# ON-LINE PRECONCENTRATION AND DETERMINATION OF LEAD IN WATER BY FLOW INJECTION- FLAME ATOMIC ABSORPTION SPECTROSCOPY USING AMBERLITE XAD-16 FUNCTIONALIZED WITH XYLENOL ORANGE

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## ABSTRACT

*An on-line system for preconcentration and determination of Pb(II) by FAAS at $\mu g\ L^{-1}$ level is proposed. A mini column is packed with Amberlite XAD-16 functionalized with Xylenol Orange via azo coupling and the resulting resin is explored for enrichment of Pb(II) at pH range 4 – 5. All chemical and flow injection variable were optimized for the quantitative preconcentration and determination of Pb(II). The calibration graph obtained was linear over the concentration range of 11.3 – 350 $\mu g\ L^{-1}$. The limit of detection and preconcentration factor at 180s loading time were 1.9 $\mu g\ L^{-1}$ and 65 respectively. The precision (relative standard deviation) at 200 $\mu g\ L^{-1}$ Pb(II) concentration level was 3.9%. A sample frequency of 30 $h^{-1}$ was obtained for 60s preconcentration time of sample solution at flow rate of $5mLmin^{-1}$. The accuracy of the proposed preconcentration procedure was validated by performing the spiked recovery studies in water sample using certified Pb(II) nitrate solution traceable to NIST and analyzing standard reference material, SRM1643e.*

*Keywords: Atomic Absorption Spectroscopy,  Online Flow Injection, Preconcentration, Amberlite XAD-16, Xylenol Orange, Lead*

## I INTRODUCTION

The analytical monitoring of heavy metals (lead, cadmium, zinc, etc.) in different environmental samples and waste water is an important issue.  Pb(II) is one of the most toxic metals, which can be detected in practically all phases of the inert environment and in all biological systems. Pb(II) is extensively used in storage batteries, solders, cable sheaths, pigments, anti-knock products, and radiation shields [1]. According to Australian Drinking Water Guidelines, the maximum permissible limit of Pb(II)  in water is 0.01 mg $L^{-1}$ [2] and industrial effluent discharges must limit the Pb(II) content to less than 100 $\mu g\ L^{-1}$ (as per Indian Standards) [3]. The determination of Pb(II) in biological material, such as blood and tissues, provides an important basis for the diagnosis of clinical disorders, intoxication, and for monitoring

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environmental pollution. Even at very low concentrations, Pb(II) is toxic to animals and humans. As the limits for Pb(II) encountered in environmental samples are very low, one needs very sensitive analytical techniques of detection are required as Electrothermal Atomic Absorption Spectrometry (ETAAS) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) and Flame Atomic Absorption Spectrometry (FAAS) are not sensitive enough for some determinations and hence may require the use of a preconcentration step in order to reach an appropriate detection level. Flame Atomic absorption spectrometric (FAAS) determinations are either insensitive (Flame) or nonselective due to pronounced matrix interference (Graphite furnace). Hence, preconcentration coupled to FAAS is often used, as it offers higher sensitivity, selectivity, better precision and accuracy. Conventional off-line preconcentration procedures, although effective, are usually time consuming, tedious and require large quantities of sample, reagents and results into contamination and analyte losses. On the other hand, flow injection (FI) methods provide an opportunity to avoid contamination and large reagent consumption by working with closed systems. In addition, FI methods offer higher sample throughput and much better precision and accuracy compared to off-line methods [4]. There is a critical need for preconcentration and separation of the trace metals from matrices prior to their determination due to their frequent presence in environmental samples and higher matrix interferences. The techniques which have been used for separation and preconcentration are coprecipitation, electrodeposition, liquid–liquid extraction, membrane filtration, ion exchange or solid phase extraction (SPE). Among all of these, solid phase extraction is the most suited for trace elements analysis. There are several types of solid phase extractor or ion exchanger, such as cation exchangers, anion exchangers, and chelating resins. Chelating resins are superior for preconcentration of trace metals because of its several major advantages, high enrichment factors, better removal of interfering ions, high performance and rate of reaction process, and the possibility of the combination with several detections methods [5]. The combination of flow injection on-line separation and preconcentration techniques using solid-phase reagents i.e. FIA-FAAS has proved to be of considerable interest in the last few years. This on-line solid phase extraction (SPE) in a flow injection (FI) system offers automation and advantages such as higher precision and accuracy as well as minimization of reagent and sample consumption. On-line SPE is based on the analyte adsorption onto appropriate SPE which may be in form of beads and are packed in the preconcentration column. It is followed by the elution of analyte and the passed to the detector like FAAS. The selectivity and sensitivity of the method can be improved by selecting a wide range of sorbent materials, chelating agents, and eluents. The major requirements of a sorbent are the ability of adsorbing a large number of elements over a wide pH range, fast sorption and elution, high sorption capacity and reusability. The use of chelating solid phase materials in flow injection system has been summarised in a review [6] written by Derya Kara. Various sorbents have recently been used for the on-line solid phase preconcentration and determination of metal ions by FAAS in different samples. Some of these sorbents are surface coated alumina [7], cellulose [8], activated carbon [9], silica nanoparticles [10] and Amberlite XAD resin. The most widely used support materials for this purpose are XAD-2[11, 12], XAD-4 [13] and XAD-16 [14] in the Amberlite XAD series. Amberlite XAD- 16 (polystyrene-divinylbenzene copolymer) [15] has an edge over these resins due to the high surface area in comparison to the XAD-2 and XAD-4 resins. The large surface area also makes it possible

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to increase the number of chelating sites and to make them more accessible towards the adsorption of metal ions. The choice of a complexing ligand is of great importance here, as it directly influences selectivity of the sorbent, also the co-ordination geometry and the co-ordination of the metal ion together with charge and the size of the ion play an important role in obtaining selective sorbent. Xylenol Orange [16,17] was chosen as the chelating agent for this study due to its multi-dentate nature.   In the present work an on-line preconcentration system is developed for the trace determination of  Pb(II)  in water samples using minicolumn packed with  Xylenol Orange modified Amberlite XAD-16 in flow-injection (FI) system with flame atomic absorption spectroscopy  (FAAS)  for detection.

## II EXPERIMENTAL

### 2.1 Instrumentation

A PerkinElmer (Shelton, CT, USA) FIAS-400, flow injection analysis system was coupled with AAnalyst™ 400, flame atomic absorption spectrometer for automatic processing of the method and operated in pre-concentration mode. The whole system was controlled by a personal computer and winlab32 (version 6.5.0.0266) application software. The FIAS-400 system consist of two peristaltic pumps P1, P2, a 5-port 2-position injection valve and a pre-concentration column[18]. It was connected to the spectrometer's nebuliser, using a short PTFE capillary 20.0 cm length and 0.35mm i.d., in order to minimise the dead volume and eluent dispersion. pH-meter (Elico Ltd, India) was used for pH measurements. CHNS Elemental analysis was carried out on an Elementor, Model Vario EL-III. Thermal analysis was carried out using a PerkinElmer Diamond DSC. IR spectra (4000-400 cm$^{-1}$) were recorded on a Perkin Elmer, Model Spectrum RX-1.

### 2.2 Preparation of Standards, reagents and samples

A 1000 mg L$^{-1}$ stock solution of  Pb(II) was prepared by dissolving appropriate amount of analytical reagent grade Pb (II) nitrate   in double distilled water ( Double Distillation unit-WDU-2000) and standardized titrimetically with EDTA before use. Standard solutions were prepared by dilution of the stock solutions with double distilled water. pH adjustments were made with acetate and phosphate buffers (1-5 mL). Mixture of 0.2mol L$^{-1}$ KCl, 0.2 mol L$^{-1}$ HCl, 0.1 mol L$^{-1}$sodium acetate and 0.1 mol L$^{-1}$ acetic acid in appropriate ratio was used for making acidic buffer solutions. Buffer solution of pH 7 was prepared by mixing 0.1M sodium hydroxide and KH$_2$PO$_4$. Basic buffer solutions were prepared by mixing 0.1 mol L$^{-1}$ Na$_2$HPO$_4$, 0.1 mol L$^{-1}$ HCl and 0.1 mol L$^{-1}$ NaOH in appropriate ratio. The laboratory glassware's were kept overnight in a 10% (v/v) nitric acid solution, and was washed before use with deionized water. Double distilled water was used to wash the glassware and to prepare all solutions. Amberlite XAD-16 resin  (Sigma – Aldrich)  has surface area approximately 800 m$^2$/g , its moisture holding capacity is 62-70% , Particle size is 20-60 mesh ,  pore diameter is 100 Å (mean pore size) , and pore volume is 1.82 mL/g . Xylenol Orange used was of analytical reagent grade. All reagents used were at least of Analytical reagent Grade and were procured from E- Merck and Thomas Baker. Certified Pb (II) nitrate solution traceable to NIST was procured from E-Merck. Water samples were collected from Rishikesh (U.P), Mayapuri industrial area and from

Yamuna river in Delhi. Standard reference material (SRM-1643e),Trace elements in water was supplied by NIST Gaithersburg, MD, USA.

## 2.3 Synthesis of Amberlite XAD-16 functionalized with Xylenol Orange (AXAD16-XO)chelating resin

The Amberlite XAD-16 (styrene-divinylbenzene copolymer) was modified according to the procedure reported in the literature [18]. The synthesis involves nitration of XAD-16, followed by the reduction to form an aromatic amine. This amine facilitates the formation of a stable diazonium salt. The diazotized resin was filtered, washed with cold water and reacted with Xylenol Xrange at 0-3°c for 24 h. The resulting brown-colored beads were filtered, washed with water and finally air-dried. The structure of Amberlite XAD16- Xylenol Orange (AXAD16-XO) is shown below:
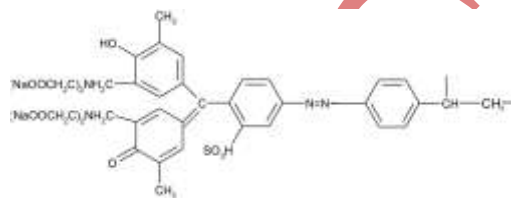


**Fig.1 Proposed structure of Amberlite XAD-16 functionalized with Xylenol Orange resin**

## 2.4 Preparation of minicolumn

A minicolumn for solid phase extraction preconcentration of Pb(II) was prepared by packing 130 mg of the synthesized AXAD16 – XO resin in a glass column (3.0 cm length and 3.0 mm internal diameter). The two ends of the column were sealed with cotton. The prepared column was washed with 2mol $L^{-1}$ HNO$_3$, and was washed with water before use. The column had a constant performance during all experiments, and there was no need for any regeneration or repacking.

## 2.5 Sample Preparation

Water samples were collected from three different places, Rishikesh (U.P), Yamuna water and Mayapuri industrial area. For these samples, the only pretreatment done was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the Pb(II) ions on the flask walls. The samples were filtered through a 0.45 µm pore size filter to remove any suspended particulate matter prior to its preconcentration. After the samples were filtered the filtrate was adjusted to pH 4.5 by addition of buffer solution.

## 2.6 Online preconcentration system

The preconcentration and determination of Pb(II) was made using two lines FI-manifold and a two step procedure. Acid resistant tubes (tygon) were used to pump the sample through the minicolumn with peristaltic pump P1. A suitable aliquot of the solution containing Pb (II) was passed through this column after adjusting its pH to an optimum value. The enriched Pb(II) - Amberlite XAD-16 – Xylenol Orange resin complex was then eluted with

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$HNO_3$ at an optimum flow rate of 5.0 mL $min^{-1}$ by using peristaltic pump P2 and then subjected to on-line flame atomic absorption spectrometric determination. Calibrations were linear in the range 11.3-350 μg $L^{-1}$ of Pb(II). In a similar manner, unknown water sample solutions were also subjected to analysis and the Pb(II) content was determined with reference to the calibration graph. For every standards and sample solution three replicates of measurements were carried out. FI-FAAS analysis program was controlled by a computer program [19] which includes: pre-filling, filling, and loading and elution steps.

## III RESULTS AND DISCUSSION

### 3.1 Characterization of the Amberlite XAD-16 functionalized with Xylenol Orange (AXAD16 – XO) chelating resin

#### 3.1.1 FT-IR spectrum of AXAD-16-XO resin

FT-IR spectrum of resin (Fig.2) has additional bands at 3424 $cm^{-1}$ (O-H stretching), 2924 $cm^{-1}$ (C-H), 1630$cm^{-1}$ ($COO^-$), 1536$cm^{-1}$ (N=N), 1350 $cm^{-1}$ (C-N) and 1265 $cm^{-1}$ (C-OH aromatic). This supports the loading of Xylenol Orange onto Amberlite XAD-16 with diazotized (N=N) coupling.
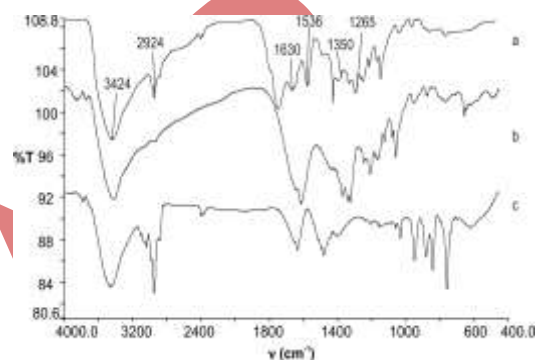


**Fig. 2 FT-IR spectra of (a)Amberlite XAD-16 functionalized with Xylenol Orange (b) Xylenol Orange and (c) Amberlite XAD-16**

### 3.1.2 Thermo- Gravimetric Analysis (TGA)

The thermogram of freshly prepared AXAD16 – XO resin showed a very slow but steady weight loss up to 500$^0$C. Up to 130$^0$C the observed weight loss is 15.3%, this is due to the removal of physisorbed water on the resin, which supports the presence of eight water molecules per repeat unit of chelating resin. This may be due to very big size of Xylenol Orange. It is reasonable to assume that with each ring one dye molecule is covalently bonded through an azo group. Most probably it occupies a position para to the –CH-CH$_2$–group, owing to electronic effect and steric reasons.

### 3.1.3 CHN Elemental Analysis

Elemental analysis provides a means for the rapid determination of carbon, hydrogen, and nitrogen in organic matrices and other types of materials.  The C H N % in AXAD16 – XO resin was found to be Carbon, 47.35%; Hydrogen, 5.07%; Nitrogen, 5.37%; sulphur, 3.20%; while calculated for $C_{38}H_{51}N_2O_{21}SNa_4N_2$ shows Carbon,
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45.22%; Hydrogen, 4.93%; Nitrogen, 5.41%; sulphur, 3.09%. This further confirmed that eight water molecules were present per repeat unit of chelating resin.

## 3.2 Optimum condition for sorption and desorption

In order to get the best performance for the flow system, the effect of various chemicals and instrumental parameters on the preconcentration and determination of Pb(II) were studied and optimized using online preconcentration procedure . The absorbance of Pb (II) was used as an analytical signal in this procedure.

### 3.2.1 Effect of pH

The pH value for the sample solution is one of the most important variables controlling the  Pb (II) ions  sorption limit because the sorption process of  Pb (II) ions is a complex formation reaction and hydrogen ions affect this complexation reaction. The effect of pH was investigated in the range of 2 – 10. In this study, pH values of sample solutions containing 200 μg $L^{-1}$ Pb (II) was adjusted to the desired pH value using an appropriate buffer.  Sample solutions were passed through a mini column packed with chelating resins with a flow rate of 5mL $min^{-1}$. The adsorbed Pb (II) was eluted by stream of 0.5mol $L^{-1}HNO_3$ with a flow rate of 5 $mLmin^{-1}$. Fig.5 shows that the absorbance signal has a maximum value at pH 4 - 5 for Pb (II) sample.

At low pH range, Pb enrichment was hindered due to strong protonation of the active sites in the sorbent. The medium pH facilitated complex formation. For higher pH values the signal decrease was observed due to hydroxide formation. Thus the pH values for all samples and standard solution were adjusted to the optimum value of 4.0-5.0 for subsequent studies.

### 3.2.2 Effect of Eluent Concentration

Desorption of adsorbed Pb(II) ions was carried out directly in the flow system using various acidic eluents. So, to choose the best type of acid as eluent hydrochloric, sulphuric and nitric acid of the same concentration (2.0 mol $L^{-1}$) were tested. The results obtained show that nitric acid has high elution ability and the reproducibility of signals was better with nitric acid. Thus, nitric acid was selected as the eluent for further studies. The effect of nitric acid concentration was studied in the range of 0.01–2.0 mol $L^{-1}$. The results show (Fig. 6) that with increase in the nitric acid concentration up to 0.5mol $L^{-1}$, absorbance increases and then decreases slightly at higher concentrations. Therefore, 0.5mol $L^{-1}$nitric acid was chosen as eluent, while the elution time was fixed at 20s in order to ensure the complete elution of adsorbed Pb (II) ions even at high concentration.
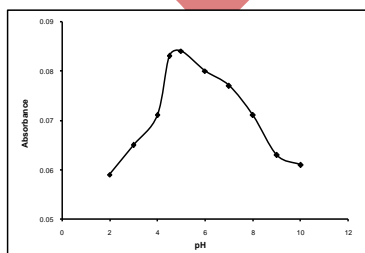


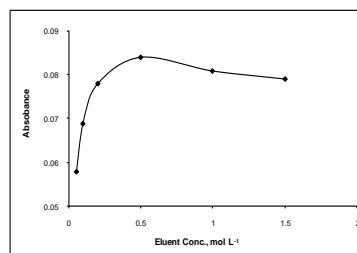|  |  |
|---|---|
| Fig. 3 Effect of pH | Fig. 4 Effect of eluent concentration |

### 3.2.3 Effect of Sample Flow Rate and Eluent Flow Rate

On-line time-based preconcentration systems are influenced by the loading flow rate because it regulates maximum mass transfer from liquid to solid phase .The amount of sample varies with flow rate if preconcentration time is constant, for this experiment. Therefore , at fixed 5mL min$^{-1}$ eluent flow rate, the effect of the sample flow rate on the preconcentration of  4.0 mL of 200 μg L$^{-1}$ Pb(II) solutions were investigated in the range of 2–7mL min$^{-1}$. Analytical signals decreased at flow rates more than 5mLmin$^{-1}$ as shown in Fig. 7. These results indicate that Pb (II) sorption is less at high flow rates because Pb (II) ions pass by column too quickly so that the time between the phases is not sufficient for a significant retention. Moreover, high flow rates increase back   pressure and this could cause leakage. Thus, a flow rate of 5mL min$^{-1}$ was chosen for subsequent experiments as a compromise between efficiency and stability of system.

The eluent flow rate is an important parameter, and the elution efficiency could be influenced by this parameter. The effect of HNO$_3$ flow rate was studied (Fig.8) within the range of 2.0–7.0 mL min$^{-1}$ at a fixed sample flow rate of 5 mL min$^{-1}$.The maximum absorbance was achieved at the flow rate  of   5mL min$^{-1}$ for 200 μg L$^{-1}$ Pb(II). Thus 5mL min$^{-1}$ flow rate of 0.5mol L$^{-1}$ HNO$_3$ was used in subsequent experiments.
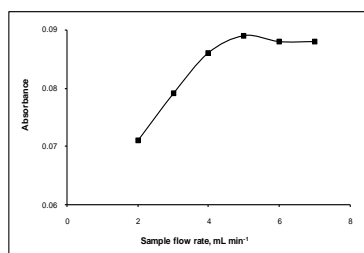


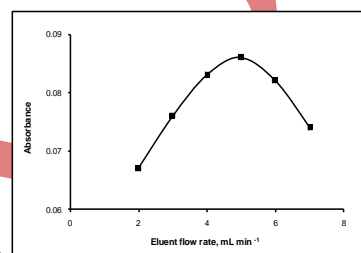**Fig. 5 Effect of sample flow rate**               **Fig. 6 Effect of Eluent flow rate**

## 3.3 Analytical performance of online precocentration system

The characteristic data for the online preconcentration system are shown in Table 1. The efficiency of solid phase extractor (SPE) was determined by analyzing the Pb(II) contents of column eluents. From the result obtained by repeated precocentration retention efficiency > 98% was calculated. The results are highly reproducible giving an overall precision of 3.9% R.S.D for five successive determinations of 200 μg L$^{-1}$ levels of Pb(II). Preconcentration Factor was calculated as a ratio of the calibration curve slopes obtained when applying the preconcentration step (FI-FAAS) and the slope obtained without it (FAAS). At pH 4.5 for sample loading time 60s, 120s and 180s the PF calculated were 19, 36 & 65 respectively. The detection limit corresponds to three times the standard deviation for five determinations of the blank was found to be 3.4, 2.7 and 1.9 μg L$^{-1}$ for 60s, 120s and 180s preconcentration time respectively. The limit of quantification is defined as concentration that gives a response equivalent to ten times the standard deviation of the blank it is 6.3 μg L$^{-1}$ for 180 s preconcentration time.  The limit of quantification is defined as concentration that gives a response equivalent to ten times the standard deviation of the blank. With total analysis time of 121 s (1+ 10 +20s for prefill, 60s for preconcentration, & 30s for elution), a sampling frequency of 30 h$^{-1}$ was

obtained for 5 mL of sample solution. Higher sensitivities can be obtained by modifying the method i.e. using longer preconcentration time of 3 min at the expense of lower sample throughput.

### 3.4 Effect of matrix ions on precocentration

The chloride, nitrate, sulfate and phosphate ions commonly found in natural water samples have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the chelating resins   to bind metal ions may be hampered resulting in the reduction of overall enrichment. Thus, the effect of  $NaCl$, $NaNO_3$ , $Na_2SO_4$ $Na_3PO_4$ , $NaBr$ , $MgCl_2$ ,  citric acid , tartaric acid & ascorbic acid on the sorption efficiency of  AXAD16-XO  resin for  $200\mu$  $L^{-1}$ Pb(II)  were  studied  using  the  recommended  flow-injection  column  method  under  the  optimum conditions. They were added to the metal ion solution before applying the recommended column procedure. The tolerance limits for electrolytes are given in Table 2. A species is considered to interfere when it lowers the recovery of metal ions by more than $\pm5\%$ compared to the value observed in its absence. In general, the tolerance limits suggest that common ions & organic acids like citric acid, tartaric acid & ascorbic acid   ions do not adversely affect sorption on the present resin when present in moderate amounts.

**Table 1 Analytical performance of the FI on-line method for Pb(II) determination**

| Parameter | Optimum conditions | | |
|---|---|---|---|
| pH range | 4-5 | | |
| Sample flow rate (mL min$^{-1}$) | 5.0 | | |
| Eluent flow rate (mL min$^{-1}$) | 5.0 | | |
| Acid conc. for desorption | 0.5 mol L$^{-1}$ HNO$_3$ | | |
| Preconcentration time (PT, S) | 60 | 120 | 180 |
| Linear range (μg L$^{-1}$) | 11.3-350 | 9-250 | 6.3-140 |
| Limit of detection (μg L$^{-1}$) | 3.4 | 2.7 | 1.9 |
| Sample throughput (h$^{-1}$) | 30 | 20 | 15 |
| Enhancement factor (EF) | 19 | 36 | 65 |
| Regression equation (7 standards, Pb(II)] /μg L$^{-1}$) (with preconcentration) | $A_{60}$= -0.00216+ 0.00043[Pb(II)] $A_{120}$= 0.00504+ 0.00080[Pb(II)] $A_{180}$=0.00742 + 0.00146[Pb(II)] | | |
| Regression equation (7 standards, Pb(II)] /μg L$^{-1}$) (without preconcentration) | $A = 0.00014+0.0000225$[Pb(II)] | | |
| Correlation coefficient | 0.99566 | 0.99847 | 0.99612 |
| Precision (RSD %) | 3.9, [Pb(II)] = 200 μg L$^{-1}$ ] | | |

### 3.5 Accuracy of the Method

In order to evaluate the accuracy of developed procedure, certified reference material NIST SRM 1643e (National Institute of Standard and Technology, Trace elements in water) was analyzed for Pb(II). The results are described in Table 3. It was found that there is no significant difference between achieved results by proposed method and certified results.

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**Table 2 Effect of neutral electrolytes and diverse ions on the FI on-line preconcentration of Pb(II)**

| Foreign species | Tolerance limit | Foreign species | Tolerance limit |
|---|---|---|---|
| NaCl[a] | 0.3 | Fe(III)[b] | 20 |
| Na$_2$SO$_4$[a] | 0.04 | Cu(II)[b], Cd(II)[b,] | 10 |
| NaI[a] , NaNO$_3$[a] | 0.05 | Al(III)[b,] Zn(II)[b] | 10 |
| Na$_3$PO$_4$[a] | 0.003 | EDTA[c] | 0.5 |
| NaBr[a] | 0.03 | Citric acid[a] | 0.3 |
| MgCl$_2$[a] | 0.07 | Tartaric acid[a] | 0.04 |
| K(I)[b] Ca(II)[b] | 5 | Ascorbic acid[a] | 0.03 |

[a]mol L$^{-1}$ , [b]mg L$^{-1}$ , [c]mmol L$^{-1}$

**Table 3 Pb(II) determination in Standard reference material using AXAD16-XO resin**

| Sample | Pb(II) (μg L$^{-1}$) | | Recovery (%) |
|---|---|---|---|
| | Certified value | Proposed methodology | |
| SRM1643e, Trace elements in water | 19.63 ± 0.21 | 19.03 ± 0.39 | 96.9% |

## 3.6 Analysis of Pb(II) in water samples

After validating the proposed method using standard reference material, the recommended procedure was applied to analyze Pb(II) in water collected from three different places, Rishikesh (U.P), Yamuna water & Mayapuri industrial area. Since analyte concentration of water sample was too low by direct method, therefore water samples were spiked with certified Pb(II) nitrate solution traceable to NIST. The accuracy of the preconcentration procedure was performed by the recovery experiments for spiked sample. The results are given in Table 4. It has been found that the addition of Pb(II) ions gives very good recovery.

**Table 4 Results for the determination of Pb(II) in water sample**

| Sample | Pb(II) added (mg L$^{-1}$) | Pb(II)[a] found (mg L$^{-1}$) | Recovery (%) |
|---|---|---|---|
| Mayapuri Area, Delhi, India | --- | 0.045 ± 0.002 | --- |
| | 0.05 | 0.09 ± 0.004 | 95 |
| | 0.15 | 0.19 ± 0.02 | 97 |
| | 0.30 | 0.34 ± 0.018 | 99 |
| Yamuna Water, Delhi, India | --- | 0.03 ± 0.002 | --- |
| | 0.05 | 0.075 ± 0.004 | 94 |
| | 0.15 | 0.175 ± 0.002 | 98 |
| | 0.3 | 0.32 ± 0.016 | 97 |

| | --- | $0.02 \pm 0.006$ | --- |
|---|---|---|---|
| Ganges Water, Rishikesh, India | 0.05 | $0.067 \pm 0.002$ | 96 |
| | 0.15 | $0.165 \pm 0.006$ | 97 |
| | 0.30 | $0.315 \pm 0.008$ | 98 |

[a]Confidence interval 95%

For comparative purposes, the performance characteristics of the proposed method and other selected on-line SPE preconcentration FAAS methods reported in the literature are given in Table 5. The proposed method shows good detection limit (DL), high sample throughput with reasonable enhancement factor (EF) over other on-line preconcentration methods.

## IV CONCLUSION

The results obtained in the present work confirm the performance of the synthesized AXAD16-XO resin as a new solid phase extractor in the online preconcentration and determination of Pb(II) in water sample using flow injection with flame atomic absorption spectrometry (FAAS) for detection. The developed resin shows high sorption capacity of 213 $\mu mol \ g^{-1}$ for Pb(II) as compared to other reported resins. The difference is due to large surface area of Amberlite XAD-16 and multidentate nature of ligand loaded. The proposed method is simple and fast with reasonable performance characteristics and high sample throughput as compared to other reported resins. The proposed resin possesses high stability and it can remain stable in strongly acidic and basic media. This feature provides the advantage of using this resin for several times (70-80 cycles). The flow injection analysis system provides simplicity, flexibility and good precision. The efficiency of the online preconcentration systems were tested by determining Pb(II) in a water samples using certified Pb(II) nitrate solution traceable to NIST by standard addition method. The accuracy of the developed on-line FI-FAAS procedure employing four chelating resins as column material were tested by analyzing Pb(II) determination in standard reference material (SRM-1643e) supplied by NIST Gaithersburg, MD, USA.

**Table 5 Comparison of the performance characteristics among selected on-line SPE methods the developed one for Pb(II) determination with FAAS.**

| Support | Chelating Agent | Eluent | EF | f (h$^{-1}$) | RSD (%) | DL ($\mu gL^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|
| Amberlite XAD-2 | Xylenol Orange | $HNO_3$ | 22 | 36 | 1.69 | 1.058 | [11] |
| Amberlite XAD-2 | 2-(2'Benzothiazolylazo)p cresol(BTAC) | HCl | 43 | 27 | 6.5 | 4.3 | [20] |
| Amberlite XAD-4 | 4-(2 pyridylazo) resorcinol | HCl | 9 | 16 | 2.3 | 7 | [21] |
| Polyurethane foam | 4-(2-pyridylazo)- resorcinol | HCl | 51 | - | 2.1 | 0.4 | [22] |

| | | | f | DL | RSD | EF | |
|---|---|---|---|---|---|---|---|
| ---- | Dimethylglyoxime | Triton X-114 | 44 | - | 1.0 | 1.4 | [23] |
| Polyurethane foam | 2-(6′-methyl-2′-benzothiazolylazo) chromotropic acid | HCl | 37 | 19 | 3.1 | 0.80 | [24] |
| Polyurethane foam | 2 benzothiazolyl azo-p-cresol | HCl | 26 | 48 | 6.0 | 1.0 | [25] |
| Polyurethane foam | 2-(2-thiazolylazo)-5 dimethylamino phenol | HCl | 45 | 27 | 6.8 | 2.2 | [26] |
| Microcrystalline naphthalene | Ammonium pyrrolidine dithiocarbamate | HCl | 65 | - | 2.7 | 4.6 | [27] |
| **Amberlite XAD-16** | **Xylenol Orange** | **HNO₃** | **65** | **32** | **3.9** | **1.9** | **This work** |

f: sampling frequency; DL: detection limit; RSD: precision (relative standard deviation); EF: enhancement factor.

## V ACKNOWLEDGEMENT

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