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journal homepage: www.elsevier.com/locate/sbsrEffect of KNO₃ to remove silver interferences in the determination of mercury(II): Application in milk and breast milk samplesA. Farahi^{a,b}, S. Lahrich^a, M. Achak^c, M. Bakasse^b, M.A. El Mhammedi^{a,*}^a Univ Hassan 1, Laboratoire de Chimie et Modélisation Mathématique, 25000 Khouribga, Morocco^b Univ Chouaib Doukkali, Equipe d'Analyse des Micropolluants Organiques, Faculté de Sciences, Morocco^c Univ Chouaib Doukkali, Ecole Nationale des Sciences Appliquées, Laboratoire des Sciences de l'Ingénieur pour l'Energie, El Jadida, Morocco

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ABSTRACT

Mercury determination was performed at rotating silver electrode (RSE) using square wave voltammetry (SWV) in electrolytic mixture of HCl (0.1 mol L⁻¹) and KNO₃ (0.2 mol L⁻¹). The reproducibility, sensitivity and accuracy are good, provided the proper instrumental parameters and supporting electrolyte are used. The relationship between the peak current of mercury(II) and its concentration is linear with regression equation: $I(\mu\text{A}) = 0.784 [\text{Hg(II)}] + 49.5$ ($r^2 = 0.9878$) in the dynamic range from 1.0×10^{-7} to 8.0×10^{-4} mol L⁻¹. The detection limit (DL, 3σ) and quantification limit (QL, 10σ) were 4.61×10^{-8} mol L⁻¹ and 15.3×10^{-8} mol L⁻¹, respectively. The relative standard deviation (RSD) for seven replicate analysis of a solution containing 5.0×10^{-5} mol L⁻¹ was 2.19%. Possible effects of Cu, Co, Fe, MnO₄, Zn, were investigated but did not cause any significant interferences. Immobilization of mercury(II) on the surface of rotating silver electrode obeyed to the Langmuir adsorption isotherm. The calculated $\Delta G^{\circ}_{\text{ads}}$ value showed that the interaction between mercury and silver electrodes is mainly controlled by a chemisorption process. This methodology was potentially applied for mercury determination in milk and breast milk samples.

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1. Introduction

Mercury is regarded as one of the most toxic elements impacting on human and ecosystem health, which is released into the environment from both anthropogenic and natural sources [1]. As the result of population growth and urbanization, more and more human activities have been contributing to significantly elevated mercury emission. More than 2500 tons of mercury is emitted annually from global anthropogenic sources [2].

Mercury can cross the placental barrier and also was secreted to milk and, because of that, it is important to control the presence of mercury in all milk samples [3]. Currently, there are only few studies on mercury concentration in milk, the main part of which was focused on the contamination of human milk. It was indicated the presence of mercury in concentrations ranging from <0.2 to 6.86 μg L⁻¹ in human milk [4]. Very large amounts of mercury in breast milk closely correlated with both the presence of the number of amalgam deposits in the teeth of the mother and fish consumption. In the Faroe Islands the average concentration of

mercury found in breast milk was 2.45 μg L⁻¹ [5], where the typical diet includes whale meat and blubber, and only 0.6 ± 0.4 ng g⁻¹ in Sweden [6]. The concentration of mercury in infant formula was found from 0.4 to 2.5 μg L⁻¹ [4] and from <0.25 to 11.7 μg L⁻¹ [7] and no studies were found on the presence of mercury forms in commercially cow milk.

Conventional analytical techniques were investigated to determine mercury in environmental samples, including cold vapor atomic absorption spectrometry (CVAAS) [8], cold vapor atomic fluorescence spectrometry (CVAFS) [9], or inductively coupled plasma mass spectrometry (IC-PMS) [10]. Although these methods are very powerful for heavy metal analysis, they are known to be expensive and not suitable for on-site monitoring owing to their size, and require highly trained personnel. Electroanalytical stripping techniques, however, appear as a valid alternative in these situations. They are attractive for the determination of trace heavy metals because of the low cost associated with them, the short analysis time, the low power consumption and the ease of use, without compromise the speed of analysis and the sensitivity or reliability of the measures [11–13]. In literature, different electroanalytical approaches for mercury determination were studied [14,15]; they are mainly based in the anodic stripping voltammetry technique and the employing of gold as the best material for the

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working electrodes, due to its high affinity for mercury, which enhances the preconcentration effect [16–19].

In this paper, we present results of detecting mercury at rotating silver electrode (RSE) in a mixture of 0.1 mol L^{-1} HCl and 0.2 mol L^{-1} KNO_3 solution. This method features fast experimentation time, good suitability for field trace mercury analysis and an acceptable electrode lifetime. Analytical performances of the method and the silver interaction were investigated using square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Instrument and reagent

All chemicals used were of analytical grade or of the highest purity available. Potassium nitrate, potassium chloride, sodium hydroxide and hydrochloric acid were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies and were used as received. $\text{Hg}(\text{NO}_3)_2$ was dissolved into distilled water (DW) to form $1.0 \times 10^{-3} \text{ mol L}^{-1}$ stock solutions. Then the working standard solutions were prepared by successive dilution of the stock solutions in 0.1 mol L^{-1} HCl and 0.2 mol L^{-1} KNO_3 mixture solutions. The milk was purchased from a local official centers (Morocco).

The working electrodes were constructed from 5 mm diameter silver wire, which was inserted into glass tubing of approximately 10 mm internal diameter, and insulated with Epoxy resin. After the drying of the resin the electrodes were polished with a mechanical polisher and glass paper of different sizes and then cleaned with distilled water. Square wave voltammetry and electrochemical impedance spectroscopy were carried out with a PGZ 100 potentiostat (Radiometer Inc.) driven by the general purpose electrochemical systems data processing software (votalab master 4 software). The electrochemical cell was configured to work with three electrodes; using rotating silver electrode (RSE) as the working, platinum plate for counter and a system Ag/AgCl (3.00 mol L^{-1} KCl) as reference electrodes. The pH-meter (Radiometer, SENSION™, PH31, Spain) was used for adjusting pH values.

2.2. Working procedure

The initial working procedure consisted of measuring the electrochemical response at rotating silver electrode (RSE) of a fixed concentration of mercury. Standard solution of mercury was added into the electrochemical cell contained 40 mL of supporting electrolyte (HCl 0.1 mol L^{-1} and 0.2 mol L^{-1} KNO_3). The mixture solution was kept quiet for 20 s at open to each electrochemical measurement. The square wave voltammetry was recorded in the range from 0.3 to -0.3 V , for which the scan rate is 1 mVs^{-1} , pulse 50 mV, amplitude 1 mV and duration 1 s. Optimum conditions were established by measuring the peak currents in dependence on all parameters. The suitability of the electroanalytical method in the determination of mercury in milk was tested under optimal condition. All experiments were carried out under ambient temperature and performed in triplicate.

3. Results and discussion

3.1. Preliminary voltammetric characterization

Fig. 1 shows square wave voltammograms when silver and mercury are stripped off by anodic oxidation after the reduction to a conducting rotating silver electrode (RSE). The oxidation potential of silver and mercury are almost identical and a mixture

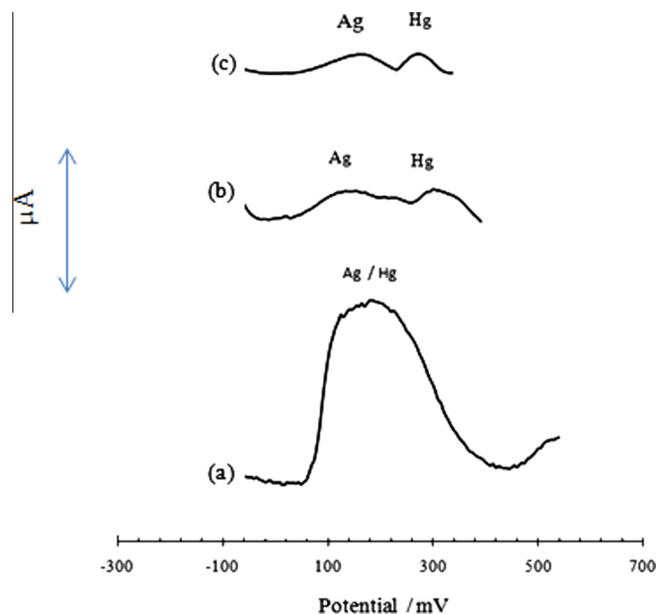


Fig. 1. Various oxidation of mercury in different electrolytes; (a) 0.1 mol L^{-1} HCl, (b) 0.1 mol L^{-1} HCl and KNO_3 , (c) 0.1 mol L^{-1} HCl and KCl.

of these metals gives a single wave when they are oxidized together.

The electrochemical behavior of mercury was studied in three electrolytes (HCl, HCl + KCl, HCl + KNO_3). When the sweep anodic of mercury was studied in 0.1 mol L^{-1} HCl, a trained band was observed indicating the presence of two peaks of the oxidation of silver and mercury. The addition of potassium chloride and potassium nitrate in 0.1 mol L^{-1} HCl solutions shows a separation of the two peaks by displacing mercury peaks in the direction of positive potentials. The best electrochemical response, in term of the highest analytical signal, was obtained in a mixture of HCl and KNO_3 . Utilization of KNO_3 opens the possibility of analytical applications of silver electrodes for the selective detection of mercury, without silver interferences, via calibration of the square wave response which was found to be linear and reproducible.

3.2. Optimization of experimental conditions

The conditions which most affect the SWV measurement process were optimized to determine mercury like the pulse, modulation amplitude, frequency (ν), pH solution, time deposition, concentration of added electrolyte KNO_3 and speed of the rotating electrode (Fig. 2). Electrochemical response of RSE in a mixture of 0.1 mol L^{-1} HCl and 0.2 mol L^{-1} KNO_3 electrolytes, contained $1.0 \times 10^{-4} \text{ mol L}^{-1}$ mercury(II), were performed for evaluating the heights and the shapes of the signals obtained. The effect of pulse was investigated in the range from 10 to 50 mV. As expected, a significant increase of the signal intensity was observed up to 50 mV. Modulation amplitude was also evaluated for the reduction of Hg(II) in the range from 1 to 15 mV. Results obtained demonstrated that an increase in amplitude results in a decrease in scan rate and intensity of current peak, which indicate an adsorption process as the rate-determining step. In subsequent experiments, a value of 1 mV was adopted.

The effect of frequency (ν) on the current intensity of mercury(II) using RSE was evaluated in the range from 0.2 to 1 Hz. The signal increased up to 1 Hz. Nevertheless, the maximum acceptable value to be in SWV program, which is 1 Hz and which corresponds to 1 s of duration for each step, was used in the present experimental study to ensure the maximum diffusion of the

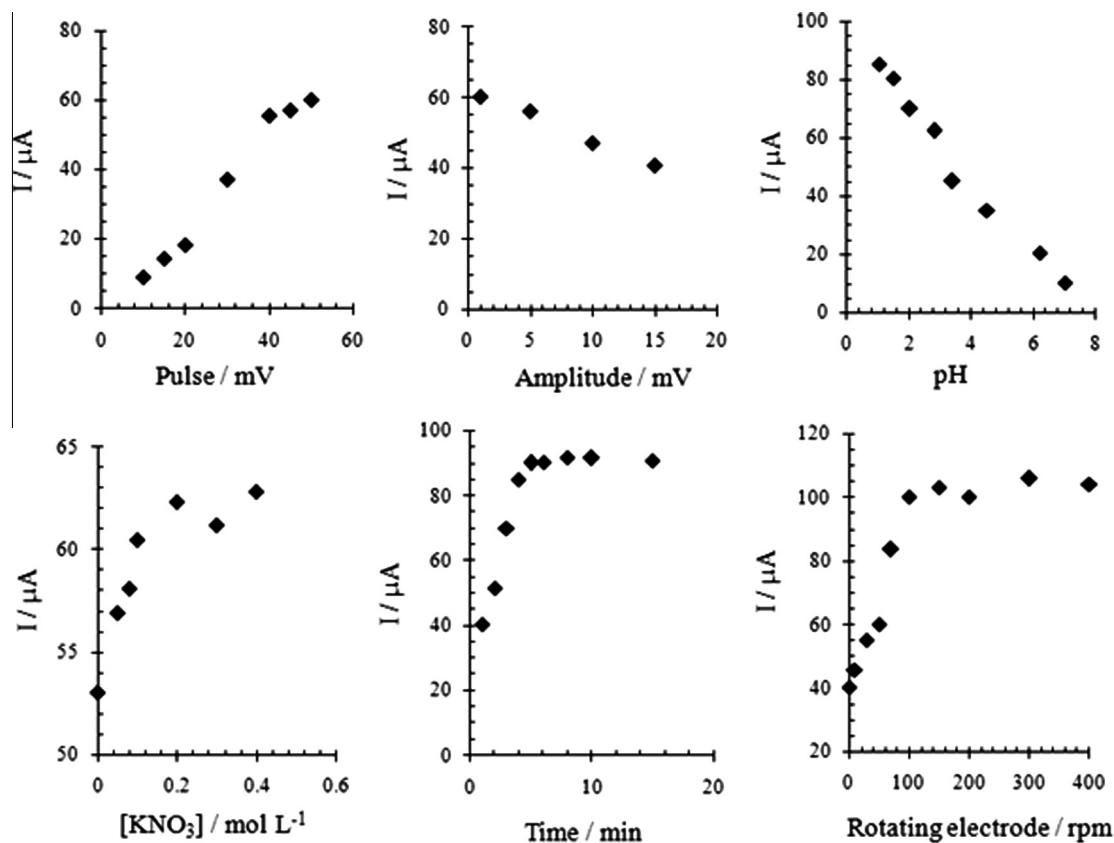


Fig. 2. Influence of the experimental variables (pulse, modulation amplitude, pH, time deposition, concentration of electrolyte KNO_3 , speed of the rotating electrode) involved in the SWV method. Response to $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Hg(II)}$ using a rotating silver electrode (RSE).

electroactive species. In agreement with the high peak current values, good shapes of the signal and better signal to noise ratio, the selected optimal values were 50 mV, 1 mV, 1 Hz for pulse, modulation amplitude and frequency respectively.

The effect of pH on the SWV response of the electrode in the range of 1.0 to 7.0 was investigated under the same conditions as above. The cathodic peak current increases significantly when decreasing the pH up to 1.0. At higher pHs the decrease of the cathodic peak current may be due to the cation hydrolysis [20].

The influence of KNO_3 concentration on the stripping peak currents was investigated. The Fig. 2 indicates that low concentration of KNO_3 can improve the sensitivity of determining mercury(II). The stripping peak currents firstly increase linearly with increase of KNO_3 concentration over the range from 0 to 0.2 mol L^{-1} and then remain stable when KNO_3 concentration changes from 0.2 to 0.4 mol L^{-1} . The KNO_3 concentration was fixed at 0.2 mol L^{-1} for all further experiments.

The amount of mercury deposited onto a RSE surface should be carefully controlled to avoid saturation and to maintain linearity with increased loading. Therefore, we investigated the effect of deposition time on the response of mercury(II), in the range 1–15 min. The cathodic SWV peak current increases by increasing of deposition time up to 5 min, above which it remained nearly constant. Therefore, a deposition time of 5 min was selected for further works.

The effect of rotation speed of the rotating electrode on the square wave voltammetry response of mercury was studied. Consecutive measurements at different stirring speeds were carried out in the range from 0 to 400 r.p.m. Voltammetric signal stability was found to be strongly dependent on stirring speed variable. Significant differences in terms of peak height were

observed at different stirring speed values. The working electrode showed a stable behavior for the determination of mercury up 100 r.p.m. with a relative standard deviation of 2.19%. Efficient analyte deposition at moderate stirring is a typical advantage of the silver electrodes in stripping analysis, probably due to enhanced mass transfer to the silver electrode by diffusion [21]. In subsequent experiments, a value of 100 r.p.m was adopted to obtain a representative calibration curve and a higher repeatability.

3.3. Electrochemical impedance spectroscopy measurements

The interaction between rotating silver electrode (RSE) and mercury was investigated utilizing electrochemical impedance spectroscopy. The charge transfer resistance R_{ct} decrease with the increase of the mercury concentration (Fig. 3), these results shows that the silver surface adsorbs mercury and the transfer process is controlled by diffusion [22]. The silver electrode response is attributed to the electron-exchange mechanism at the electrode–contact interface and the ion exchange at the electrode–solution interface [23–24]. The fixation efficiency of mercury onto the surface of the electrode (RSE) is due to its ability to be adsorbed onto a silver surface to form a mercury compounds coating. The establishment of isotherms that describe the adsorption behavior of attack ion is important as they provide important clues about the nature of metal–mercury interaction. Values of degree of surface coverage (θ) corresponding to different Hg(II) concentrations at 25°C after 30 min of immersion were used to determine which isotherm best described the adsorption process. In the present study, values of θ were calculated using the impedance results according to the equation [25]:

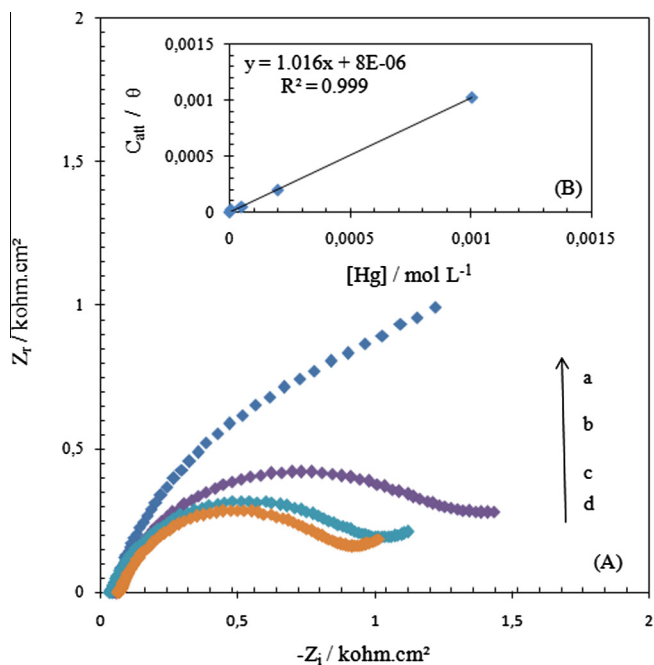


Fig. 3. (A) Nyquist diagrams at rotating silver electrode (RSE) in electrolytic mixture; 0.1 mol L⁻¹ HCl and 0.2 mol L⁻¹ KNO₃ containing different concentrations of mercury(II): (a) 0.0 mol L⁻¹, (b) 5.0 × 10⁻⁶ mol L⁻¹, (c) 5.0 × 10⁻⁵ mol L⁻¹, (d) 2.0 × 10⁻⁴ mol L⁻¹ at room temperature, (B) Langmuir's isotherm adsorption of mercury(II).

$$\theta = (R_{ct}^0 - R_{ct})/R_{ct}^0 \quad (1)$$

where R_{ct}^0 and R_{ct} are the charge-transfer resistance values without and with mercury respectively. The results obtained for Hg(II) solution fit well Langmuir adsorption isotherm (Fig. 3), given by:

$$\frac{C_{att}}{\theta} = \frac{1}{K_{ads}} + C_{att} \quad (2)$$

where θ is the degree of surface attack, C_{att} is the mercury concentration in the electrolyte and K_{ads} the equilibrium constant of the adsorption process. From Fig. 3, it can be seen that the linear correlation coefficient (r^2) is close to 1 and the slope of straight line is also close to 1, which suggests that the adsorption of Hg(II) from electrolytic solution on the rotating silver electrode (RSE) obeys the Langmuir model and exhibit single-layer adsorption characteristic. From the intercept of the straight line C_{att}/θ -axis, K_{ads} value can be calculated. The equilibrium constant of the adsorption process K_{ads} , is related to the standard free energy of adsorption, ΔG_{ads}° , with the following equation [26]:

$$K_{ads} = \frac{1}{55.5} \exp(-\Delta G_{ads}^\circ/RT) \quad (3)$$

where R is the universal gas constant and T is the absolute temperature. At 25 °C, the calculated ΔG_{ads}° of Hg(II) was -43.36 kJ mol⁻¹. The negative value of ΔG_{ads}° suggests that the adsorption of Hg(II) is a spontaneous process [27]. Generally speaking, the adsorption type is regarded as physisorption if the absolute value of ΔG_{ads}° is lower than 20 kJ mol⁻¹. The attack behavior is attributed to the electrostatic interaction between the mercury and silver. When the absolute value of ΔG_{ads}° is higher than 40 kJ mol⁻¹, the adsorption could be seen as chemisorption. The obtained ΔG_{ads}° in this work indicates that the adsorption mechanism of Hg(II) on surface rotating silver electrode (RSE) involves two types of interactions, predominant chemisorption (ionic) and weak physisorption (ionic) [25].

3.4. Analytical measurements

Fig. 4 shows the cathodic peak current of mercury(II) versus its concentration. Under the optimized conditions, the relationship between the peak current of mercury(II) and its concentration is linear with regression equation: $I(\mu A) = 0.784 [Hg(II)] (\text{mol L}^{-1}) + 49.5$ ($r^2 = 0.9878$) in the dynamic range of 1.0×10^{-7} to 8.0×10^{-4} mol L⁻¹. The detection limit ($DL, 3\sigma$) and quantification limit ($QL, 10\sigma$) for the determination of mercury(II) were 4.61×10^{-8} mol L⁻¹ and 15.3×10^{-8} mol L⁻¹, respectively. The relative standard deviation (RSD) for seven replicate analysis of a solution containing 5.0×10^{-5} mol L⁻¹ was 2.19%. It should, however, be pointed out that even though the DL obtained in the present study are comparable to the values obtained in the literature. However, it was slightly less sensitive than those obtained by, vibrating gold microwire electrode (3.5×10^{-10} mol L⁻¹) [14], electrode modified with a novel ion imprinted polymeric (5.0×10^{-9} mol L⁻¹) [28], carbon nanotubes paste electrode modified with crosslinked chitosan (2.4×10^{-9} mol L⁻¹) [29], glassy carbon electrode modified by gold nanoparticles/carbon nanotubes (3.0×10^{-10} mol L⁻¹) [30] and is near than those obtained with carbon paste electrode (4.1×10^{-8} mol L⁻¹) [20].

3.5. Interferences

The selectivity of this approach for the determination of mercury was evaluated by introducing concentrations of other ions into the mercury sample solution during the preconcentration

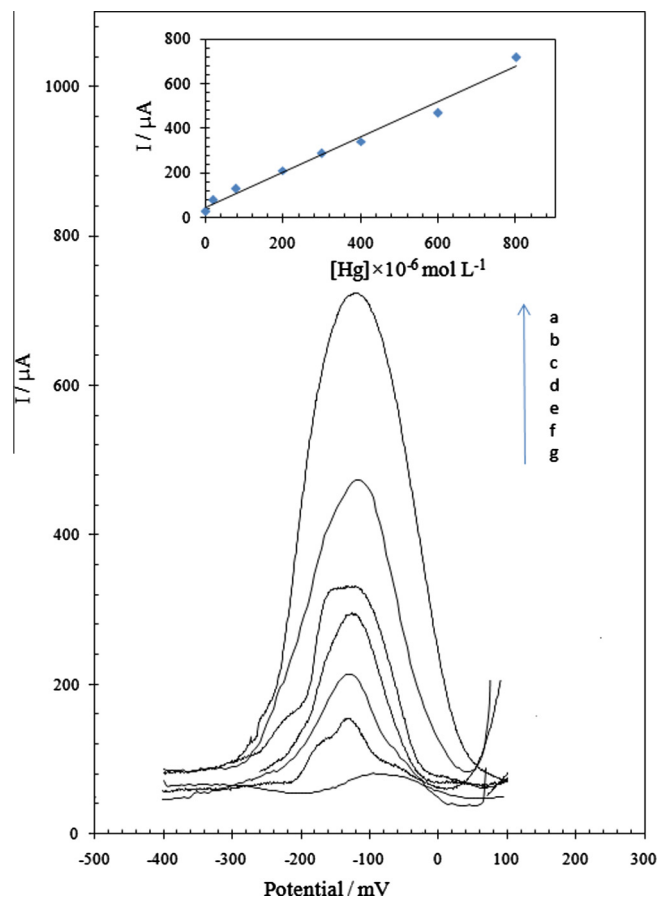


Fig. 4. Square wave voltammograms at rotating silver electrode in 0.1 mol L⁻¹ HCl and 0.2 mol L⁻¹ KNO₃ mixture solution, under the optimized conditions, of different concentrations of mercury, (g) 1.0×10^{-7} , (f) 8.0×10^{-5} , (e) 2.0×10^{-4} , (d) 3.0×10^{-4} , (c) 4.0×10^{-4} , (b) 6.0×10^{-4} , (a) 8.0×10^{-4} mol L⁻¹.

step. The interferences of some metal ions on the determination of mercury(II) were investigated. The rotating silver electrode was immersed in a mixture of Hg(II), Cu(II), Co(III) and Zn(II). Metal interference studies were performed to examine the effect of other metals on the stripping signal of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ Hg(II). No significant effect was observed after the addition of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of Zn(II) and Co(III). The voltammogram of Fig. 5 shows one reduction signal attributed to Hg(II) in position -0.2 V , no interfering under the optimized condition described above (pulse of 50 mV , modulation amplitude of 1 mV , frequency of 1 Hz pH of 1.0 and rotation speed of the rotating electrode of 100 r.p.m.). The clean separation of the potential peaks offers us the possibility of the determination of Hg(II) without any harmful interference from other common heavy metals. The addition of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of MnO_4^- did not modify the SWV response of Hg(II). The addition of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of Fe(II) decreased by 8% the signals of Hg(II). But the addition of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ Cu(II) shows a band related of the mercury and copper peaks.

Reduction peak potentials of Hg(II) and Cu(II) were located at -0.2 V , in HCl solution at $\text{pH} = 1.0$. The peak potentials were swapped regarding their position on the (RSE) electrode. The Cu(II) interferences can be removed by separating the two peaks of mercury(II) and copper(II) using the mixture of 0.1 mol L^{-1} HCl, 0.2 mol L^{-1} KNO_3 and 0.5 mol L^{-1} NaCl as supporting electrolyte [14].

3.6. Analytical application

Milk and Breast milk can contains toxic trace elements, such as mercury, cadmium and lead, potentially toxic heavy metals with hematotoxic, neurotoxic and nephrotoxic properties even at very low concentrations. Occurrence of mercury in the milk samples from lactating women in Morocco makes a major public health hazard for the inhabitants, especially neonatal and children, of the industrial locations. The determination of mercury in Breast milk serves as a means of minimizing the hazardous effect of such metals. Moreover, more complex matrixes, such as blood, fish and milk, were rarely analyzed. Hence it is necessary to apply some pre-treatment to avoid any matrix interference and maintain the mercury under the preferable mercury(II) ion form [31].

The applicability and feasibility of the proposed electrode for analysis of real samples with different matrixes was assessed by its application to determine mercury(II) ions in milk and breast milk samples. Retail packaged milk was purchased from a local supermarket (Morocco) at defatted version. The analysis of milk samples was carried out without any processing (extraction process) to prevent the binding of mercury by proteins. The support electrolytes were prepared by addition of electrolyte (HCl and KNO_3) to breast and commercial defatted milk samples which contain the following elements and concentrations (mg per 100 mL^{-1}): calcium (120), protein (3), fat material (3), vitamin A (4.3), vitamin B_2 (0.16), vitamin D_3 (0.18) and vitamin B_{12} (0.00031). The electroanalytical curves were obtained by using square wave voltammetry, in commercial milk spiked with mercury(II) in the range from 5.0×10^{-7} to $4.0 \times 10^{-4} \text{ mol L}^{-1}$ (Fig. 5), it was observed that peak currents versus mercury added into real sample solution increased linearly, and hence the proposed methodology is suitable for the determination of mercury in commercial milk samples. The statistical calculations for the assay results showed suitable precision of the proposed method (Table 1). The recovery experiments were carried out by adding a $5.0 \times 10^{-5} \text{ mol L}^{-1}$ of mercury(II) in milk solution containing HCl and KNO_3 . The volume change does not exceed 1%. The value of mercury(II) found refers to the concentration obtained by extrapolating the analytical curve of the corresponding spiked samples. The accuracy of methodologies was tested with different solutions of mercury and the relative standard deviations (R.S.D.) were calculated in quadruplicates.

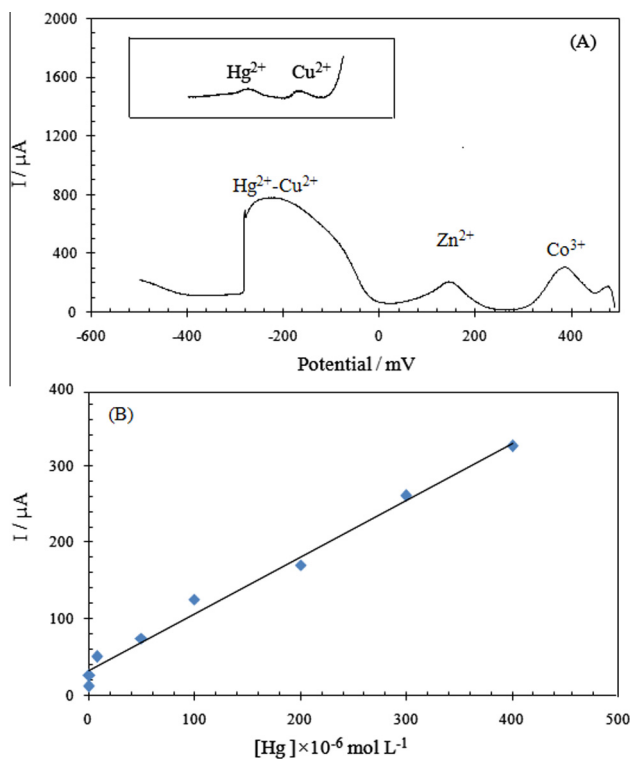


Fig. 5. (A) Voltammogram obtained after electrode exposure to a solution containing Hg(II), Zn(II), Cu(II) and Co(III) under the optimized conditions. (B) Calibration curves obtained in commercial milk spiked with mercury(II) in the range from 5.0×10^{-7} to $4.0 \times 10^{-4} \text{ mol L}^{-1}$.

Table 1
Analytical characteristics of the method used to determine mercury(II) in milk samples.

Techniques	Analyte	Comments	References
SWV	Mercury(II)	<ul style="list-style-type: none"> - Milk: Calibration range: 5.0×10^{-7} to $4.0 \times 10^{-4} \text{ mol L}^{-1}$; DL: $3.62 \times 10^{-7} \text{ mol L}^{-1}$ QL: $12.08 \times 10^{-7} \text{ mol L}^{-1}$; RSD (%): 2.34; Recovery (SWV) (%): 94.0; Recovery (ICP-MS) (%): 94.0. - Breast milk: Recovery (SWV) (%): 93.50% - Milk cow's: Recovery (SWV) (%): 92.0% - Milk powder: Recovery (SWV) (%): 91.0% - Full cream cow milk: Recovery (SWV) (%): 89.0% 	This work
CV-AFS	Mercury(II)	Milk powder: DL: $5.5 \times 10^{-5} \text{ nmol g}^{-1}$; RSD (%): 3.4%	[32]
ICP-MS	Mercury(II) and toxic elements	<ul style="list-style-type: none"> Milk: Calibration range 5.0×10^{-10} to $5.0 \times 10^{-8} \text{ mol L}^{-1}$; DL: $4.1 \times 10^{-11} \text{ mol L}^{-1}$; RSD (%): ≤ 5; Recovery (%): 84.0 	[33]

CV-AFS: Cold vapor atomic fluorescence spectrometry.
ICP-MS: Inductively coupled plasma-mass spectrometry.

The interferences coming from the milk samples, resulting probably from protein and fat material, which can inhibit the adsorption process of mercury(II) on silver electrode.

The comparative determination of mercury(II) in milk by the proposed method and inductively coupled plasma-atomic emission spectrometric method was investigated in solution containing 2.0×10^{-6} mol L⁻¹ of mercury(II). The mean percentage recoveries were found to be 94.0% and 94.4% using the RSE and ICP-MS, respectively. The excellent average recoveries in milk samples, observed in confidence interval of 95.0%, suggest that the silver rotating electrode developed in this work has practical significance and is able to determine mercury(II) in milk.

4. Conclusion

A silver electrode was successfully applied in quantifying mercury in milk matrices using square wave voltammetric procedure. In the present work, the primary goal, on using electrodes, was to verify the possibility of obtaining responses using SWV in the cathodic sweep which are much more convenient since at this level. The novelty of the proposed methodology is rooted in the use of electrodes in breast milk without any pre-treatment or extraction procedure. The reproducibility, sensitivity and accuracy are good, provided the proper instrumental parameters and supporting electrolyte are used. The use of the rotating silver electrode makes the direct analysis of the milk samples possible without any necessity of pre-treatments or chemical preparation stages. The observed recovery percentage values were exceeded 94.0%, which is considered very satisfactory for analytic applications. Adsorption of Hg(II) on the electrodes solid rotating silver (RSE) obeyed to the Langmuir adsorption isotherm. The calculated $\Delta G^{\circ}_{\text{ads}}$ value showed that the attack of the RSE in electrolyte (HCl and KNO₃) is mainly controlled by a chemisorption process.

5. Conflict of interest

The authors have declared that there is no conflicts of interest.

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