

## Magnesium Ferrite-Based Solid Phase Extraction for Preconcentration and Quantification of Lead Ions

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In efforts of trace analysis of heavy metals from a water sample, the sample preparation based on solid phase extraction (SPE) addressing the elimination of matrix interferences and the enrichment of metal ions is of vital importance in terms of selectivity and sensitivity. In this framework, the sorbents have been chosen depending on adsorbed target, adsorption capacity and ease in operation. The purpose of this work focused on magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ ) as an efficient sorbent toward divalent lead ions from water, which was applied to their preconcentration prior to quantifying by flame atomic absorption spectrometry (FAAS). Using a co-precipitation approach, the crystalline  $\text{MgFe}_2\text{O}_4$  was obtained as evidenced by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR). The existence of nanospheres with a mean diameter of 50 nm was observed on scanning electron microscope (SEM) and their surface area was estimated to be  $52.6 \text{ m}^2 \text{ g}^{-1}$  by  $\text{N}_2$  adsorption-desorption isotherm. As a sorbent in a SPE technique, lead ions in a water sample were preconcentrated and then eluted from  $\text{MgFe}_2\text{O}_4$  using  $2.0 \text{ mol L}^{-1}$  HCl, prior to being quantified by FAAS.  $\text{MgFe}_2\text{O}_4$  showed the highest recovery of lead ions (100.7 %) in comparison with ferrite ( $\text{Fe}_3\text{O}_4$ , 48.1 %) and nickel ferrite ( $\text{NiFe}_2\text{O}_4$ , 81.7 %). The effects of lead ions preconcentration were examined involving time, dosage of sorbent, pH condition and eluting solution. Method validation was also carried out in compliance with the International Conference on Harmonisation (ICH Q2(R1)), including linearity, recovery, repeatability, limits of detection and quantification. The present report established a simple, fast, non-toxic and efficient procedure in the separation and enrichment of heavy metal ions from water with validated results.

### 1. Introduction

In the field of trace analysis of heavy metals from a water sample, atomic spectroscopic methods are of vital importance, leading to a series of advancement opportunities for various modes, typically flame atomic absorption spectroscopy (FAAS) (Manousi et al., 2021), flame atomic emission spectroscopy (FAES), inductively coupled plasma optical emission spectroscopy (ICP-OES) (Samadifar et al., 2022), inductively coupled plasma mass spectrometry (ICP-MS) (Xu et al., 2022). In principle, FAAS technique has been normally acknowledged in terms of simplicity, low-cost, time-saving; it still faced with challenges of inadequate sensitivity at a trace level and matrix effect for direct quantification of metal cations in a real water sample (Manousi et al., 2021). In conquest of such problems, the most frequently used strategy focused on sample preparation (separation and enrichment of analytes), prior to proceeding quantitative instrumental analysis, such as liquid-liquid extraction (Bagherian et al., 2019) and chemical precipitation (Ipeaiyeda and Ayoade, 2017). The above-mentioned methods faced some drawbacks regarding to complicated multiple-step procedures and high consumptions of hazardous chemicals. Solid phase extraction (SPE) has been recently paid great attention, taking advantage of the elimination of matrix interferences and the preconcentration of metal ions (Khan et al., 2020). The principle of analyte separation on SPE relies on the partition efficiency between mobile (containing analytes) and solid phases (acting as sorbents); in which, the selection of sorbents generally depends on adsorbed target, adsorption capacity and ease in operation.

In this context, nano-sorbents applied to the uptake of metal ions has been assigned for their preconcentration in SPE technique, due to their large surface area and being capable of chemical surface modifications (Khan et al., 2020). Spinel ferrites ( $MFe_2O_4$ , in which M presents divalent metal ion) have been evidenced to be stable in acid environments (pH varied from 2 to 6), being beneficial to the extraction and enrichment of metal cations from a water sample (Abdolmohammad-Zadeh and Salimi, 2018). Taking into account the magnetic property, spinel ferrites could be efficiently collected from an aqueous solution by employing an external magnet, facilitating the further elution step (Lam et al., 2020).

Based on the structure of  $Fe_3O_4$ , the displacement of  $Fe^{2+}$  ions by other divalent metal ions could be obtained by a co-precipitation approach (Dang-Bao et al., 2023), typically  $MgFe_2O_4$  and  $NiFe_2O_4$ . As inverse spinel ferrites, divalent metal ions are placed in the octahedral sites,  $Fe^{3+}$  ions equivalently occupy both the octahedral and the tetrahedral sites (Soufi et al., 2021). The above-mentioned displacement can engender surface and internal pores, leading to raising their surface areas. In contrast to a series of reports on  $Fe_3O_4$ -based (Khan et al., 2020) and  $NiFe_2O_4$ -based SPE methods (Abdolmohammad-Zadeh and Salimi, 2018), it is necessary to exploit other ferrites, typically  $MgFe_2O_4$ , in a similar framework. In the present work, a simple, fast, non-toxic and efficient SPE approach based on  $MgFe_2O_4$  was reported for the preconcentration of divalent lead ions from a water sample prior to their quantification by FAAS. The influences of adsorption and elution conditions on the recovery of lead ions were evaluated and the analytical method was also validated.

## 2. Experimental

### 2.1 Fabrication of $MgFe_2O_4$

All the chemicals in this section were supplied from Xilong Scientific, China.  $MgFe_2O_4$  was fabricated by a co-precipitation, being similar to our previous report for the fabrication of spinel ferrites (Dang-Bao et al., 2023).  $Fe_2(SO_4)_3 \cdot 9H_2O$  ( $5 \times 10^{-3}$  mol) and  $MgSO_4 \cdot H_2O$  ( $5 \times 10^{-3}$  mol) were completely dissolved in 50.0 mL of deionized water. A 100.0-mL aqueous solution of  $2.0 \text{ mol L}^{-1}$  NaOH was then poured dropwise into the above solution; the reaction was taken place at  $80 \text{ }^\circ\text{C}$  for 2 h, under a vigorous stirring condition. After being collected by employing an external magnet, the dark precipitate was washed using deionized water, air dried at  $100 \text{ }^\circ\text{C}$  overnight, and air sintered at  $900 \text{ }^\circ\text{C}$  for 3 h. In a similar approach,  $Fe_3O_4$  and  $NiFe_2O_4$  were also fabricated using  $FeSO_4 \cdot 7H_2O$  or  $NiSO_4 \cdot 7H_2O$  instead of  $MgSO_4 \cdot H_2O$ .

Characteristics of ferrites were examined by XRD on a Bruker D2 phaser ( $Cu\text{-}K\alpha$ , a wavelength of  $1.5406 \text{ \AA}$ ), FT-IR on a Tensor 27 Bruker spectrometer, SEM on a JEOL JSM 7400F instrument.

### 2.2 Recovery of divalent lead ions from an aqueous solution by $MgFe_2O_4$ -based SPE

Lead(II) nitrate solution of  $1000 \text{ } \mu\text{g mL}^{-1}$  as a lead standard solution for AAS and hydrochloric acid (HCl, 37 %) were purchased from Merck. The preconcentration of divalent lead ions was carried out under static adsorption conditions at room temperature. A 100-mL aqueous solution of  $10 \text{ ng mL}^{-1}$  Pb(II) ions containing  $MgFe_2O_4$  (200.0 mg) was adjusted to pH 4.5 and then ultrasonicated for 15 min. After employing an external magnet, the dark solid was separated from an aqueous solution and the elution of Pb(II) ions from the collected dark solid was then carried out by shaking with 2.00 mL of  $2.0 \text{ mol L}^{-1}$  HCl aqueous solution for 10 min.

The lead quantification was performed on ZA3000 Series Atomic Absorption Spectrophotometer, using an air-acetylene flame atomizer with a fuel flow of  $2.0 \text{ L min}^{-1}$ , an oxidant pressure of 160 kPa, an oxidant flow of  $15.0 \text{ L min}^{-1}$  and a burner height of 7.5 mm. At a wavelength of 283.3 nm, the absorbance was measured with an instrument setup including a slit width of 1.3 nm, a lamp current of 7.5 mA and photoelectron multiplier tube (PMT) voltage of 290 V. The lead concentration was quantified by an external standard method; the calibration curve was established based on a linear response between lead concentration and absorbance, in a range of 40–800  $\text{ng mL}^{-1}$ . The blank test was carried out under the same conditions, with a sample containing only matrix (without adding lead standard solution).

The lead recovery was assigned to a ratio of lead amounts eluted from  $MgFe_2O_4$  and in the initial solution sample, estimated from the following Eq(1). The result was represented as a median value of three replicates.

$$\text{Recovery} = \frac{C}{C_0 \times EF} \times 100 \quad (1)$$

Where C represents the lead concentration in the elution solution quantified by FAAS (subtracted with the blank sample);  $C_0$  represents the lead concentration of the initial solution ( $10 \text{ ng mL}^{-1}$ ); EF represents the enrichment factor ( $EF = 50$ ).

### 3. Results and Discussion

#### 3.1 Physicochemical features of $\text{MgFe}_2\text{O}_4$

The formation of ferrites ( $\text{MgFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ ) was admitted via two sequential steps, involving metal hydroxides and then corresponding metal oxides (Dang-Bao et al., 2023). Their crystal structures were characterized via XRD (Figure 1), evidencing the presence of face-centered cubic spinel signaled at the diffraction planes of (220), (311), (400), (511) and (440), corresponding to the standard JCPDS files for  $\text{MgFe}_2\text{O}_4$  (JCPDS 77-1547),  $\text{NiFe}_2\text{O}_4$  (JCPDS 89-4927) and  $\text{Fe}_3\text{O}_4$  (JCPDS 76-1470). According to the Debye-Scherrer equation (Dang-Bao et al., 2023), their crystallite sizes were calculated and briefed in Table 1. Their chemical compositions in the solid were analysed by EDTA (ethylenediaminetetraacetic acid) complexometric titration method, being consistent with the corresponding chemical formulas (Table 1).

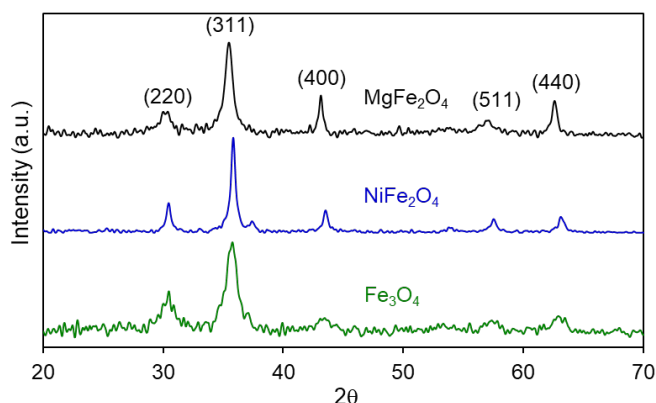


Figure 1: XRD patterns of various ferrites

Table 1: Crystallite sizes and chemical compositions of various ferrites

Sample	XRD		Chemical composition	
	Diffraction plane	Crystallite size (nm)	Fe (wt.%)	Mg or Ni (wt.%)
$\text{MgFe}_2\text{O}_4$	(311)	10.9	58.6	11.3
$\text{NiFe}_2\text{O}_4$	(311)	19.4	43.5	23.3
$\text{Fe}_3\text{O}_4$	(311)	8.7	68.5	-

Taking into account the highest lead recovery from an aqueous solution (see next section), the thorough characterization of  $\text{MgFe}_2\text{O}_4$  was accomplished. Based on FT-IR,  $\text{MgFe}_2\text{O}_4$  indicated the absorption bands at  $3410\text{ cm}^{-1}$  (O–H stretching) and  $1630\text{ cm}^{-1}$  (O–H bending) associated to absorbed hydroxyls on the surface (Figure 2) (Thach-Nguyen et al., 2022). The doublet vibrational bands at  $533\text{ cm}^{-1}$  and  $515\text{ cm}^{-1}$  could be respectively contributed by the stretching of metal-oxygen placed at tetrahedral and octahedral sites of inverse spinel ferrites (Figure 2, inset) (Durrani et al., 2017).

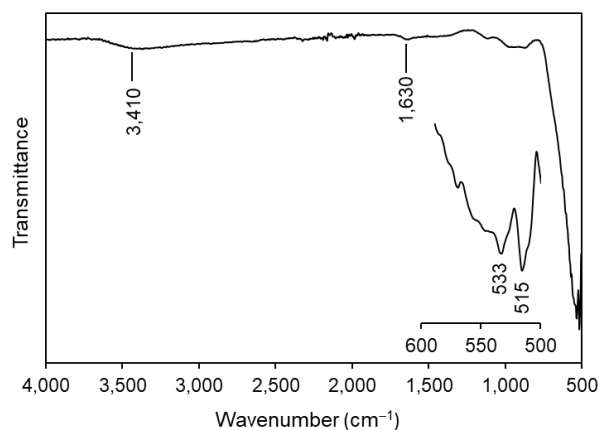


Figure 2: FT-IR spectrum of  $\text{MgFe}_2\text{O}_4$  in a wavenumber range of  $4000\text{--}500\text{ cm}^{-1}$  and  $600\text{--}500\text{ cm}^{-1}$  (inset)

The surface of  $\text{MgFe}_2\text{O}_4$  was examined by  $\text{N}_2$  adsorption-desorption isotherm, obeying type IV with the H3 type hysteresis loop at a high relative pressure (IUPAC classification), regarding to a mesoporous structure (Figure 3a) (Heidari and Masoudpanah, 2020). The BET surface area of such a ferrite was estimated to be  $52.6 \text{ m}^2 \text{ g}^{-1}$ . The BJH pore size distribution of  $\text{MgFe}_2\text{O}_4$  was mainly centred in a range of 5–40 nm, with the corresponding average pore diameter of 18.9 nm and pore volume of  $0.2485 \text{ cm}^3 \text{ g}^{-1}$  (Figure 3b).

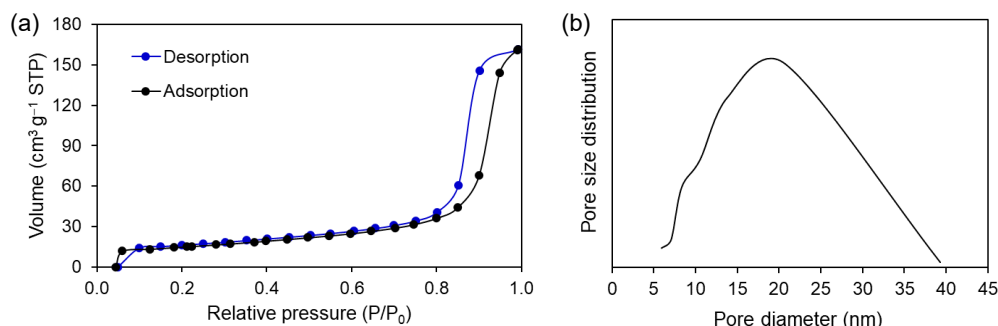


Figure 3: (a)  $\text{N}_2$  adsorption-desorption isotherm, and (b) BJH pore size distribution of  $\text{MgFe}_2\text{O}_4$

The size, shape and distribution of  $\text{MgFe}_2\text{O}_4$  was inspected via SEM (Figure 4), indicating that the ferrite was spherical in shape and around 50 nm in size. Although some aggregates were observed due to the magnetic property of such a spinel ferrite and a lack of stabilizers, the clusters consisted of nano-sized spheres could be concluded (Dang-Bao et al., 2023).

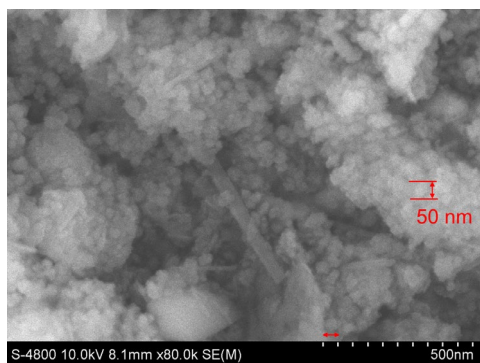


Figure 4: SEM image of  $\text{MgFe}_2\text{O}_4$

### 3.2 Recovery of divalent lead ions from an aqueous solution by $\text{MgFe}_2\text{O}_4$ -based SPE

The recovery efficiency of lead ions from various spinel ferrites was presented in Figure 5, showing the highest value of  $\text{MgFe}_2\text{O}_4$  (100.7 %) in comparison with  $\text{NiFe}_2\text{O}_4$  (81.7 %) and  $\text{Fe}_3\text{O}_4$  (48.1 %). When  $\text{Fe}^{2+}$  ions or  $\text{Ni}^{2+}$  ions were replaced by  $\text{Mg}^{2+}$  in the octahedral sites (Soufi et al., 2021), the porosity of  $\text{MgFe}_2\text{O}_4$  was enlarged due to the difference in their ionic radius (Abdolmohammad-Zadeh and Salimi, 2018), raising the surface area and favouring the uptake of lead ions from water.

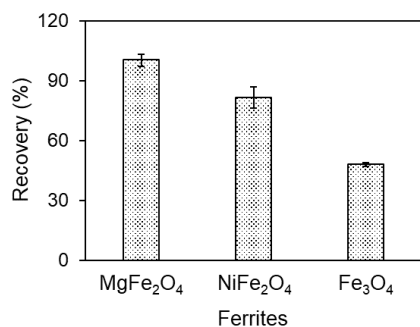


Figure 5: Recovery of lead ions from various spinel ferrites

As the best sorbent in a SPE method, the preconcentration and the elution of lead ions from  $\text{MgFe}_2\text{O}_4$  were successively controlled via time, pH condition, dosage of sorbent and concentration of HCl eluting solution (Figure 6). The uptake of lead ions could be contributed by their anchoring in mesopores, or their interaction with the surface charge of  $\text{MgFe}_2\text{O}_4$ . The presence of surface hydroxyls as proven by FT-IR analysis could provoke the protonation or deprotonation, depending on pH condition. In a low pH condition, the protonation was favour and the surface was positively charged, and the repulsive force was occurred with positively charged lead ions. With increasing the pH condition, the deprotonation of surface hydroxyls was beneficial to electrostatic force between opposite charged counterparts. At  $\text{pH} > 5$ , the precipitation of lead ions interfered their uptake on the surface of sorbent (Abdolmohammad-Zadeh and Salimi, 2018). The suitable conditions were established involving time of 10 min, 0.20 g sorbent at pH 4.5 using  $2.0 \text{ mol L}^{-1}$  HCl as an eluting solution for the recovery of lead ions from  $\text{MgFe}_2\text{O}_4$ .

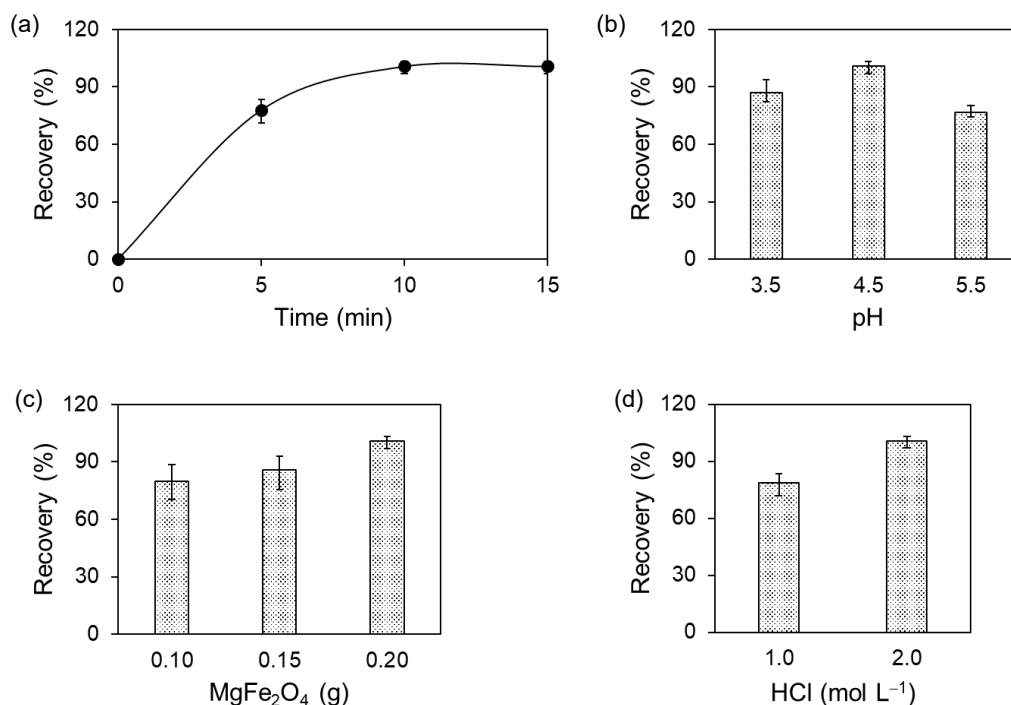


Figure 6: Influences of preconcentration conditions on the lead recovery of  $\text{MgFe}_2\text{O}_4$

### 3.3 Method validation

The above-mentioned  $\text{MgFe}_2\text{O}_4$ -based SPE for the quantification of Pb(II) ions in an aqueous solution by FAAS was validated in compliance with the ICH Q2(R1) (ICH Harmonised Tripartite Guideline, 2005); including linearity, accuracy (%recovery), repeatability (relative standard deviation, %RSD), limits of detection (LOD) and quantification (LOQ). The linear regression equation was plotted based on the linear response between absorbance and Pb(II) concentration ( $40\text{--}800 \text{ ng mL}^{-1}$ ). The above-mentioned values were estimated on the blank samples spiked with Pb(II) for six replicates and briefed in Table 2. The proposed analytical method was adequate with a good repeatability (%RSD of 5.2 %) and a good accuracy (%recovery of 100.7 %).

Table 2: Validated parameters for  $\text{MgFe}_2\text{O}_4$ -based SPE method

Parameters	Results
Linear range ( $\text{ng mL}^{-1}$ )	40–800
Linear regression	$y = 0.0109x - 6.36 \times 10^{-5}$
Determination coefficient ( $R^2$ )	0.9999
LOD = $3.3 \times \text{SD}$ ( $\text{ng mL}^{-1}$ )	0.086
LOQ = $10 \times \text{SD}$ ( $\text{ng mL}^{-1}$ )	0.26
Enrichment factor	50
%Recovery	100.7
%RSD	5.2

#### 4. Conclusions

A simple, fast, non-toxic and efficient SPE approach based on MgFe<sub>2</sub>O<sub>4</sub> (spherical in shape and 50 nm in diameter, 52.6 m<sup>2</sup> g<sup>-1</sup> in BET surface area) was reported for the preconcentration of divalent lead ions from a water sample prior to their quantification by FAAS. In a spinel ferrite, when Mg<sup>2+</sup> ions are placed in the octahedral sites, the porosity of MgFe<sub>2</sub>O<sub>4</sub> was enlarged, raising the surface area and favouring the uptake of lead ions. The suitable conditions were established involving time of 10 min, 0.20 g sorbent at pH 4.5 using 2.0 mol L<sup>-1</sup> HCl as an eluting solution for the recovery of lead ions from MgFe<sub>2</sub>O<sub>4</sub>. Achieving an enrichment coefficient of 50, the present method evidenced good recovery and repeatability, widening its application for the lead quantification in real samples.

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