# Nano TiO2 based hollow fiber solid/liquid phase microextraction for the detection of Pb(II) from water samples

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*Abstract*— **Nano TiO2 were applied to preconcentration and determination of Pb (II) in water samples using hollow fiber based solid-liquid phase microextraction (HF-SLPME) combined with flame atomic absorption spectrometry (FAAS). The effect of experimental conditions was investigated. The method was linear in the range of 0.6 -3000 µgmL-1. The relative standard deviations and relative recovery of Pb (II) was 4.9 % and 99.3 %, respectively (n=5).**

*Keywords*— **TiO2, Hollow fiber, Solid/liquid phase microextraction, Pb (II), Flame atomic absorption**

## I.    Introduction

Some of heavy metals are classified as nonessential trace elements (1). Non-essential trace elements are well recognized to be highly toxic to human health. Meanwhile, due to the unique properties and a wide range of chemical processing industries, lead is one of the most widely disturbed heavy metal in the environment. The maximum contaminant level of Pb (II) in drinking water according to US environmental protection agency (USEPA) is 0.015 mgL$^{-1}$(2). Hence, determination of Pb (II) ions at trace levels is very important in the context of environmental protection, food and agricultural chemistry. Several analytical techniques such as; flame atomic absorption spectrometry are available for the determination of trace Pb (II) with sufficient sensitivity in various samples. However, the direct determination of trace Pb (II) is difficult due to their low concentrations, matrix effects. To overcome these limitations, in this study, combination of HF-SLPME with FAAS leads was used to determination of Pb (II) in aqueous samples.

## II.    Experimental

### A.    HF-SLPME procedure

Membrane-supported extraction with a solid/liquid interface used in this research, which consisted of the aqueous feed: organic solvent/nanosorbent phases operated in direct immersion sampling mode.

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### B.    Instrumentation and reagents

Flame atomic absorption spectrometer equipped with D$_2$ lamp background correction (GBC Scientific Equipment Co., Australia) was used for determination of lead ions. A lead hollow cathode lamp with wavelength 217.0 nm and air-acetylene flame atomizer were used for measurements.

All chemicals and reagents used in this study were of analytical grade and obtained from Merck (Darmstadt, Germany).The hollow fiber membrane with the inner diameter of 600 µm, wall thickness of 200µm, and pore size of 0.2 µm was purchased from Membrana (Wuppertal, Germany).

## III.    Results and discussions

Nanometer material that has been known as ultrafine grained particle is a solid material that gained importance due to its specific properties such as high specific surface area. Nanoparticles are described as clusters of atoms or molecules, falling between single atoms or molecules and bulk materials and ranging in size from 1~100 nm. The particle size of these materials has an important role in the physical and chemical properties because the specific surface area, the chemical stability, and the chemical reactivity of the nanomaterial are all highly correlated with the particle size. One of the most important properties of nanoparticles is that high percent of the atoms of a nanoparticle are on the surface and usually, the surface atoms are unsaturated and can easily bind with other atoms. Thus, nanoparticles having high chemical activity and can strongly chemisorb many substances, such as metal ions with very high adsorption capacity. In the present work, the TiO$_2$ nanoparticles were dispersed in octanoic acid immobilized in the lumen of the porous hollow fiber as an efficient reinforcement factor for extraction of metal ions and to prevent the dispersion of nanoparticles into sample solution via solid-liquid phase's trapping. The structure of synthesized nano – sorbent was shown in Fig 1.



Fig 1.Scanning electron microscopy(SEM) micrographs of TiO2

reinforced located in the pores of the fiber.

## A.  *Influence of pH*

The reaction between Pb (II) ions and the octanoic acid as an extraction agent can be influenced by changes of pH value. To investigation of pH effect, a set of similar experiments at fixed values of all variable in the pH range of 3-10 has been carried out.As the results, to achieve high extraction efficiency without metal hydroxide precipitation, pH 6 was selected for further experiments.

## B. *Effect of the donor phase volume*

Generally, due to the low concentration of heavy metal ion in real samples, large sample volume is required for effective pre-concentration and determination of trace metals. On the other hand, in the two phases LPME, enrichment factor can be improved by increasing the volume ratio of donor to acceptor phases. In the present work, the volume of the donor phase was varied in the range of 3-8 ml while the volume of the acceptor phase was kept constant at 6 µl. The optimal volume of donor phase was obtained 6 ml.

## C. *Extraction time*

Like to the other LPME procedures, HF-SLPME is not an exhaustive extraction technique and is based on the extraction equilibrium between the organic and aqueous solutions, that requires a period of time to be established. When the partition equilibrium is reached, the amount of extracted analyte has a linear relationship with the initial concentration of the analyte in the sample solution (4). Different extraction times from 5 to 60 min were tested. By increasing the extraction time the extraction efficiency of the HF-SLPME system is increased up to the period of time 30 min and then decreased with the increasing of the extraction time. This may be due to the loss of organic solvent into the aqueous solution. Therefore, 30 min was selected as the extraction time for the further experiment.

## D. *Effect of stirring rate*

Agitation of sample solution provides a fresh donor solution for the acceptor phase to extract analyte and increase the mass transfer rate by decreasing the thickness of the diffusion film at the outer membrane surface and improve the repeatability of extraction method. The experimental results showed that extraction efficiency was increased with the increase of strring rate up to 400 rpm. On the other hand, further stirring speed may also cause lower extraction efficiency because the higher stirring speed led to mechanical stress and vibration of the fiber by surrounding flow and air bubbles on the surface of the hollow fiber reduced contact area between analyte and membrane. The stirring speed of 400 rpm was chosen in the subsequent experiments.

## E. *Effect of TiO2 content*

The influence of TiO2 nanoparticles on the extraction capacity have been examined by adding TiO2 nanoparticles at range 20, 40 and 60 mgmL-1, respectively. It was observed that as the TiO2 concentration increased, the percent of adsorbed Pb (II) increased which was expected since the amount of available surface sites increased with the sorbent concentration.(Figure 2).
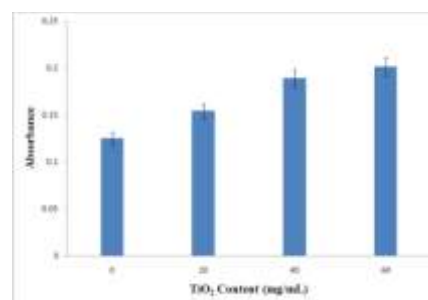


Fig.2. Influence of TiO2 amount on the extraction

## F. *Surfactant& ionic strength effect*

- In many conventional extraction processes, the addition of salts might decrease the solubility of analyte compounds in the aqueous solution and improve the extraction efficiency due to salting out effect. Whereby water molecules form hydration spheres around the ionic salt molecules, so that the amount of free water available to dissolve analyte molecules in water reduce, therefore, the analyte compounds will drive into the extractor phase. Usually, sodium chloride is used for this purpose. In this research, to investigate the salt effect on the HF-LPME, the extraction was performed with 6 ml sample solution containing various concentrations of NaCl in the range of 0.5-10%. The results showed that the salt almost had a positive effect on the extraction efficiency of lead ions. On the other hand, further salt concentration may also cause lower extraction efficiency because the viscosity of aqueous solution would increase by the addition of salt, which resulted in difficult mass transfer. Therefore the HF-LPME was done with the addition of NaCl with a concentration of 2 % W/V (5).

The effect of nonionic surfactant, Triton X-100 on the extraction efficiency was also investigated. The experimental results showed that the surfactant has not a positive effect on the Pb(II) extractions and the absorption signal generally decreased by the addition of surfactant. Thus, the extraction experiments were carried out without adding surfactant.

## G. *The tolerance of coexisting ions*

By fixing the concentration of Pb (II) at 0.3 µgmL-1, the interference of common coexisting ions found in the real aqueous sample, such as $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Zn^{2+}$, $Cu^{2+}$, $SO_4^{2-}$, $CO_3^{2-}$, $NO_3^-$, and $Cl^-$ on the extraction and determination of Pb (II) were investigated for three concentration level of each interfering ion. The results indicated that except for $Fe^{3+}$, that has precipitated under the optimum conditions described above; the other ionic species have not serious interfering on the preconcentration of Pb (II)

## III. **Method validation**

Based on the above studies, the optimal HF-LPME conditions for Pb (II) ions were as follow: 6.0 ml of feed solution (pH 6) was extracted with 6.0 µl of solid/liquid acceptor phase for 30 min with a stirring rate of 400 rpm,

and desorbed ultrasonicately by 1.0 mL of MeOH:HNO3 (1:1 V/V) for 5 min.

The analytical performance for proposed method has been validated and the linear range, limit of detection (LOD), enrichment factor (EF), and relative standard deviations (RSDs) are listed in Table 1. The linear range was found to cover 4 orders of magnitude (0.6 -3000 µgL-1) for lead ion, with a correlation coefficient of R2 = 0.9960. According to the 3δ blank approach as recommended by IUPAC for spectrochemical measurements, the LOD of the proposed method was found 0.2 µgL$^{-1}$. The enrichment factor that is a ratio of concentration between acceptor phase and initial donor phase aqueous solution for Pb (II) was determined too. For determination of this factor, absorbance after extraction of analyte should be divided to absorbance before extraction at the same concentration and same conditions. Since, after extraction of analyte onto the fiber containing 6.0 µl of acceptor phase, analyte was desorbed with 1.0 mL of MeOH-HNO3 (1-1 V/V) mixture, thus absorbance after extraction divided to observe before extraction multiplied by the dilution factor (1000/6).

Table 1. Figure of merit of the proposed method in the determination of Pb (II) in aqueous samples.

| Calibration equation[a] | LR µgL$^{-1}$ | EF | r$^2$ | LOD µgL$^{-1}$ | RR% [b] | RSD % (n=5) |
|---|---|---|---|---|---|---|
| y = 0.0005x + 0.0971 | 0.6-3000 | 790 | 0.996 | 0.2 | 99.3 | 4.9 |

a  y: Absorbance, x: Concentration (µgL-1)

b Sample Concentration: 0.3 µgmL-1 of Pb (II)

# IV. Real sample analysis

To investigate method accuracy and matrix effects and applicability of the HF-LMPE technique to environmental samples, the method was carried out on two environmental water samples including tap and river water. Tap water was collected from Ardabil, Iran. River water was collected from Baliqly Chay River in Ardabil, Iran. As no lead contamination was found in any of the water samples analyzed, relative recovery (RR%) studies were carried out (Table 2).

Table 2.Relative recovery (RR) %  and RSD % for  environmental water samples.

| Water sample | RR % | RSD % within day (n=5)[a] | RSD % with day (n=9)[b] |
|---|---|---|---|
| Tap water | 102.3 | 3.40 | 2.41 |
| River water | 93.4 | 5.10 | 6.82 |

a five samples in one day, b nine sample in three consecutive days

# V. Conclusion

The aim of this study was to develop a simple, reliable and inexpensive method for the determination of Pb (II) ions from aquatic environmental samples using hollow fiber-solid/liquid phase microextraction combined with FAAS. The ability of Caprylic acid in the extraction of metal ions using the formation of metal soap molecules makes it a suitable organic solvent with low toxicity and high efficiency in the liquid phase microextraction. The single use of the hollow fiber due to the disposable nature of it reduces the risk of sample carry-over problems and ensures high reproducibility. On the other hand, nano-TiO2 small size can be acting as nano-solid trap. Due to high surface areas of TiO2 nanoparticles, high enrichment factor with good selectivity can be obtained, in addition to the effect of caprilic acid that was disscussed before

## *References*

[1]. Y. Tan, M. Chen, Y. Hao, "High efficient removal of Pb (II) by amino-functionalized Fe3O4 magnetic nano-particles" Chem. Eng. J., Vol. 191, pp. May 2012.

[2]. L. Niu, S. Deng, G. Yu and J. Huang, " Efficient removal of Cu(II), Pb(II), Cr(VI) and As(V) from aqueous solution using an aminated resin prepared by surface-initiated atom transfer radical polymerization", Chem. Eng. J., Vol. 165, pp 751-757, August 2010.

[3]. H. G. Seiler, H. Sigel and A. Sigel, Handbook on toxicity of inorganic compounds, Dekker, New York, 1988.

[4]. Z. Es'haghi," Determination of widely used non-steroidal anti-inflammatory drugs in water samples by in situ derivatization, continuous hollow fiber liquid-phase microextraction and gas chromatography-flame ionization detector", Anal. Chim. Acta, Vol. 641, pp 83-89, May 2009.

[5].  A. A. Boyd-Boland and J. B. Pawliszyn, " Solid Phase Microextraction of Nitrogen Containing Herbicides", J. Chromatogr. A, Vol. 704, pp163-172, October 1995.