

RESEARCH PAPER

# A sandwich-type three-dimensional layered double hydroxide nanosheet array as a novel fiber coating for headspace solid-phase microextraction of phenols from water samples

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## ABSTRACT

In the present study, graphene oxide nickel-titanium layered double hydroxide (NiTi-LDH/GO) was synthesized. NiTi-LDH/GO was used as a fiber coating for the determination of phenolic compounds for headspace solid-phase microextraction methods in water samples. These extracted components were introduced into a gas chromatography-mass spectrometry (GC-MS) injection port for further analysis. The following analytical merits were used under optimal conditions: temperature of extraction: 80 °C, desorption duration: 2 min, extraction time: 40 min, temperature time: 270 °C, salt concentration: 10% (w/v), 0.01–100 µg L<sup>-1</sup> and 0.004–0.09 ng mL<sup>-1</sup> for dynamic linear rang (DLR) and limit of detection (LOD), respectively. The repeatability under optimal conditions for one fiber (n = 3) is given as the relative standard deviation (R.S.D. %) which was between 6.5 % and 9.9% for these compounds. The results of the experiments clearly indicate that the NiTi-LDH /GO nanostructure fiber is an appropriate choice for HS-SPME of phenols analysis. By combining HS-SPME using NiTi-LDH /GO nanostructure fiber and GC-MS, low LODs can be achieved which can be used for determining phenols from water samples.

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## INTRODUCTION

Layered double hydroxide (LDH) is defined as the non-organic layered anionic clay, which is generally given using the relation  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} [A^{n-}]_{x/n} \cdot mH_2O$ , where M<sup>3+</sup> and M<sup>2+</sup> denote trivalent and divalent metal cations, and A<sup>n-</sup> indicates an interlayer anion. LDHs have been investigated because of their possible application in various significant fields, including polymerization, catalysis, biomedical science, environmental application, electrochemistry, and magnetization in laboratory and industrial scales. The common approaches utilized for the preparation of LDHs allow confined control

over the size of particles, morphology, pore architectures, and surface area. These parameters define the practical performances. Easy tuning of the chemical composition of LDH configuration is the main advantage. Mainly, hybrid materials can be created due to the potential intercalation of organic anions. Thus, the application areas of LDH structures could be extended and they can be used as multifunctional materials, compatible inorganic fillers, and supported catalysts. Various attractive carbonaceous materials can be accessed by carbonization of these hybrid layered materials in inert conditions and elimination of the inorganic side by acid demineralization [1].

Solid-phase microextraction (SPME) is a

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straightforward and low-cost approach which does not involve any organic solvents. It is the capability of SPME for integrating steps of sampling, extracting, pre-concentration, and sample representation as a single one. Thus, this method has drawn considerable attention, and it is known as an exciting alternative to conventional sampling methods, especially for semi-volatile and volatile compounds [2-14].

We synthesized a new sandwich-like configuration through growing NiTi-LDH / GO nanosheets (NSs) in situ on the reduced GO. We believe that LDH modulation on graphene oxide provides a new nanostructure which can be an innovation for expanding the solid-phase microextraction method. To this end, we tested phenols as models in aqueous samples at a trace level. The factors affecting the efficiency of selected phenolic compounds extraction were investigated and optimized. These factors include the temperature of the sample, pH, ionic strength, extraction duration, and stirring rate.

## EXPERIMENTAL

### Chemicals and reagents

Phenol, 4-chlorophenol, 2, 4-dichlorophenol, 3-nitrophenol, 2, 4-dichlorophenol, titanium isopropoxide ( $\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4$ ), urea,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , graphite powder,  $\text{H}_2\text{O}_2$  (30%),  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  (98%), deionized distilled water, citric acid, and all chemical solvents were obtained from the Sigma (Buchs, Switzerland) and Merck (Darmstadt, Germany) companies. All solvents used in this study were of analytical reagent grade.

### Apparatus

A laboratory-made SPME tool was used in all tests. A splitless mode model of injector was used for injections. In the headspace SPME process, a 25 mL glassy vial was employed. Phenolic compounds were separated, and quantified with the split/splitless modes of an injector using an Agilent 5975C mass-selective (Agilent Technologies, Palo Alto, USA) detector system. EI mode (70 eV) was used for operating MS. An HP-5 capillary column (30 m×0.32 mm id×0.25µm film thickness) was utilized as the column for determination. The Wiley 7N (Wiley, New York, NY, USA) Mass Spectral Library was utilized for identifying organic compounds. The temperature of the initial column was fixed at 70 °C. Then, the temperature was raised to 190 °C at a rate of 15 °C min<sup>-1</sup>, and it was

subsequently raised at a rate of 20 °C min<sup>-1</sup> to 260 °C and it was kept for two minutes. The temperature in the injector was set at 275 °C, and the splitless mode was used for conducting injections for 2 minutes. The temperatures of the ion source, GC-MS interface, and quadrupole were at 230, 280, and 150 °C, respectively. Seron AIS-2100 SEM was utilized to investigate the surface of the fiber.

### Synthesis of the graphene oxide

Graphite powder was first converted to graphene oxide by the Hummer method [10]. Next, 2.5 g of graphite powder in an ice bath was added to 50 ml of sulfuric acid, followed by adding 2 g of potassium permanganate slowly to the mixture at a low temperature. The prepared solution was then stirred for 2 h. After that, 50 ml of deionized distilled water was carefully added to the mixture. The mixture was stirred for 1 h and then diluted with 100 ml of additional deionized distilled water. Finally, 10 ml of 30% oxygenated water was added to the mixture such that it turned yellow. After centrifugation, the final product was washed for several times with hydrochloric acid and its pH was neutralized with distilled water. The resulting solid was placed in an oven at 60°C for 24 h and the brown powder was obtained. At the end, the resulting powder was subjected to an ultrasonic bath.

### Synthesis of titanium-hydrogen peroxide (TiOOH)

Initially, about 15.63 g of titanium isopropoxide solution was dissolved in 100 ml of water and magnetically stirred at 85°C for 20 min. Then, 1 M citric acid was added to the solution for hydrolysis of titanium isopropoxide, until the pH of the solution reached about 3-4. The solution was subjected to magnetic stirring for 2 h at 85°C and then slowly cooled until reaching room temperature. Afterward, 2.5 g of solid TiOOH was obtained by the evaporation of the above solution and grinding of the resulting powder. The powder was dispersed in 1 % of the nitric acid solution under magnetic stirring and then placed under the reflux condition for 6 h. Finally, the resulting TiOOH sol was slowly cooled to room temperature.

### Preparation of the nanostructure GO- TiOOH

To prepare the aqueous suspension of graphene oxide, 36 ml of solution was first prepared at a concentration of 1 mg/ml. Next, 20 ml of TiOOH sol was mixed with the aqueous graphene oxide solution and subjected to magnetic stirring for 12

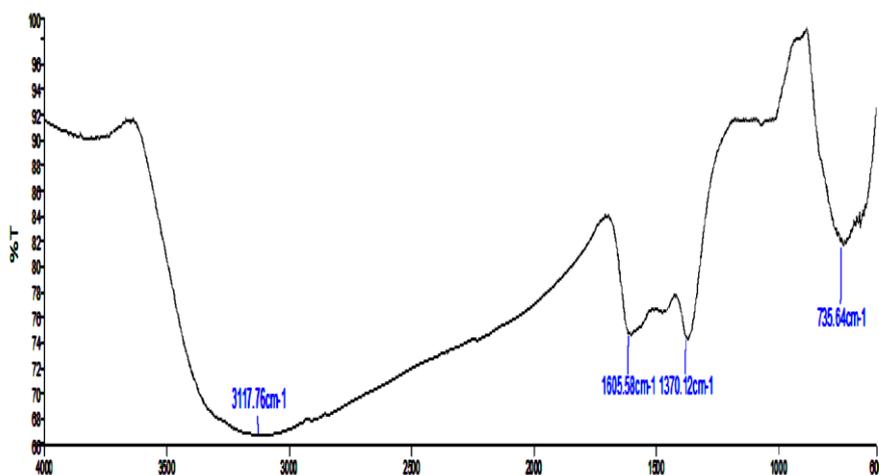


Fig.1. FTIR spectra of the NiTi- LDH /GO nanostructure.

h. The product was separated as sediment from the solution by centrifugation. Finally, it was washed with absolute ethanol for five times and dried at room temperature.

#### Synthesis Ni-Ti- LDH /GO

The Ni-Ti layered double hydroxide was grown on the surface of graphene oxide according to the in-situ crystallization method. The GO-TiOOH gray powder was subjected to an ultrasonic bath (40 kHz) in 30 mL of deionized water and was uniformly dispersed. About 1 mL of nickel nitrate and 0.3 g of urea were added to the solution. After mixing for half an hour, the mixture was transferred to a 50 mL Teflon autoclave and placed at 100°C in the oven for 24 h. Finally, the resulting sediment was collected by centrifugation and washed with deionized water and ethanol for several times and dried at 60°C.

#### Solid-phase microextraction (SPME) fiber preparation

We cleaned a part of stainless steel wire (diameter: 300- $\mu$ m) twice using methanol in the ultrasonic bath, lasting for ten minutes. The cleaned wire was dried under N<sub>2</sub> atmosphere. Epoxy glue was used for immobilizing of the NiTi-LDH/GO on steel wire. The wire was warmed up to 70 °C for 2 days using an oven. It was then mildly scrubbed for the removal of non-bonded parts and was put in an SPME made in the laboratory. Finally, the fabricated SPME fibers were conditioned at 190 °C for one hour to remove the fiber contaminations.

#### Analytical procedure

The water sample was separated in 5 mm and was put in a vial (25 mL), which contained 1.0 g NaCl. The vial then was sealed using the silicone septum. The temperature used for microextraction from the sample's headspace at solid phase was 80 °C which was carried out in a thermostatic water bath lasting for 40 minutes. The sample was stirred by a magnetic stirrer (300 rpm) as the agitation approach. After the extraction phase, we removed the SPME fiber from the vial, and it was then placed in the hot injection part of GC in the splitless state, keeping for two minutes. Thermal desorption of the analytes was done, and they were transferred into the column using a carrier gas. Finally, analytes were identified using the GC-MS library.

## RESULTS AND DISCUSSION

#### NiTi-LDH /GO nanostructure characterization

For establishing LDH structure, FT-IR spectroscopy was employed, where the interlayer anions and their effects on the compounds were identified (see Fig. 1). Regarding NiTi-LDH, it has a robust wide band with its central part at 3430 cm<sup>-1</sup>, which shows the presence of an O-H bond. In addition, it was found that there was a shift in the peak of the hydroxyl group toward a lower frequency in comparison with that of (MII/MIII) LDH. It is because of the electron density change on O-H bond via Ti<sup>4+</sup>. The IR spectrum related to NiTi- LDH /GO indicates that the stretching vibrations of C-O-C (epoxy) at 1224 cm<sup>-1</sup>, C-O-H (alkoxy) at 1050 cm<sup>-1</sup>, and C-O (carboxylic

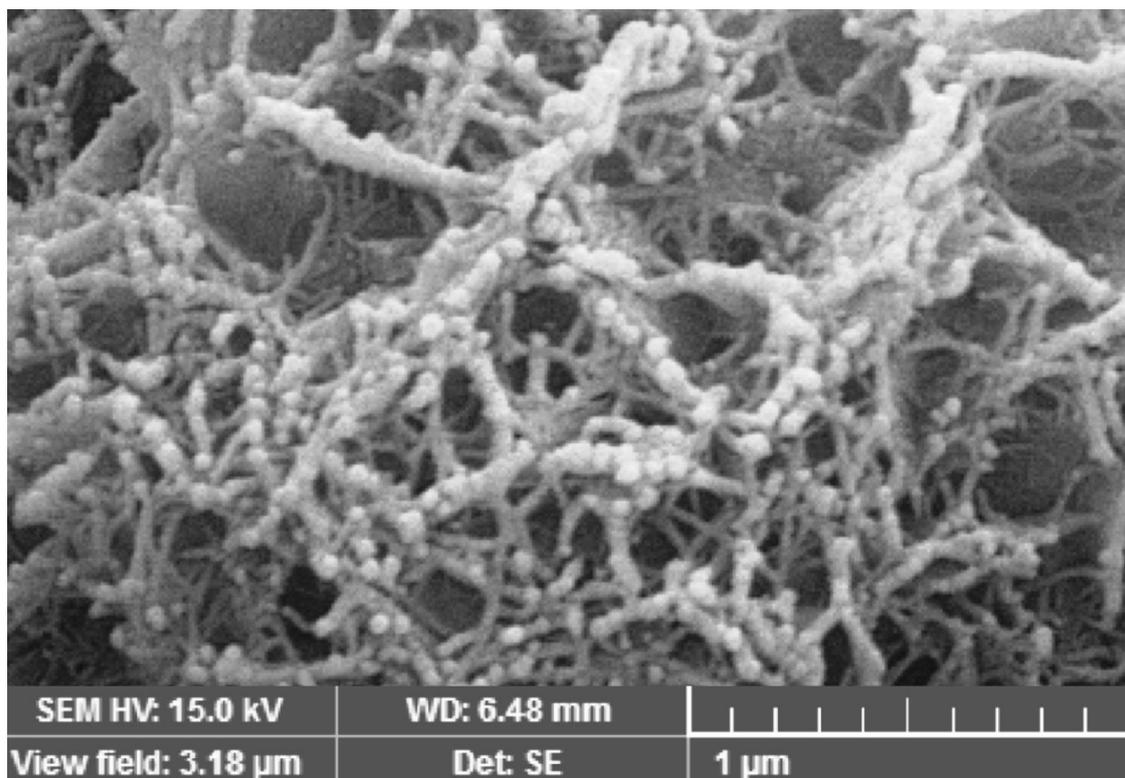


Fig.2. SEM image of the NiTi- LDH /GO nanocomposite.

acid) at  $1720\text{ cm}^{-1}$  approximately disappeared in comparison to original graphene oxide, which shows the effective decrease of graphene oxide. In addition, a peak was observed at  $3440\text{ cm}^{-1}$ , which is attributed to O-H. Further, there are stretching vibrations at  $735$  and  $1370\text{ cm}^{-1}$ , attributed to  $\text{CO}_3^{-2}$  in the compounds that are considerably increased. These demonstrate the successful intercalation of carbonate ions and water molecules into NiTi-LDH interlayer spaces within the assembly process. Furthermore, some bands under  $800\text{ cm}^{-1}$  are attributed to distinctive bending vibrations of the M-O bond, which confirms that there exists NiTi-LDH in the compound.

Through SEM image, the morphology and structure were obtained (Fig. 2). It is obvious that the NiTi-LDH/GO contains numerous layers. The energy-dispersive X-ray spectroscopy was also investigated. As shown in Fig. 3, the only elements observed at the products are carbon, nickel, titanium, and oxygen.

#### Microextraction temperature optimization

It is appropriate to use higher temperatures in headspace SPME to increase analytes volatility and establish the distribution equilibrium of analytes

between the gaseous and fiber phases. However, it is not desirable to adsorb analytes on fiber at higher temperatures. Nevertheless, the extraction temperature must be optimized. To this end, phenols were extracted from 5 mL aqueous samples, which contained  $10\text{ }\mu\text{g L}^{-1}$  of each composite at varying temperatures. Fig. 4 presents plots of the resulting peak areas versus temperature. It is observed that the components were mostly extracted at  $80\text{ }^\circ\text{C}$  using the suggested fiber. Thus, we selected  $80\text{ }^\circ\text{C}$  as a suitable empirical temperature for other investigations.

#### Extraction time optimization

If the aim is to achieve an equilibrium for the distribution of the analytes between sample and fiber, the fiber exposure time in water samples should be considered. Exposure time is a definitive factor in extraction efficiency improvement. Thus, the suggested extraction process was performed at varying times at a range of 20-50 minutes. The plot of peak areas versus exposure times is shown in Fig. 5. Our findings indicate that equilibrium was reached within 40 minutes. Hence, the exposure time of fiber to the sample's headspace was 40 minutes in further extractions.

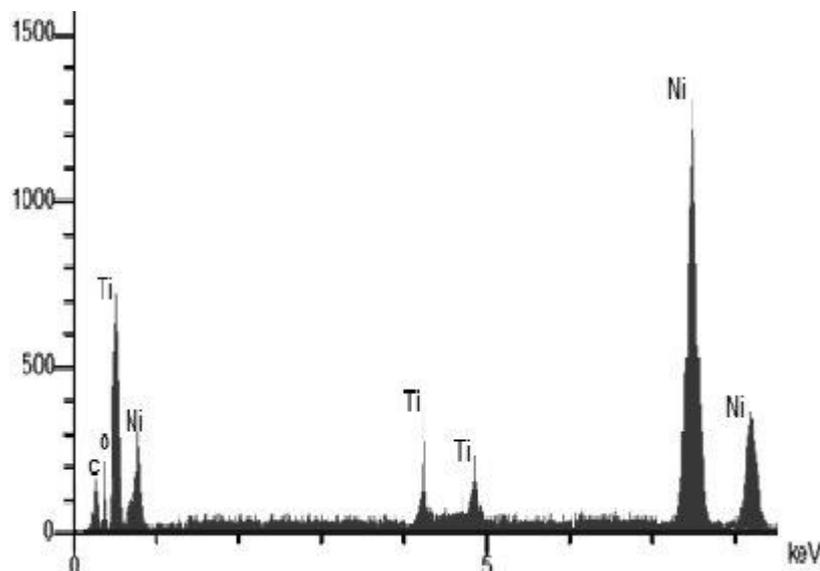


Fig.3.X-ray spectroscopy of the NiTi- LDH /GO nanocomposite.

#### Optimization of desorption time and temperature

In the SPME method, the mechanism of introducing analytes to GC is thermal desorption from the surface of fiber in the hot injection port of GC. Therefore, desorption temperature is required to be optimized for the quantitative transfer of the analytes. For finding the optimal desorption temperature, different temperatures (160 to 280 °C) were investigated for carrying out the injections. The results demonstrated that the optimum desorption temperature is 270 °C. Fiber time should also be considered in the injection part of the GC (Fig. 6). When desorption occurs faster, sharper peaks are provided and the separation efficiency is increased. According to the experimental studies on desorption times in the range of 0.5 to 4 minutes, desorption requires two minutes for completion (Fig. 7).

#### Effect of salt addition

Since the salting out effect is crucial in the transfer of organic compounds to headspace in the SPME methods, the microextraction procedure was carried out with NaCl (0–30% w/v). Based on the results, adjusting the concentration of NaCl at 10% w/v provided the highest extraction efficiency. Since the solubility of phenols in the water is lowered when NaCl is present in the aqueous sample solution, the presence of salt is an essential parameter. The water molecules are attracted and

held by the ions of the dissolved salt, making these molecules less free for interaction with the solute. Therefore, the solubility of the solute molecules is lowered which causes precipitation or separation to occur.

#### Impact of pH

We also studied the impact of pH because of its significance for the extraction of phenols and their acid–base characteristics. The pH of aqueous solution has a crucial role in the process of extraction. In addition, the pH sample solution is an essential factor progressing the transfer of the analyte to the headspace from the sample solution. Thus, following an investigation of the impact of the pH in the range of 2–9, the right HCl or NaOH solution was added to the aqueous phase. The highest extraction efficiency was achieved at pH 4. There were significant shifts in the acid–base balance for the phenols at a lower pH to the neutral forms, which showed a higher affinity toward the fiber and higher vapor pressure. Therefore, the extraction efficiency is increased.

#### Impact of sample agitation rate on efficiency of microextraction

Agitation is an important factor for transferring the analytes to the fiber surface from the solution which can be accomplished by sonication, magnetic stirring, etc. Here, magnetic stirring was

Table 1. Some analytical data obtained for microextraction of phenolic compounds using the honeycomb NHA/AAO in optimum conditions and comparison of the developed method with other SPMEa fibers (3-(trimethoxysilyl) propylamine/ PDMS (TMSPA/PDMS) (Abolghasemi et al 2014), Polyacrilate (85µm) (Ribeiro et al. 2002), and CNT/LDH nanocomposite (Abolghasemi et al 2015).

Compound	Current method				TMSPA/PDMS		Polyacrilate		LDH/CNT	
	DLR <sup>a</sup>	(R <sup>2</sup> ) <sup>b</sup>	LOD <sup>c</sup>	%RSD <sup>d</sup>	LOD	%RSD	LOD	%RSD	LOD	%RSD
Phenol	0.1-100	0.999	0.09	7.5	0.05	9.2	2.5	5.2	0.08	6.5
4-Chlorophenol	0.01-100	0.997	0.004	5.8	0.05	6.8	-	-	0.04	7.3
2, 4-Dichlorophenol	0.1-100	0.998	0.006	6.3	0.02	9.2	0.05	3.6	0.005	9.9
2, 6-Dichlorophenol	0.01-100	0.995	0.005	7.4	-	-	0.05	4.9	0.008	8.8
2, 4, 6-Trichlorophenol	0.01-100	0.998	0.007	6.5	0.02	8.7	-	-	0.005	7.2

a Dynamic Linear Rang (ngml-1).

b Regression coefficient

c Limit of detection calculated as three times the baseline noise (ngml-1).

d Relative Standard Deviation

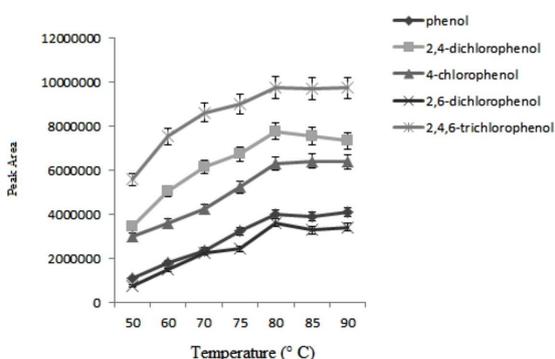


Fig. 4. Effect of temperature on microextraction of phenols.

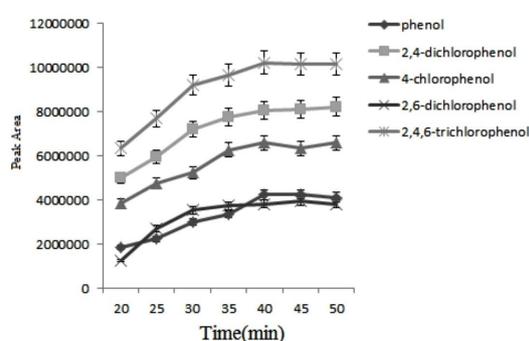


Fig. 5. Effect of time on microextraction of phenols.

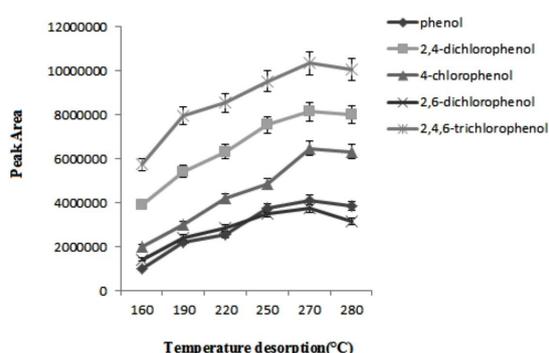


Fig. 6. Effect of desorption temperature on microextraction of phenols.

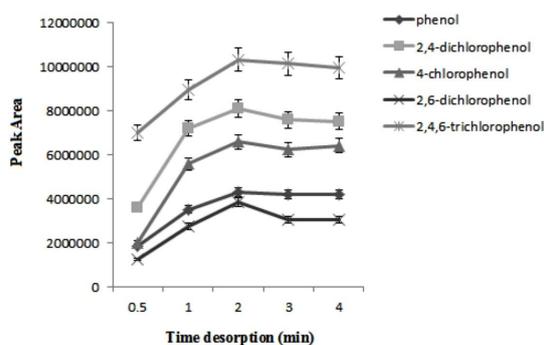


Fig. 7. Effect of desorption time on microextraction of phenols.

used at varying agitation rates (0–600 rpm), and we obtained the optimum outcomes at 300 rpm.

#### Validation of Method

For evaluating the precision of the method, 5 replicate determinations were carried out by a single fiber. Then, we calculated the relative

standard deviations, the outcomes of which are given in Table 1. The range of relative standard deviations (R.S.D.) was from 5.8 to 7.5 %, and all analytes showed acceptable calibration linearity. Four spiking levels of phenols were used in the range of 0.01–100 µg L<sup>-1</sup> concentrations to draw calibration curves. Three replicate extractions and



Table 2. The results obtained for the analysis of the spiked water samples (10 ngml-1) by the proposed method, under the optimized conditions

Compound	Seymere river	khoramrod river
Phenol	10.1(0.4)	10.1(0.5)
4-Chlorophenol	10.2(0.3)	10.5(0.2)
2, 4-Dichlorophenol	10.1(0.2)	10.1(0.1)
2, 6-Dichlorophenol	10.4(0.2)	10.3(0.5)
2, 4, 6-Trichlorophenol	10.4(0.3)	10.2(0.3)

a The figures within parentheses are standard deviations for three replicates.a

determination were conducted for each level under optimum conditions. The correlation coefficient values were calculated between 0.995 and 0.999, which shows good linearity in the dynamic ranges.

#### Real sample analysis

We collected water samples (October 2013) from Lorestan, Iran (contaminated areas of the Khoramrod and Seymere river). Prior to analysis, the samples were kept at 4 °C. Table 2 gives the resulting outcomes.

#### CONCLUSION

In the present study, we synthesized and examined the NiTi-LDH /GO nanostructure which was employed as a new SPME fiber coating. The NiTi-LDH/GO nanostructure SPME fiber was presented and studied for extracting phenol from aqueous samples. The experimental results clearly indicate that NiTi- LDH /GO nanostructure fiber is an appropriate choice for HS-SPME of phenols analysis. By combining HS-SPME using NiTi- LDH /GO nanostructure fiber and GC-MS, low LODs can be achieved, and it can be used for determining phenols form water samples.

#### CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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