

## New Determination of Lead in Edible Oil and Water Samples by High Selective Adsorptive Stripping Voltammetry with SPADNS

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The complex formed by lead and 4,5-Dihydroxy-3-(p-Sulfophenylazo)-2,7-Naphthalene Disulfonic Acid Trisodium Salt (SPADNS) was able to be adsorbed on the HMDE. In this investigation we were able to determine lead (II) in water and edible oil samples, using Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV) technique. The influence of variables is completely studied. Linear dependence between the peak current and lead concentration in the (NH<sub>3</sub>/NH<sub>4</sub>Cl) buffer in pH=7.5 observed in the range 0.7 – 115.0 ng ml<sup>-1</sup> of Pb(II), for accumulation time 100 s and sweep rate 24 mV s<sup>-1</sup>. The detection limit for Pb(II) was 0.110 ng ml<sup>-1</sup>, and the RSD at a concentration level of 45 ng ml<sup>-1</sup> was 1.48%. This method has been applied for the determination of Lead in Edible Oil and Water Samples with satisfactory results.

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**Keywords:** Pb (II); adsorptive stripping voltammetry; SPADNS; Edible Oil

### 1. INTRODUCTION

Determination of heavy metals such as lead is very important because it shows toxic effect on living systems. The manifestations of lead exposure include dullness, restlessness, irritability, poor attention span, headache, tremor, hallucination and loss of memory, which can progress to delirium, mania, convulsions, paralysis, coma and death 1.. Lead is also known to be able to cross the placental barrier and, thus, may cause possible damage to the fetus and newborn 2-4.. Pb<sup>+2</sup> is listed by EPA as a class-B2 carcinogen 5.. Human absorbs Pb<sup>+2</sup> in small amounts from food, water and air. The Pb<sup>+2</sup> ions inhibit a select group of enzymes, including thiol-dependent enzymes involved in heme synthesis and

mitochondrial energetic. The toxicologic effect of lead may result from the ability of  $Pb^{+2}$  to uncouple oxidative phosphorylation and modify mitochondrial ion transport 5.. Lead also decreases glucose-6-phosphate dehydrogenase activity in human, and thus decreases the glutathione level in red blood cells. When the blood  $Pb^{+2}$  concentrations are near to  $80 \text{ mg L}^{-1}$  or greater, basophilic stripping occurs in erythrocytes 6.

Determination of trace elements in vegetable oil is one of the criteria for the assessment of quality of oil in regard to freshness, keeping properties and storability. Trace heavy metals in vegetable oils are known to have an effect on the rate of oil oxidation. The determination of trace level of lead in vegetable oil could be important 7.. The usual methods for the determination of  $Pb^{2+}$  in solution involve potentiometry, spectrophotometry, atomic absorption spectrometry 8-10., inductively coupled plasma–mass spectrometry, graphite furnace atomic absorption spectroscopy, neutron activation analysis, inductively coupled plasma–atomic emission spectroscopy and direct current plasma atomic emission spectrometry 11-15. Electrochemical method is one of the most favorable techniques for the determination of heavy metal ions, because of its low cost, high sensitivity, easy operation and the ability of analyzing element speciation. In previous works the determination of heavy metal ions were mostly carried out at mercury electrodes 16-19. A literature survey reveals that metal ions may be preconcentrated on different adsorbent, such as silanized glass beads 20., polythioether foams 21. and ion-exchange and chelating resin 22.. Some of these adsorbents may be fairly effective for the preconcentration of the sorption of ions, but their preparation methods are lengthy and involve rigid control of the conditions. However, the use of extraction methods is usually time consuming and labor-intensive, and requires relatively large volume of high-purity and toxic solvents 6.. Stripping voltammetry, especially with adsorptive collection, has been widely used as a simple, sensitive and inexpensive technique without anymore preconcentration steps, directly to determine heavy metals in natural waters and food stuffs. In this paper, a method for the adsorptive voltammetric determination of  $Pb^{+2}$  in presences of 4, 5-Dihydroxy-3-(p-sulfophenylazo) 2, 7-naphthalene disulfonic acid, trisodium salt (SPADNS), as a complexing agent, at hanging mercury drop electrode is presented. This method provides a very low detection limit with good accuracy and precision and excellent selectivity against the other co-existing ionic species. The method was applied to determination of lead in tap water and oil samples

## 2. EXPERIMENTAL PART

### 2.1. Apparatus

Voltammetric measurement made using a 746 VA-Trace Analyzer, (Metrohm, Switzerland) connected to an electrode stand, 747 VA-Stand, (Metrohm, Switzerland) The three-electrode configuration was used comprising a Metrohm multi mode electrode (MME) in HMDE state as working electrode, a double junction Ag/AgCl (3M KCl, saturated AgCl, and 3M KCl in the bridge) reference electrode and a Pt wire auxiliary electrode. All potentials quoted are relative to this Ag/AgCl reference electrode. A rotating Teflon rod stirred solutions in the voltammetric cell. The mercury was

triple-distilled quality, and the medium drop size of the HMDE was selected. All experiments were done at room temperature (approximately 20 °C) pH measurements were made with a Metrohm pH meter model 780 (Switzerland). Eppendorf reference variable micropipettes were used to pipette microlitre volume of solutions. Each sample was filtered with a whatman filter paper (ashless-42, 12.5 cm, England) was used.

## 2.2. Chemicals and reagents

All the chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany). Doubly-distilled water was used throughout. Working metal ion solutions were prepared by appropriate dilution of 1000 mg l<sup>-1</sup> atomic absorption standard solutions (alpha-line, Chem Tech Analytical, Ltd. England) Stock Solutions used in the preparing buffer solutions for influence of pH were 0.05 M NaHCO<sub>3</sub>, 0.1 M NaOH, 0.05 M borax, 0.1 M K<sub>2</sub>HPO<sub>4</sub>, 0.2 M NH<sub>3</sub>, 0.2 M NH<sub>4</sub>Cl, 0.1 M H<sub>3</sub>BO<sub>3</sub> and 0.1 M KCl, preparation was according to the procedure in Ref. 23..

## 2.3. Sample preparation

Tap water was collected from taps in our laboratory. For the determination of Pb(II), 10 ml filtered tap water sample, 1 ml of the 0.2 mol l<sup>-1</sup> NH<sub>4</sub>Cl/NH<sub>3</sub> buffer and 0.2 ml of the 1.75×10<sup>-3</sup> mol l<sup>-1</sup> SPADNS were placed in the cell and the analysis was carried out as described below.

The oil samples prepared according to the procedure in Ref. 24. by dry ashing technique. 5 ml of this solution, 1 ml of the 0.2 mol l<sup>-1</sup> NH<sub>4</sub>Cl/NH<sub>3</sub> buffer and 0.2 ml of the 1.75×10<sup>-3</sup> mol l<sup>-1</sup> SPADNS diluted to 10 ml with Doubly-distilled water, were placed in the cell and the analysis was carried out as described below.

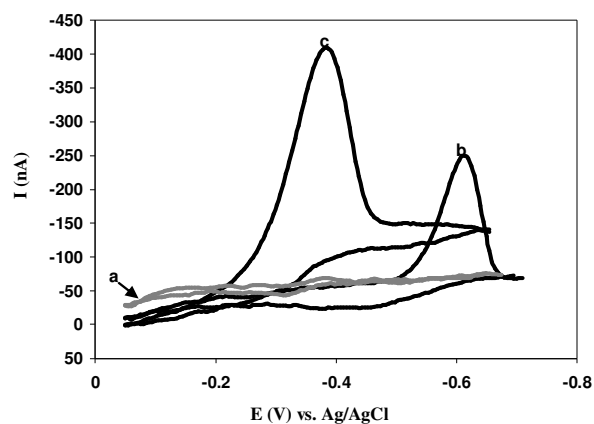
## 2.4. Measurement procedure

The mixture solution (contain sample, buffer and ligand solution) was stirred and deaerated by purging for 3 min with water-saturated nitrogen gas prior to analysis. The nitrogen flow was stopped and a new mercury drop was extruded, and the adsorption potential was set to -495 mV for 100 s, while the solution was stirred 2000 rpm. Then the stirrer was switched off and a quiescence time of 10 s was allowed. The potential scan was carried out from -150 to -550 mV and voltammogram was recorded using differential pulse modulation (DP) with a potential scan rate of 24 mV s<sup>-1</sup>.

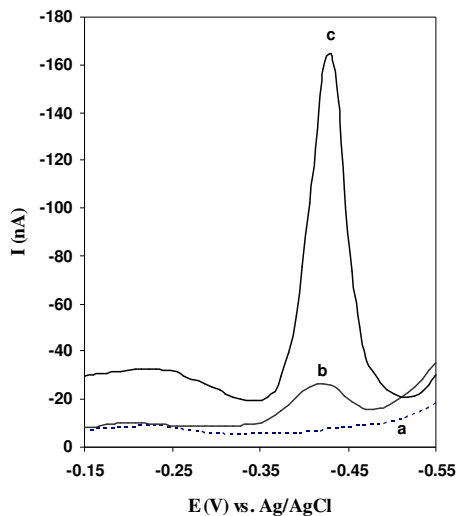
## 3. RESULTS AND DISCUSSION

The reagent of 2-(parasulfophenylazo)-1, 8-dihydroxy-3, 6-naphthalene-disulfonate (SPADNS) is a ligand with -N and -O functional groups and used for the spectrophotometric determination of

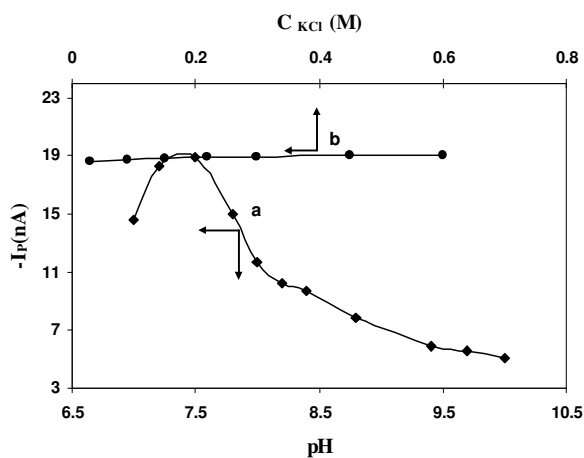
fluoride 25.. In regard to previous report for the 1:1 (Pb (II)-SPADNS) complex formation 26., cyclic voltammetric investigation was carried out. As shown in fig 1a, cyclic voltammogram of Pb (II) in pH=7.5 shows a very small reversible pick for reduction of Pb (II) at -367 mV vs. Ag/AgCl. CV of SPADNS in the same condition demonstrates an adsorptive irreversible cathodic peak for reduction of SPADNS at -604 mV vs. Ag/AgCl (Fig 1b). Results for CV of Pb (II) in the presence of SPADNS are shown a large and clear cathodic peak for reduction of Pb-SPADNS complex at -372 mV vs. Ag/AgCl (Fig 1c). As can be seen from Fig 1c, the cathodic peak current of lead is more extended than same cathodic peak of lead in Fig 1a. Increase of reduction peak current in Fig 1c as a result of increasing concentration of lead on electrode surface and strongly supports the adsorption of Pb-SPADNS complex on the electrode surface. The shape of cathodic peak in Fig 1c is another irrefutable evidence of adsorptive behavior in electrode process. Hence, because of complex adsorptive process on electrode surface, adsorptive stripping voltammetry was selected for further study. The stripping voltammogram for the blank and sample solution was shown in fig 2. As can be seen in this figure, for the blank solution containing SPADNS at pH 7.5, no obvious current peaks were observable between 150 to -550 mV. On the other hand, with the addition of small amount of Pb a peak can be seen located approximately -430 mV vs. Ag/AgCl electrode. All peaks current ( $I_p$ ) measured from linear base line at -430 mV. The current of the complex generally increases at large values due to its adsorption properties on the HMDE. The spontaneous adsorption process can be utilized as an effective preconcentration. The peak current increased with increasing accumulation time, showing evidence for the adsorption of complex on surface of the electrode. This phenomenon indicates that the complex is strongly adsorbed on the mercury electrode surface. In this way, highly sensitive measurements of Pb with SPADNS can be achieved by using the method of adsorptive differential stripping voltammetry.



**Figure 1.** Cyclic voltammograms for (a) Pb(II) (b) SPADNS (c) complex of Pb(II)-SPADNS. Conditions:  $C_{\text{SPADNS}}$ ,  $2.0 \times 10^{-5}$  M; pH, 7.5; sweep rate,  $500 \text{ mV s}^{-1}$ ; Pb(II),  $200 \text{ ng mL}^{-1}$ .



**Figure 2.** Differential pulsed voltammograms for (a) Pb(II) (b) SPADNS (c) Pb(II)- SPADNS. Conditions:  $C_{\text{SPADNS}}$ ,  $3.5 \times 10^{-5}$  M; pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -495 mV; accumulation time, 100 s; sweep rate,  $24 \text{ mV s}^{-1}$ ; Pb(II),  $35 \text{ ng mL}^{-1}$ .



**Figure 3.** The effect of (a) pH ( $C_{\text{SPADNS}}$ ,  $1.75 \times 10^{-5}$  M; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -470 mV; accumulation time, 50 s; sweep rate,  $20 \text{ mV s}^{-1}$ ; Pb(II),  $35 \text{ ng mL}^{-1}$ ) and (b) supporting electrolyte on peak current ( $C_{\text{SPADNS}}$ ,  $1.75 \times 10^{-5}$  M; pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -470 mV; accumulation time, 50 s; sweep rate,  $20 \text{ mV s}^{-1}$ ; Pb(II),  $35 \text{ ng mL}^{-1}$ ).

### 3.1. Effect of Buffer Solutions

Diverse buffer solutions were tested for their suitability in the determination of Pb in presence of SPADNS, as follows:  $\text{NaHCO}_3\text{-NaOH}$ , borax- $\text{NaOH}$ ,  $\text{K}_2\text{HPO}_4\text{-NaOH}$ ,  $\text{K}_2\text{HPO}_4\text{-borax}$ ,  $\text{NH}_3\text{-NH}_4\text{Cl}$ ,

NaOH-H<sub>3</sub>BO<sub>3</sub>-KCl, NH<sub>3</sub>-HCl, CH<sub>3</sub>COONa-CH<sub>3</sub>COOH. The most suitable buffer system for the determination of Pb was found to be NH<sub>3</sub>-NH<sub>4</sub>Cl. In this buffer solution, peak height is more than other buffers (Table 1).

### 3.2. Effect of pH and Supporting Electrolyte

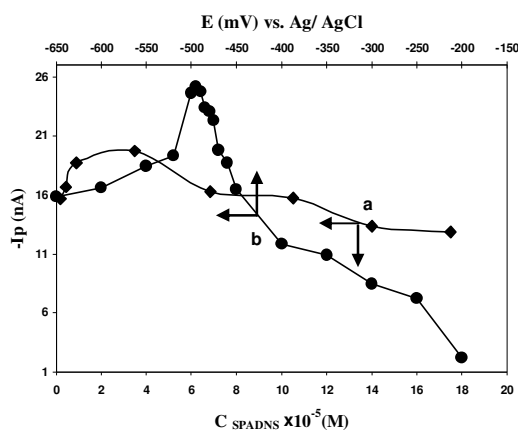
In order to investigate the effect of pH on the peak height, pH was increased from 7.0 to 10.0 by addition of ammonia. The peak height of lead increased strongly at pH 7.5. Thus, the pH of 7.5 was selected for further studies. The results given in Fig 3a at duration also examined ionic ability changes with different concentration of KCl but results showed that current remained constant without signal alteration (Fig 3b).

**Table 1.** Comparison of results with diverse buffer.

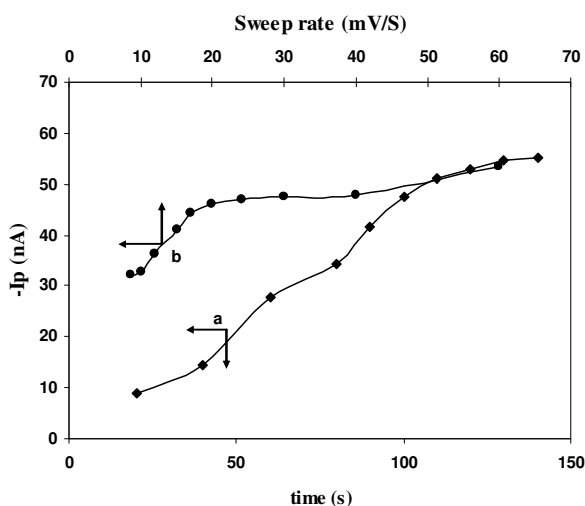
Buffer type	pH	-Ip (nA)
NaHCO <sub>3</sub> + NaOH	9.6	2.4
	11.0	1.1
Na <sub>2</sub> B <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub> + NaOH	9.5	2.2
	10.6	0.9
K <sub>2</sub> HPO <sub>4</sub> + Na <sub>2</sub> B <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub>	9.0	3.5
	8.0	4.4
K <sub>2</sub> HPO <sub>4</sub> + NaOH	7.0	1.8
	8.0	2.3
NH <sub>4</sub> Cl + NH <sub>3</sub>	8.0	11.5
	9.0	8.0
	10.0	5.1
H <sub>3</sub> BO <sub>3</sub> + NaOH + KCl	8.6	4.8
	9.0	5.3
CH <sub>3</sub> COONa + CH <sub>3</sub> COOH	4.0	2.4
	5.0	3.0
NaH <sub>2</sub> PO <sub>4</sub> + Na <sub>2</sub> HPO <sub>4</sub>	6.0	5.6
	7.0	4.9
KH <sub>2</sub> PO <sub>4</sub> + Na <sub>2</sub> HPO <sub>4</sub>	7.0	3.8
NaOH + C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	4.0	4.6

### 3.3. Effect of Ligand Concentration and Accumulation Potential

The ligand gives one peaks at -430 and the peak height increases with increasing concentration of the ligand. The optimum ligand concentration was  $3.5 \times 10^{-5}$  M., the dependence of the peak height on ligand concentration is shown in Fig 4a. On the other hand, accumulation potential was varied between -200 to -650 mV. The optimum accumulation potential -495 mV was selected for determination of Pb (Fig 4b).



**Figure 4.** The effect of (a) Ligand Concentration (pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -470 mV; accumulation time, 50 s; sweep rate,  $20 \text{ mV s}^{-1}$ ; Pb(II),  $35 \text{ ng mL}^{-1}$ ) and (b) Accumulation Potential on peak current ( $C_{\text{SPADNS}}$ ,  $3.5 \times 10^{-5} \text{ M}$ ; pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation time, 50 s; sweep rate,  $20 \text{ mV s}^{-1}$ ; Pb(II),  $35 \text{ ng mL}^{-1}$ ).



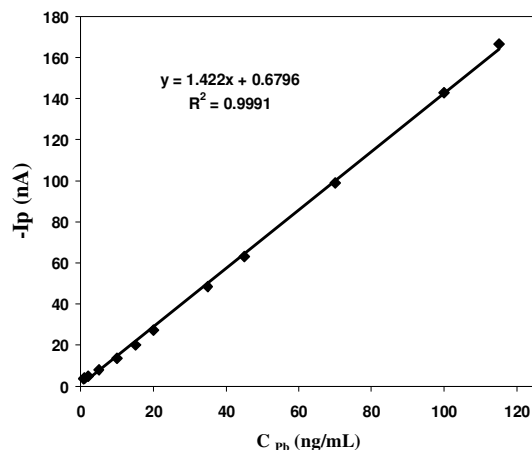
**Figure 5.** The effect of (a) Time ( $C_{\text{SPADNS}}$ ,  $3.5 \times 10^{-5} \text{ M}$ ; pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -495 mV; sweep rate,  $20 \text{ mV s}^{-1}$ ; Pb(II),  $35 \text{ ng mL}^{-1}$ ) and (b) Sweep rate on peak current ( $C_{\text{SPADNS}}$ ,  $3.5 \times 10^{-5} \text{ M}$ ; pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -495 mV; accumulation time, 100 s; Pb(II),  $35 \text{ ng mL}^{-1}$ ).

### 3.4. Effect of Time and Sweep Rate

Variation of the deposition time between 20 to 140 s at deposition potential of -495 mV showed that the peak height of Pb increase up to 100 and after longer deposition a plateau was reached. The independence of Pb on the deposition time is attributed to diffusion controlled currents. Also for the study of sweep rate effect on the determination of Pb the peak current was recorded as a function of sweep rate over the range of 8.6-60  $\text{mV s}^{-1}$  and 24  $\text{mV s}^{-1}$  was used for subsequent experiment, as the best sweep rate. The dependence of the peak height on time and sweep rate, are shown in Fig 5a and 5b respectively.

### 3.5. Linear range

Under the optimal voltammetric conditions, different concentrations of Pb were applied and the peak current was recorded. The recorded data showed that the peak current increased linearly with the Pb concentration over the range of 0.7-115  $\text{ng mL}^{-1}$ . Hence, a linear calibration graph was demonstrated from 0.7 to 115  $\text{ng mL}^{-1}$  of Pb with a correlation coefficient of 0.9991 ( $n=13$ ) (Fig. 6).



**Figure 6.** Linear calibration curves obtained by varying the concentration of Pb 0.7–115  $\text{ng mL}^{-1}$  ( $C_{\text{SPADNS}}$ ,  $3.5 \times 10^{-5}$  M; pH, 7.5; initial potential, -150 mV; final potential, -550 mV; accumulation potential, -495 mV; sweep rate, 24  $\text{mV s}^{-1}$ ).

### 3.6. Analytical performances

The limit of detection  $C_L$  of the proposed method for the determination of Pb according to the IUPAC definition 27. was obtained 0.110  $\text{ng mL}^{-1}$  of Pb under the optimal experimental conditions by measuring nine blank samples and using as the criterion the equation:  $C_L = 3s_b/S$ , where  $s_b$  is the standard deviation of the blank measure and  $S$  is the slope of the calibration curve. The results obtained on 9 replicate measurements for 5.00 and 45  $\text{ng mL}^{-1}$  of Pb revealed RSDs of 2.05 and 1.48 %, respectively.



### 3.7. Interferences

The influence of several anions and cations on determination of Pb was studied. For a fixed concentration of  $40 \text{ ng ml}^{-1}$  Pb, the maximum tolerance levels which do not modify the peak current of Pb, beyond the limits of  $I_p \pm 3s$  of those obtained in the absence of interferences, were established and results reported in Table 2 were found. Most of the examined ions are tolerated at high levels, almost  $1000 W_{\text{ion}}/W_{\text{Pb}}$ . As can be seen, only  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  (at  $750 W_{\text{ion}}/W_{\text{Pb}}$ ),  $\text{Sb}^{3+}$  (at  $500 W_{\text{ion}}/W_{\text{Pb}}$ ),  $\text{Sn}^{4+}$  and  $\text{F}^-$  (at  $75 W_{\text{ion}}/W_{\text{Pb}}$ ) weakly were interfered.

**Table 2.** Interferences study for the determination of Pb under optimum conditions

Species	Tolerance limit ( $W_{\text{ion}}/W_{\text{Pb}}$ )
Ag(I), Ce(III), Ba(II), Mo(VI), Mg(II), Na(I), Bi(III), Li(I), Cr(III), K(I), Ti(II), Mn(II), Ni(II), Co(II), Cd(II), Al(III), Cu(II), $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{HPO}_4^{2-}$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ , $\text{CN}^-$	1000 <sup>a</sup>
Zn(II), Ca(II), Fe(III)	750
Sb (III)	500
Sn(IV), $\text{F}^-$	75

<sup>a</sup> maximum concentration of ions tested

### 3.8. Application of the proposed methods to real samples.

To evaluate the applicability of the proposed method, it was applied to the separation and recovery of Pb from tap water, oil of fish conserve and solid hydrogenated oil samples. The results of recommended procedure, with a standard addition method are summarized in Tables 3. Satisfactory agreement exists between the results obtained by the proposed method and those reported by reference standard method.

The precision of the proposed method, for the analysis of Pb in real samples, were compared with the reference method (ETAAS) using two-sided *F*-test. The results of *F*-test in Table 4 showed that there is not any statistically difference between the precise of the methods in the uncertainty level of 5%.

**Table 3.** Determination of Pb in real samples

Sample	Pb added (ng ml <sup>-1</sup> )	Pb found (ng ml <sup>-1</sup> )	R.S.D. (%) (n=5)	Recovery (%)	Pb found by ETAAS <sup>a</sup>
Tap water	-	3.21	0.18	-	3.03
	10	13.32	0.23	101.1	
	20	23.08	0.25	99.3	
Oil of fish conserve	-	18.71	0.28	-	19.12
	20	38.92	0.23	101.1	
	40	58.40	0.20	99.2	
vegetable hydrogenated oil	-	15.92	0.32	-	15.73
	20	35.71	0.25	99.0	
	40	55.43	0.28	98.8	

<sup>a</sup> Electrothermal Atomization Atomic Absorption Spectrometry

**Table 4.** Results of tow-sided *F* test for comparison precision proposed method and reference method (ETAAS).

Sample	S <sub>1</sub>	S <sub>2</sub>	Critical F (P=0.05)	Experimental F
Tap water	0.26	0.23	9.605	1.278
Oil of fish conserve	0.32	0.25	9.605	1.638
vegetable hydrogenated oil	0.31	0.23	9.605	1.816

**Table 5.** comparison of figure of metric of the present work with other studies

Reference number	Figure of metric		
	LOD	% RSD	Accomolation time (s)
28.	5.00 × 10 <sup>-7</sup> M	-	900
29.	10.00 × 10 <sup>-9</sup> M	-	300
30.	1.00 × 10 <sup>-9</sup> M	3.70-5.00	30
31.	4.83 × 10 <sup>-9</sup> M	2.00-6.00	-
32.	1.74 × 10 <sup>-7</sup> M	2.14	180
33.	9.66 × 10 <sup>-10</sup> M	-	600
34.	5.81 × 10 <sup>-11</sup> M	3.20	100
Present work	5.32 × 10 <sup>-10</sup> M	2.05	100

#### 4. CONCLUSIONS

The proposed voltammetric method, for the determination of Pb, offers several advantages over other previously reported procedures. The proposed methods provided better LOD for the determination of SDS, relative to the previously presented methods 28, 29, 30, 31, 32., also lower deposition time 28, 29, 32, 33. and RSD 30, 31, 32, 34. On the other hand, the purposed method has no interfere of species that were interference at previously methods 30, 34, 35, 36. (Table 5).

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