

On-line separation and preconcentration of lead(II) by solid-phase extraction using activated carbon loaded with xylenol orange and its determination by flame atomic absorption spectrometry

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Abstract

Activated carbon loaded with xylenol orange in a mini-column was used for the highly selective separation and preconcentration of Pb(II) ions. An on-line system for enrichment and the determination of Pb(II) was carried out on flame atomic absorption spectrometry. The conditions of preconcentration and quantitative recovery of Pb(II) from diluted solution, such as pH of aqueous phase, amount of the sorbent, volume of the solutions and flow variables were studied as well as effect of potential interfering ions. Under the optimum conditions, Pb(II) in an aqueous sample was concentrated about 200-fold and the detection limit was 0.4 ng mL^{-1} Pb(II). The adsorption capacity of the solid phase was 0.20 mg of lead per one gram of the modified activated carbon. The modified activated carbon is stable for several treatments of sample solutions without the need for using any chemical reagent. The recovery of lead(II) from river water, waste water, tap water, and in the following reference materials: SRM 2711 Montana soil and GBW-07605 tea were obtained in the range of 97–104% by the proposed method.

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1. Introduction

Lead is a toxic metal, which accumulates in the vital organs of human and animals. Its cumulative poisoning effects are serious hematological damage, brain damage, anemia and kidney malfunctioning. In natural water it is typical concentration lies between 2 and 10 ng mL^{-1} , whereas the upper limit recommended by WHO is less than 10 ng mL^{-1} [1]. Thus, there is a great interest concerning the implementation of a reliable preconcentration system for lead(II) for analytical determinations. Flame atomic absorption spectrometry (FAAS) and ICP-AES are very available techniques for the determination of heavy metals in water samples. However, the main problem is a low sensitivity at ng/mL level, and high levels of matrices are the main problem [2,3]. Several methods extensively used for preconcentration include liquid–liquid extraction, ion exchange, solid-phase extraction and chelating matrices. To solve the prob-

lem of main problem of FAAS and ICP-AES techniques for trace analysis, solid-phase extraction is the one of the important preconcentration method. On-line separation and preconcentration have received considerable attention during recent years, and this technique is widely applied for selectivity and sensitivity enhancement.

Activated carbon has proved to be an excellent collector for numerous metal ions. Solid-phase extraction procedures based on the sorption of metal complex on activated carbon have been recently reviewed [4]. Zaporozhets and Tsyukalo [5] have been introduced a new solid-phase based on XO adsorbed on silica for preconcentration of lead(II) and then determined by diffuse reflectance spectroscopy. The method is a batch method, has higher limit of detection ($>2 \text{ ng mL}^{-1}$ Pb(II)) and suffer from many interfering ions such as Fe(II), Mn(II), Cd(II), Zn(II) and phosphate. In addition, Amberlite XAD-16 loaded with XO [6], Amberlite XAD-2000 [7] and Amberlite XAD-1180 [8] have been reported by M. Soylak et al. as suitable solid phases for preconcentration of heavy metals including Cr, Cu, Ni, Zn and Pb. However, those methods are not selective for Pb(II). Table 1 shows the sorption capacity, preconcentration factor, detection

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Table 1
Comparison of sorption capacity, preconcentration factor, detection limit and interferences

Immobilized ligand	Parameters			
	Sorption capacity ($\mu\text{mol g}^{-1}$)	Preconcentration factor	Detection limit (ng mL^{-1})	Interferences
Support: Amberlite XAD-2				
Chromotropic acid [14]	186.3	200	–	Fe, Cu
Thiosalicylic acid [15]	89.3	100	–	–
Pyrocatechol [16]	104.7	100	–	Na_3PO_4
Salicylic acid [17]	2.22	140	5.5	F^- , Cl^- , NO_3^- , Zn
Pyrocatechol violet [18]	6.56	23	44	Cd, Cu, Ni, Zn
<i>o</i> -Vanillinthiosemicarbazone [19]	9.65	100	50	Cu, Zn, Cu, Co, Cd, Ni
<i>o</i> -Aminophenol [20]	16.02	40	25	Cu, Cd, Co, Ni, Zn, Mn
Tiron [21]	60.3	25	24	Cd, Co, Cu, Fe, Ni, Zn
Dithiocarbamate [22]	–	20	10	Na_3PO_4
Alizarin Red S [23]	1.5	40	10	Zn, Cd, Ni
Pyrocatechol violet [24]	6.5	500	8	Cd, Cu, Ni, Zn
Support: Amberlite XAD-4				
7-Dodeceny1-8-quinolinol [25]	52	500	–	Ti, Ni, Mn, Fe, Cr, Co, Cu
Support: Amberlite XAD-7				
Xylenol orange [26]	16.89	100	10	–
Dimethylglyoxalbis(4-phenyl-3-thiosemicarbazone) [27]	19.7	100	–	Hg, Cd, Cu, Pd
Support: Polyacrylonitrile				
Amino phosphoric and dithiocarbamate[28]	27.16	200	–	Cu, Cd, Co, Ni, Zn, Mn
Support: Silica gel				
Acid Red 88 [29]	12.1	–	10	Cd, Cu, Co, Mn, Ni, Zn
5-Amino-1,3,4-thiadiazole-2-thiol [30]	130.0	80	–	Cd, Cu, Co, Zn
Other resins				
Chelex-100 [31]	–	1000	20	Cd, Cu, Co, Mn, Ni, Zn
Metalfix chelamine resin [32]	–	25	–	–
Support: Activated carbon				
8-Hydroxyquinoline and cupferron [33]	–	100	2.4	Cd
Xylenol orange	125	200	0.4	Present work

limit, and interferences of the reported solid-phase extraction for lead(II) based on activated carbon and Amberlite. In all of the reported method except Ref. [4], the solid phases were not reversible; it is meaning that a ligand solution was needed for each experiment, because the chelating agent was removed when the solid phase is washed for the determination of metal ions.

In this paper, a new on-line column separation/preconcentration method is described for determination of lead(II) ions using activated carbon loaded with xylenol orange (XO) and FAAS. The modified activated carbon with XO is tightly bound. Thus, it does not wash away with the eluent solution that used to remove Pb(II) ions from the sorbent. The sorbent is highly selective for separation of Pb(II) ions from other cations. Automation of the procedure cause reducing the risk of operational errors, increase the speed of analysis and the precision of the method.

2. Experimental

2.1. Apparatus

A Perkin-Elmer flame atomic absorption spectrometer, Model 2380, furnished with a Pb hollow cathode lamp, operated with 10 mA, and with air–acetylene flame was used. The

instrument was set at a wavelength 217.0 nm and slit width of 0.7 nm. A short mini-column with an inner diameter of 7.0 mm and a length of 42.9 mm equipped with glass wool plugs at the end of the column, was filled up to a height of about 10 mm with XO loaded activated carbon. After each experiment, the column was rinsed with water and stored for the next experiment. A Jasco UV–vis spectrophotometer (Tokyo, Japan), Model V-570, was used to measure the absorbance of XO solution. A pH-meter, Schott Model GC-825, equipped with a glass electrode was employed for measuring pH in the solutions.

The schematic diagram of the on-line preconcentration system is shown in Fig. 1. The hardware of the system was composed of 32 channel I/O card (PCL-720, Advantech, Taiwan) which has a power relay module to convert the output of I/O card to 220 V AC, a peristaltic pump (Ismatic, ISM 404), three 220 V AC electrical valves, a silicon rubber tubing pump (2.06 mm i.d.) and a PC computer, Pentium III. A program was written in Borland C++ by the authors to monitor and to control the system.

2.2. Chemicals

All chemicals were used of analytical reagent grade and all solutions were prepared with doubly distilled water.

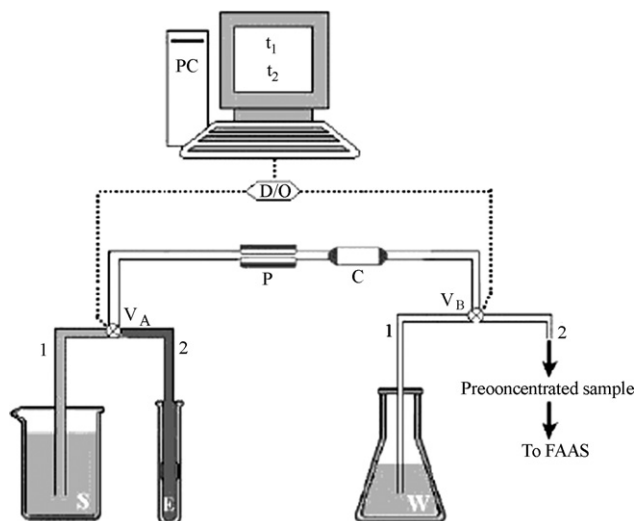


Fig. 1. The schematic diagram of the on-line pre-concentration system (P, pump; C, microcolumn; D/O, analog to digital converter; S, sample solution; V_A , valve A; V_B , valve B; E, eluent solution (2.0 M HNO_3); PC, computer).

A XO solution was prepared by dissolving 6.0 mg of the reagent (Merck) in 100 mL water.

Standard solution of Pb(II) was prepared by dissolving lead granulated in dilute HNO_3 (1:1).

Acetic acid, boric acid, plus sodium hydroxide was used for preparation of buffer solutions (0.04 M).

Activated carbon powder (Merck No. 2180) was treated with concentrated HCl, washed with doubly distilled water and dried at 110 °C for 1 day.

The following certified reference materials were used: SRM 2711 Montana soil and GBW-07605 tea.

2.3. Preparation of modified activated carbon

In a 1000 mL beaker, 2.0 g of activated carbon was added to 800 mL of XO (6.0 mg/100 mL) and mixed well at pH 10.0 (0.04 M). After 36 h, the mixture was filtered and washed with water three times, each time with 10 mL of water, and then dried out. A Teflon column (42.9 cm length and 7.0 mm in diameter) was packed with 0.20 g of the modified activated carbon.

2.4. Preconcentration procedure

The method was tested with model solution before its application to real samples. A 100 mL Pb(II) solution buffered at pH 6.0, was passed through the column at a flow rate of 4.0 mL min^{-1} by opening the position 1 of electrical valves A and B (Fig. 1). After finishing the solution, position 1 of valves A and B is closed automatically, and position 2 of valves A and B is opened. Therefore, 6 mL of 0.5 M nitric acid was passed through the column at a flow rate of 0.5 mL min^{-1} to elute the Pb(II) ions. The eluent was collected and analyzed for Pb(II) by flame atomic absorption spectrometry. The percent of the metal ions adsorbed on the column for the concentration of Pb(II) was calculated from the amount of Pb(II) ions in the starting sample and the amount of Pb(II) eluted from the column.

2.5. Real sample analysis

GBW-07605 tea was digested with 6 mL of HNO_3 (65%) and 2 mL of H_2O_2 (30%). After digestion the samples, the pH of the digested samples was neutralized by the addition of 0.1 mol L^{-1} sodium hydroxide solution [9,10]. A blank digest was carried out in the same way. Then the separation/preconcentration procedure given above was applied to the final solutions.

SRM 2711 Montana soil standard reference materials (250 mg) was digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in microwave digestion system and diluted to 40 mL with deionized water [9,10]. After digestion the samples, the pH of the digested samples was neutralized by the addition of 0.1 mol L^{-1} sodium hydroxide solution. A blank digest was carried out in the same way. Then the separation/preconcentration procedure given above was applied to the final solutions.

Water samples were collected in prewashed (with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water, respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 μm . The samples were stored in 1 L polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4 °C in a refrigerator. To apply the presented method, 250 mL of water sample was taken in a beaker, and then the pH of the sample was adjusted to pH 6 with the buffer. Then the separation/preconcentration method given above was applied.

3. Results and discussion

Xylenol orange (XO) is a metal indicator, which is widely used for analytical determination [6,11,12]. It has a large formation constant with Pb(II). This ligand acts as a selective complexing agent for Pb(II) at pH 6. On the other hand this ligand can be adsorbed on the activated carbon. After the adsorption, the modified activated carbon is completely stable and does not wash off when using HNO_3 solution as a washing solvent. This means that the activated carbon that is treated with XO can be used several times for separation and preconcentration of lead(II) without decreasing the enrichment factor of the solid phase. This may be due to the similarity of the XO structure to that of activated carbon, producing strong π - π interaction [13].

For the first of all, to obtain the best quantitative recoveries of Pb(II) ions from the sample solution and then from the solid phase, the parameters such as pH of adsorption of XO on activated carbon, pH of sample solution containing Pb(II) adsorbed on the column, sample volume, type and volume and the concentration of eluent solution, velocity of the sample solution through the column, capacity of the modified activated carbon and the effect of matrix should be studied.

First, to find the optimum pH for adsorption of XO on activated carbon, buffer solutions were used. For this purpose, 6.0 mg of XO and 25.0 mL of buffer solution (pH 4.0–11.0) were added into a 100 mL volumetric flask and the solution was diluted to 100 mL with water. The absorbance of the solution was measured spectrophotometrically at the appropriate wavelength (at the λ_{max}) to find the molar absorption coefficient of XO at dif-

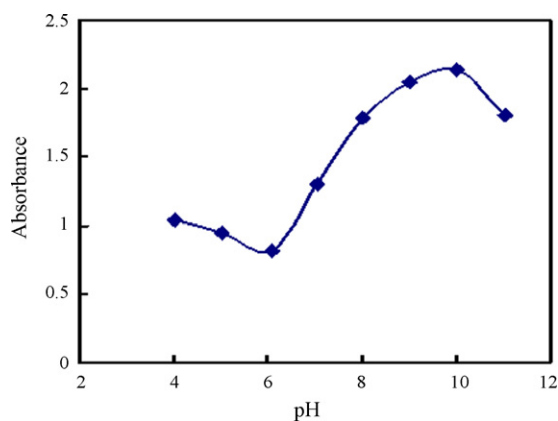


Fig. 2. Influence of pH on the adsorption of XO on activated carbon. Conditions: 200.0 mg activated carbon; 6.0 mg XO; diluted to 100 mL with buffer solution at different pHs (1.0–11.0), mixed well and stored for 24 h.

ferent pHs. Then, 6.0 mg of XO and 25 mL of buffer solution (pH 4.0–11.0) plus 0.20 g activated carbon were mixed in a 100 mL beaker. After 24 h, the mixture was filtered, and the absorbance of the filtered solution was measured spectrophotometrically to find the unadsorbed XO, according to the calibration curve. The results show that the best pH for adsorption of XO on activated carbon is 10.0 (Fig. 2). Therefore, a buffer solution of pH 10.0 (0.04 M) was used to prepare the modified activated carbon.

The influence of time on the modification of activated carbon was studied by treating 6.0 mg of XO, 0.20 g activated carbon and 25.0 mL buffer solution at pH 10.0 for different time. The results showed that maximum adsorption of XO on the surface of activated carbon takes place after 36 h (Fig. 3).

The capacity of activated carbon for XO was also checked. In order to measure the capacity of activated carbon for adsorption of XO at pH 10.0, 25 mL of the buffer solution (pH 10.0) plus 3.0–9.5 mg XO was added into a series of 100 mL beakers and mixed with 0.20 g activated carbon. After 36 h, the mixture was filtered, and the absorbance of the solution was measurement spectrophotometrically to find the free XO (unadsorbed). The results are shown in Fig. 4. The results showed that one gram of activated carbon can adsorb more than 30.0 mg XO.

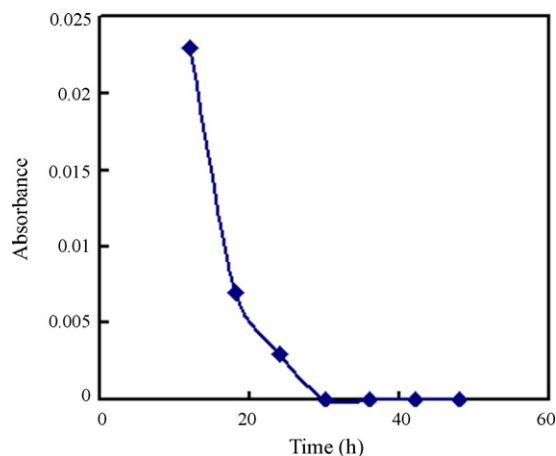


Fig. 3. Influence of time on the modification of activated carbon with XO. Conditions: 200.0 mg activated carbon; 6.0 mg XO; diluted to 25 mL at pH 10.0.

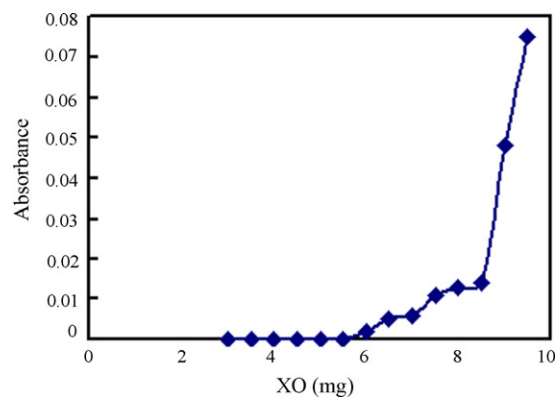


Fig. 4. The capacity of activated carbon for XO. Conditions: 200.0 mg activated carbon; pH 10.0; mixed well and stored for 36 h.

The influence of pH of sample solution on the preconcentration step of Pb(II) was also studied. For this purpose, 100 mL of 50.0 ng/mL Pb(II) at different pH values (3.0–11.0) was passed through the modified solid phase, then the solid phase was washed with 5.0 mL of 2.0 M HNO₃ solution. The eluent solution was checked for Pb(II) concentration using FAAS (Fig. 5). The results show that a suitable pH for adsorption of Pb(II) on the modified activated carbon was about 6.0. This is due to the fact that, in acidic solution the formation constant of Pb(II)–XO complex decreases due to the protonation of XO. Therefore, a buffer solution with pH 6.0 (0.04 M) was used for the preconcentration step.

Different concentrations of HNO₃ (8 mL, with flow rate of 0.5 mL/min) in the interval range of 0.5–3.0 M on the quantitative elution of preconcentrated lead(II) ions from the column was checked. The results showed that 1.5 M HNO₃ is suitable to remove (100 ± 1.2)% of Pb(II) from the solid sorbent. In order to optimize the volume of 1.5 M HNO₃ solution, 50 mL of 400 ng/mL Pb(II) was passed through the modified activated carbon under the optimum conditions. Then, the solid phase was washed with different volumes of 1.5 M HNO₃ (2.0–6.0 mL). The results solution was checked by FAAS to measure the Pb(II) contents. The results showed that 5.0 mL of 1.5 M HNO₃ is suitable to remove (100 ± 1.5)% of Pb(II) from the modified solid phase.

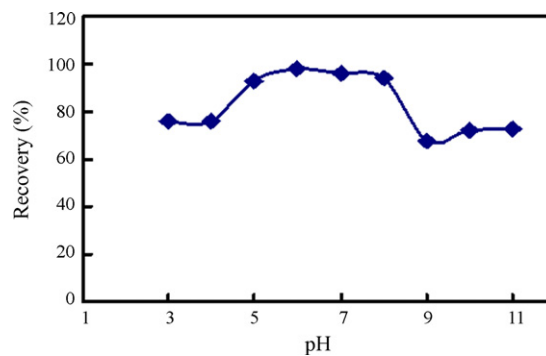


Fig. 5. Influence of pH on adsorption of Pb(II) on the modified activated carbon. Conditions: initial lead(II) value, 100 mL 50.0 ng/mL Pb(II); washing solution, 5.0 mL of 0.50 M HNO₃.

Table 2
Determination of Pb(II) in water and reference standard material samples ($n = 4$)

Sample	Pb(II) added (ng mL ⁻¹)	Pb(II) found ^a (ng mL ⁻¹)	Recovery (%)
Tap water	–	5.7 ± 0.5	–
	40.0	45.8 ± 0.3	104.0
	80.0	85.4 ± 0.2	103.0
	120.0	125.5 ± 0.4	101.0
Zayandeh Roud river water	–	11.2 ± 0.6	–
	40.0	51.5 ± 0.3	101.0
	80.0	91.4 ± 0.5	103.0
	120.0	129.8 ± 0.4	100.0
Waste water	–	3.5 ± 0.4	–
	40.0	43.8 ± 0.2	104.0
	80.0	83.2 ± 0.3	99.0
	120.0	123.8 ± 0.6	101.0
GBW-07605 tea ^b	–	4.3 ± 0.3 (μg/g)	–
GBW-07605 tea ^b	10.0 μg/g	14.3 ± 0.4 (μg/g)	100.0
SRM 2711 Montana soil ^c	–	1142 ± 25 (μg/g)	–
SRM 2711 Montana soil ^c	200 μg/g	1350 ± 28 (μg/g)	104.0

^a Mean values expressed as 95% tolerance limit.

^b Certified value: 4.4 μg/g.

^c Certified value: 1162 μg/g.

The influence of the sample flow rate for adsorption of lead(II) onto the column was also investigated. For this purpose, 50 mL of 400 ng mL⁻¹ Pb(II) solution was passed through the modified column at various flow rates between 2.0 and 11.8 mL min⁻¹. Then the adsorbed lead(II) was washed with 5.0 mL of 1.5 M HNO₃ solution, and the lead(II) content was measured by FAAS. The results showed that increasing the flow rate of the sample solution up to 4.0 mL min⁻¹ did not affect the recovery of Pb(II) from the modified activated carbon, and the recovery was 100 ± 1.5%. Therefore, a flow rate of 4.0 mL min⁻¹ was used for further study.

The effect of eluent flow rate (HNO₃, 1.5 M) was also checked in the range of 0.5–2.0 mL min⁻¹. The results showed that the recovery of lead(II) was maximum when using elution rates up to 0.5 mL min⁻¹.

The capacity of the modified activated carbon for adsorption of Pb(II) was checked by passing series of 50 mL solutions containing 50–1000 ng of Pb(II) through the column (containing 0.20 g of the modified activated carbon). The results showed that the capacity of the solid adsorbent is equal to 0.20 mg of lead per one gram of the modified activated carbon.

The influence of matrix ions in water samples on the separation and recovery of lead(II) ions was also investigated by passing different amounts of potential interfering ions plus 50 ng/mL Pb(II). The results showed that 100,000-fold of alkali and alkaline earth, 5000-fold Zn(II), Fe(II), Ni(II), Cd(II), V(III), Mn(II), Cu(II), Hg(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), chloride, nitrate, hydrogen carbonate, carbonate and sulfate did not interfere. The results confirm that the modified solid phase is highly selective for Pb(II) and it was not any interference. The method was used for three different water samples for Pb(II) determination containing Zayandeh Roud river water (Isfahan), tap water, industrial waste water, and the following

reference materials: SRM 2711 Montana soil and GBW-07605 tea.

The river and industrial waste water samples were directly measured by the proposed method after filtering the samples with a Millipore cellulose nitrate membrane of pore size 0.45 μm. For each sample, 250 mL was passed through the column as explained by the recommended procedure. Then the lead(II) contents in the washed solution were determined by FAAS. SRM 2711 Montana soil and GBW-07605 tea solution were spiked with various amounts of lead(II) then the separation/preconcentration method given above was applied. After that, Pb(II) was determined using FAAS. The results given in Table 2 shows good precision plus the recoveries.

4. Conclusion

The new developed method is both a repeatable method for lead(II) preconcentration and is a selective separation/preconcentration method for ultra trace of lead(II). The method can be used for preconcentration of lead(II) down to 0.4 ng mL⁻¹. The modified activated carbon phase is stable for several treatments of sample solutions without the need for any chemical reagents. Under the optimum conditions, lead in aqueous samples was concentrated about 200-fold. The relative standard deviation for six independent determinations reached values of 3.2% for a lead concentration of 4.0 ng mL⁻¹.

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