

Evaluation and determination of occupational and environmental exposure of lead in workplace air and human workers based dispersive ionic liquid solid phase micro extraction in battery manufacturing factories from Iran

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ABSTRACT

The exposure of lead in workplace air and human workers of battery manufacturing factory was evaluated determined by nanotechnology since 2019-2020. Human whole blood (HWB) for subject and healthy peoples (25-55, Men, 40 N) and workplace air (40N) was prepared based on NIOSH sampling. 10 mL of HWB samples added to 20 mg of mixture ionic liquid/ ligand ([HMIM][PF₆]/APDC) modified on graphene oxide nanostructures(GONs) at pH=6. After sonication, the lead ions separated/extracted by dispersive ionic liquid solid phase micro extraction (DIL-SPME) and determined by flame atomic absorption spectrometry (F-AAS). All air samples in workplace were analyzed based on NIOSH process. The results showed us the negative correlation between Pb concentration in human blood subject and healthy peoples ($r=0.24$). The range concentrations of lead in human subject, healthy peoples and workplace air were obtained 193.4-543.7 $\mu\text{g L}^{-1}$, 85.6-175.9 $\mu\text{g L}^{-1}$ and 44.7-81.5 $\mu\text{g m}^{-3}$, respectively. The LOD, linear rang, enrichment factor(EF) and RSD% were achieved 1.25 $\mu\text{g L}^{-1}$, 5.0- 310 $\mu\text{g L}^{-1}$, 19.6 and less than 5% by procedure. The method was validated by standard reference material (SRM), the electrothermal atomic absorption spectrometry (ET-AAS) and ICP-MS analyzer for human samples.

1. Introduction

Heavy metals have toxic effects in environmental and human health which it causes main problem in many human organs such as brain. Lead (Pb) with dangerous properties in human consider as a hazardous chemical [1]. The battery and chemical factories use the lead in their products. The lead enters in environment by various sources such as, water, soil, the medical

industries, air dust, water and gas pipes, paint factories and chemical products [2-5]. Lead causes many problem in human organs such as, the nervous central system (insomnia, delirium, cognitive deficits and tremor), kidney, liver, gastrointestinal and bone disorders [6,7]. Also, an acute poisoning of lead cause to neurological defect include, pain, muscle weakness and numbness. In biochemistry, the lead can be seen in various of proteins and amino acids. Also, lead bonded to sulfur groups of aminoacids such as cysteine (Cys) and a homoleptic and hemidirectic (SR)₃ complex [8,9]. Moreover,

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lead can be complexed to copper/ zinc and caused brain problems. Therefore, the lead determination in the human biological samples (blood, serum and urine) with accurate and precise method must be considered. The environmental protection agency (EPA), NIOSH, OSHA, the National toxicology program (NTP) and food and drug administration (FDA) reported that the lead concentration in water, air and human blood samples are between 0.01-0.1 mg L⁻¹, less than 50 µg m⁻³ and 250 µg L⁻¹, respectively [10-12]. Recently, many researchers reported the different lead analysis in water and human blood samples [13]. The various techniques such as flame atomic absorption spectrometry (F-AAS) [14,15], the electrothermal atomic absorption spectrometry (ET-AAS) [16], the inductively coupled plasma mass spectrometry (ICP-MS), the microwave plasma atomic emission spectrometry (MP-AES) [17, 18], the gas chromatography mass spectrometry GC-MS [19] and laser-induced breakdown spectroscopy (LIBS) [20] were used for lead determination in different matrixes. Due to difficulty of matrixes and interferences, the extraction/preconcentration method for lead determination in blood samples is used. Various methodology such as, solid-phase extraction (SPE) [21], the magnetic-SPE [22], the dispersive liquid-liquid microextraction (DLLME) [23], the cloud point extraction (CPE) [24], the dispersive solid phase extraction (D-SPE), the ultrasound-assisted dispersive micro solid phase extraction (USA-µ-SPE) [25], and the emulsification microextraction using a ionic liquid (IL-EME) [26] were reported. Recently, the dispersive ionic liquid solid phase micro extraction (DIL-SPME) for separation/determination of heavy metals in liquid phases was used. The DIL-SPME method has many advantages such as high efficiency/recovery and easy to use in short time. The various sorbents include, the carbon nanotubes (CNTs) [27], the silica gel functionalized with thiosalicylic acid [28], and graphene/graphene oxide [29] was used for extraction/removal of heavy metals from solutions by scientists. The Ionic liquids were used for the separation of heavy metals from samples. Currently, safety, health and environmental assessments in factories can help manage pollutants

in industry and pollutants are reduced in the long run after analysis [30].

In this study, the mixture of ionic liquid/ ligand ([HMIM][PF₆]/APDC) modified on graphene oxide (NGO) was used for lead extraction from blood samples at pH=6. The speciation of lead was achieved based on IL/APDC/NGO adsorbent before the DIL-SPME procedure. The method was validated in blood and water samples by spiking samples and ICP-MS analyzer.

2. Experimental

2.1. Apparatus

The GBC atomic absorption spectrophotometer equipped with flame and graphite tube (electrical furnace) were used for the determination of lead in blood and serum samples (F-AAS, ET-AAS, GBC 932 plus, Australia). The Pal GF3000 as auto sampler accessory for ET-AAS was used as a low volume of samples for lead determination by injecting 1-100 µL of sample to graphite tube (wavelength 283.3 nm, slit 0.5 nm, lamp current 5.0 mA). Also, the auto sampler accessory for flame technique was used (0.5-5 mL). After atomization process in flame or graphite tube, the ppm and ppb concentration of lead was determined in liquid samples, respectively (Table 1). The ICP-MS analyzer with high sensitivity was used for as ultra-trace lead determination in human blood samples (Perkin Elmer, USA, 1100 W; 14 L min⁻¹; 1.2 sec per mass; auxiliary gas 1.1 L min⁻¹). The pH meter was used for measuring pH in blood samples (Metrohm, E-744, Switzerland). The shaking of samples was achieved by 300 rpm speeds by vortex mixer (Thermo, USA) and samples centrifuged with Falcon accessory (4000 rpm, 5-30 mL of polypropylene conical tubes, USA). An ultrasonic bath was used for dispersing of solid phase in blood samples with the temperature controlling accessory between 10-100°C (HB120, USA). The X-ray diffraction (XRD) based on a Panalytical X'Pert PRO X-ray diffractometer was used. The scanning electron microscopy (SEM) images were obtained using a Tescan Mira, Field Emission Scanning Electron Microscope (FEG-SEM).

Table 1. The AT-F-AAS and ET-AAS conditions for lead (Pb) determination

Features	AT-F-AAS	ET-AAS
Linear range	0.1-6.2 (mg L ⁻¹)	5-145 (μg L ⁻¹)
Wavelength	283.3 nm	283.3 nm
Lamp current	5.0 mA	5.0 mA
Slit	0.5 nm	0.5 nm
Mode	Peak Area	Peak Area
Atomization	Air-Acetylene	Electrical
Auto Sampler	0.5-5.0(mL)	1-100(μL)
LOD	0.03(mg L ⁻¹)	1.2(μg L ⁻¹)
R ²	0.9998	0.9995

2.2. Reagents

The standard solution of lead (Pb²⁺) was purchased from Merck with a concentration of 1000 mg L⁻¹ in 1 % HNO₃ (CAS N: 119776, 1 Li, Germany). The calibration standard of lead between 0.5-60 μg L⁻¹ was daily prepared by diluting of lead stock. Ammonium pyrrolidinedithiocarbamate as ligand (APDC, CAS N.: 169209-63-6) was prepared from Merck, Germany. Ultrapure water was purchased from Millipore Company (USA) for dilution of solutions or standards. The hydrophobic ionic liquid of 1-Hexyl-3-methylimidazolium hexafluorophosphate was prepared from Sigma Aldrich (CAS N: 304680-35). The pH of 6 was adjusted by sodium phosphate buffer solution (Merck, Germany, (Na₂HPO₄/NaH₂PO₄)). The polyoxyethylene octyl phenyl ether (TX-100), HNO₃, HCl, acetone, and butanol were purchased from Sigma Aldrich, Germany.

2.3. Human and air sample

For preparation of blood samples, the glass mixed in nitric acid (1 M) for 24 h and washed with DW for 8 times. The low concentrations of lead in blood samples (<250 μg L⁻¹), caused to the effect on accurate results. So, the process of blood sampling was carefully done based on standard methods. The 5 mL of blood samples were prepared from battery workers from Iran (40 Men, 25-55 age) due to world medical association declaration of Helsinki and dilution with DW up to 10 mL. Clean tubes and syringes with plastic needles were purchased for Merck, Germany for blood sampling. The 10 μL

heparin (pure metals) was added to human blood sample. The blood samples were maintained frozen in refrigerator below -4°C.

The air sampling for lead was prepared based on Filter (0.8 μm cellulose ester membrane) by 7082 NIOSH method. The flowrate adjusted 1 to 4 L min⁻¹ and ashing process with 6 mL of HNO₃, 1 mL of H₂O₂ (30%) at 140 °C was achieved. The working standards covering the range 0.25 -20 μg mL⁻¹ of Pb used for calibration method (2.5-200 μg lead per sample). The lead concentration in workplace air was determined by F-AAS and D₂ or H₂ continuum or Zeeman background correction used to control flame or molecular absorption. The working range between 0.05 -1 mg m⁻³ for a 200 L of air sample was selected. In addition, the flow rate between 1.0 - 4.0 L min⁻¹ for 8 h was used by personal pump.

2.4. Synthesis of IL/GONPs

The mixture ionic liquid with ligand ([HMIM][PF₆]/APDC) modified on graphene oxide nanostructures(GONs) and used as adsorbent for lead extraction. The synthesis of graphene oxide (GO) was followed by the modified Hummers method [31-33]. First, 10 g of graphite powder was mixed with 500 mL of H₂SO₄ and stirred for one day. Then, KMnO₄ (48 g) was mixed to the above mixture at 55 °C. Next, the mixture was moved into a beaker with 1000 mL of ice. Also, 100 mL of H₂O₂ in 1000 mL of DW was added to the mixture up to create a yellow color. The product was washed with deionized water and HCl for many times and dried at 70 °C. Then, 0.1 g of APDC mixed with 0.25 g

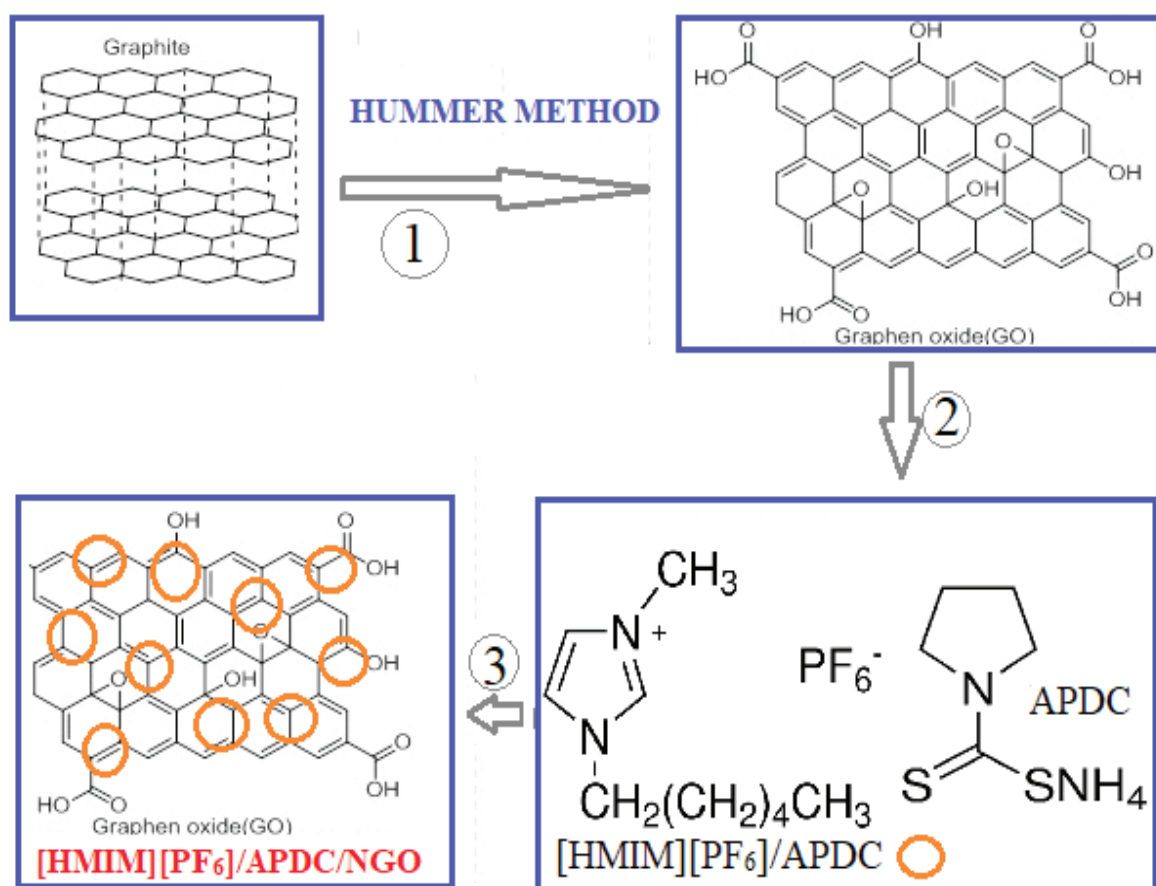


Fig.1. Synthesis of ([HMIM][PF₆]/APDC) modified on graphene oxide

of IL in presence of 2 mL of acetone and 0.2 g of GO. After increasing temperature up to 50°C, the mixture of IL/APDC were uniformly modified on Go (Fig.1). Finally, 20 mg of adsorbent selected for lead extraction in blood samples.

2.5. Extraction Procedure

In the DIL-SPME method, 10 mL of blood samples were used for extraction and determination of lead ions at pH 6.0. By procedure, 20 mg of IL/APDC modified on GO were injected to human blood samples and standard solution (5 - 310 µg L⁻¹) at pH=6.0 (Fig.2). After sonication of samples for 3.0 min, the lead separated and extracted with the APDC on adsorbent as sulfur coordination bonding in liquid phase (Pb²⁺ → APDC/IL-GONPs). By centrifuging (5 min; 4000 rpm), the solid phase trapped in [HMIM][PF₆] phase and collected from the samples in the end of the conical tube. The liquid phase was set aside and the lead ions back-extracted from ([HMIM][PF₆]/

APDC)/NGO adsorbent in pH=2 (HNO₃, 0.5 M, 200 µL) and diluted with 300 µL of DW before determined by F-AAS. In addition, On the other hand, the 10 mL of standard solution was used based on the DIL-SPME procedure by the same conditions at pH=6.0. A blank run without any lead ions was used for ten times. The calibration curve for lead in standards solutions was prepared. The analytical procedure was showed in Table 2. Validation was followed by CRM of lead and real samples, which was analyzed by ETAAS and ICP-MS analyzer. The concentration lead in work place air was achieved based on 7082 NIOSH method for 40 workers and the mean concentration in air were obtained 65.6 µg m⁻³ for TWA measurements. The recovery of lead procedure in blood samples based on APDC/IL-GONPs was obtained by the equation 1. The C_i is the primary concentrations and C_f is the secondary concentration of Pb(II), which was determined by APDC/IL-GONPs coupled DIL-SPME procedure (n=8).

$$R\% = (C_i - C_p) / C_i \times 100 \quad (\text{Eq. 1})$$

For workplace air, after determination lead in filter, the concentrations (C_s , $\mu\text{g mL}^{-1}$) of lead in the sample air was achieved by NIOSH method (The average blank, C_b). The concentration in air calculated based on equation 2, the volumes (mL) of the sample and media blanks is V_s and

V_b , respectively. Finally, the C (mg m^{-3}), of lead showed the concentration lead in air where the air volume sampled was V (L).

$$C = \frac{C_s V_s - C_b V_b}{V} \quad (\text{Eq. 2})$$

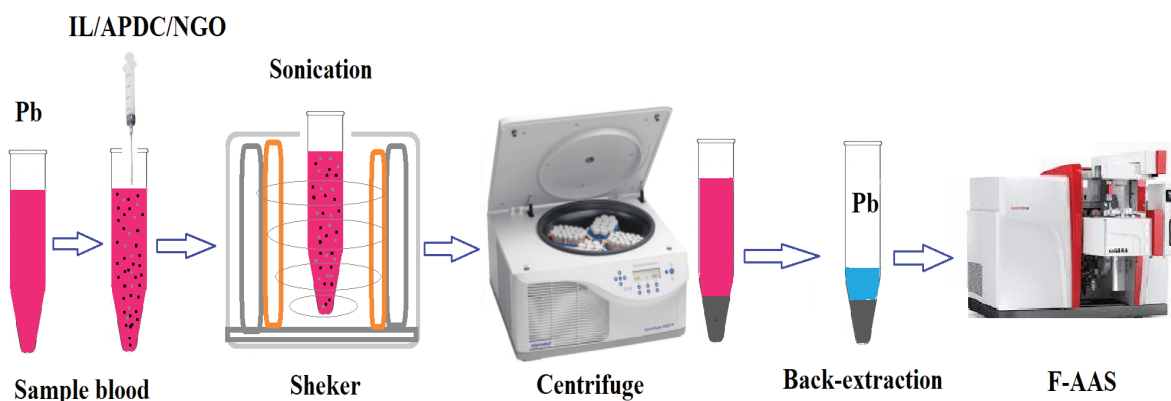


Fig.2. Lead extraction based on APDC/IL/NGO coupled to DIL-SPME procedure

Table 2. The analytical features for determination lead in human blood samples by DIL-SPME procedure

Features	value
pH	6.0
Amount of APDC/IL modified on GONPs (mg)	20.0
Sample volume of blood, serum (mL)	10 .0
Volume of sample injection	0.5 mL
Linear range for blood	5-310 $\mu\text{g L}^{-1}$
Mean RSD %, n=8	4.6
LOD for blood	1.25 $\mu\text{g L}^{-1}$
Enrichment factor for blood	19.6
Volume and concentration of HNO_3	0.2 mL, 0.5 M
Shaking/Centrifuging time	3.0 min, 5 min
Correlation coefficient	$R^2 = 0.9995$

3. Results and discussion

3.1. Characterization

XRD patterns of GO and APDC/IL/GO are similar and shown in Figure 3. Graphene oxide exhibits the sole main diffraction peak at $2\theta = 12^\circ$ corresponding to the oxygen functional groups which are intercalated between graphene sheets in the course of oxidation. The peaks at $2\theta = 12^\circ$ and 42.58° are related to the diffraction planes of (002) and (100) respectively, which can be observed in the XRD patterns of both GO and APDC/IL/GO. However, existence of this peak at about $2\theta = 12^\circ$ agrees well with the modification of graphene oxide with APDC and IL.

The morphology of GO and APDC/IL/GO are evaluated by scanning electron microscope (SEM) (Fig. 4). According to the SEM images (Fig. 4I and 4II), Comparison between the SEM images of GO and APDC/IL/GO revealed that, the modification

of GO had no prominent effect on the morphology of the graphene sheets.

3.2. Optimization of proposed procedure

The DIL-SPME procedure with new IL/APDC/NGO was applied for the extraction and separation of lead ions in human blood samples. The high recovery for lead extraction was obtained by optimizing of parameters.

3.2.1. The pH optimization

The pH is the main factor for lead extraction in human blood samples by APDC ligand which was mixed with IL and modified on NGO. The various pH for lead extraction in blood samples was used and studied between 2-12. The results showed, the IL/APDC/NGO had highly lead extraction at pH of 5.5-6.5 (<95%). The complexation of lead with APDC were decreased at pH less than 5 and

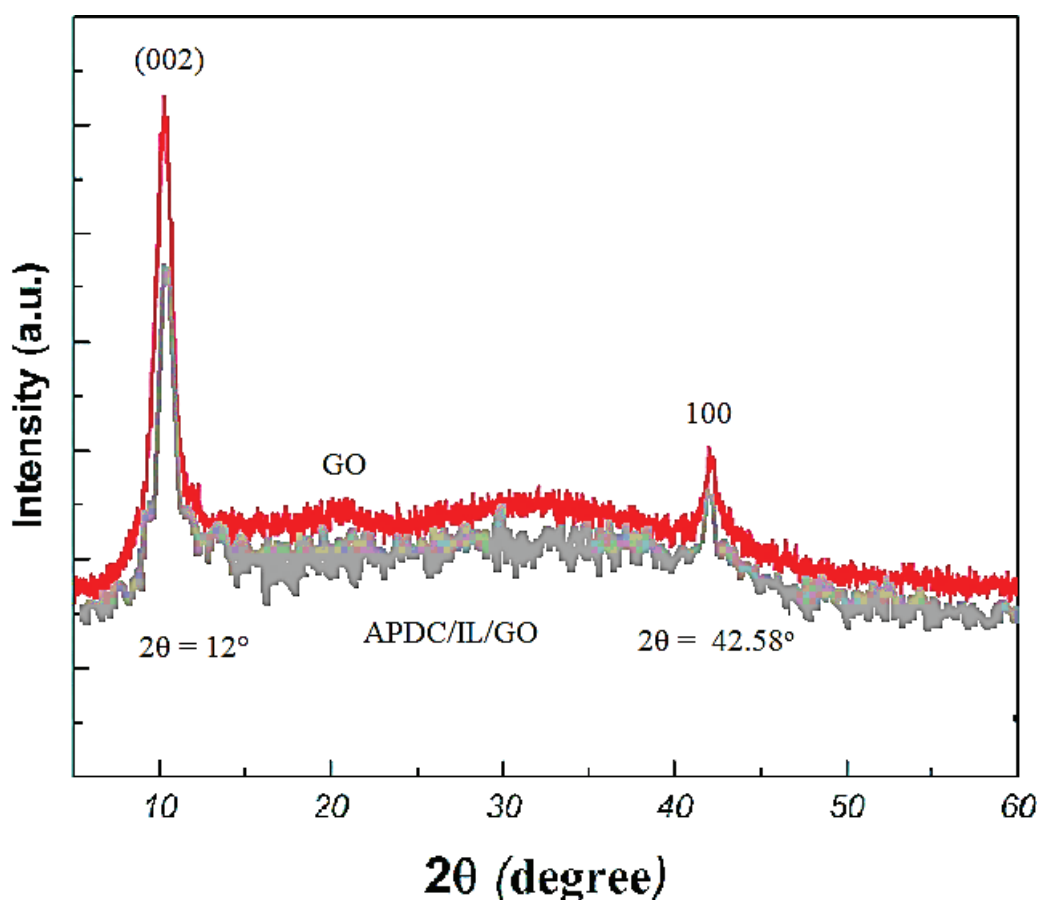


Fig.3. XRD of NGO and IL/APDC/NGO

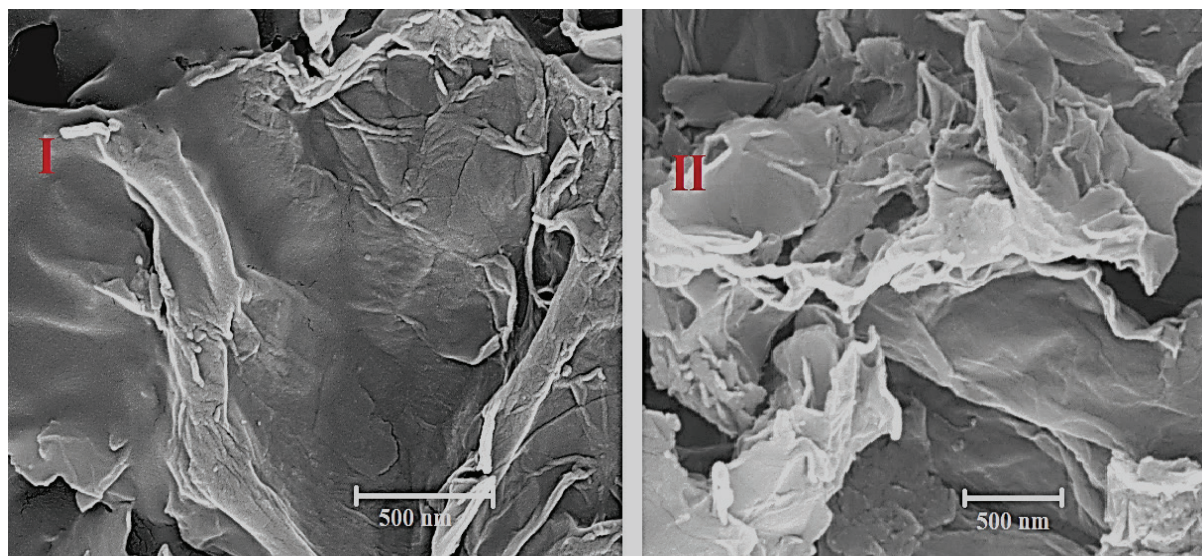


Fig.4. I (SEM of NGO II) SEM of IL/APDC/NGO

pH more than 6.5. So, the pH=6 was selected as optimum pH for lead extraction in blood samples (Fig. 5). The mechanism of lead extraction depended on sulfur group in APDC which was created a dative bond with Pb ions in liquid phase ($\text{Pb}^{2+} \rightarrow \text{S} \dots \text{APDC/IL/NGO-GO}$). At lower pH the surface of adsorbent had positive-charge (S^+) and extraction decreased due to similarity charges law. At pH of 6.0, the surface of APDC/IL/NGO have negatively charged (S^-) and Pb (+) complexed by sulfur groups. Moreover, the lead participated in liquid phase ($\text{Pb}(\text{OH})_2$) and the extraction efficiency was decreased at more than pH of 7. Therefore, the pH=6 used for further studies in blood samples.

3.2.2. Optimization of APDC/IL/NGO mass

The high extraction was achieved based on APDC/IL/NGO mass which was depended to sulfur group of APDC as complexation. So, the mass of APDC/IL/NGO must be optimized conditions. The amounts of APDC/IL/NGO between 2-50 mg in human blood samples and standard solution were studied for lead extraction by DIL-SPME procedure. As Figure 6, the maximum recoveries were achieved for Pb extraction by 20 mg of APDC/IL/NGO in human blood samples. So, 20 mg of APDC/IL/NGO was selected for experimental run by DIL-SPME procedure. The extraction efficiency of lead had constant rate for more than 20 mg of APDC/IL/NGO in blood samples.

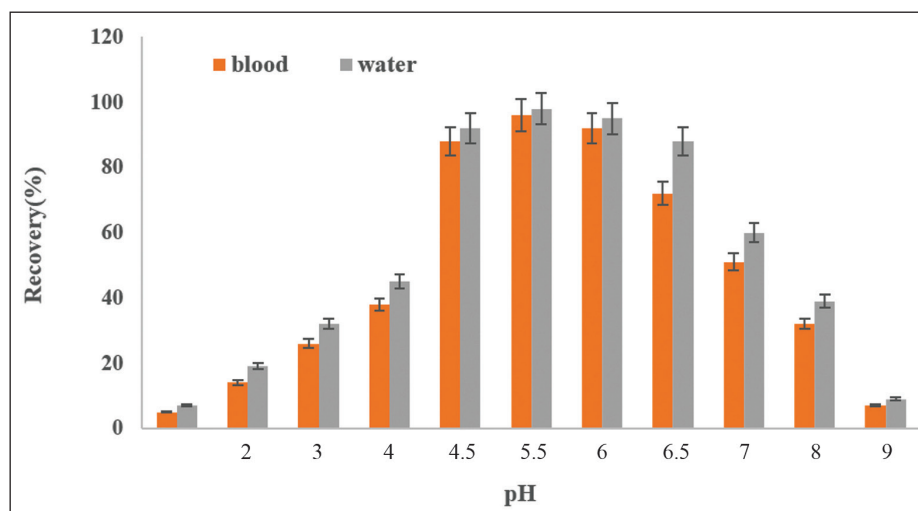


Fig.5. The effect of pH on lead extraction based on APDC/IL/NGO by DIL-SPME procedure

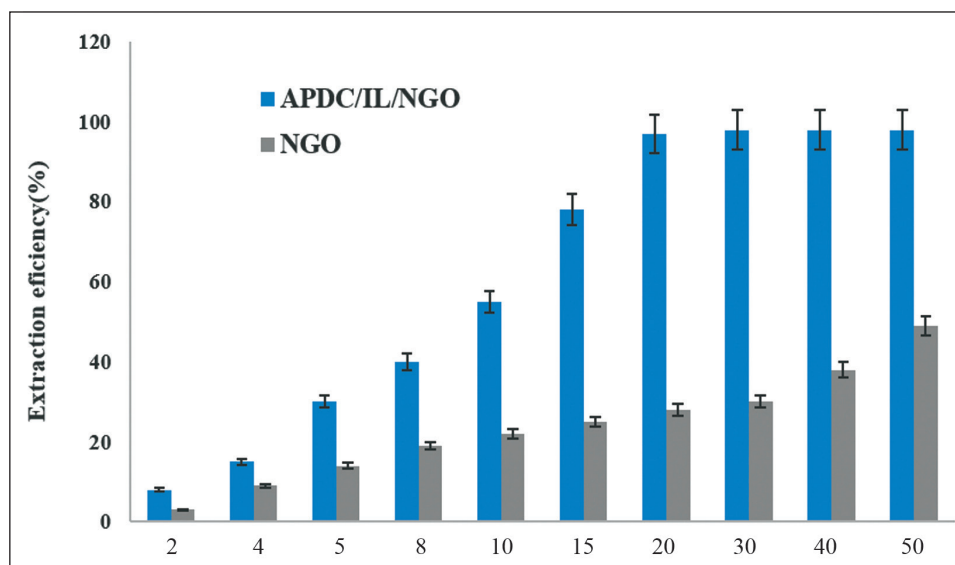


Fig.6. The effect of amount of APDC/IL/NGO on lead extraction based on APDC/IL/NGO by DIL-SPME procedure

3.2.3. Optimization of sample volume and eluent

The volume and concentration of eluents such as acid or bases is important for back extraction Pb ions from APDC/IL/NGO were studied. The low/ high pH caused to dissociate the sulfur-Pb covalent bonds and released the Pb ions from adsorbent. So, the different reagents (HCl, HNO₃, CH₃COOH, H₂SO₄, H₂CO₃) were used for the back-extraction of lead from APDC/IL/NGO to liquid solutions. The 0.1-1.0 molar of various eluents with different volumes from 0.1 to 0.7

mL was studied. Due to Figure 7, the efficient recovery obtained by 0.2 mL of HNO₃ (0.5 M). In addition, the volume of blood and standard solutions for lead extraction based on APDC/IL/NGO adsorbent was optimized from 1.0 mL to 20.0 mL for LLOQ and ULLOQ concentration of Pb(II) (5.0-310 µg L⁻¹). The results showed that the best recovery was achieved less than 10 mL for in blood samples at pH=6. therefore, the 10 mL of blood or standard solution was used for further work (Fig. 8).

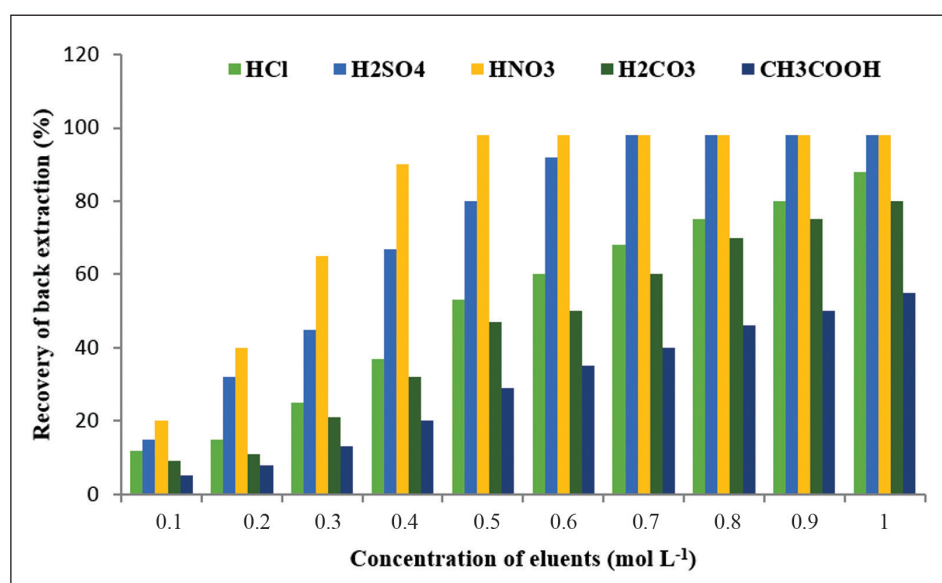


Fig.7. The effect of eluents on lead extraction based on APDC/IL/NGO by DIL-SPME procedure

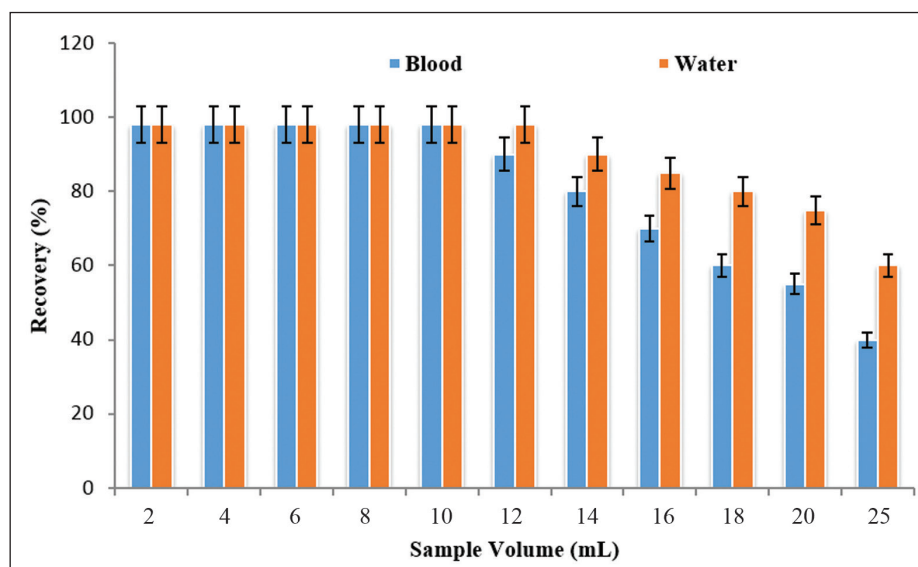


Fig.8. The effect of sample volume on lead extraction based on APDC/IL/NGO by DIL-SPME procedure

3.2.4. Optimization of time, reusability and absorption capacity

The time dispersion of APDC/IL/NGO adsorbent in blood or standard samples had a main factor for efficient extraction of lead. Moreover, the mass-transference between APDC/IL/NGO and Pb ions was occurred at pH=6 by DIL-SPME procedure. In optimized conditions, the sonication time was evaluated between 1 - 8 min. the results showed that the sonication time of 3.0 min has maximum extraction of lead in blood samples. In addition, the centrifuging time between 1-10 min (4000 rpm) was used for collecting sorbent in end of conical tube. Based on results, 5 min of centrifuge time is enough time for efficient extraction of lead. Finally, the lead ions were back-extracted from APDC/IL/NGO by changing pH and determined by F-AAS. The reusability of APDC/IL/NGO was obtained with many times extraction process by DIL-SPME procedure. The results showed, the DIL-SPME can be used for less than 7 cycles for lead extraction at optimized pH in room temperature. The absorption capacities for lead depended on chemical and physical properties of APDC/IL/NGO in bath system. The absorption capacities of APDC/IL/NGO for Pb ions examined with 50 mg L^{-1} in

optimized conditions. The adsorption capacity of APDC/IL/NGO and NGO for Pb ions was achieved 154.7 mg g^{-1} and 28.9 mg g^{-1} , respectively.

3.2.5. Interference cations and anions

For extraction lead in blood samples, the effect of interference of ions was studied by DIL-SPME procedure. So, the concentrations of cations and anions in human blood such as Cu, Zn, Mn, Mg, Ca, Fe and etc. (1-2 ppm) added to 10 mL of standard solution or human blood samples in presence of $300 \mu\text{g L}^{-1}$ of lead at pH=6. The recovery of lead extraction in presence of the concomitant cations/anions couldn't decreased at pH=6. Therefore, the Pb ions can be extracted based on APDC/IL/NGO in blood samples in presence of some coexisting ions (Table 3).

3.2.6. Real sample analysis

The concentration of lead in human blood and standard samples was determined by DIL-SPME procedure. The lead was efficiently extracted based on APDC/IL/NGO adsorbent from human blood samples and obtained results were validated by electrothermal atomic absorption spectrometry (ET-AAS) and ICP-MS techniques (Table 4). In this study, the validation based on spiking real

Table 3. The effect of interference cations and anions for lead extraction by the DIL-SPME procedure

Interfering Ions in blood (A)	Mean ratio ($C_A / C_{Pb(II)}$)	Recovery (%)
	Pb(II)	Pb(II)
Co ²⁺ , Fe ²⁺	550	99.3
Zn ²⁺ , Cu ²⁺	850	98.1
Mn ²⁺ , Mo ²⁺	600	96.5
I ⁻ , Br ⁻ , F ⁻ , Cl ⁻	1100	97.4
Na ⁺ , K ⁺	1000	99.3
Ca ²⁺ , Mg ²⁺	1200	98.4
CO ₃ ²⁻ , PO ₄ ³⁻ , NO ₃ ⁻	650	97.4
Ni ²⁺	300	98.1
Al ³⁺ , V ³⁺ , Cr ³⁺	900	97.7
Hg ²⁺ , Ag ⁺	120	98.2

samples with a standard solution were achieved in human blood and serum samples by APDC/IL/NGO adsorbent (Table 5). The results demonstrated the efficient recovery for lead ions in difficult matrixes in blood samples. The spiked samples showed accurate results for separation/extraction/

determination /preconcentration of human blood samples by APDC/IL/NGO adsorbent. As intra-day and inter-day analysis, the 40 human blood workers of battery manufacturing factories determined by same procedure ((25-55, Men, Iran) and compared to office people as control markers (Table 6).

Table 4. The validation of proposed method for lead extraction in human matrixes by ICP-MS and ET-AAS (μg L⁻¹)

Samples	ICP-MS*	DIL-SPME /F-AAS *	ET-AAS*
Serum	253.8 ± 7.2	244.9 ± 10.2	248.3 ± 12.7
Blood	302.7 ± 7.8	290.6 ± 11.6	295.1 ± 14.2
Plasma	142.5 ± 3.8	139.4 ± 5.5	145.6 ± 6.9

*Mean of three determinations ± confidence interval (P= 0.95, n=5),

As low LOD for ET-AAS and ICP-MS the samples diluted with DW before analysis

Table 5. Spiking real samples with a standard solution in human blood, serum and plasma samples by APDC/IL/NGO adsorbent(μg L⁻¹)

Sample	Added	* Found	Recovery (%)
Serum	-----	123.2± 5.3	----
	50	170.9 ± 7.6	95.4
	100	225.4± 9.8	102.2
Blood	-----	111.3± 4.9	-----
	50	159.4 ± 6.1	96.2
	100	209.8± 9.2	98.5
Plasma	-----	84.5 ± 4.2	-----
	50	133.6 ± 5.8	98.2
	100	183.7 ± 8.8	99.2

* Mean of three determinations ± confidence interval (P= 0.95, n=5)

Table 6. Comparing of mean lead concentration in human blood of battery workers with control peoples by DIL-SPME procedure (μgL^{-1})

Sample	*Mean of Subjects (n=40)		*Mean of Controls (n=40)		+Data Subject	
	Intra-day	Inter day	Intra-day	Inter day	r	P value
Plasma	194.2 \pm 8.7	191.5 \pm 8.6	47.1 \pm 2.3	48.4 \pm 2.5	0.090	<0.001
Serum	401.2 \pm 19.3	397.7 \pm 18.9	94.4 \pm 4.6	90.8 \pm 4.4	0.088	<0.001
Blood	382.5 \pm 18.4	386.3 \pm 18.6	88.2 \pm 4.1	85.9 \pm 3.9	0.101	<0.001

*Mean of three determinations of samples \pm confidence interval (P = 0.95, n =10)

+Correlations are based on Pearson coefficients (r). Statistical significance will be observed if P < 0.001
Subject and control groups belong to *battery* workers and control peoples

Table 7. The validation of methodology for lead extraction with certified reference material (CRM, ICP-MS) by DIL-SPME procedure(μgL^{-1})

SRM	Added	Found by μ -SPE +	Recovery (%)
ICP-MS A	-----	120.4 \pm 5.7	-----
	50	168.1 \pm 7.3	95.4
	100	218.5 \pm 9.9	98.1
ICP-MS B	-----	208.7 \pm 9.8	-----
	50	260.1 \pm 14.2	102.8
	100	305.4 \pm 14.2	96.7

+ Mean value \pm standard deviation based on three replicate measurements

ICP-MS: blood analysis for lead, A=122.5 ngL^{-1} , B=210.3 (μgL^{-1})

In addition, the blood samples were validated by certified reference materials (CRM, NIST) by DIL-SPME procedure (Table 7). Based on table 4-7, the precision and accuracy of results was satisfactorily confirmed in human blood samples.

4. Conclusions

An applied adsorbent based on APDC/IL/NGO was used for separation, preconcentration and determination of lead in blood samples by the DIL-SPME procedure. The IL was helped to separate the solid phase from liquid matrixes in bottom of conical tube which was modified on NGO. By DIL-SPME procedure, the simple, perfect recovery and fast analysis was achieved for lead at pH=6.0 by APDC/IL/NGO sorbent. The modification of NGO surface with IL/APDC helped to enhance the lead extraction in blood samples. Also, some advantages of proposed method such as, fast separation, low cost, and high extraction

caused to comparable to ICP-MS analyzer. The LOD and linear range(LR) has acceptable level for lead analysis in human biological samples. Therefore, the extraction and determination lead with APDC/IL modified on NGO in human blood were simply achieved based on sulfur dative bond in optimized conditions by DIL-SPME procedure before determined by F-AAS. The lead analysis in workplace air was achieved based on NIOSH method for 40 workers and range/mean concentrations in air were obtained 44.7-81.5 μgm^{-3} and 65.6 μgm^{-3} , respectively for a 200 L of air sample which was higher than standard of lead in air by NIOSH (50 μgm^{-3}).

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