
| SPE | 1-NS, 2-NS and DPA-4-S | Capillary zone electrophoresis | NM | 1-20 | 3 |
| Online ion pair solid phase extraction | 2-NS, 2, 7- NDS, 1, 5- NDS, 1-NS-2-NH$_2$, 2, 6- NDS, 6-NH$_2$-4-OH-2-NS, 5-NH$_2$-1-NS, 7-NH$_2$-4-OH-2-NS, 4-NH$_2$-1-NS, 5-NH$_2$-2-NS, 1-NS-4- OH and 8-NH$_2$-2-NS, | Ion pair liquid chromatography with fast scanning fluorescence detection | NM | 0.07- 15.00 | 4 |
| SPE | 1-NS, 2-NS, 1, 5- NDS, 1, 6- NDS, 2, 6- NDS and 2, 7- NDS | HPLC | NM | 0.007- 2.00 | 6 |
| MIPSB | 1-NS, 2-NS, 5-NH$_2$-1-NS and 3, 6-NDS- 1- OH | UV | 0.32- 0.95 | 5- 500 | This work |

* Not mentioned

*Abbreviations*: (SPE) solid phase extraction, (2, 7-NDS) naphthalene-2,7-disulfonic acid, (1-NS-4- OH) 4-naphthol-1-sulfonic acid, (1-NS-2- $NH_2$) 2-naphthylamine-1-sulfonic acid, (1, 5- NDS-2-$NH_2$) 2-naphthylamine-1,5-disulfonic acid, (1, 5- NDS) naphthalene-1,5-disulfonic acid, (DPA-4-S) diphenylamine-4-sulfonate, (1, 5- NDS) 1,5-naphthalene disulfonate, (2, 6-NDS) 2,6-naphthalene disulfonate, (6-$NH_2$-4-OH-2-NS) 6-Amino-4-hydroxy-2-naphthalenesulfonate, (1,6-NDS) 1,6-naphthalene disulfonate, (5-$NH_2$-1-NS) 5-Amino-1-naphthalenesulfonate, (7-$NH_2$-4-OH-2-NS) 7-Amino-4-hydroxy-2-naphthalenesulfonate, (4-$NH_2$-1-NS) 4-Amino-1-naphthalenesulfonate, (5-$NH_2$-2-NS) 5-Amino-2-naphthalenesulfonate, (8-$NH_2$-2-NS) 8-Amino-2-naphthalenesulfonate.

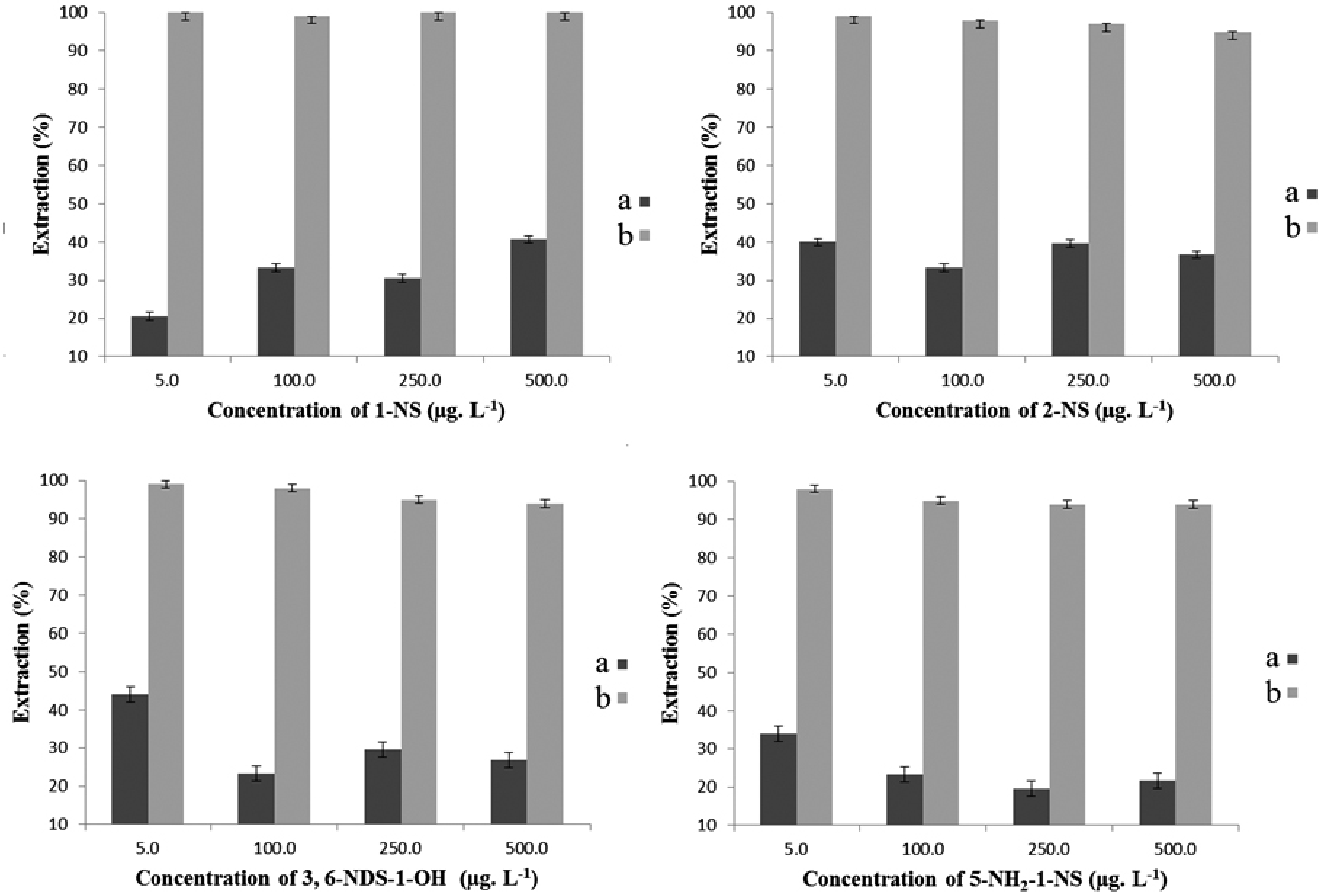

**Figure 5**. Behavior of the NIP-coated stir bar *(a)* and *(b)*MIP-coated stir bar for four NSs uptake at different concentrations of NSs.

**Selectivity of naphthalene sulfonates MIPSB**

Five compounds, naphthalene, phenol, 4- nitrophenol, 2- chlorophenol and 4- chlorophenol were applied for selectivity studies. for selectivity studies MIPSB for the extraction of four NSs in the solutions contain similar compounds, aliquots of 10 mL of aqueous solution containing 5 µg of each of the analytes and potential interferences was taken and the proposed procedure was followed. Compounds were used in this study without any interference.

**Determination of naphthalene sulfonates in Chabahar Bay**

In order to assess the applicability of the method to real samples with different matrices, it was applied to the extraction and separation of NSs from 10 mL of four different samples taken from five stations beside Chabahar Bay (southern east of Iran) and each one spiked at the concentration of 20 µg $L^{-1}$ with the target analytes. Moreover, MIP-coated stir bar could eliminate the matrix interferences successfully. The recoveries for 5 stations are presented in Table 3. Reproducibility of the method (as RSD %) was within 1-9.4%. These results indicate that the developed method can be successfully applied for the determination of NS in very complicated matrices such as seawater samples.

The proposed MIPSB could be used at least 50 times without apparent damage and kept in dried air for 8 months without reduce of extraction ability. The repeatability between MIPSB (n=5) was obtained to be better than 6 %.

## CONCLUSION

In this work, a novel 1-NS molecularly imprinted polymer (MIP)-coated stir bar was prepared for the selective extraction of four NSs in seawater samples. This method shows that proposed MIPSB for the separation of NSs has the potential to be a new type of carrier. Under the optimized extraction conditions, the MIPSB showed much higher extraction than that of the NIP coated stir bar. The linear ranges had a wide concentration and the MIPSB could selective extract NSs for analysis even at the low concentration of 20 µg /L. The MIPSB has the advantages of easy to prepare, repeatability and rapid separation, low cost, with high extraction capability and good selectivity in complex matrix. The MIPSB could be used for at least 50 times extraction without substantial change in the absorption signal.

**Table 3.** Recovery results for seawater samples obtained from 5 different locations of Chabahar Bay (Iran).

| Analyte added | Sampling location | Recovery % at spiked level of 20 (μg $L^{-1}$) | NSs found (μg $L^{-1}$) | RSD (%)[**] |
|---|---|---|---|---|
| 1-NS | Station1, Chabahar Maritime University[*] | - | 0.30 | 1 |
| | Chabahar Maritime University | 97.9 | 19.87 | 2.10 |
| | Station 2, Konarak[*] | - | 0.26 | 3.47 |
| | Station 2, Konarak | 94.0 | 19.05 | 4.86 |
| | Station3, Tis[*] | - | 0.43 | 3.55 |
| | Station3,Tis | 84.2 | 17.20 | 2.95 |
| | Station 4, Kalantary[*] | - | 0.23 | 1.5 |
| | Station 4, Kalantary | 90.5 | 18.30 | 1.7 |
| | Station 5, Beheshti[*] | - | 0.52 | 1.3 |
| | Station 5, Beheshti | 97.9 | 20.10 | 1.1 |
| 2-NS | Station1, Chabahar Maritime University[*] | - | 0.36 | 2.5 |
| | Station1, Chabahar Maritime University | 98.2 | 20.00 | 1.8 |
| | Station 2, Konarak[*] | - | 0.41 | 2.0 |
| | Station 2, Konarak | 94.2 | 19.23 | 3.4 |
| | Station3, Tis[*] | - | 0.26 | 3.5 |
| | Station3, Tis | 89.3 | 18.10 | 6.8 |
| | Station 4, Kalantary[*] | - | 0.46 | 1.1 |
| | Station 4, Kalantary | 98.2 | 20.09 | 4 |
| | Station 5, Beheshti[*] | - | 0.53 | 3.1 |
| | Station 5, Beheshti | 81.8 | 16.80 | 4 |
| 3, 6- NDS- 1-OH | Station1, Chabahar Maritime University[*] | - | 1.85 | 4.5 |
| | Station1, Chabahar Maritime University | 96.1 | 21.00 | 4.9 |
| | Station 2, Konarak[*] | - | 1.74 | 2.5 |
| | Station 2, Konarak | 92.4 | 20.09 | 9 |
| | Station3, Tis[*] | - | 1.62 | 3.5 |
| | Station3, Tis | 86.4 | 18.69 | 1.6 |
| | Station 4, Kalantary[*] | - | 2.15 | 1.8 |
| | Station 4, Kalantary | 99.5 | 12.09 | 2.1 |
| | Station 5, Beheshti[*] | - | 1.16 | 2.2 |
| | Station 5, Beheshti | 90.7 | 19.20 | 2.5 |
| 5-$NH_2$-1-NS | Station1, Chabahar Maritime University[*] | - | 1.63 | 2.8 |
| | Station1, Chabahar Maritime University | 97.5 | 21.10 | 9.4 |
| | Station 2, Konarak[*] | - | 1.16 | 2.1 |
| | Station 2, Konarak | 95.0 | 20.09 | 4.6 |
| | Station3, Tis[*] | - | 0.93 | 1.3 |
| | Station3, Tis | 86.72 | 18.15 | 5.2 |
| | Station 4, Kalantary[*] | - | 0.58 | 2.6 |
| | Station 4, Kalantary | 83.58 | 17.20 | 3 |
| | Station 5, Beheshti[*] | - | 1.74 | 2 |
| | Station 5, Beheshti | 84.33 | 17.49 | 6 |

* No spiking

** RSD, relative standard deviation, for seven replicate measurements

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