

*Full Paper*

## **Validation of Sequential Cathodic-anodic Stripping Voltammetric Determination of Ultratrace Level of Copper, Lead, Cadmium, Zinc, and Selenium in Milk and Dairy Products of Iran**

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*Received: 27 May 2016 / Received in revised form: 17 August 2016 /*

*Accepted: 10 October 2016 / Published online: 31 December 2016*

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**Abstract-** The concentrations of Pb, Cd, Cu, Zn and Se metal ions in milk and dairy products (pasteurized milk, doogh, cheese and yoghurt) were determined with differential pulse anodic and cathodic stripping voltammetry technique at HMDE electrode. For more accurate and selective metal ions determination the samples were digested by dryness-HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub> heat digestion method. The concentration linear ranges of Pb, Cd, Zn, Cu and Se in fermented milk sample were in the range of 0.5-200, 0.3-220, 0.1-500, 0.1-450, and 0.4-120 ppb, respectively. The recovery for metal ions in all samples was in the range of 89 to 99%. The intermetallic effect of metal ions was omitted by change of pH. This study shows that nearly in all cases the concentration of the measured amounts are lower than the international permissible limits and there is no health threatening concern due to the consumption of milk and dairy products in Iran.

**Keywords-** Stripping voltammetry, Milk, Dairy products, Heavy metals, Health risk assessment

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## 1. INTRODUCTION

It would definitely be said that the milk and its products were making a great part of daily diet of all peoples. Therefore, the determination and analyses of contaminants such as: pesticides, aflatoxins, poly aromatic hydrocarbons, heavy metals, and also essential elements [1], may have great help to control problems that affects the human's health and their quality of life. In this regards the presence of trace amounts of heavy metals in milk and its products are easily absorbed in the body and induced their poisonous. It is well established that the Pb and Cd can cause the damage of nervous connections, brain damage, poisoning, and various cancers [2]. In opposite, the beneficial elements such as Zn, Cu and Se at low concentrations are essential and have a variety of biochemical functions in all living organisms, but at high level concentrations they can be toxic and this both toxicity and necessity vary from element-to-element [3]. These reasons emphasize that the determination and control of concentration level of trace elements in milk, and dairy products which consumed daily are so important. Various analytical methods such as: inductively coupled plasma-mass spectrometry (ICP-MS) [4], inductively coupled plasma-optical emission spectrometry (ICP-OES) [5], atomic absorption spectroscopy (AAS) [6], potentiometric stripping [7], anodic stripping voltammetry (ASV) methods [8], have been employed for the determination of elements in milks. The international standard methods for the analysis of elements such as Pb in milk and milk products are based on the ashing, extraction by some reagents such as 1-pyrrolidinedithioate and/or HNO<sub>3</sub>, and determination by AAS or anodic stripping voltammetric methods [9]. For other metal ions, the atomic absorption spectrometry coupled with dry ashing is recommended as standard method [10]. Although, the AAS method has been issued for the determination of most elements in milk and related products, but for simultaneous analyzing of several elements in many samples, it is so tedious and uneconomic. In addition, the ICP-OES is a selective instrument that able to determine the simultaneous elements, but it is very expensive and for large amount of samples is not economic.

Today the electrochemistry science has been widely used in various fields such as: analysis of metal ions [11], develop of sensors [12], investigation of chemical interactions [13,14] and biological evaluations of drugs [15] and etc. Among these methods the anodic stripping voltammetric (ASV) and cathodic stripping voltammetric (CSV) methods are widely consider as an economic and high sensitive and selective method for simultaneous determination of several metal ions [16-19]. It is well established that for determination of Zn, Cu, Pb and Cd in many matrices the ASV is a suitable method whereas CSV has proved to be most sensitive for Se [20]. Therefore, these two techniques can be used for simultaneous determinations of these metals in a single sample solution that caused to reduce the total time needed for individual determination of each element. The important point in the simultaneous determination of these metal ions is the possibility of intermetallic interferences

that may occur in analyses [21]. However, by elimination of this effect the concurrent use of both techniques for the determination of a number of elements in a single sample solution would be possible. To our library search, in this work we firstly describe an ASV-CSV method for the determination of Se, Cu, Pb, Cd and Zn in a single sample solution after acid digestion of milk and dairy samples. By change of pH of electrolyte the intermetallic effect of studied metal ions was completely removed. This method is selective, fast, accurate, reproducible, sensitive and economic for analysis of these metal ions in large samples of milk and dairy products.

## **2. EXPERIMENTAL SECTION**

### **2.1. Materials**

Se, Cu, Pb, Cd and Zn standard solutions (1000 mg L<sup>-1</sup>) were obtained from Merck Company (Darmstadt, Germany). Triple-distilled deionized water used in the present study was of ultrapure quality (>18.2 MΩ cm resistivity). The individual standard solutions with the desired concentrations were prepared every day by appropriate diluting of the stock solutions with the chosen electrolyte. Super pure nitric acid (67-69%), super pure sulfuric acid (94-98%) and hydrogen peroxide obtained from Merck and were used for soaking glassware, sample digestions and cleaning of voltammetric cell. Moreover, all other reagents and chemicals were of analytical grade unless otherwise stated.

### **2.2. Sampling**

The five samples of raw milk (250 ml) were obtained from two different industrial dairy herds and also four dairy products (pasteurized milk, cheese, doogh, and yoghurt) were purchased from local super markets in order to analyses of the elements of interest by proposed method. Each sample was analyzed in three different pH. Also, three replicate determinations were carried out on each sample.

### **2.3. Apparatus**

All voltammetric measurements of elements were carried on a voltammeter model VA 797 Computrace (Metrohm, Switzerland) that controlled with 797 PC software package (version 1.2). Measurements were carried out using a hanging mercury drop electrode (HMDE). The instrument contains three-electrode: a platinum wire as the auxiliary electrode with a considerably larger surface area than that of HMDE; Silver/silver chloride (KCl 3 M) as the reference electrode and a mercury electrode as working electrode. The samples were stirred using a large Teflon rod at 2000 rpm. Solutions were purged with high-purity nitrogen for 3.0 minutes prior to each analysis under a nitrogen atmosphere. Experimental analysis

conditions for ASV and CSV are demonstrated in Table 1. The pH values of the buffer solutions were measured with a Metrohm pH meter (model 827).

**Table 1.** Instrument conditions for ASV and CSV analyses of metal ions

	ASV				CSV
	Zn	Cd	Pb	Cu	Se
Instrument operation					
Drop Size	5	5	5	5	5
Start Potential (V)	-1.15	-1.15	-1.15	-0.5	-0.1
End Potential(mV)	0.0	0.0	0.0	0.0	-0.9
Pulse Amplitude (mV)	50	50	50	50	50
Pulse time (s)	0.04	0.04	0.04	0.04	0.04
Voltage Step (mV)	5	5	5	5	5
Voltage Step Time (s)	0.125	0.125	0.125	0.125	0.125
Scan Rate (mV s <sup>-1</sup> )	40	40	40	40	40
Accumulation Potential (mV)	-1100	-1100	-1100	-200	-300
Accumulation Time (s)	20	20	20	20	20
Equilibrium time (s)	5	5	5	5	5
Peak Potential (mV)	-1020	-613	-452	-140	-558

## 2.4. Sample digestions

3 ml of milk and doogh and/or 3 g of cheese and yoghurt were taken accurately and transfer into a beaker, then 4.0 mL of HNO<sub>3</sub> (65 %W/W) was added and the mixture was heated to dryness for digestion of samples. After that, 1.0 mL of H<sub>2</sub>SO<sub>4</sub> (95% w/w) was added to each sample and the temperature was adjusted to 180-200 °C until the solution was going to complete dryness and the digestion completed. After that 1.0 mL of H<sub>2</sub>O<sub>2</sub> (30% v/v) was added to the digested material and the mixture was heated until become colorless and dry. Finally, the residues were re-dissolved in triple distilled water to achieve the final volume 1.0 mL.

## 2.5. Experimental procedure

### 2.5.1. Anodic stripping voltammetric determination of Zn, Cd and Pb

For simultaneous determining of Zn, Cd and Pb, the voltmeter was set at its determination mode, and then 10.0 mL of buffer solution (0.3 molL<sup>-1</sup> of phosphate buffer pH 6.0) containing digested material (50 µl) was transferred into the voltammetric cell and purged with nitrogen for 3.0 minutes. The accumulation potential of HMDE for each metal ion was adjusted according to Table 1 while the solution was stirred at 2000 rpm.

Following the accumulation period, the stirring of solution was stopped and after 5 seconds the voltammograms of cations were recorded by applying a positive-going potential scan (from -1.5 to 0.0 V). The concentrations of Zn, Cd and Pb were quantified by the standards addition method.

#### 2.5.2. Anodic stripping voltammetric determination of Cu

For determination of Cu, 10.0 ml of buffer solution ( $0.3 \text{ mol L}^{-1}$  of ammonium buffer, pH 9.5) containing digested material (50  $\mu\text{l}$ ) was added to the voltammetric cell and deoxygenated with a nitrogen flow for 3.0 min. The accumulation potential of -0.2 V was applied to the working electrode for 20 seconds under stirring condition of 2000 rpm. Following the accumulation period, the stirrer was stopped and after 5 seconds of reset the voltammogram was recorded by applying a positive-going potential from -1 to 0.0 mV. The instrument worked at its determination mode and the concentration of Cu was quantified by the standard addition method.

#### 2.5.3. Cathodic stripping voltammetric determination of Se

In the present study, in order to completely eliminate blank signals and gain accurate signal intensity of the Se, the instrument was set in the determination mode. Briefly, the phosphate buffer solution (pH 2.0) containing digested material (50  $\mu\text{l}$ ) was purged with nitrogen for 3.0 min to remove oxygen and then analyzed by CSV mode. The experimental analysis conditions of CSV method was shown in Table 1. Determination of Se concentration in the sample solutions was carried out using the standard addition method, by adding appropriate concentrations of Se from 10 to 30 ppb to the voltammetric cell and re-purging the solution in the cell with nitrogen gas for 10 s prior to each experiment. All experiments in the current research were conducted in triplicates.

### 2.6. Statistical analysis

All experiments were conducted in triplicate. Analyses were done for each replicate. The analysis was performed using SPSS 16.0 for Windows (SPSS, Chicago, IL, USA) software package. Significance level was considered  $P < 0.05$  in all experimental data.

## 3. RESULTS AND DISCUSSION

The possibility of intermetallic interferences in ASV and CSV techniques may be make a big problem for simultaneous determination of metal ions and should be removed by selective deposition of the analyte(s) and or use of masking or oxidizing agents [22]. Most recently Mahesar reported the simultaneous determination of Zn, Cd, Pb and Cu in

commercial broiler poultry feeds by ASV method and acetate buffer (pH 5) as a supporting electrolyte [23]. However, under reported conditions we observed a significance intermetallic effect from Zn, Cd, Pb on Cu peak current and we tried to remove this effect. Three different parameters such as: pH of solution, accumulation potential and accumulation time were for improving of sensitivity of method and reducing of intermetallic effect.

### 3.1. Optimization of analysis parameters

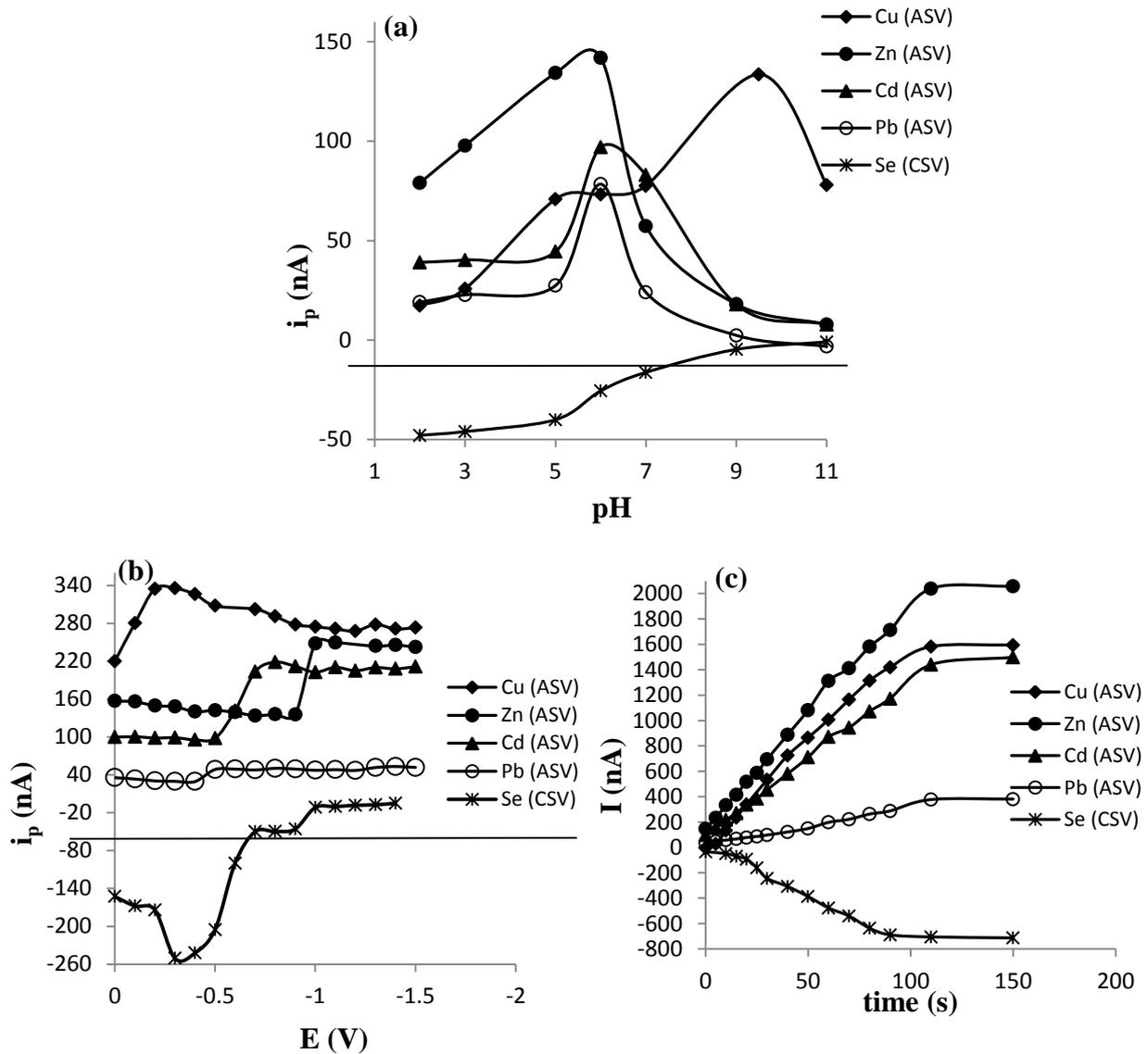
#### 3.1.1. The effect of pH on peak current of metal ions

The effect of pH on the anodic peaks correspond to Zn, Cd, Pb, and Cu and also the cathodic peak corresponds to Se were separately determined for each metal ion. The concentration of all metal ions in solution was fixed at 50 ppb. The results were shown in Fig. 1a. As shown, the anodic peak current of Zn, Cd and Pb increased in parallel increasing value of sample pH from 2.0 to 6.0, and after that the peak currents of Zn, Cd and Pb were reduced. For Cu, the corresponded peak was increased when the value of sample pH increased from 2.0 to 9.5 and after that the peak was reduced. Therefore, for ASV determination of Zn, Cd and Pb, a phosphate buffer ( $0.3 \text{ mol L}^{-1}$ ) with pH of 6.0 was selected; while for ASV determination of Cu an ammonium buffer ( $0.3 \text{ mol L}^{-1}$ ) with pH of 9.5 was used. In addition, our finding indicate that at pH 9.5 the peaks of Zn, Cd, and Pb significantly decreased ( $P < 0.05$ ), and have not any intermetallic effect on Cu peak current. The effect of pH on cathodic peak of Se was also evaluated. According to our findings, the peak corresponding of Se significantly decreased when the value of sample pH increased from 3.0 to 11 (Fig. 1a). Hence, the pH of 2.0 was selected as optimum pH for further studies.

#### 3.1.2. The effect of accumulation potential

The accumulation potential effect on sensitivity of studied metals was studied too. The determined accumulation potentials of Zn, Cd, Pb, Cu during ASV procedure and the assessed accumulation potential of Se during CSV procedure were shown in Fig. 1b. All accumulation potentials were evaluated on the HMDE ( $t_{\text{acc}}=10 \text{ s}$ ) at several selected potentials between 0.0 and -1.5 V. As shown in Fig. 1b, in pH 6.0, at accumulation potentials of -1.1, -0.5, and -0.8 V, the Zn, Pb and Cd are being accumulated efficiently on the HMDE, respectively, while the Cu is being accumulated efficiently at -0.2 V in pH 9.5. At more positive deposition potentials, all peak corresponding were remarkably reduced and this result likely related to the incomplete reduction of all cations to form an amalgam with the HMDE electrode. However, simultaneous analyses of Zn, Pb and Cd was performed on the accumulation of -1.1 as suitable potential for achieving a reproducible peak corresponding. Fig.1b shows the relationship between the peak current of Se and deposition potential in the CSV method. As exhibited in this Fig.1b, the Se is being accumulated efficiently on the

HMDE at -0.3 V in phosphate buffer (pH 2.0). At a more negative deposition potential than -0.3 V, the peak current of Se reduced rapidly and reached zero at -0.6 V.



**Fig. 1.** Effect of (a) pH on peak currents of 50 ppb of, Zn, Cd and Pb ( $t_{acc}=20$  s,  $E_{acc}= -0.5$  V), and 50 ppb of Cu ( $t_{acc}=20$ s,  $E_{acc}= -0.5$  V) and 50 ppb of Se ( $t_{acc}=20$ s,  $E_{acc}=-0.5$  V); (b) Effect of  $E_{acc}$  on peak currents of 50 ppb of, Zn, Cd, Pb in phosphate buffer (pH=6.0,  $t_{acc}=20$ s) Cu in ammonium buffer (pH=9.5,  $t_{acc}=20$ s) and Se in phosphate buffer (pH=2.0,  $t_{acc}=20$ s); (c) Effect of  $t_{acc}$  on peak currents of 50 ppb of, Zn, Cd, Pb in phosphate buffer (pH=6.0,  $E_{acc}= -1.1$  V) Cu in ammonium buffer(pH=9.5,  $E_{acc}= -0.2$  V) and Se in phosphate buffer (pH=2.0,  $E_{acc}=-0.3$ V)

This could be attributed to the reduction of Se (IV) to Se (-II) during the deposition step. The continuous decrease of CSV peak for Se at accumulation potentials more positive than -

0.3 V may be due to the incomplete reduction of Se (IV) to Se (0). In continue the accumulation potential of -0.3 V was used for next studies.

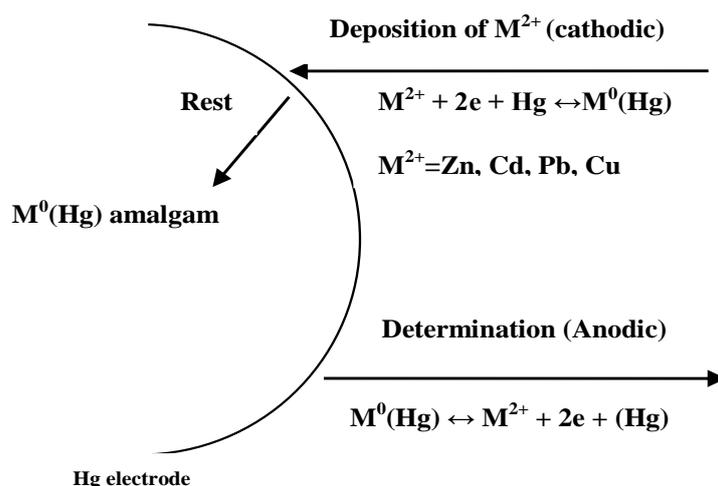
### 3.1.3. The effect of accumulation time

The effect of accumulation time, on ASV and CSV peak currents of metal ions was investigated for each analyte (See Fig. 1c). As it is observed for up to 110 sec adsorption, the CSV peak currents of Pb, Cd, Cu and Zn were increased linearly and after that the peak currents levels off because of adsorption saturation. In ASV mode the Se was saturated at 90 s. In this work an accumulation time of 20 sec was selected for all metal ions by comparison between sensitivity and time of analysis.

### 3.2. The mechanism of ASV and CSV for determination of Zn, Cd, Pb, Cu and Se

The ASV determination of Zn, Cd, Pb, and Cu is based on the deposition of metal ions at the surface of mercury electrode and then oxidation of them in stripping step (Fig. 2).

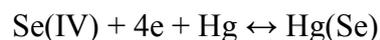
Our previous works were shown a two electron reduction for Zn, Cd and Pb ions [24]. The diagram of ASV is shown as follows (scheme 1):



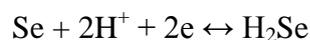
**Scheme 1.** The ASV mechanism of Zn, Cd, Pb, Cu metal ions on surface of HMDE

At pH=2.0 the peak reduction of Se(IV) have two peaks (Fig. 2) that means the reduction may be performed via two steps.

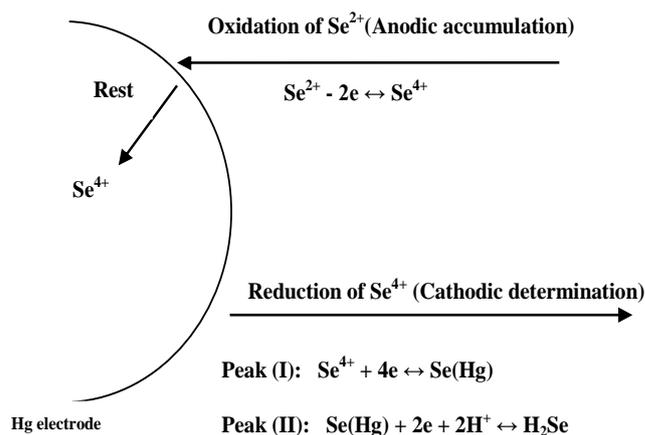
In the first step, the Se(IV) is reduced to Se(0) on HMDE,



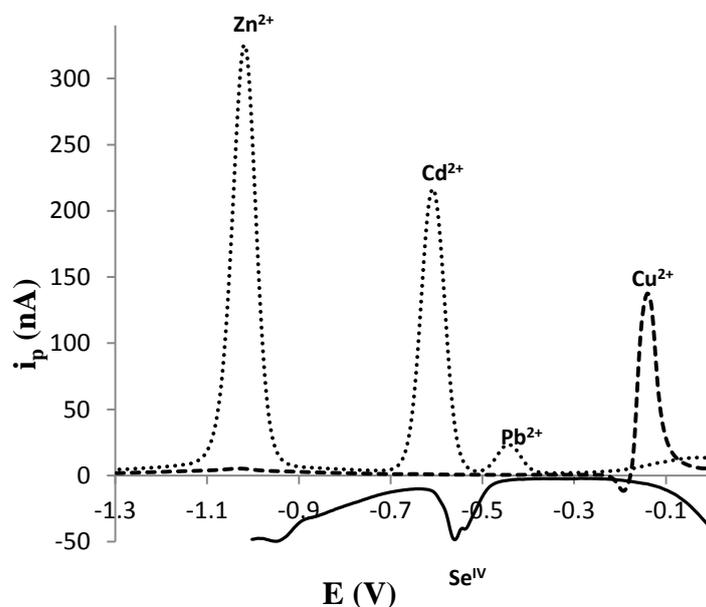
In the second step, the Se(0) is reduced to hydrogen selenide as follows:



The diagram of CSV is exhibited as follows (scheme 2):



**Scheme 2.** The CSV mechanism of Se metal ion on surface of HMDE

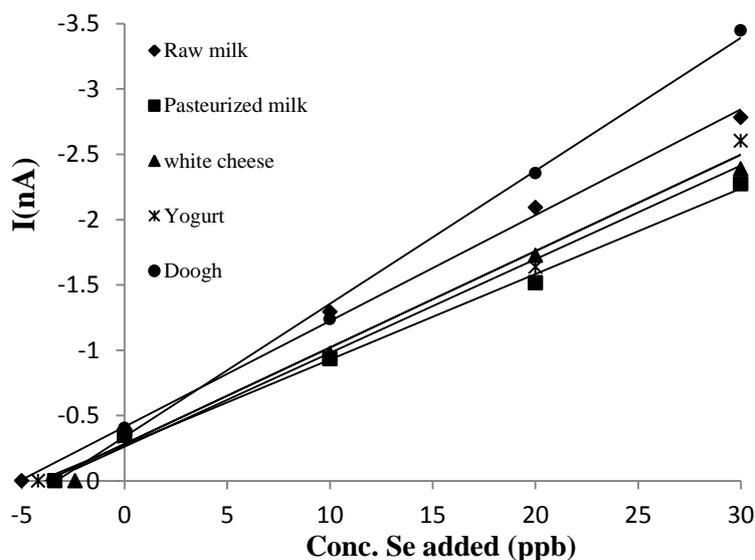


**Fig. 2.** Anodic stripping voltammograms of 50 ppb of, Zn, Cd, Pb at pH=6.0,  $t_{acc}=20$  s,  $E_{acc}=-1.1$  V (round dot line); 50 ppb of Cu at pH=9.5,  $t_{acc}=20$  s,  $E_{acc}=-0.2$  V (square dot line); cathodic stripping voltammogram of 50 ppb of Se at pH=2,  $t_{acc}=20$  s,  $E_{acc}=-0.3$  V (solid line)

### 3.3. Method validation

In order to validate the method, a recovery test was conducted by spiking of a standard milk sample (Institute of Standard of Iran) with 20 ppb of Zn, Cd, Pb, Cu and Se using standard addition technique. All experiments were done in triplicates. The recovery values were  $\%95\pm 1.5$  for Zn,  $\%96\pm 1.2$  for Cd,  $\%97\pm 1.4$  for Pb,  $\%98\pm 1.3$  for Cu and  $\%91\pm 1.4$  for Se. Based on our results, the sensitivity of the proposed method is not restricted by the

voltammetric methods themselves and/or by the digested blank values, because the concentrations of metal ions are higher than 1 ppb and therefore the digested blank value is insignificant. At optimum conditions, quantitative determination of metal ion concentrations was conducted using the standard addition method. Three standard additions are adequate to determine the concentration. The concentrations of the ion metals were assessed by calculating the determination of the intercept of the linear regression lines with the x-axis. For this purpose, 10  $\mu\text{l}$  of 50 ppb of Zn standard was transferred into the voltammetric cell and then concentration of Zn in milk and dairy product samples was assessed from the increments of the peak current at -1.1V.



**Fig. 3.** A sample of standard addition curves for determination of Se in raw milk, pasteurized milk, doogh, white cheese and yoghurt that obtained under optimum condition as described in section 2.5.3

The intercept range and calculated coefficients of determination ( $r^2$ ) value of Zn were found to be 0.5-1.5 ppb and 0.9977, respectively. In this work, following transferring 10  $\mu\text{l}$  of 50 ppb Cd, Pb and Cu standards, increasing at the -0.8, -0.5 and -0.2 V was observed and hence the determination of Cd, Pb, and Cu concentrations in the sample made possible. The intercept ranges of Cd, Pb, and Cu were found to be 0.5-1.5 ppb. The corresponding calculated coefficients of determination ( $r^2$ ) values of Cd, Pb, and Cu ion metals were 0.9989 and 0.9969 and 0.9897, respectively. Moreover, following transferring the standard additions of 10  $\mu\text{l}$  of 50 ppb Se, increasing at the -0.3 V was found and hence the determination of Se concentration in the sample made possible. The intercept range and calculated coefficients of determination ( $r^2$ ) value of Se was found to be 0.5-1.5 ppb and 0.9997. An example was exhibited in Fig. 3.

In addition, in the current research, five calibration curves was made for each metal ion at optimum conditions in raw milk and corresponding results were shown in Table 2.

**Table 2.** The analytical merit of proposed method in raw milk for five metal ions

Sample	Metal ions	Linear equation	Regression	Linear range (ppb)	LOQ (ppb)	LOD (ppb)
Raw milk <sup>a</sup>	Pb	$I_{(nA)}=1.231 C_{ppb}+5.16$	0.9915	0.5-200	0.5	0.25
	Cd	$I_{(nA)}=5.499 C_{ppb}+17.35$	0.9969	0.3-220	0.3	0.12
	Zn	$I_{(nA)}=3.463 C_{ppb}+28.58$	0.999	0.1-500	0.1	0.05
	Cu	$I_{(nA)}=6.720 C_{ppb}+3.61$	0.9989	0.1-450	0.1	0.04
	Se	$I_{(nA)}=-1.852 C_{ppb}+1.44$	0.9965	0.4-120	0.4	0.14

<sup>a</sup> samples were prepared from Institute of Standard of Iran

### 3.4. Occurrence of Zn, Cd, Pb, Cu and Se in milk and dairy products

The analytical findings of milk and dairy product samples (mean±SD; n=5) were shown in Table 3.

Taking the results of the present study, all the samples contained detectable amount of investigated heavy metals. The metal detected at lowest concentration was Cd (raw milk: 1.18±0.09 ppb; pasteurized milk: 1.01±0.12 ppb; cheese: 1.45±0.3 ppb; yoghurt: 0.818±0.14 ppb; and doogh: 0.804±0.44 ppb). Moreover, Zn was the metal detected at highest level in samples (raw milk: 568.82±21.15 ppb; pasteurized milk: 467.79±23.66 ppb; cheese: 624.3±97.33 ppb; yoghurt: 419.91±91.00 ppb; and doogh; 393.55±12.07 ppb). The presence of heavy metals in milk and milk based products may be due to environmental sources such as equipment used during the production processing (lead or cadmium pipes in dairies), packaging materials, contaminated water, fodder and feed stuffs with industrial wastes, fertilizers, organic and inorganic chemicals and also fumes and dusts from the industrial activities [25]. Hence, water and soil investigation should be one of the important topics for future study in this part of Iran. Concentration of heavy metals in this work was higher than the amount reported by previous studies [3, 26-28], but it was lower than those reported from other countries such as Croatia [29] and Turkey [30]. In agreement with our findings, Khan et al., [4] reported that the concentration of Cu in collected milk and yoghurt from South Korea were 383.4 and 328.9 ppb, respectively. Generally, the observed differences in concentrations of heavy metals in milk and dairy products, when compared with previous studies, could be attributed to several factors including different analytical techniques used, samples size, season of the year, geographical variation and livestock management [26].

It has been suggested that heavy metals are mainly related to the protein fractions of milk especially the low molecular weight protein fraction (metallothionein). Indeed, heavy metals bind to the thiol group of cysteine residues of this protein in mammillary glands [4, 26]. The significantly higher concentration of cheese samples in compare with other products is not unexpected since heavy metals are preferentially bound to the milk proteins, as described above, and during the curdling of cheese move in curd [31]. On the other hands, the presence of the all five heavy metals in pasteurized milk and dairy products in the current research indicated that these elements have high stability in various thermal processing such as pasteurization and ultra-high-temperature (UHT) treatment and also under refrigeration storage [32]. As the heavy metals have high stability in milk and dairy products, further investigation should be performed on metal contamination sources for controlling and reduce metal residues in these products. The application of this approach along with development of strict regulatory legislations can decrease metal levels in foods especially milk and dairy products.

**Table 3.** The concentration level of element (ppb) in milk and dairy products (mean±SD; n=5)

Samples	Toxic element		Essential element		
	Pb	Cd	Zn	Cu	Se
Raw milk	11.53±0.12 <sup>b</sup>	1.18±0.09 <sup>b</sup>	568.82±21.15 <sup>a</sup>	522.46±32.07 <sup>b</sup>	2.47±0.15 <sup>a</sup>
Pasteurized milk	9.34±0.24 <sup>c</sup>	1.01±0.12 <sup>bc</sup>	467.79±23.66 <sup>b</sup>	335.81±18.39 <sup>d</sup>	2.26±0.11 <sup>a</sup>
Cheese	13.56±0.12 <sup>a</sup>	1.45±0.3 <sup>a</sup>	624.3±97.33 <sup>a</sup>	598.58±17.08 <sup>a</sup>	1.42±0.27 <sup>b</sup>
Yoghurt	7.20±0.19 <sup>d</sup>	0.818±0.14 <sup>c</sup>	419.91±91.00 <sup>bc</sup>	406.21±69.02 <sup>c</sup>	1.07±0.06 <sup>c</sup>
Doogh	6.83±0.38 <sup>d</sup>	0.804±0.44 <sup>c</sup>	393.55±12.07 <sup>c</sup>	317.09±8.44 <sup>d</sup>	0.96±0.05 <sup>d</sup>

<sup>a,b,c,d</sup> Means ± SD indicate significant different (P<0.05) between milk and dairy product

#### 4. CONCLUSION

An anodic-cathodic stripping voltammetric method for the simultaneous determination of Se, Cu, Pb, Cd and Zn has been developed. The proposed method was carried out in three different pHs and therefore, the intermetallic effect was completely removed. The accumulation of metal ions on HMDE offers a useful multi-element pre-concentration technique in milk and its product samples with acceptable precision and accuracy. The content of metal ions at levels of ng g<sup>-1</sup> was determined by standard addition method. Although, the AAS and ICP-AES methods have high sensitivity, favorable selectivity and reasonable detection limits, but their application require expensive equipment and involves a higher running cost and not suitable for in situ measurement. Moreover, they require

preliminary separation steps, such as extraction and ion-exchange procedures for sample preparation. Other disadvantages associated with these procedures include the use of large volumes of organic solvents and acids, resulting in large volumes of generated waste. Despite these methods, anodic-cathodic stripping voltammetric method is a reliable, low cost, and quick analytical technique and is very suitable for routine analysis. In addition, it has several other advantages such as speed of analysis, good selectivity and sensitivity, good performance with saline matrices like river water and the possibility of simultaneous analysis of mixtures.

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