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# Speciation of As(III)/As(V) in water samples by a magnetic solid phase extraction based on $Fe_3O_4$/Mg–Al layered double hydroxide nano-hybrid followed by chemiluminescence detection

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ABSTRACT

A novel magnetic solid phase extraction method was developed for the speciation of As(III)/As(V) in aqueous solutions utilizing $Fe_3O_4$-doped Mg–Al layered double hydroxide (LDH) as a nano-sorbent. The method is based on the separation and pre-concentration of As(V) by $Fe_3O_4$/Mg–Al LDH nano-hybrid prior to determination by a chemiluminescence (CL) technique. The CL route involves the oxidation of luminol by vanadomolybdoarsenate heteropoly acid in a basic media. Since the existing cations cannot be adsorbed by positively charged layers of the LDH and other potentially interferent anions had no considerable effect on the CL reaction, it provides a very selective and sensitive determination approach for As(V). The determination of total arsenic and hence indirectly As(III) involve the pre-oxidation of As (III) to As(V) by a mixture of hydrogen peroxide and potassium hydroxide. Several factors affecting the extraction and determination of the analyte were investigated and optimized. Under optimum conditions, the calibration graph was linear in the range of 5.0–5000 ng $L^{-1}$. The limit of detection and enrichment factor was 2.0 ng $L^{-1}$ and 80, respectively. The method was validated by the analysis of a standard reference material (NIST SRM 1643e), and successfully applied to the speciation of arsenic in several water samples with recoveries in the range of 93.3–106.7% for the spiked samples.

## 1. Introduction

Arsenic (As) is a widely spread heavy metal in the Earth's crust, which exists in four oxidation states of As(V), As(III), As(0) and As (–III). In oxidized environment, appears mostly as oxyanions [1]. It is used in various fields such as medicine, agriculture, livestock, electronics, industry and metallurgy [2]. In water, it is mostly present as As(V), but in anaerobic conditions, it is likely to be present as As(III). Although the vital source of As is geological, human activities such as mining, burning of fossil fuels and pesticides application also cause As pollution. The most important routes of As exposure are through food and drinking-water. According to the World Health Organization, the maximum permissible concentration of As in drinking water is 10 μg $L^{-1}$ [3]. In view of these facts, there is a continuing challenge in the trace determination of As in all environmental compartments.

Chemiluminescence (CL), as an analytical technique, has widely been applied for trace determination (ng $mL^{-1}$–pg $mL^{-1}$) of metals and organic compounds in different fields, from the life sciences to clinical, environmental, food and pharmaceutical analyses [4–6]. The main problem limiting applicability of chemiluminescent method is its low selectivity. Thus, an efficient sample pretreatment methodology is often necessary for separation of analyte from interfering matrix before CL detection [7]. As a promising sample pretreatment technique, magnetic solid phase extraction (MSPE) has recently caught considerable attention because it avoids the main disadvantages of other conventional pretreatment methods such as consumption of organic solvents [8,9]. On the other hand, a magnetic separation process can be performed in a rapid and easy way by an applied magnetic field in which several stages of sample pretreatment (especially centrifugation, filtration and membrane separation) would be eliminated. In MSPE procedures, the sorbent should have some inherent properties such as superparamagnetic nature, high surface area, highly dispersion and small diffusion resistance. Recently, considerable research interests have been focused on the synthesis of novel magnetic nano-particles or introducing magnetic properties to nano-materials to produce magnetic nano-hybrids and nanocomposites [10–15].

Layered double hydroxides (LDHs), consisting of stacked brucite-type octahedral layers with anions and water molecules occupying the interlayer space are expressed by a general formula, $[M^{II}_{1-x} M^{III}_{x}(OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$, where $M^{II}$ and $M^{III}$ are divalent

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and trivalent cations, respectively, in which the positively charged brucite-like layers are balanced by the interlayer anions ($A_n^-$) [16]. Due to their many advantages such as large surface areas, exchangeable interlayer anions, compositional flexibilities, ease of preparation and low cost, LDHs have been used as ion-exchangers and adsorbents [17–19]. Recently, we have developed a dispersive solid phase extraction methodology based on the colloidal suspension of Ni–Al LDH for in situ determination of dopamine [20]. By adding the magnetic properties to the colloidal LDHs, the resultant nano-hybrids could be applied in MSPE methodologies and the separation and recycling of the sorbents from bulk sample solutions during MSPE procedures would become more easy and fast. Several magnetic LDH based nano-hybrids have recently been synthesized and used for removal of some analytes [15,21–23]. However, so far, no attempt was made to apply the LDHs in MSPE procedures in order to speciation analysis of metal ions.

The purpose of the present work is to combine a MSPE procedure with chemiluminescence (CL) detection for separation, pre-concentration and determination of ultra-trace amounts of As(V) in water samples. Although Mg–Al-carbonate LDH has recently been used as an adsorbent material for the pre-concentration of sodium dodecyl benzene sulfonate prior to its determination by CL detection system [24], to the best of our knowledge, this is the first time that $Fe_3O_4$/Mg–Al-nitrate LDH is used in MSPE procedures and followed with CL detection for speciation of inorganic species. The CL route involves the oxidation of luminol by vanadomolybdoarsenate heteropoly acid (VMoAs-HPA) in a basic media. The concentration of As(V) was obtained by direct measurement, and total concentration of As was determined after pre-oxidation of As(III) to As(V) with hydrogen peroxide in a basic solution. The As(III) content was estimated by subtracting the content of As(V) from the total As concentration. Effects of several parameters on the extraction efficiency of As(V) and its CL signal were systematically investigated and optimized. The combined MSPE–CL method was successfully applied to the determination of As(V) and As(III) in several water samples.

## 2. Experimental

### 2.1. Apparatus and instruments

Chemiluminescence spectra and intensity measurements were carried out using a FP–6200 spectrofluorometer (JASCO Corporation, Tokyo, Japan). The instrument equipped with a 150 W xenon lamp, 1.0 cm quartz cell, Peltier thermostatted single cell holder (model ETC-272), and supported with PC–based Windows® Spectra Manager TM software for JASCO Corporation version 1.02, which is capable of recording both spectra and time course measurements. Chemiluminescent reaction was occurred within the quartz cell ($10 \times 10 \times 40\ mm^3$) just after injection of CL reagent. For injection of CL reagent, a homemade injection port was designed and used. For this purpose, the quartz cell holder was completely covered with a rubber cap and a 0.5 mL syringe pump was positioned in center of the rubber after its drilling. To fix the syringe, it was located through a hole of another piece of rubber which was glued on top of the rubber cap. The third piece of rubber, which has a hole with the same diameter of inner piston of the syringe, was attached behind the instrument shutter to fix the piston before its pushing in the injection step (Fig. 1A). It is worth noticing that the designed structure is fully re-establishable and for each measurement, new portion of analyte was injected into the quartz cell by means of the syringe pump. The complete injection of CL reagent existing in the syringe pump was done by fast shutting the outer shield of the cell holder (Fig. 1B), so that, the inner piston of syringe pump was pushed forward and its content was emptied at once. At this time, the CL signal was recorded in a time course measurement mode.

In order to study the structure of the nano-materials, XRD measurements were performed on a Siemens D5000 X-ray powder diffractometer (Cu Kα radiation source, $\lambda = 0.154056$ nm) between 2° and 70° generated at 40 kV and 35 mA at room temperature. Samples for XRD were ground into powder and then pressed flat in the sample slot. In addition, FT-IR spectra (4000–400 $cm^{-1}$) were recorded on a (Shimadzu 8400 series, Japan)

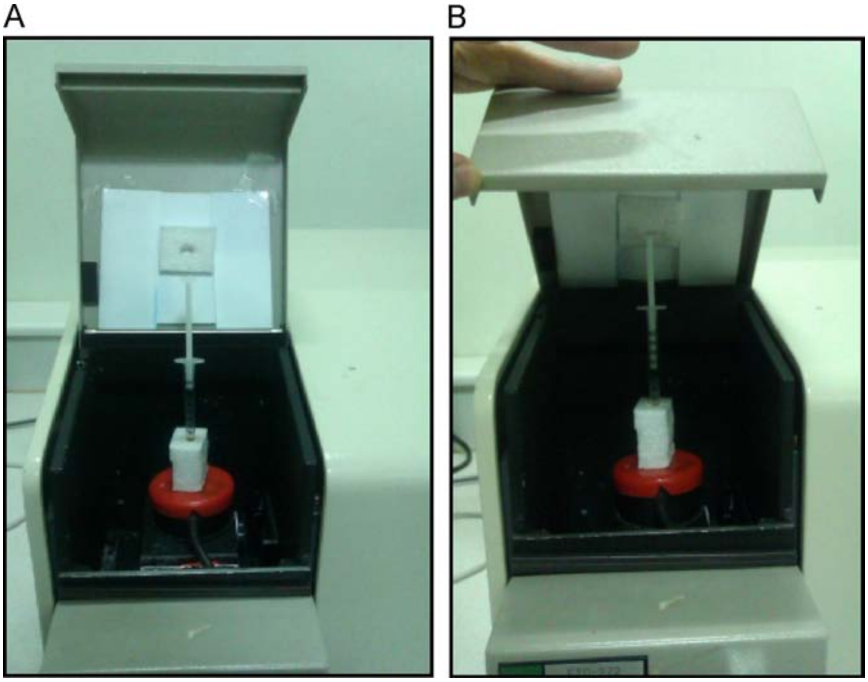

**Fig. 1.** **(A)** A designed injection port for CL detection, and **(B)** injection of CL reagents by shutting the outer shield of the cell holder.

Fourier transform infrared spectrometer using the KBr disk method with a ratio sample/KBr of 1:100 by mass. A field emission scanning electron microscope (FESEM), model MIRA3 TESCAC (Czech Republic) was additionally used to study the morphological characteristics of the nano-hybrid. Chemical composition analysis of the synthesized nano-materials was carried out on an electron dispersive X-ray analyzer attached to the FESEM.

Hot plate stirrer model Jenway 1000 (U.K.), Selecta lab centrifuge model Tl320 and nitrogen gas (99.9995%, Azaroxide Co., Iran) were used during the magnetic nano-particles preparation process. A 45 mL Teflon lined autoclave and an electrical furnace (EX.1200-30L; Exciton Co., Iran) was used throughout the LDH synthesis procedure. An ultrasonic bath (SONICA, Italy) is used to disperse the $Fe_3O_4$/Mg–Al LDH in a sample solution vial, and a mechanical stirrer (Pars Azma Co., Iran) was used for stirring the vial. The pH values were measured with a Metrohm pH-meter (model 827), supplied with a glass-combined electrode. An electronic analytical balance (GR-200, Japan) was used for weighting the solid materials.

### 2.2. Standard solutions and reagents

All chemicals used were of analytical reagent grade and all solutions were prepared with high purity deionized water (Shahid Ghazi Co., Tabriz, Iran). The standard stock solution of 1000 mg $L^{-1}$ As (V) is obtained from Chem-Lab (Belgium). A 1000 mg $L^{-1}$ stock solution of As(III) is prepared by dissolving 0.1732 g of $NaAsO_2$ (Panreac) in 100.0 mL deionized water using a calibrated flask. Working standard solutions for As(III) and As(V) are prepared by serial dilutions with deionized water. NaOH, $Al(NO_3)_3.9H_2O$ (99%), $FeCl_2.4H_2O$ (99%), $FeCl_3.6H_2O$ (99%), ammonia solution (28%v/v), $NH_4VO_3$ (99%), $(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$ (99%), $H_2SO_4$, $H_2O_2$ (30%v/v) and other salts used for the interference study were all purchased from merck (Darmstadt, Germany). Other precursors such as $Mg(NO_3)_2 \cdot 6H_2O$ (99%), citric acid, potassium hydroxide (85%) and luminol (5-amino-2,3-dihydro1,4-phthalazinedione) were purchased from Fluka (Switzerland).

### 2.3. Synthesis of $Fe_3O_4$ magnetic nano-particles

$Fe_3O_4$ nano-particles ($Fe_3O_4$-NP) capped with citrate groups were synthesized using the procedure described in the literature [21]. Briefly, 8.73 mmol of $FeCl_3 \cdot 6H_2O$ and 4.37 mmol of $FeCl_2.4H_2O$ were dissolved in 40 mL of deionized water and the solution was heated to 80 °C under $N_2$ purging. Then, 5 mL of ammonia solution (28%v/v,) was added quickly into the vigorously stirred solution. After 30 min, the precipitates were collected by a magnet followed by washing with deionized water and then re-dispersed into 80 mL of deionized water at 80 °C. To this mixture, 0.5 g of citric acid in 5 mL of deionized water was added with continuous stirring and purging with $N_2$ for 2 h. The final solid sample was collected by a magnet. One half was dispersed in 25 mL of deionized water to form a stable aqueous dispersion and the other half was washed and dried in vacuum at room temperature for characterization.

### 2.4. Synthesis of Mg–Al-nitrate LDH

For this purpose, 10 mL of a solution containing 3.0 mmol of $Mg(NO_3)_2 \cdot 6H_2O$ and 1.0 mmol of $Al(NO_3)_3 \cdot 9H_2O$ was added quickly into 40 mL of 0.15 mol $L^{-1}$ NaOH solution under vigorous stirring and nitrogen purging. The mixture was continuously stirred for another 10 min. The precipitate was centrifuged and washed with decabonated deionized water, and then re-dispersed in water to get a 40 mL suspension. The resulting suspension was transferred into a 45 mL Teflon-lined autoclave and hydrothermally treated at 100 °C for 16 h.

### 2.5. Preparation of $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid

The $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid was prepared according to the procedure described elsewhere [21]. Firstly, 5 mL of the $Fe_3O_4$ and Mg–Al-nitrate LDH suspensions were individually ultrasonicated for 1 h. The $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid was prepared by directly mixing the two suspensions followed by ultrasonication for 2 h at room temperature. By applying a magnet, all the particles in the final suspension were separated from the aqueous phase within one minute. The obtained material was dried in a vacuum oven overnight at room temperature.

### 2.6. Sample preparation

Water samples including tap water, spring water, well water and rain water were collected from local sources. After sampling, they were filtered through a Round filter paper (blue band, no. 300210) to remove suspended particulate matter and then aliquots of 200.0 mL were analyzed within 24 h of collection without previous treatment by the procedure described in “General procedure”. In the case of certified reference material, SRM 1643e, a suitable aliquot was diluted with deionized water prior to analysis.

### 2.7. General procedure

150 mg of $Fe_3O_4$/Mg–Al-nitrate LDH was placed in a 250 mL glass beaker as a nano-sorbent. Afterward, 200 mL portion of standard or sample solution containing As(V) in the range of 5.0–5000 ng $L^{-1}$ was transferred into the beaker. In order to disperse the nano-sorbent homogenously through the whole solution, the beaker was placed in an ultrasonic bath for 1 min. Under continuous mechanical stirring of the mixture, the separation and pre-concentration of As(V) ions by the nano-sorbent was proceed at room temperature for 10 min. Then, the nano-sorbent was gathered at one side of the beaker under an external magnetic field (Nd–Fe–B, 10,000 G) and the clear supernatant was directly decanted. To desorb the extracted analyte, 1 mL of 2 mol $L^{-1}$ NaOH solution was added on the isolated nano-sorbent. After 5 min, the nano-sorbent particles were gathered again, with the aid of a magnet, and the supernatant containing the concentrated As (V) ions was transferred into a small vial. Prior to detection, the solution was acidified by adding 0.5 mL of 3.75 mol $L^{-1}$ sulfuric acid. Then, 0.3 mL of 5.5 mmol $L^{-1}$ ammonium molybdate and 0.2 mL of 2.5 mmol $L^{-1}$ ammonium vanadate were added. To accelerate the vanadomolybdoarsenate heteropoly acid (VMoAs-HPA) formation, the resultant solution was heated in a water bath at 60 °C for 5 min. Finally, after cooling to room temperature, the solution was transferred into a spectrofluorometer cell and the CL intensity was recorded by injection of 0.5 mL of 25 mmol $L^{-1}$ luminol solution.

## 3. Results and discussion

### 3.1. Characterization of the synthesized nano-sorbent

The powder X-ray diffraction (XRD) is a very powerful technique for characterizing the structure of materials. (Fig. 2a–c) show XRD patterns of Mg–Al-nitrate LDH, $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid and $Fe_3O_4$ nano-particles, respectively. Fig. 2a indicates the XRD pattern and the characteristic reflections of the Mg–Al-nitrate LDH structure with a series of sharp and intense lines corresponding to a well crystallized layered structure. Fig. 2c shows the diffraction peaks of prepared citrate capped $Fe_3O_4$ nano-particles occurred at $2\theta$ region of 30–70°, which are ascribed

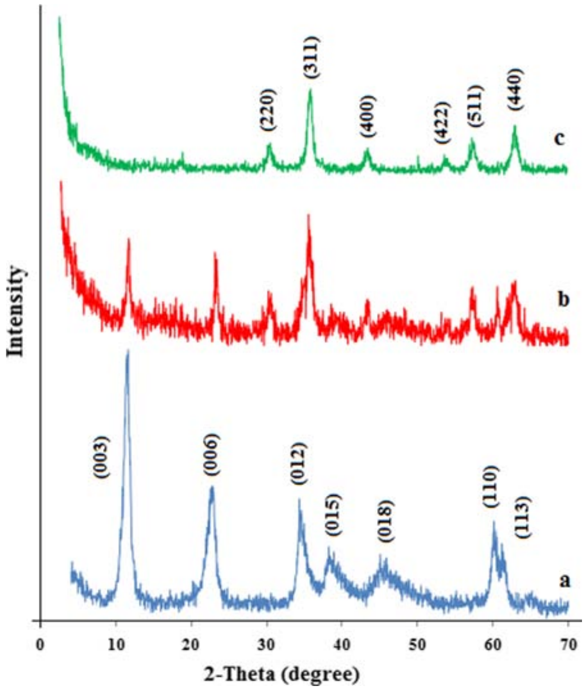

**Fig. 2.** XRD patterns of (**a**) Mg–Al-nitrate LDH, (**b**) $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid and (**c**) $Fe_3O_4$ nano-particles.

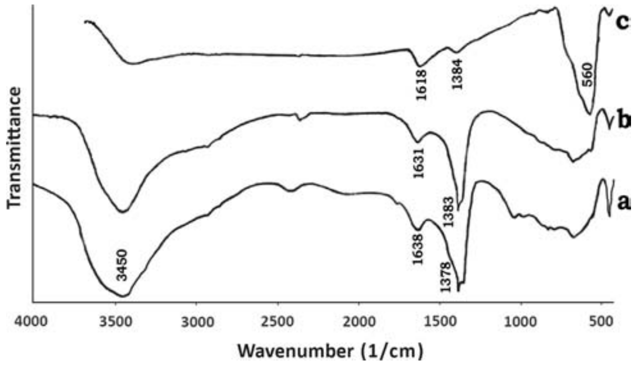

**Fig. 3.** FT-IR spectrum of (**a**) Mg–Al-nitrate LDH, (**b**) $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid and (**c**) $Fe_3O_4$ nano-particles.

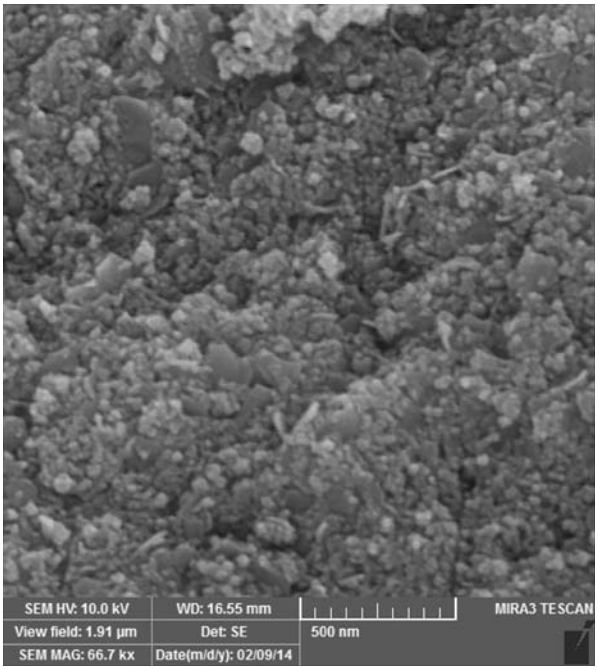

**Fig. 4.** SEM image of $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid.

to crystal plate of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0), respectively. The XRD pattern shown in Fig. 2b indicates a mixture of Mg–Al-nitrate LDH and $Fe_3O_4$ phases as all their diffraction peaks can be observed in the nano-hybrid sample, which is in agreement with the results from the literature [21]. The FT-IR spectra of the LDH, $Fe_3O_4$/LDH nano-hybrid and $Fe_3O_4$ nano-particles, are shown in Fig. 3a–c. The broad band around 3450 $cm^{-1}$ in FT-IR spectra of the LDH and nano-hybrid is attributed to the stretching mode of hydroxyl groups of LDH layers and interlayer water molecules. The presence of water molecules is also responsible for the medium intensity band close to 1638 $cm^{-1}$ and 1631 $cm^{-1}$ (bending mode) in the LDH and nano-hybrid structures, respectively. A sharp and intense band is observed at 1378 $cm^{-1}$ and 1383 $cm^{-1}$ corresponding to stretching vibration of intercalated $NO_3^-$ ions in the LDH and nano-hybrid structures, respectively. The small absorption bands at region 400–900 $cm^{-1}$ are associated with M–O stretching and M–OH bending vibrations in both Mg–Al-nitrate LDH and $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid structures. The FT-IR spectrum of magnetic nano-particles can clearly justify the citrate capped $Fe_3O_4$ nano-particles structure. Because, the broad and weak bands around 560 and 3400 $cm^{-1}$ are respectively due to the stretching vibration mode of Fe–O and Fe–O–H. On the other hand, the adventure of bands at 1384 $cm^{-1}$ and 1618 $cm^{-1}$ indicates that citric acid was coated on the surface of the nano-particles via the –COOH because these bands are assigned to the symmetric and asymmetric stretching of C═O in the –COOH group.

Field emission scanning electron microscopy was employed to explore the morphology of the synthesized nano-hybrid. FESEM image of $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid (Fig. 4) shows an aggregate that consists of crystallites were collected as small pseudo-spherical particles. Electron dispersive X–ray (EDX) analysis was applied for accurate assigning and comparing the chemical composition of each synthesized sample. Table 1 summarizes the obtained EDX analysis data for citrate capped $Fe_3O_4$-nano-particles, Mg–Al-nitrate LDH and $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid.

### 3.2. *Optimization of magnetic solid phase extraction conditions*

To evaluate the capability of the presented method for separation and pre-concentration of As(V), the effect of several variables on the extraction efficiency including pH, the amount of sorbent, the sample volume and the eluent concentration were studied and optimized. One at a time method was used for optimization of the parameters affecting the extraction efficiency. A 250 ng $L^{-1}$ of As (V) solution was used for all the measurements and three replicates were performed for each experiment.

#### 3.2.1. *Effect of pH*

The influence of the pH value on the recovery of As(V) was studied by adjusting the pH values of sample solution in the range of 4–12 with minimum volume of 0.01 mol $L^{-1}$ $HNO_3$ and/or NaOH. Solutions with $pH < 4$ were not tested due to the probability of the layered materials and $Fe_3O_4$ nano-particles dissolving in strongly acidic media. The obtained results indicate that the retention of As(V) on the nano-sorbent is not affected by pH and recovery value is almost constant in the wide pH range. At pH values higher than 2.5 the major forms of As(V) are $H_2AsO_4^-$ and

**Table 1**
Elemental analysis data of the synthesized nano-materials obtained from EDX.

| Sample | Mg% | Al% | Fe% | N% | O% | C% |
|---|---|---|---|---|---|---|
| Mg–Al-nitrate LDH nano-crystals | 22.54 | 13.17 | – | 12.3 | 50.45 | 1.4 |
| Citrate capped $Fe_3O_4$ nano-particles | – | – | 74.95 | 0.93 | 17.8 | 7.25 |
| $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid | 15.89 | 10.12 | 33 | 10.84 | 24.61 | 5.54 |

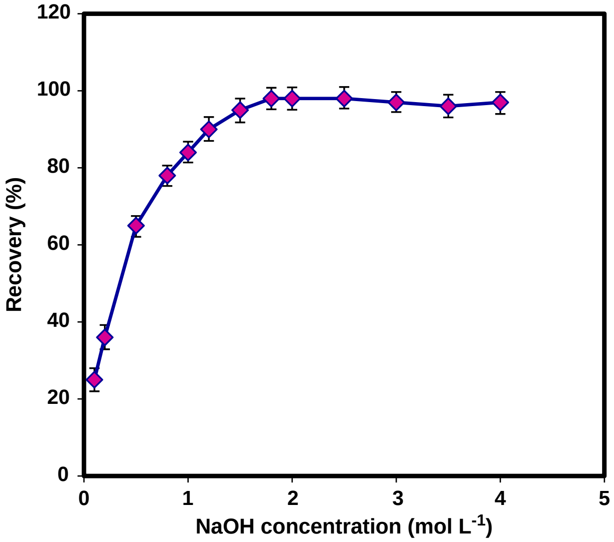

**Fig. 5.** Effect of eluent concentration on the recovery of 250 ng L$^{-1}$ As(V). Other conditions are given in Table 3.

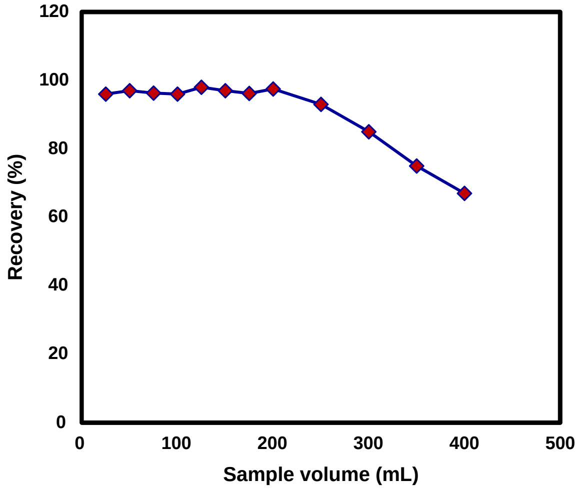

**Fig. 6.** Effect of sample volume on the recovery of As(V). Conditions are as Fig. 5.

$HAsO_4^{2-}$ [25]. On the other hand, the main mechanisms of analyte uptake with LDH based structures are electrostatic interactions between negatively charged analyte and positively charged surface of the LDH, and exchanging of the analyte with the interlayer anions [18]. Therefore, considering both these mechanisms, retention of As(V) in the form of the mentioned oxyanions can be quantitative at pH values higher than 2.5. Accordingly, there is no need to adjust the pH in the studied real samples.

### 3.2.2. Optimization of elution conditions

According to our previous studies [17–19], NaOH solution is nominated as the best eluent solution for complete stripping of negatively charged retained analyte from the LDH based nano-sorbents. In this work, NaOH solution was also selected as an eluent, and the effect of its concentration (0.1–4 mol L$^{-1}$) on the recovery of the analyte was studied. As revealed in Fig. 5, 2.0 mol L$^{-1}$ NaOH solution was sufficient for complete elution of the retained As(V) from the nano-sorbent. Keeping the NaOH concentration of 2.0 mol L$^{-1}$, the effect of eluent volume (0.5–3.0 mL) on the recovery was investigated. The recovery value of As (V) increased by increasing the NaOH volume up to 1 mL and remained constant afterward. So, to achieve the highest pre-concentration factor, 1 mL of 2.0 mol L$^{-1}$ NaOH solution was chosen as an optimum value.

### 3.2.3. Effect of amount of the nano-sorbent

The effect of the amount of $Fe_3O_4$/Mg–Al-nitrate LDH on the recovery of As(V) ions was examined in the range of 50–500 mg. The results demonstrated that the recovery values higher than 95% were obtained when the amount of the nano-sorbent was above 100 mg. Therefore, 150 mg of the synthesized nano-sorbent was employed in further experiments.

### 3.2.4. Effect of sample volume

The possibility of enriching low concentrations of analyte from large volumes of samples could be examined by studying the effect of sample volume on the recovery of the analyte. For this aim, 25–400 mL sample solutions containing 250 ng L$^{-1}$ As(V) were prepared and the analyte in each sample solution was pre-concentrated and determined by applying the presented MSPE–CL method. As shown in Fig. 6, quantitative recovery values obtained up to 200 mL of sample solution. So, by analyzing 2.5 mL of the final solution containing As(V), after pre-concentration of 200 mL of sample solution, an enrichment factor was found as 80 by this method.

### 3.2.5. Effect of sorption/desorption time

Due to the superparamagnetic property of the $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid, the sorbent could rapidly be separated from the sample solution in about 2 min using an external magnetic field instead of filtration or centrifugation. However, to achieve satisfactory recoveries during the determination of the analyte, the effect of sorption and desorption times on the recovery of As(V) ions were investigated. For this purpose, both of them were varied in the range of 1–20 min. It was observed that 10 and 5 min was sufficient for sorption and desorption stages, respectively.

### 3.2.6. Sorption capacity and regeneration of the nano-sorbent

To determine the sorption capacity, 200 mg of the nano-sorbent was added to 50 mL of solution containing 10 mg L$^{-1}$ of the analyte and ultrasonicated for 5 min. The extraction process was continued for 45 min by stirring the solution on a mechanical stirrer. Afterward, the nano-sorbent was separated from the solution under magnetic field. Then, the extracted As(V) was stripped from the nano-sorbent with 5 mL of 2.0 mol L$^{-1}$ NaOH solution. Finally, the concentration of the analyte was determined by CL detection after appropriate dilution. As a result, capacity of the nano-sorbent for As(V) was found to be 12.7 mg $g^{-1}$. The potential regeneration and stability of the sorbent were also investigated. The nano-sorbent could be reused after regenerating with 2 mL of 1 mol $L^{-1}$ NaOH and 10 mL deionized water, respectively. Moreover, based on the obtained results, the prepared magnetic nano-hybrid can be reused for 100 times without obvious loss of analytical performance or magnetic properties.

### 3.3. *Optimization of detection conditions*

Chemiluminescence is a simple and usually inexpensive detection method which provides wide dynamic range and high sensitivity. There are a few reports exploited the use of CL detection to determine inorganic arsenic species [24,26–28]. One of the proposed strategies for CL detection of arsenic is based on the oxidation of luminol by vanadomolybdoarsenate-heteropoly acid (VMoAs-HPA) in a basic media as follows [26].

$$\mathrm{Mo(VI)+As(V)+H^{+}\rightarrow[AsMo_{10}O_{33}]^{9-}} \qquad (1)$$

$$\mathrm{[AsMo_{10}O_{33}]^{9-}+Mo(VI)+V(V)\rightarrow[AsVMo_{11}O_{40}]^{4-}} \qquad (2)$$

$$\mathrm{Luminol+[AsVMo_{11}O_{40}]^{4-}+OH^{-}\rightarrow Aminophthalate+N_2+other\ products}+h\nu \qquad (3)$$

Due to a slow kinetic of VMoAs-HPA complex formation, and to promote the rate of the whole procedure, the complex formation reaction was done at was 60 °C. Fig. 7 shows the CL spectrum obtained by the oxidation of luminol in the presence of VMoAs-HPA. To reach the accurate and highest CL intensity, it is necessary to investigate the effect of parameters influencing the VMoAs-HPA complex formation and the luminol oxidation.

#### 3.3.1. *Optimum conditions for VMoAs-HPA complex formation*

The formation of the hetropoly acid is completely pH dependant process and it was proved that the reaction should be done in acidic medium. So, the effect of acid concentration should be studied. As described former, in this work, VMoAs-HPA complex is formed after elution of the analyte from the sorbent by NaOH solution. Accordingly, to provide proper acidic conditions for HPA formation, first the alkalinity of the reaction media should be neutralized by the acid. Based on the obtained results, 0.5 mL of 0.75 mol $L^{-1}$ $H_2SO_4$ solution provides the optimum acidic conditions for VMoAs-HPA complex formation. The effect of concentration of the ammonium molybdate and ammonium vanadate on VMoAs-HPA complex formation was also studied. The influence of ammonium molybdate concentration on VMoAs-HPA complex formation was studied over the range (0.15–1 mmol $L^{-1}$) and gave a maximum CL response at 0.65 mmol $L^{-1}$ (Fig. 8A). The effect of ammonium vanadate concentration was investigated (0.01–0.5 mmol $L^{-1}$) and the maximum response was observed for 0.2 mmol $L^{-1}$ as shown in Fig. 8B.

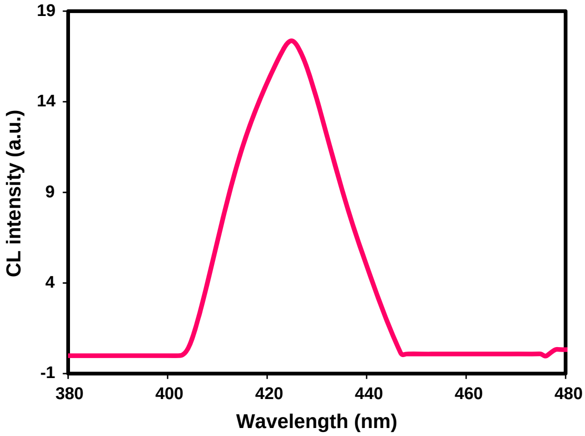

**Fig. 7.** CL spectrum obtained from the oxidation of luminol by VMoAs-HPA. Utilized conditions: As(V) concentration; 0.2 μg $L^{-1}$, ammonium molybdate, ammonium vanadate, sulfuric acid and luminol concentration; $10^{-2}$ mol $L^{-1}$, $10^{-3}$ mol $L^{-1}$, 0.1 mol $L^{-1}$ and $5\times10^{-3}$ mol $L^{-1}$, respectively.

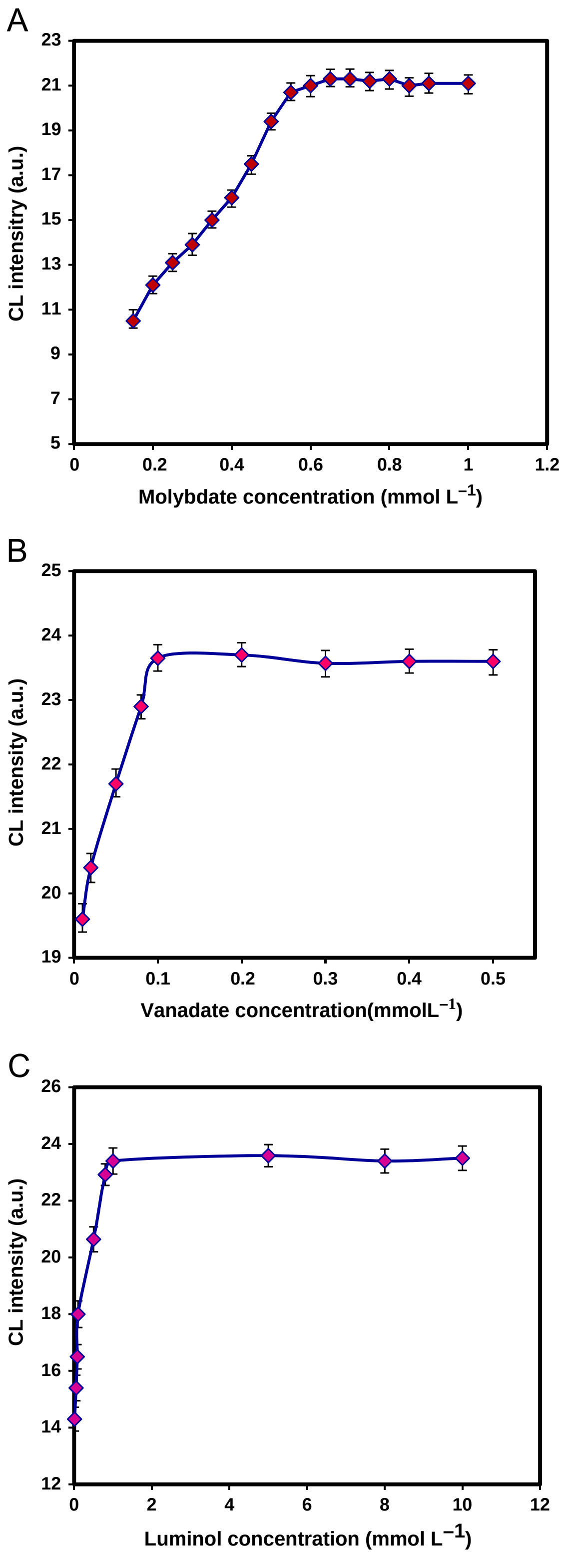

**Fig. 8.** Effect of (**A**) ammonium molybdate concentration, (**B**) ammonium vanadate concentration and (**C**) luminol concentration on the CL intensity.

### 3.3.2. *Effect of CL reagent concentration*

The CL reagent was composed of luminol and NaOH. The ability of the HPA complex of the arsenic oxyanion to stimulate luminol CL emission is well known [25,26]. The effect of luminol concentration on the CL intensity was studied over the range from $10^{-5}$ to $10^{-2}$ mol $L^{-1}$ in 0.15 mol $L^{-1}$ NaOH. The results are given in Fig. 8C. The CL intensity increases by increasing the concentration of luminol from $10^{-5}$ to $10^{-3}$ mol $L^{-1}$ and then remains constant. Consequently, 5.0 mmol $L^{-1}$ luminol solution was used for further experiments.

Since the efficiency of luminol based CL is highly dependent on pH [25], the effect of NaOH concentration in the CL reagent was further studied. The concentration of NaOH was varied from 0.01 to 2 mol $L^{-1}$. The results showed that the CL intensity increases by increasing the NaOH concentration from 0.01 to 0.4 mol $L^{-1}$ and then remains constant. Hence, 0.5 mol $L^{-1}$ NaOH solution was selected as an optimum.

## 3.4. *Study of interferences*

In order to demonstrate the selectivity of the developed extraction method for pre-concentration and determination of As(V) the effect of alkali and alkaline earth metals and several potentially interfering ions on the recovery of As(V) was investigated. In these experiments, different amounts of ions were added to the test solutions containing 250 ng $L^{-1}$ of As(V) and then followed according to general procedure. An ion was considered to interfere when its presence produced a variation of more than ± 5% in the analytical signal of the analyte. The results are shown in Table 2. The results reveal that the developed method is fairly free from the interference resulting from the coexisting ions commonly found in natural water samples.

## 3.5. *Analytical figures of merit*

Optimized experimental parameters and analytical characteristics of the method are given in Table 3. In the optimum conditions, a calibration graph was constructed for As(V) by pre-concentration of standard solutions according to the “General procedure”. Linear relationships were attained between CL intensity and As (V) concentration within two different concentration ranges. The calibration graphs using the pre-concentration system for As (V) were linear in the range of 5.0–800 ng $L^{-1}$ and 800–5000 ng $L^{-1}$, with regression equations of $I_{CL}=96.856\ C_{(As)}+0.0254$ and $I_{CL}=43.23\ C_{(As)}+23.48$ by correlation coefficients of 0.999 and 0.998, respectively, where $I_{CL}$ is the chemiluminescence intensity and $C_{(As)}$ is As(V) concentration (ng $L^{-1}$). The limit of detection was found to be 2.0 ng $L^{-1}$. In order to study the precision of the method a series of six solutions containing 200 and 2000 ng $L^{-1}$ As (V) were measured at the same day. The relative standard deviations were 0.85% and 2.17%, respectively.

**Table 2**
Tolerance limits of potentially interfering ions in the determination of 250 ng $L^{-1}$ of As(V).

| **Interfering ions** | **Interferent to analyte ratio** |
|---|---|
| $Na^{+}$, $K^{+}$, $Ca^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Bi^{3+}$, $Co^{2+}$, $Zn^{2+}$, $Ba^{2+}$, $Ni^{2+}$, $Pb^{2+}$, $Cr^{3+}$, and $Fe^{3+}$ | 1000:1 |
| Mn(VI), $F^{-}$, $Cl^{-}$, $BrO_3^{-}$, $CH_3COO^{-}$, $SO_4^{2-}$, and $NO_3^{-}$ | 500:1 |
| $CO_3^{2-}$, $CrO_4^{-}$, and $BO_3^{3-}$ | 250:1 |
| $PO_4^{3-}$, $H_2PO_4^{-}$, and $HPO_4^{2-}$ | 100:1 |

**Table 3**
Optimized experimental parameters and analytical characteristics of the presented method for As(V) determination.

| Experimental conditions | Unit | |
|---|---|---|
| Amount of sorbent | mg | 150 |
| Sample volume | mL | 200 |
| Eluent concentration | mol $L^{-1}$ | 2 |
| Eluent volume | mL | 1 |
| *Detection conditions* | | |
| Molybdate concentration | mmol $L^{-1}$ | 0.65 |
| Vanadate concentration | mmol $L^{-1}$ | 0.2 |
| Sulfuric acid concentration | mol $L^{-1}$ | 0.75 |
| Luminol concentration | mmol $L^{-1}$ | 5.0 |
| *Analytical parameters* | *Unit* | |
| Linear ranges | (ng $L^{-1}$) | 5.0–800 and 800–5000 |
| Intercepts | – | 0.025 and 23.48 |
| Slopes | – | 96.86 and 43.23 |
| Limit of detection[a] | (ng $L^{-1}$) | 2.0 |
| Correlation coefficients | – | 0.999 and 0.998 |
| RSD (%) ($n=6$) | – | 0.85 (200)[b], 2.17 (2000)[b] |
| Pre-concentration factor | – | 80 |

[a] Calculated as thrice the standard deviation of the blank signal divided by the calibration curve slope.

[b] Values in parentheses are the As(V) concentrations (ng $L^{-1}$) for which the RSD was obtained.

## 3.6. *Method validation and analysis of real samples*

To verify the accuracy of the developed method, it was first applied to the determination of total arsenic in a standard reference material (NIST SRM 1643e, Trace elements in water). The certified amount of arsenic in the SRM is 60.45 ± 0.72 μg $L^{-1}$. The obtained value for total arsenic by using the presented MSPE–CL method was 61.76 ± 0.84 μg $L^{-1}$, (mean of five determinations ± standard deviation), which is in good agreement with the certified value. The method was then used for the determination of As(V) and As(III) in several water samples. Table 4 shows the obtained results. The recovery tests were also performed by spiking the samples with different amounts of As(III) and As(V) before any pre-treatment. As can be seen, the relative recovery values between 93.3% and 106.7% were obtained, which again confirm the accuracy of the method.

## 3.7. *Comparison of the MSPE with other pre-concentration methods*

We compared in Table 5 the linear range, LOD, enhancement or enrichment factor, and sorption capacity of the presented technique with those of other related pre-concentration methods for the extraction and determination of As(V). The presented method has relatively low LOD, good enrichment factor and sorption capacity, and short extraction procedure (about 20 min) with a sample volume of 200 mL. The RSD was 0.85% for 200 ng $L^{-1}$ As(V) level ($n=6$), indicating favorable precision of the presented method. So, the combination of MSPE cleanup system based on the $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid with CL detection provided excellent precision, selectivity and sensitivity, and has other advantages such as simplicity and environment-friendly.

## 4. Conclusions

In this work a novel magnetic solid phase extraction approach based on $Fe_3O_4$/Mg–Al-nitrate LDH nano-hybrid followed by a chemiluminescence detection was developed for the determination of As(V). Due to the selectivity of the synthesized nano-hybrid toward As(V) ions and the sensitivity of the presented chemiluminescence method, the whole methodology resulted in a separation,

**Table 4**
Determination of As(V) and As(III) in real samples (result of recoveries of spiked samples).

| Sample | Added ($\mu g\ L^{-1}$) | | Founded ($\mu g\ L^{-1}$)[a] | | Recovery (%) | |
|---|---|---|---|---|---|---|
| | As(V) | As(III) | As(V) | As(III) | As(V) | As(III) |
| Tap water[b] | 0 | 0 | $0.25 \pm 0.02$ | $0.19 \pm 0.04$ | – | – |
| | 0.15 | 0.15 | $0.40 \pm 0.03$ | $0.34 \pm 0.04$ | $100.0 \pm 3.5$ | $100.0 \pm 1.3$ |
| | 0.25 | 0.25 | $0.49 \pm 0.02$ | $0.45 \pm 0.03$ | $96.0 \pm 1.6$ | $104.0 \pm 1.2$ |
| Spring water[c] | 0 | 0 | $0.24 \pm 0.02$ | $0.30 \pm 0.03$ | – | – |
| | 0.15 | 0.15 | $0.39 \pm 0.02$ | $0.45 \pm 0.03$ | $100.0 \pm 3.1$ | $93.3 \pm 2.7$ |
| | 0.25 | 0.25 | $0.48 \pm 0.04$ | $0.56 \pm 0.03$ | $96.0 \pm 2.4$ | $104.0 \pm 0.8$ |
| Well water[d] | 0 | 0 | $0.66 \pm 0.04$ | $0.92 \pm 0.04$ | – | – |
| | 0.15 | 0.15 | $0.80 \pm 0.03$ | $1.06 \pm 0.04$ | $93.3 \pm 1.8$ | $93.3 \pm 0.4$ |
| | 0.25 | 0.25 | $0.92 \pm 0.03$ | $1.17 \pm 0.05$ | $104.0 \pm 2.0$ | $100.0 \pm 1.1$ |
| Rain water[e] | 0 | 0 | $0.30 \pm 0.01$ | $0.27 \pm 0.02$ | – | – |
| | 0.15 | 0.15 | $0.46 \pm 0.02$ | $0.42 \pm 0.02$ | $106.7 \pm 2.6$ | $100.0 \pm 0.8$ |
| | 0.25 | 0.25 | $0.55 \pm 0.04$ | $0.53 \pm 0.03$ | $100.0 \pm 0.8$ | $104.0 \pm 1.4$ |

[a] Mean of five experiments ± standard deviation.
[b] From drinking water system of Azarshahr, Iran.
[c] Obtained from local source, Khoy, Iran.
[d] Obtained from local source, Khoy, Iran.
[e] Collected at Tabriz, Iran (25 February, 2014).

**Table 5**
Comparison of the presented MSPE method with other pre-concentration methods.

| Sorbent/Detection | Linear range ($\mu g\ L^{-1}$) | LOD ($\mu g\ L^{-1}$) | EF | Sorption capacity ($mg\ g^{-1}$) | Ref. |
|---|---|---|---|---|---|
| Mg–Al–Fe($NO_3^-$) LDH/ET-AAS | 0.015–0.650 | 0.0046 | 300 | 8.7 | [18] |
| ESM/HG-AFS | 0.005–2 | 0.001 | 33 | 0.039 | [25] |
| Polystyrene/CL | $10^{-7}$–$10^{-5}$ ($mol\ L^{-1}$) | $8.9 \times 10^{-8}$ ($mol\ L^{-1}$) | – | – | [26] |
| Modified Sepabeads SP 70 resin/HG-AAS | 1–25 | 0.013 | 36 | 7.3 | [29] |
| Nano $ZrO_2$–$B_2O_3$/HG-AAS | 5–800 | 0.009 | 50 | 98.04 | [30] |
| Modified mesoporous $TiO_2$/ICP–OES | – | 0.1 | 50 | 1.9 | [31] |
| Modified activated carbon /ET-AAS | – | 0.05 | 50 | 7.3 | [32] |
| MSPE–CL | 0.005–5 | 0.002 | 80 | 12.7 | This work |

EF: Enrichment factor, ET-AAS: electrothermal-atomic absorption spectrometry, ESM: eggshell membrane, HG-AFS: hydride generation-atomic fluorescence spectrometry, CL: Chemiluminescence, HG-AAS: hydride generation-atomic absorption spectrometry, ICP–OES: inductively coupled plasma–optical emission spectrometry, MSPE: magnetic solid phase extraction.

pre-concentration and determination of As(V) with high recovery and enrichment factor. In addition, speciation analysis of As was performed utilizing the introduced methodology. The presented method possesses some advantages such as environmentally benign, simplicity, high kinetic sorption on the target analyte, excellent precision and accuracy. To the best of our knowledge, this is the first time that a magnetic solid phase extraction method based on LDHs is combined with chemiluminescence detection system for quantitative determination and speciation analysis of inorganic anions.

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