

Trace analysis of Pb(II) in milk samples by $\text{Fe}_3\text{O}_4@\text{SiO}_2@3\text{-chloropropyltriethoxysilane}@o\text{-phenylendiamine}$ nanoparticles as an unprecedented adsorbent for magnetic dispersive solid phase extraction

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In the present work, a magnetic dispersive solid-phase extraction method followed by flame atomic absorption spectrometry was used for extraction, preconcentration and determination of trace amounts of Pb(II) in milk samples. $\text{Fe}_3\text{O}_4@\text{SiO}_2@3\text{-chloropropyltriethoxysilane}@o\text{-phenylendiamine}$ nanoparticles were synthesised and used as the adsorbent in the extraction procedure. The effective parameters of the extraction efficiency comprising pH of the sample solution, sorbent amount, extraction time, acidic concentration of the eluent and desorption time were optimised using a face-centred central composite design. Under the optimal conditions, the applied method offered suitable linearity in the range of 2.0–250 ng mL⁻¹, the limit of detection as low as 0.11 ng mL⁻¹, and high preconcentration factor of 66. The precision of the proposed method was evaluated by calculating the intra-day and inter-day relative standard deviation, which were <3.4 and 5.5%, respectively. The applicability of the method in real sample analysis was tested by analysing bovine milk samples. The relative recoveries in the range of 81.6–97.2% showed the suggested method is of appropriate accuracy in real sample analysis.

1. Introduction: During the past century and as a result of the industrialisation, heavy metal ions have drastically contaminated many resources which human beings and other species directly or indirectly deal with [1]. Many newly arrived stuff such as fertilisers, synthetic dyes, industrial oils and fabrications and many other human-made products are polluting our ecosystems with toxic heavy metals. These elements can easily penetrate from wastewaters to soil and as a result, they can easily enter to vegetation. When the livestock and poultry consume the vegetation and seeds, which were cultivated in heavy metal-contaminated soils, the toxic heavy elements can easily spread out through our food chains [2, 3]. The most well-known heavy metals are cadmium (Cd), zinc (Zn), chromium (Cr), manganese (Mn), cobalt (Co), mercury (Hg) and lead (Pb). Although some of them like zinc and manganese are considered as essential elements for our body at trace levels, most of these elements have different levels of toxicity to human health as well. Pb(II) is one of the most important toxic elements which has been catastrophically increased in geologic parent materials as a result of industrialisation. One of the food products that we routinely consume is milk and related dairy samples because of the essential nutrients and elements. Pb(II) appears to be the most common heavy metal in milk. The maximum permissible limit of Pb(II) by Codex Alimentarius Commission is 20 µg L⁻¹. Thus, quantitative analysis of such metal ions in these products would be definitely valuable [4–6]. Chemical analysis of many real samples required different pretreatment steps due to the high levels of contaminants and interferences in complex matrices which are potentially detrimental to analytical instruments. Conventional sample preparation techniques such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) need high amounts of hazardous organic solvents as well as labour-intensive steps [7]. Alternatively, modern extraction methods bring about simple and labour-saving steps with the lowest consumption of organic solvents and other hazardous material. These methods are miniaturised form of the conventional extraction techniques termed as microextraction methods [8, 9]. In 1990, Pawliszyn and

co-worker [10] introduced solid-phase microextraction methods, in which just micrograms of a solid phase was considered as the acceptor phase. Similarly, as an alternative for LLE, Jeannot and Cantwell [11] introduced the liquid-phase microextraction method in 1996 in which the target analytes were extracted into an organic droplet. Since then, different miniaturised extraction methods have been released by research groups worldwide such as hollow-fibre liquid-phase microextraction (LPME) [12], dispersive liquid–liquid microextraction [13], electromembrane extraction [14], in-tube solid-phase microextraction [15], pipette-tip SPE (PT-SPE) [16], magnetic dispersive SPE (MDSPE) [17], and many other formats with innovative approaches. During the past decade, the exploitation of nanostructured materials in microextraction methods have facilitated these methods thanks to the ease of preparation, availability of required materials which are usually environmentally friendly, with high cleanup values and extraction efficiencies (EEs) [18]. Among different nanomaterials, Fe_3O_4 nanoparticles (NPs) has been utilised as an excellent substrate which can be easily modified with different functional groups. Moreover, thanks to the superparamagnetic feature of this nanomaterial, it can be easily eliminated from the sample solutions with a strong external magnet. Up to now, different functional groups have been used to modify the Fe_3O_4 surface [19]. With the aim of this strategy, different analytes with diverse physicochemical properties can be selectively extracted from a wide variety of sample matrices making an extraction method more selective.

In the present study, novel $\text{Fe}_3\text{O}_4@\text{SiO}_2@3\text{-chloropropyltriethoxysilane}@o\text{-phenylendiamine}$ (OPSF) NPs were synthesised and utilised as an adsorbent in MDSPE for selective and efficient extraction and preconcentration of Pb(II) at trace levels in milk samples. Next, the determination of the analyte was carried out by flame atomic absorption spectrometry (FAAS) instrument. The effective parameters of the extraction were identified and optimised through face-centred central composite design (FCCD) method. The optimised method was evaluated for extraction, preconcentration and determination of Pb (II) in whole milk samples.

2. Experimental setup

2.1. Chemicals and reagents: In this research, all the chemicals and reagents were analytical grades. A 1000 mg L⁻¹ stock solutions of Pb(II) was prepared by dissolving an appropriate amount of Pb(NO₃)₂ in 1.0% HNO₃. Other standard samples were freshly prepared by diluting of the stock solution with ultrapure water. Ferric chloride (FeCl₃·6H₂O), ferrous chloride (FeCl₂·4H₂O), tetraethyl orthosilicate (TEOS), acetylacetone, sodium hydride, toluene, tetrahydrofuran, 3-chloropropyltrimethoxysilane, o-phenylenediamine, triethylamine, sodium hydroxide, sulphuric acid, nitric acid, hydrochloric acid, trifluoroacetic acid, ethanol and hydrogen peroxide were purchased from Merck (Darmstadt, Germany). All the glassware was cleaned by soaking in diluted HNO₃ (1:5) for 24 h and then washed several times with ultrapure water.

2.2. Instruments and apparatus: FT-IR spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellet. Scanning electron micrograph images were taken with VEGA-TESCAN. Energy-dispersive X-ray (EDX) spectra were recorded with a Numerix DXP-X10P. Magnetic measurements of the solid samples were performed using a vibrating sample magnetometer (VSM) from Meghnatis Kavir Kashan (Kashan, Iran). Quantitative analysis of Pb(II) was carried out using a FAAS (GBC Scientific Equipment, Australia) equipped with a hollow cathode lamp for the lead as a radiation source (wavelength, 217.0 nm spectrum bandwidth, 1.0 nm; lamp current, 5.0 mA), a deuterium background corrector and an air-acetylene flame. The flame composition was operated according to the optimum operation conditions recommended by the manufacturer. According to the adsorption mechanism of Pb ions on the surface of prepared NPs, mentioned in Fig. 1, an electrostatic interaction can be created between pb²⁺ ions and sorbent surface. Moreover, due to the presence of chelating agents on the sorbent surface, pb²⁺ ions can also be adsorbed via complex formation.

2.3. Real samples: Bovine milk samples were bought from a local supermarket. In order to precipitate the proteins in milk samples, 1.0 mL of trifluoroacetic acid was added to 10 mL of each milk sample and vortexed for 5 min. Then, the sample was centrifuged at 3500 rpm for 15 min to precipitate milk proteins. The supernatant was diluted with distilled water, its pH was adjusted to 8.72 and finally transferred to a 100 mL volumetric flask and diluted up to the mark.

2.4. Synthesis of OPSF NPs: A schematic presentation for the synthesis of OPSF NPs is shown in Fig. 2. Synthesis of superparamagnetic Fe₃O₄ NPs was carried out using chemical co-precipitation of Fe(III) and Fe(II) according to the published methods in the literature [20]. Briefly, 2.82 g of FeCl₃ and 1.72 g of FeCl₂·4H₂O were dissolved in 80 mL of distilled water. Next, the reaction was warmed to 80°C and stirred with a mechanical stirrer. Then, 10 mL of ammonia was added drop-wise to the mixture. At the next step, the mixture was then stirred for 40 min and then cooled to room temperature. Finally, the black precipitate was collected using an external magnet and washed several times with ethanol and distilled water. The synthesised black solid was dried at 80°C in an oven. Then, 45 mg of the obtained Fe₃O₄ NPs were dispersed

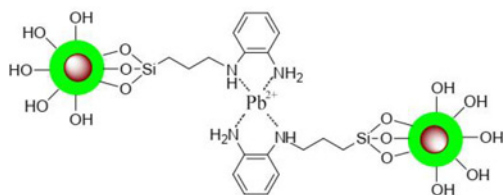


Fig. 1 Proposed mechanism Fe₃O₄@SiO₂-OPDA

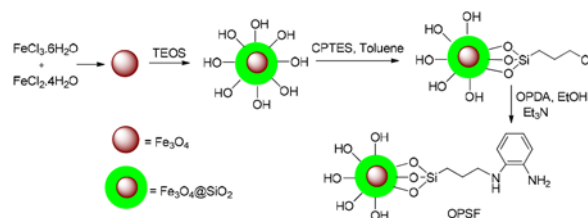


Fig. 2 Schematic presentation of the synthesised Fe₃O₄@SiO₂@3-chloropropyltriethoxysilane@o-phenylenediamine (OPSF) NPs

in 16 mL of deionised water under ultrasound irradiation by using an ultrasonic water bath.

To prepare Fe₃O₄@SiO₂ core@shell NPs, 0.8 mL of TEOS was added drop-wise into the mixture and stirred vigorously for 24 h at room temperature. Then, the products were separated by an external magnet and washed several times with distilled water. The final product was collected and dried at 50°C [21]. To synthesise Fe₃O₄@SiO₂@3-chloropropyltriethoxysilane NPs, 1.00 g of the synthesised Fe₃O₄@SiO₂ NPs was added in 100 mL dried toluene. After that, 1.0 mL of 3-chloropropyltriethoxysilane was added drop-wise to the mixture under stirring for 16 h at 60°C. The resultant solid precipitate was collected by an external magnet and washed several times with ethanol and distilled water, and then the synthesised product was dried under vacuum for 2 h at 60°C. Finally, in order to prepare OPSF NPs, 1.00 g of the synthesised Fe₃O₄@SiO₂@OSi(CH₂)₃Cl was dissolved in 50 mL EtOH in three separate flasks under ultrasound irradiation. After that, 1.0 mmol (1.08 mg) of o-phenylenediamine with 0.1 mL Et₃N was added to the mixture under ultrasound irradiation and then refluxed for 12 h. Lastly, the obtained mixture was separated from reaction mixture by an external magnet and the washed with EtOH and dried at 60°C for about 12 h [22].

2.5. MDSPE procedure followed by FAAS: The MDSPE procedure was carried out as follows: 48 mg of the synthesised sorbent was added into 100 mL of the sample solution (pH 8.72) and the mixture was stirred for 9 min. Then, using a strong external magnetic field, NPs were separated from the mixture very quickly. Afterwards, the supernatant was decanted and the adsorbent, which still contained residuals of the sample, was transferred into a conical tube. After removing the residuals of the sample solution from the sorbent, NPs were washed using 1.5 mL of HNO₃ 1.1 mol L⁻¹ under the vigorous vortex for 15 min. Finally, the extract was introduced to the FAAS instrument for analytical detection and quantification.

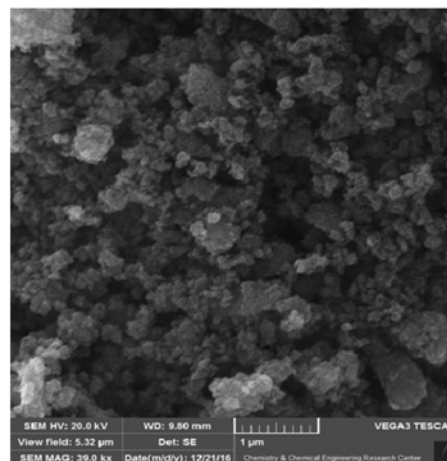


Fig. 3 SEM image of the OPSF NPs at 39,000 magnification

3. Results and discussion

3.1. Characterisation of the prepared OPSF NPs: To evaluate the morphological shape as well as the size of the synthesised sorbent, scanning electron microscopy (SEM) was utilised

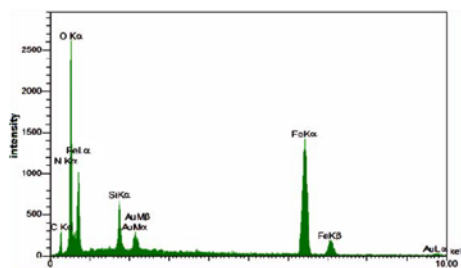


Fig. 4 EDX spectrum of the OPSF NPs

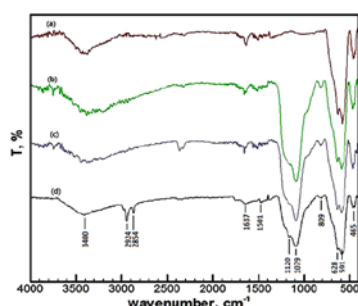


Fig. 5 FT-IR spectra of
a Bared Fe₃O₄
b Fe₃O₄@SiO₂
c Fe₃O₄@SiO₂@3-chloropropyltriethoxysilane
d OPSF NPs

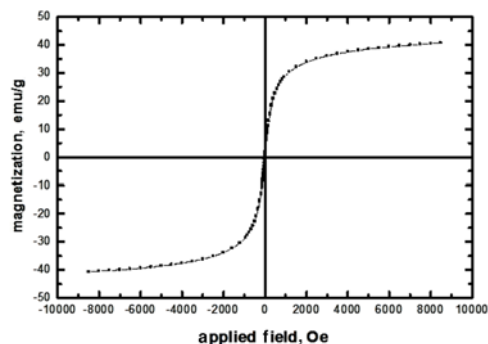


Fig. 6 VSM curve of the synthesised OPSF NPs

(Fig. 3). The synthesised NPs were of spherical shape and uniform size with the average diameters of 30 nm.

In order to ensure that the synthesised sorbent contains the desired functional groups, EDX analysis was used. As can be seen in Fig. 4, the obtained EDX spectrum was of peaks indicating the elemental analysis of the synthesised sorbent. As is shown the distinguishable separate peaks of Fe, O, Si, C and N confirm the successful synthesis of the desired nanosorbent.

The above results were accompanied by the FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@3-chloropropyltriethoxysilane, and OPSF. Fig. 4 depicts the obtained FT-IR spectra of these particles. According to this Fig. 5, the absorption band at 591 cm⁻¹ is corresponded to stretching vibration of Fe–O. Also, the sharp peak illustrated at 1079 and 1120 cm⁻¹ are related to asymmetric stretching vibration of Si–O group. The stretching vibrations of aliphatic C–H groups are illustrated at 2854 and 2924 cm⁻¹. Moreover, the absorption band at 3400 cm⁻¹ is related to the stretching vibration of the N–H and O–H groups.

To test the magnetic properties of the synthesised sorbent, VSM analysis was carried out at room temperature. As is shown in Fig. 6, the magnetic saturation of the synthesised sorbent was around 40.73 emu g⁻¹. Although these values are less than bared Fe₃O₄ NPs (60 emu g⁻¹), the magnetic properties of the sorbent were strong enough to be separated from the sample solution via an external magnet.

3.2. Optimisation of the MDSPE procedure: To achieve the best analytical performance of the proposed methods, the effective parameters on the EE of the method were identified and optimised. For this purpose, response surface methodology was performed using a central composite design as the optimisation protocol [23, 24]. The effective parameters were pH of the sample solution, adsorption time and sorbent amount for the adsorption step, as well as the acid concentration in the desorption solvent, the eluent volume, and desorption time for the desorption step. Table 1 shows the selected range and the optimum values of the effective parameters. During the optimisation step, a concentration of 250 ng mL⁻¹ of Pb (II) was used.

Figs. 7a and b graphically show the relationships between the effective parameters of the adsorption step of the MDSPE procedure in three-dimensional (3D) response surface graphs. According to these figures, the optimal value for the pH of the sample solution was 8.72. The next variable was sorbent amount which was investigated in the range of 10–50 mg. Low amounts of the sorbent are not capable of adsorbing the analyte effectively, while high amounts of the sorbent lessen the ability of the eluent for successful desorption. According to the obtained results, the sorbent amount of 48.0 mg was selected as the optimal value of this parameter.

Just like other extraction methods, MDSPE is an equilibrium procedure in which the extraction time directly determine the quality of this equilibrium. In accordance with this point, the effect of the extraction time was evaluated using different

Table 1 Optimum values and optimised ranges of the selected parameter in the adsorption and desorption steps using a FCCD

	Factors	Symbols	Levels			Optimum value ^a
			Low (–1)	Centre (0)	High (+1)	
adsorption step	sample pH	A	5	7	9	8.72
	sorbent amount, mg	B	10	30	50	48.06 (48.0)
	adsorption time, min	C	5	15	25	8.38 (9.0)
desorption step	acid conc., mol L ⁻¹	D	0.5	1.0	1.5	1.11 (1.1)
	acid volume, mL	E	0.75	1.5	2.25	1.52 (1.5)
	desorption time, min	F	5	10	15	14.70 (15.0)

^aData in the parenthesis were selected practically.

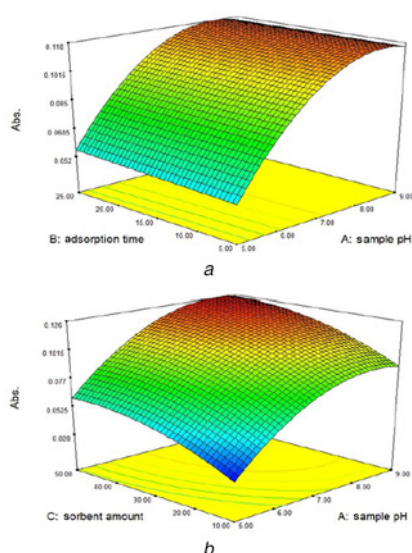


Fig. 7 Response surfaces obtained from optimisation of the adsorption step
a The relationship between adsorption time and sample pH
b The relationship between sorbent and sample pH

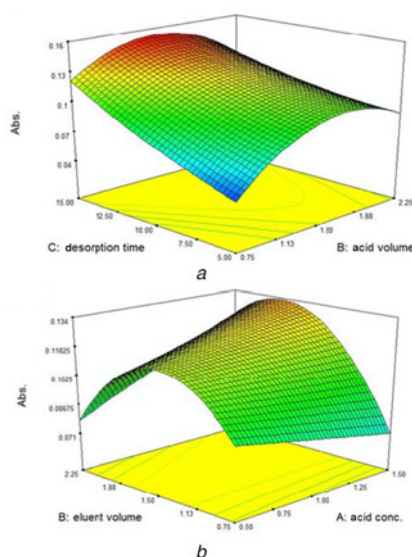


Fig. 8 Response surfaces obtained from optimisation of the desorption step
a The relationship between desorption time and acid volume
b The relationship between eluent volume and acid concentration

extraction times in the range of 5.0–25.0 min. According to the results, 9.0 min was the optimum value for this effective parameter.

Also, the obtained 3D plots for the desorption step can be seen in Figs. 7*a* and *b*. During the desorption step, desorption volume must be adequately high to desorb the target analyte efficiently, otherwise, desorption procedure would be incomplete. Another effective parameter is the acidic concentration of the eluent which should be adjusted at appropriate values to desorb the analyte from the sorbent. To this point, different concentrations of HNO_3 were evaluated in the range of 0.5–1.5 mol L^{-1} . According to the results, 1.10 mol L^{-1} of HNO_3 was considered as the optimal value of this parameter. The volume of the applied acidic solution was the other effective parameter which was investigated in the range of 0.75–2.25 mL. As this solution was, in fact, the final extract, the volume of this solution should be high enough to dissolve as much desorbed analyte as practicable. On the other hand, too much of the volumes of this solution would result in the dilution phenomenon. According to the suggested model of the FCCD protocol, 1.5 mL was the best amount of this parameter. Finally, the other parameter of this step was desorption time. This parameter had to be long enough to ensure that the desorption procedure would be completed. According to the obtained results from the optimisation of this parameter, 15.0 min was selected as the optimum value of desorption time.

3.3. Effect of interfering ions: The heavy metal analysis is usually accompanied by the interference of similar ions other than the target analyte. That is why we tried to investigate the effects of co-existence other possible metal ions on the EE of Pb(II). To this aim, different amounts of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and Fe^{2+} were added at different concentration levels into 100 mL of the sample solution contacting 50 ng mL^{-1} of the target analyte. Under the optimal conditions, the MDSPE was carried out. By definition, an ion which caused a variation $> \pm 10\%$ in the recovery was considered as an interfering species. The experimental results indicated no considerable interference effect at interfering/ion concentration ratios of 1000 for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , 125 for Zn^{2+} , Ni^{2+} , Fe^{2+} and 80 for Cu^{2+} on quantitative analysis of Pb(II).

3.4. Analytical performance: To evaluate the analytical performance of the proposed method for preconcentration and determination of Pb(II) at trace levels, figures of merits were calculated (Fig. 8). For this goal, the calibration curve was plotted for Pb(II) which was linear within the concentration range of 2.0–250 ng mL^{-1} with a calibration equation of $\text{Abs.} = 0.4884 C (\text{mg L}^{-1}) + 0.0122$ ($R^2 = 0.9993$). The limit of detection was calculated according to $\text{LOD} = 3S_b/m$ equation, where S_b is the standard deviation of five replicates of the blank signals and m is the slope

Table 2 Comparison between the figures of merit of the proposed method and some other reports published in the literature

Method	Sample volume	LOD (ng mL^{-1})	LDR (ng mL^{-1})	RR%	PF	RSD%	Ref.
$\text{Fe}_3\text{O}_4/\text{TiO}_2/\text{PAN}^a/\text{FAAS}$	50.0 mL	1.21	4.00–470	>99.0	250	2.20	[25]
$\text{CaFe}_2\text{O}_4\text{--APTES--PA}^b/\text{FAAS}$	50.0 mL	0.78	3.50–200	98.2	133	2.50	[26]
ATSA ^c resin/FAAS	125 mL	0.15	1.0–20.0	93.0	350	9.00	[27]
magnetic graphene/ETAAS ^d	50.0 mL	0.50	1.50–200	97.0	—	3.30	[28]
IL-SD-LPME ^e /ETAAS	100 mL	0.015	0.025–0.8	—	76.0	5.20	[29]
MPTS modified SiO_2 /ICP-AES	10.0 mL	0.52	—	>90.0	5.00	3.80	[30]
OPSF/FAAS	100 mL	0.11	2.00–250	>81.6	66.0	5.50	this work

^a1-(2-pyridylazo)-2-naphthol modified $\text{Fe}_3\text{O}_4/\text{TiO}_2$.

^bAnhydride calcium ferrite NPs functionalised with 3-aminopropyl-triethoxysilane (APTES) and phthalic anhydride (PA).

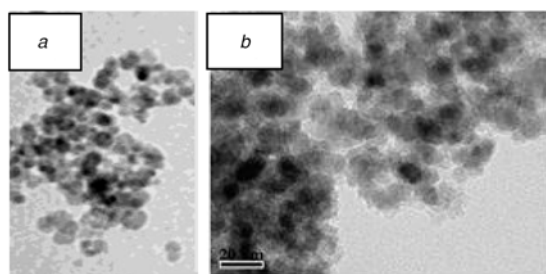
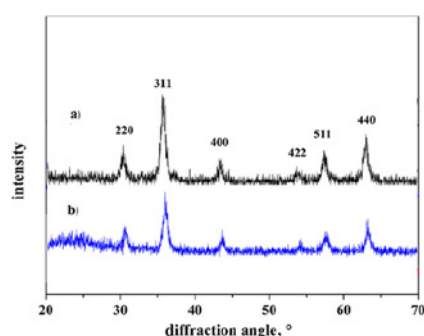
^cAminothiazole sulfonamide.

^dElectrothermal atomic absorption spectrometry.

^eIonic liquid-based single drop liquid-phase microextraction.

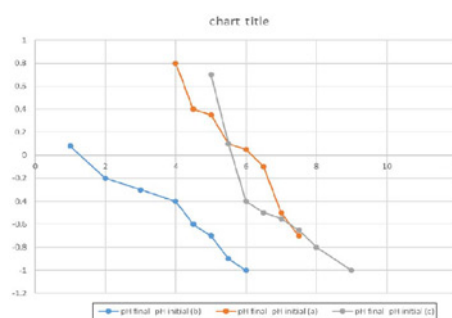
Table 3 Determination of Pb in milk samples using the proposed method

Sample	Added (ng mL ⁻¹)	Found (ng mL ⁻¹) ± SD	RR% ^a (relative error%)
milk 1	0	37.4 (±0.85)	—
	25	60.3(±1.12) ^b	91.6 (−8.4)
	100	134.6 (±1.5)	97.2 (−2.8)
milk 2	0	45.4 (±0.55)	—
	25	65.8 (±0.76)	81.6 (−18.4)
	100	141.3 (±2.2)	95.9 (−4.1)
milk 3	0	15.8 (±0.53)	—
	25	37.9 (±0.77)	88.4 (−11.6)
	100	112.3 (±2.3)	96.5 (−3.5)
milk 4	0	25.3 (±0.66)	—
	25	47.5 (±2.0)	88.8 (−11.2)
	100	121.7 (±1.8)	96.4 (−4.6)

^aRR%.^bStandard deviation for $n = 3$.**Fig. 9** TEM images ofa bare Fe₃O₄b Fe₃O₄@SiO₂**Fig. 10** XRD ofa bare Fe₃O₄b Fe₃O₄@SiO₂

of the calibration curve for the extraction procedure. The obtained detection limit was lower than 0.11 ng mL⁻¹ showing the capability of the method in trace analysis of Pb(II) in milk samples. Also, the limit of quantification was evaluated using $LOQ = 10S_b/m$ equation. The intra- and inter-assay precisions of the proposed method using relative standard deviation (RSD%) at two different concentration of 25 and 100 ng mL⁻¹ were calculated. Intra-day and inter-day RSD% values were obtained <3.4 and 5.5%, respectively. The respective preconcentration factor (PF) and EE% were obtained at 66 and 100%, respectively.

Table 2 is a summary of the obtained analytical data for the other studies reported in the literature to comparably evaluate the analytical performance of the suggested method in terms of its figures of

**Fig. 11** Zeta potential ofa Bare Fe₃O₄b Fe₃O₄@SiO₂c Fe₃O₄@SiO₂-OPDA

merit. As can be seen, in comparison with other studies mentioned in the table, the proposed method offers favourable EE, high PF, as well as suitable linear dynamic range.

3.4.1. Real sample analysis: To test the applicability of the method in determination of Pb (II) in real samples, different bovine milk samples were analysed. To begin with, all the samples were prepared based on the described procedure in Section 2.3 and then were analysed by the proposed MDSPE method. To investigate the relative recovery (RR%) of the method in each sample, Pb(II) standard solutions were spiked into the samples at two concentration levels of 20 and 100 ng mL⁻¹.

Table 3 summarises the obtained results of the quantitative analysis of Pb(II) in bovine milk samples. According to these results, the favourable RR% values in the range of 81.6–97.2% indicate that the suggested method is quite applicable for quantitative analysis of Pb(II) in bovine milk samples as a fairly complex matrix.

The TEM images, XRD and zeta potential analysis of bare Fe₃O₄ and SiO₂-coated Fe₃O₄ have been added as Figs. 9–11.

4. Conclusion: In this research, a novel magnetic NP called Fe₃O₄@SiO₂@3-chloropropyltriethoxysilane@o-phenyldiamine was used for a highly effective MDSPE of lead in milk samples followed by FAAS. As the procedure was divided into two separate steps comprising adsorption and desorption of the target analyte, both the steps were optimised through a FCCD protocol. Under the optimal conditions, the applied method showed noticeable EE, broad linear dynamic range, and desirable RSDs. Furthermore, satisfactory LOD and appropriate cleanup values made the procedure quite capable of determining Pb(II) at trace levels in complex matrices like milk samples. Also, the method is simple and fast and can be used as a suitable alternative for lead analysis in biological fluids.

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6 References

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