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Anodic Stripping Voltammetric Behavior of Mercury in Chloride Medium and its Determination at a Gold Film Electrode

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The electrochemical behavior of aqueous Hg(II) ions at a gold film electrode is described. The effects of supporting electrolyte and halide ions on the anodic stripping voltammetric behavior of Hg(II) ions was illustrated to prepare a basis for the analysis in real samples with high saline content. The concentration ratio of metallic mercury to halide ions at the electrode surface determines the resulting peak characteristics. The peak potentials in particular shift in a more negative direction as the halide concentration increases. A comparative study with Cu(II) ions revealed that a different mechanism is involved in their reoxidation steps. Mercuric ions were collected at 0.2 V from 0.1 M $HClO_4$ medium containing 3 x 10^{-3}M HCl and a detection limit of 0.12 ng/mL (S/N = 3) was attained (RSD < 5%, n = 5). The method was applied for the determination of mercury in haemodialysis concentrates. No significant interference was observed from other possibly interfering metallic ions.

Key Words: Mercury determination, gold film electrode, anodic stripping voltammetry, heamodialysis solution.

Introduction

Mercury is a highly toxic metal in the environment and its determination at trace levels is important. Many papers on the analysis of mercury have been reported in recent years including methods such as cold vapor atomic absorption CV-AAS [1-4], cold vapor atomic fluorescence CV-AFS [5,6], inductively coupled plasma mass spectrometry ICP-MS [7-9] and inductively coupled plasma atomic emission spectrometry ICP-AES[10]. Several chromatographic techniques coupled with spectrometric methods have also been used for mercury speciation [11-14]. Among these, CV-AFS is the most preferred method due to its sensitivity. However inexpensive methods are still being sought.

Electroanalytical methods can be easily adopted for the simultaneous analysis of a number of metals at trace or ultra trace levels, and these cost less. The most common electroanalytical technique is anodic

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stripping voltammetry (ASV). Other techniques such as potentiometric stripping analysis (PSA) [15,16] and subtractive anodic stripping voltammetry (SASV) [17] are also used for the determination of very low concentrations of mercury, offering a detection limit even at sub-ppb level. Different types of electrodes have been utilized in these techniques, mainly glassy carbon electrodes (GCE) [18], gold disk (GDE) [19−22], gold fiber [23], gold film (GFE) on different substrates [24], carbon paste (CPE) [25] and chemically modified electrodes (CME) [26−27]. The major drawback of solid gold electrodes is the well-known phenomenon of structural changes on the surface, caused by amalgam formation that requires complex electrochemical pretreatments to achieve better reproducibility. In acidic chloride media, the anodic range of the gold electrode is severely limited by the oxidation of the metal to chloride complexes [28]. Regeneration procedures can be simplified by employing a gold film electrode rather than solid gold electrodes. The thin layer of metallic gold deposited onto a suitable electrode support represents the film electrode. Electrochemical plating and renewal of films are simple and can be done as frequently as needed [25]. In addition to the advantages of a renewable surface, the use of gold film electrodes minimizes the cost of electrodes. The film is deposited either via external pre-electrolysis in a separate plating solution (ex-situ) or by plating in-situ. The latter method can be simply accomplished in stripping analysis, where a gold film is formed directly during the accumulation step in the sample solution, which is spiked with trivalent gold. However, during their co-deposition on the GCE surface, the strong interaction between gold and mercury results in a low stripping efficiency of mercury from the bulk of gold film, and eventually less sensitive results are obtained [18].

Another aspect of electroanalytical techniques is that they can be applied for samples with high saline content while the analysis of these samples with other techniques requires a pre-separation step to eliminate interference from the matrices. However, in the case of interaction of the metal with the matrix ions, the ASV behavior of the metal should be specified before measurement. Copper ions in particular are exposed to interference from the chloride present in many samples, i.e. seawater, wastewater, etc. It was reported that standard addition plots in the analysis of copper in seawater display a change in slope and this variability can be interpreted as a change in speciation [29,30]. This was interpreted as Cu(I) formation from the chemical reaction between metallic copper on the film surface and neighboring Cu(II) ions in the presence of excess chloride ions. A similar matrix effect was also observed for Hg(II) determination with gold electrodes [19]. In the case of voltammetric determinations with GFE, a high concentration of chloride ion irreversibly damages the electrode surface and results in the dissolution of gold at more negative potentials. However, the addition of a small amounts of HCl is necessary to shift the stripping peak to more negative potentials where the residual current is lower and the peak distortion is smaller [18,31].

Samples with high saline content are known to contain trace amounts of mercury as well as excessive chloride that causes severe disturbance during the stripping step when gold is used as the electrode material. Heamodialysis concentrates are also prepared from high amounts of salt and therefore their heavy metal content, inherited from these salts, should be rigorously controlled. However, no data were encountered in the literature about the mercury levels of such solutions.

The main objective of this study was to investigate the effect of chloride ions on the anodic stripping voltammetric behavior of Hg(II) ions at a GFE, as well as the physical conditions of the working electrode to prepare a basis for analyses in real samples.

Experimental

Instrumentation

The differential pulse (DP) ASV measurements were performed with Metrohm 693 VA Processor with a 694 VA Stand Voltammetric Analyzer. The working electrode, GFE, was prepared by means of electrochemical deposition of Au(III) ions on a rotating glassy carbon electrode (GCE) support. The active surface area of the electrode was 3.14 mm^2. The counter electrode was a platinum wire and an Ag/AgCl (3M KCl) electrode was used as the reference electrode. A double junction reference electrode (Ag / AgCl / (3M KCl) / sat. KNO_3) supplied from Tacussel was used for the analysis of the test solution to maintain the absence of chloride ions.

The optimal instrumental parameters for DP ASV; the potential scan rate was 20 mV/s, the pulse amplitude and duration were 50 mV and 0.3 s, respectively, the electrode rotation rate was 1600 rpm, the pre-electrolysis time was usually 60 s, and a rest period of 5 s was used. For square wave (SW) ASV, potential amplitude of 10 mV, a frequency of 25 Hz, a measuring time of 2 ms and a step time of 0.3 s were used. The cell content was deaerated with nitrogen for 300 s before each measurement. Water supplied from Elga Ultrapure Water System was used throughout the study.

Reagents

A stock solution of Hg(II) was prepared by adding 6.5 mL of concentrated HNO_3 solution (1:4 in mole ratio) into 4.6951 g of pure mercury. The mixture was heated to dryness. The salt was dissolved by adding several milliliters of $HClO_4$ and was diluted to 1.0 L with water. This stock solution was standardized by titrating with standard thiocyanate solution. Standard solutions were prepared daily from the stock solution.

A stock 500 mg/L solution of Au(III) was prepared by dissolving pure metallic gold (999.9% o) in a 1 mL HNO_3 (conc.) + 4 mL HCl (conc.) mixture and heating until the NO_x gases were removed. Then the solution was diluted to 500 mL with redistilled water.

Dilute solutions of $HClO_4$, HCl and HNO_3 were prepared from analytical grade concentrated solutions supplied by Merck. Stock solutions of Cu(II) and Pb(II) ions were prepared by weighing 1.0000 g of metal supplied by Merck and then dissolved in 6 M HNO_3 and diluted to 1.0 L to obtain a 1000 mg/L standard solution. The mixed standards were added to the sample solution for interference studies.

Heamodialysis liquid samples were obtained from the Ege University Dialysis Center and the analysis was performed in 24 h. The measurements were obtained at ambient temperature and all glassware was stored in a (1/10) HNO_3 solution bath and rinsed with water before use.

Procedure

The gold film was deposited on the surface of a glassy carbon electrode (GCE) supplied by Metrohm with a surface area of 3.14 mm^2. The GCE surface was polished with Al_2O_3on a piece of velvet and rinsed with water. Following sonication in water for 5 min., the electrode was placed in the voltammetric cell containing 20 mL of plating solution (0.1 M HCl containing 1 x 10^{-5} M Au(III)) and then the electrochemical cleaning process was initiated by cycling the potential 100 times at a potential range of 0.2-0.8 V.

The GFE was prepared in ex situ manner by depositing the gold from Au(III) ions in the solution by 3 successive electrolysis steps at –0.5 V for 300 s. A stirring rate of 1600 rpm was used in the deposition period.

The conditioning step was repeated between deposition periods to remove any deposited metallic impurities. Cleaning and reactivation between individual measurements are necessary for attaining reproducible results. However, the electrode allows a series of measurements without any treatment as long as it does not come into contact with the air. Mercuric ions were collected at 0.2 V from 0.1 M $HClO_4$ medium either in the absence or presence of chloride ions, usually in 3 x 10^{-3}M HCl. Then the potential was scanned a in positive direction to display the anodic peak related to the reoxidation of mercury. The heamodialysis sample was analyzed in a standard addition manner. A 5.0 mL aliquot of the sample was diluted to 100 mL with 0.1 M $HClO_4$solution, 20 mL of this mixture was transferred into the voltammetric cell and the procedure was performed.

Results and Discussion

The baseline is a major problem in mercury determination at different solid electrodes. Early experiments in this lab included DP ASV determination of mercury by using a glassy carbon rotating disk electrode (GC-RDE). No signal was observed with this electrode for Hg(II) ions in concentrations lower than 100 ng/mL. The measurement of the analytical signal for Hg(II) ions on the GCE surface may be hindered by the baseline behavior. Therefore, studies were carried out with a preformed GFE to investigate the surface properties as well as the deposition conditions to evaluate their influence on the sensitivity of the measurement.

Characteristics of GFE

The thickness of the gold film naturally depends on the Au(III) concentration of the plating solution. As the Au(III) concentration increased from 5.0 x 10^{-6} to 1.0 x 10^{-4}M, the color of the GFE changed from light green to yellow, respectively. Closer optical inspection of the surface revealed that the film was not homogeneous and there were surface defects scattered throughout the film. These defects were more apparent after depositing the mercury on the GFE from a solution containing 50 ng/mL Hg(II) ions. This effect may be attributed to the diffusion of mercury into inner layer of gold film.

Electrode performance depending on the thickness was examined in a 0.1 M $HClO_4$ solution containing 5.0 ng/mL Hg(II) ions. The mercury deposition was performed at 0.2 V for 60 s and the anodic peak currents were found to be dependent on the Au(III) concentration in the plating solution (Table). As the gold film became thicker, the ASV peak current of the mercury increased, as did the background current. As can be seen from the Table, the peak potential of the mercury changed from 0.66 to 0.73 V depending on the GFE thickness, and this shift in the peak potential made measurement more difficult as the peak approached the large oxidation peak of gold. In addition, an observed small pre-wave in the voltammograms became more evident for thicker films. Here, it should be noted that the present experiments were performed using a double junction electrode to avoid chloride interference. Therefore, the peak potentials were more positive than those obtained in previous studies performed in HCl solution[18]. For the determination of low concentration regions of Hg(II) (1-10 ng/mL), thinner films obtained by deposition of 1.0–5.0 x 10^{-5}M Au(III) solutions were preferred. For higher concentrations, thicker electrodes provided mechanically more stable surfaces.

Composition of the supporting electrolyte

The electrochemical dissolution of mercury from the GFE is strongly influenced by the supporting electrolyte. Previous studies recommend the use of a suitable mineral acid and a complexing agent capable of reducing the very strong interaction between gold and mercury [31]. Diluted solutions of sulfuric acid [31], nitric acid [25] and perchloric acid [18] containing different amounts of complexants, chloride in particular, were utilized for this purpose.

Table. Dependence of the ASV peak current of mercury (5 ng/mL) on the Au(III) concentration in 0.1 M HCl for ex situ GFE preparation.

Au (III) conc. (10^{-5}M)	Peak potential (mV)	Peak current (nA)	Film color
0.5	663	247.5	Light green
1.0	674	239.0	Green
5.0	711	273.5	Green-yellow
10.0	728	303.0	Yellow

In the present study, initial studies were carried out in $HClO_4$ solution as this provided a non-complexing medium for mercury. A deposition potential (E_{depo}) of 0.2 V and deposition time (t_{depo}) of 60 s were used for 5.0 ng/mL Hg(II) solution. As the $HClO_4$ concentration increased from 0.01 to 1.0 M, the peak current increased, as did the residual current, while the mercury dissolution peak potentials shifted from 0.61 to 0.68 V. Therefore, the 0.1 M $HClO_4$ medium was chosen since the resulting peak current was high and well separated from the large peak of gold oxidation.

On the other hand, the addition of small amount of chloride ion was recommended for shifting mercury stripping peak to more negative potentials where the residual current was lower and the peak distortion was smaller [18]. Therefore, the effects of halides on anodic peaks had to be evaluated.

Effect of halides on reoxidation peak of mercury

The effect of chloride on dissolution peaks of mercury was examined in 0.1 M $HClO_4$ with a GFE prepared from a plating solution containing 1 x 10^{-5} M Au(III) ions. The stripping cell solution included 50.0 ng/mL Hg(II) ions in 0.1 M $HClO_4$ solution. Measurements were obtained with a double junction reference electrode for controlling the actual chloride concentration in the cell. As shown in Figure 1, the peak potential shifted from 0.706 to 0.604 V as the concentration of chloride was increased from 1 x 10^{-4} to 5 x 10^{-3} M. This shift in the peak potential was attributed to the involvement of chloride in the stripping step of mercury, stabilizing the Hg_2Cl_2 species on the electrode surface. Here, the possible formation of Hg(II) complexes with chloride during the anodic dissolution was excluded since the stability constants were much smaller than that of calomel formation. Therefore, the proposed mechanism is given below:

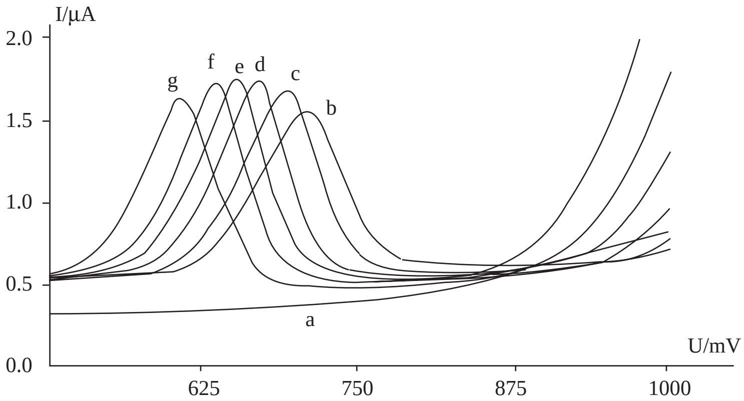

Figure 1. ASV peaks obtained for a solution containing a) 0.1 M $HClO_4$ and 50 ng/mL Hg(II) and after addition of chloride ions to the cell to be b) 1.0, c) 2.0, d) 5.0, e) 10, f) 20 g) 50 x 10^{-4} M (E_{depo}= -0.30 V, t_{depo} = 60 s).

$$\text{Deposition step: } Hg^{2+} + 2e^- \rightarrow Hg(Au) \tag{1}$$

$$\text{Stripping step: } 2Hg(Au) + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^- \tag{2}$$

$$\text{For } Hg_2Cl_2 K'_{sp} = \left[Hg_2^{2+}\right]\left[Cl^-\right]^2 \tag{3}$$

$$E = E^o(Hg_2^{2+}/Hg) + \frac{0.059}{2}\log\frac{K'_{sp}}{[Cl^-]^2} \tag{4}$$

E = constant - 0.059 log [Cl^-] can be written for 25 °C

The peak potentials measured against the Ag/AgCl double junction reference electrode were plotted against the –log [Cl^-] (Figure 2). The slope of the resulting curve was 58.80, which agrees well with the proposed mechanism. As the chloride concentration was changed in a wider range (1 x 10^{-6} – 1 x 10^{-2}M), a similar change in peak shape was observed for 5 ng/mL Hg(II). The peak potential shifted from 0.69 to 0.54 V while the peak current decreased from 276 nA to 158 nA.

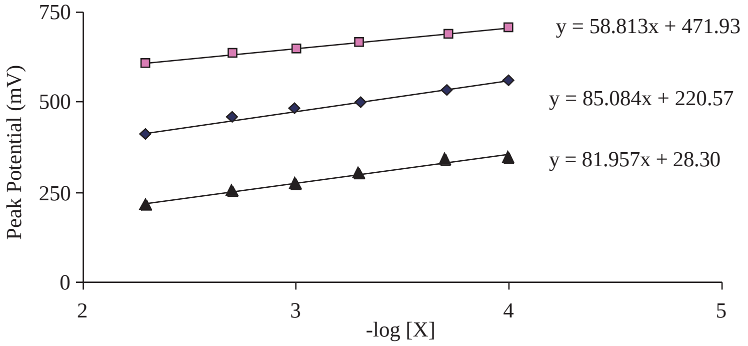

Figure 2. Dependence of anodic peak potentials of mercury deposited from 50 ng/mL solution in 0.1 M $HClO_4$ medium on the chloride (■), bromide (♦) and the iodide (▲) content of the solution (E_{depo}= -0.30 V, t_{depo} = 60 s).

It was concluded that the surface concentration ratio of metallic mercury to chloride ions determines the peak characteristics. Thus, the chloride concentration that yields the maximum peak current may yield a slight change according to this ratio. Therefore, a chloride concentration may be chosen in the range of 1.0-5.0 x 10^{-3} M for mercury determinations at the ng/mL level, in agreement with the literature [18,31].

Similarly, the influence of other halide ions on ASV peaks of mercury was investigated. The cell solution included 50 ng/mL Hg(II) ions in 0.1 M $HClO_4$ medium. Sharper peaks were obtained for mercury at +0.558 V in the presence of 1 x 10^{-4}M bromide ions. As the bromide concentration was increased, the peak potential shifted in a negative direction. The peak currents reached a maximum at a 5 x 10^{-4} M bromide concentration and then decreased. The slope of this change, obtained by plotting the peak currents against the –log [Br^-] values, was calculated as 85.05 mV, which did not fit the above mechanism (Figure 2). However, on comparison with the stability constants of chloride complexes, it is clear that bromide ions form more stable complexes with Hg(II) ions. Different type of complexes, mainly $HgBr_2$ and $HgBr_3^-$ may occur in the stripping step. The latter species dominate at high concentrations of bromide ions which is reflected in the slope.

In the presence of iodide, however, a large oxidation peak of iodide was observed at 0.59 V in addition to the anodic peak of mercury at more negative potentials. The latter peak was shifted in a negative direction from 0.34 to 0.21 V by increasing the iodide concentration. The slope was 81.95 mV, which confirmed that the mercury was deposited on GFE oxidizes to Hg(II) ions since it formed stable complexes in bromide or iodide media, unlike the chloride medium.

Although the more sensitive results were obtained in the presence of bromide ions, the peak characteristic can be altered with a small change in bromide concentrations. Therefore, an electrolyte solution containing 3 x 10^{-3} M HCl was chosen for further studies.

On the other hand, copper ions, which may be found in saline samples in trace amounts, can interfere with the measurement of mercury with gold based electrodes. Anodic stripping peaks of copper are also affected by the chloride content of the solution, and related peak potentials tend to approach mercury peaks [15]. Therefore, the voltammograms were recorded upon the addition of chloride ions into a cell containing 5.0 ng/mL of Cu(II) and Hg(II) ions. The chloride concentration was changed in a range of $5 \times 10^{-6} - 5 \times 10^{-3}$ M. As can be seen in Figure 3, the peak potential of mercury shifted in a negative direction with increasing chloride concentration, as expected, while the peak current remained nearly the same. However, the peaks related to the copper dissolution built up at the same potential with increasing chloride addition. This behavior indicated that a different mechanism was involved in the deposition and stripping steps for copper ions. In fact, a previous study carried out with copper electrodes revealed a reaction (Eq. 5) between the metallic copper and Cu(II) ions on the electrode surface [32]. The reaction product was stabilized in the presence of chloride ions.

$$Cu^{2+} + Cu^0 \rightleftharpoons 2Cu^+ \qquad (5)$$

This approach may be adopted for the dissolution of copper deposited on the GFE and so formed Cu_2Cl_2 species on the electrode surface may undergo an oxidation reaction. Therefore, the peak current built up with increasing concentrations of chloride ions while the peak potential remained the same.

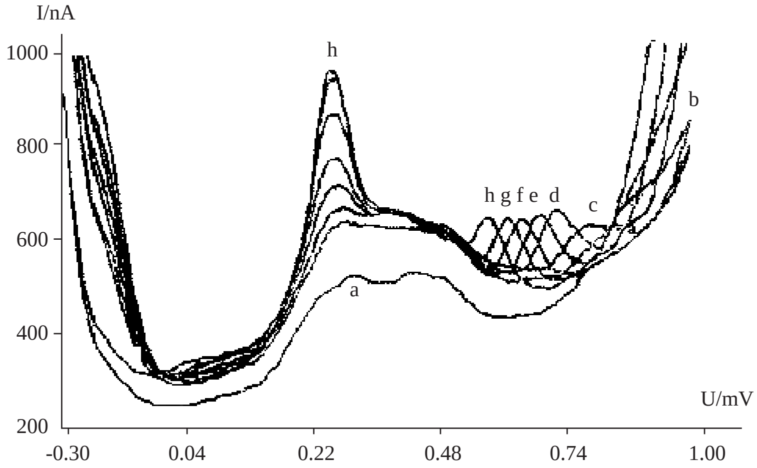

Figure 3. Effect of chloride concentrations on dissolution peaks of copper and mercury deposited from equal concentrations of 5 ng/mL in a) 0.1 M $HClO_4$ and after addition of chloride ions to be b) 5 x 10^{-6}, c) 1 x 10^{-5}, d) 5 x 10^{-5}, e) 1 x 10^{-4}, f) 5 x 10^{-4}, g) 1.5 x10^{-3} and h) 4.5 x 10^{-3} M in the final solution (E_{depo}= -0.30 V, t_{depo} = 60 s).

A similar chemical reaction may also occur between mercury deposited on the glassy carbon electrode surface as a thin mercury film and mercuric ions neighboring the electrode, resulting in calomel formation. This reaction particularly takes place under open circuit conditions and cathodic peak currents appear on the anodic scan over time [33,34]. However, the mercury deposited on the gold film behaved somewhat differently to that of glassy carbon electrodes since mercury interacted more strongly with the gold surface. As given above, Hg(II) ions were deposited as metallic mercury, but oxidized to Hg_2Cl_2 in the chloride medium according to Eq. 2. Therefore the peak potential was shifted in the cathodic region while the peak current remained nearly the same. This result agreed well with those obtained in HCl medium [15]. However, Bonfil et al. reported a reverse change in peak currents for copper dissolution peaks recorded in 0.01 M HNO_3[16]. It was pointed out that as the chloride concentration was increased, mercury and copper peaks approached each other while the latter peak gradually decreased. This could be attributed to the oxidative effect of nitric acid on the metallic copper deposited on the electrode surface.

Optimization of deposition parameters for mercury determination

Regarding analytical applications, the DP and SW anodic stripping techniques are popular because of their ability to enhance the analytical signal by removing the non-faradaic current. Further studies include the optimization of deposition parameters for mercury determination in 0.1 M $HClO_4$ medium containing 3 x 10^{-3} M HCl. The residual current tends to increase at potentials more negative than –0.5 V due to the hydrogen evolution on the gold film surface. The potential was scanned from –0.4 to more positive potentials, i.e. 0.8 V, which is the limit for the oxidation of the gold film. A well-developed peak was observed at 0.59 V for a solution containing 5 ng/mL Hg(II) ions. Another peak corresponding to the copper impurities was also observed around -0.3 V and the height of this peak increased as the deposition potential was made more negative while the peak current of mercury slightly decreased. Therefore, the deposition potential was chosen as 0.2 V for further studies.

The deposition time of mercury at a GFE should be carefully controlled to avoid saturation and to maintain linearity with increased loading. At low concentrations of Hg(II) (5 ng/mL) the anodic signal change of mercury collected on a GFE in 0.1 M $HClO_4$ containing 3 mM HCl was plotted against the deposition time. The peak current was changed linearly until 180 s and a deposition time of 60 s was used for further studies.

The optimal conditions given above were utilized for constructing a calibration graph. The anodic stripping voltammograms were obtained for Hg(II) in a concentration range of 1.0–8.0 ng/mL. The mercury dissolution peaks show an incline with Hg(II) ions and deviate linearly for higher concentrations. Figure 4 shows the calibration curve attained for a lower concentration range and the detection limit was calculated as 0.12 ng/mL (S/N = 3). RSD varied in the range of 0.3–4.3 % (n = 3).

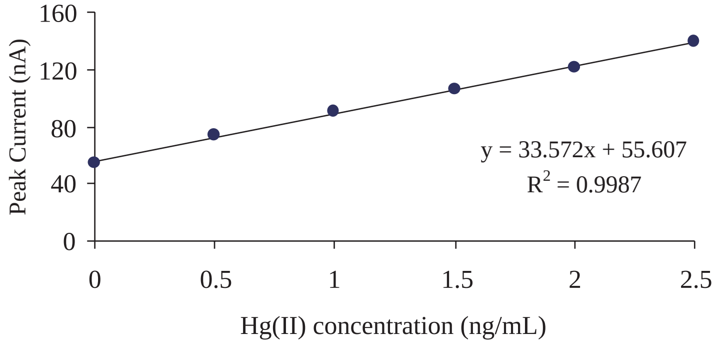

Figure 4. The calibration graph of Hg(II) for lower concentration range using the DP ASV technique.

In comparison to the DP ASV, the experiments were repeated using SW ASV mode employing the parameters given above. Although the residual current was low, the precision was poor and RSD values varied in the range of 4.9–8.3 % (n = 3). The calibration curve was linear in a rather narrow concentration range of 0.5-2.5 ng/mL Hg(II) ions. The detection limit was calculated as1.49 ng/mL. On comparing the results of the 2 modes, the DP ASV technique was the method of the choice in terms of reproducibility and sensitivity.

Interference study

In stripping analysis, gold-based electrodes have been applied to the determination of Pb, Cu, Sn, Se, Ge, As and Sb. Of these, possible interference with mercury determination may come from Pb and Cu impurities in the saline samples. The voltammograms were recorded with a solution spiked with standard solutions of Pb(II), Cu(II) and Hg(II) ions in the range of 5.0-30.0 ng/mL. The deposition was made at -0.3 V and the stripping peaks of Pb, Cu and Hg were observed at –0.14 V, +0.26 V and +0.59 V, respectively (Figure 5). The dissolution peaks of mercury and copper increased in height linearly with standard addition. However, the anodic peak of lead showed an irregularity probably due to the competition between other metallic forms for the active sites of the surface. No significant interference was observed for these concentrations.

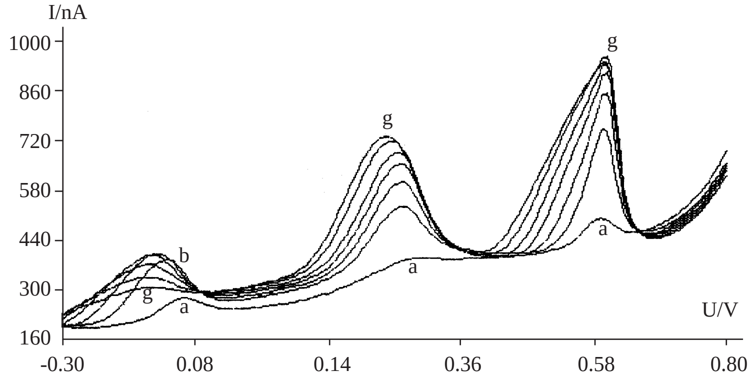

Figure 5. DP ASV peaks obtained for a solution containing a) 0.1 M $HClO_4$ and 3 x 10^{-3} M HCl after addition of Hg(II), Cu(II), Pb(II) solution to be b) 5.0, c)10.0, d)15.0, e) 20.0, f) 25.0 and g) 30.0 ng/mL.

Practical application

The method was applied for the determination of mercury in heamodialysis concentrates. The dissolved Hg(II) content of the sample was determined using standard addition. The resulting voltammograms and the standard addition curve are shown in Figure 6. Anodic peaks were located at 0.45 V due to the high chloride content of the sample solution. Further dilution of the samples to achieve optimum chloride concentration was excluded since this would have reduced the analyte concentration to a level below the sensitivity limit. The mercury content of the heamodialysis concentrate was 3.56 ± 0.15 ng/mL, subtracting the value established for the blank. RSD was calculated as 4.2% (n = 5). The accuracy of the method was tested by analyzing the spiked heamodialysis concentrates and recoveries were found in the range of 90-98%.

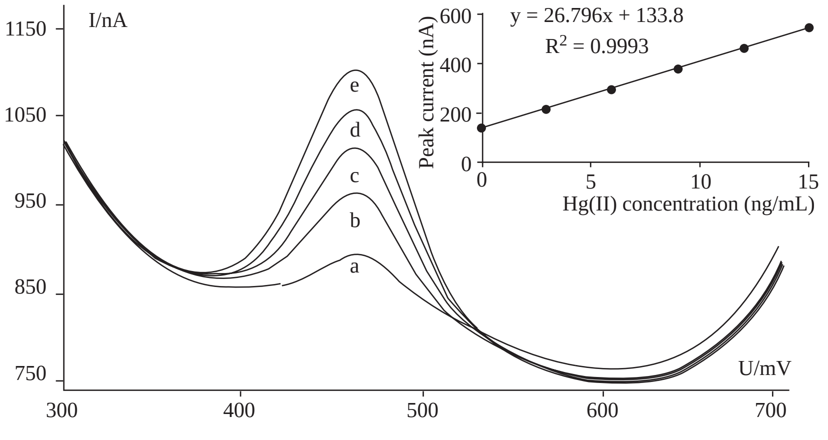

Figure 6. DP ASV peaks obtained for a solution containing a) 0.1 M $HClO_4$ and hemodialysis solution sample after addition of Hg(II) solution to be b) 4.0, c) 6.0, d) 8.0, e) 10.0 ng/mL.

The medium exchange to a deaerated stripping solution prior to the anodic scan was also tested. However, much smaller peaks with poor precision were obtained due to the loss of analyte during the electrode transfer step.

Conclusion

This study describes the effects of chloride and other halide ions on reoxidation peaks of mercury deposited on a GFE. The shift in the reoxidation peak potential of mercury was attributed to the involvement of the chloride in the stripping step of mercury stabilizing the Hg_2Cl_2 species on the electrode surface. Comparative studies revealed that the reoxidation peak of copper deposited on the GFE is also affected by chloride, but in a somewhat different manner. CuCl species thus formed on the electrode surface give an oxidation reaction and therefore, the peak current builds up with increasing concentrations of chloride ions while the peak potential remains the same.

No significant interference was observed from the several metal ions studied. Furthermore, by choosing more positive potentials for deposition, selectivity can easily be maintained. However, the main problem in working with saline samples is the difficulty in establishing a stable background current in the absence of chloride ions. It is known that even a high purity form of chloride salt contains trace amounts of mercury. Further research will focus on a procedure to stabilize the background current.

In conclusion, mercury can be determined sensitively and selectively by the DP ASV method using gold film electrodes. By using a deposition solution of 3 x 10^{-3} M HCl prepared in 0.1 M $HClO_4$ medium, a detection limit of 0.12 ng/mL (S/N = 3) was attained and the procedure was applied for heamodialysis concentrates. This method offers a sensitive and simpler procedure for mercury determination in saline samples since other techniques require a pre-separation step.

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References

1. A.W. Bott, **Bioanalytical Systems**, **West Lafeyette In USA, 47**, 906-1382 (1995).
2. W.L. Clevenger, B.W. Smith and J.D. Winefordner, **Crit. Rev. Anal. Chem. 27**, 1-26 (1997).
3. L.A. De Paz, A. Alegria, R. Barbera, R. Farre and M.J Lagarda, **Food Chem. 58**, 169-172 (1997).
4. J.M. Ombaba, **Microchemical Journal 53,** 195 -200 (1996).
5. H. Bagheri and A. Gholami, **Talanta 55**, 1141-1150 (2001).
6. E. Temmerman, C. Vandecasteele, G. Vermeir, L. Leyman and R. Dams, **Anal. Chim. Acta 236**, 371-376 (1990).
7. H.E.L Armstrong, W.T. Corns, P.B. Stockwell, G. O'Connor, L. Ebdon and E.H. Evans, **Anal. Chim. Acta 390**, 245-253 (1999).
8. E.L. Seibert, V.L Dressler, D. Pozebon and A.J. Curtius, **Spectrochim. Acta Part B 56**, 1963-1971 (2001).
9. P. Ugo, S. Zampieri, L.M. Moretto, and D. Paolucci, **Anal. Chim. Acta 434**, 291-300 (2001).
10. A.C. Barbosa, and G.A. East, **Ecological Trace Element Research 60**, 153-161 (1997).
11. H. Emteborg, H.W. Sinemus, B. Radziuk, D.C. Baxter and W. Frech, **Spectrochim. Acta Part B, 51**, 829-837 (1996).

12. Y. Cai, S. Monsalud, R. Jaffe and R.D. Jones, **J. Chromatogr. 876,** 147-155 (2000).
13. S. Rio-Segade and C. Bendicho, **Talanta 48**, 477-484 (1999).
14. J. Qvarnström, Q. Tu, F. Wolfgang and C. Lüdke, **Analyst 125**, 1193-1197 (2000).
15. R. Di Roso, M. Waeles, P. Monbet and C.J. Chaumery, **Anal. Chim. Acta 410**, 97-105 (2000).
16. M.F. Tutunji, **Fresenius J. Chem. 356**, 90-95 (1996).
17. Y. Bonfil, M. Brand and E. Kirowa-Eisner, **Anal. Chim. Acta 424**, 65-76 (2000).
18. M. Hatle, **Talanta 34**, 1001-1007 (1987).
19. I. Gustavsson, **J. Anal. Chem. 214,** 31-36 (1986).
20. F. Scholz, L. Nitschke and G. Henrion, **Anal. Chim. Acta 199**, 167-171 (1987).
21. D. Sancho, L. Deban, F. Barbosa, R. Pardo and M. Vega, **Food Chem. 74,** 527-531 (2001).
22. T.R Linstrom, and C.D Johnson, **Anal. Chem.** 1855-1857 (1981).
23. H. Huilliang, D. Jagner and L. Renman, **Anal. Chim. Acta 202**, 117-122 (1987).
24. E.A. Viltchinskaia, L.L. Zeigmann, D.M. Garcia and P.F. Santos, **Electroanal. 9,** 633-640 (1996).
25. I. Svancara, M. Matousek, E. Sikora, K. Schachl, K. Kalcher and K. Vytras, **Electroanal. 9**, 827-833 (1997).
26. R. Agraz, M.T. Sevilla and L. Hernandez, **J. Anal. Chem. 390,** 47-57 (1995).
27. C. Faller, N.Y. Stojko, G. Henze and K.Z. Brainina, **Anal. Chim. Acta 396,** 195-202 (1999).
28. J. Wang, **"Stripping Analysis"**, VCH Publishers, Deerfield Beach, FL, USA (1985).
29. A.S. Misiego, R. Garcia, M. Carra and A. Zirino, **Electroanal. 8**, 534-538 (1996).
30. J. Pinchin and J. Newham, **Anal. Chim. Acta 90**, 91-102 (1997).
31. E.P. Gil and P. Ostapczuk, **Anal. Chim. Acta 293**, 55 (1994).
32. R. Romagnoli and V.F. Vetere, **Anal. Chim. Acta 234,** 331-338 (1990).
33. F.N. Ertaş, H.İ. Gökçel and H. Tural, **Turk. J. Chem. 24**, 261-267,(2000).
34. D. Jagner, E. Sahlin and L. Renman, **Anal. Chem. 68**, 1616-1622 (1996).