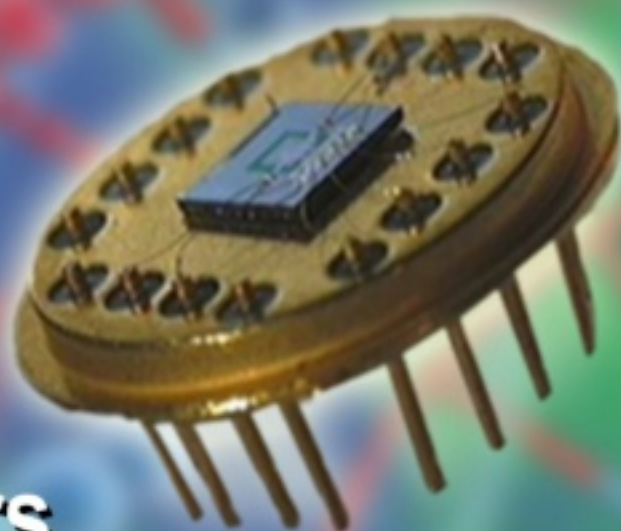


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## Glutathione Modified Gold Piezoelectric and Voltammetric Sensors for Determination of Mercury in a Wide Concentration Range

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**Abstract:** Glutathione-modified Au electrodes (Au-SG) deposited on a piezoelectric quartz crystal resonators were investigated for sensor applications for mercury(II). Owing to the stable background resulting from well ordered Au-SG self-assembled monolayer film, very small accumulations of mercury could be utilized in Hg(II) determination. Typically, the accumulations ranging from  $\theta_{\text{Hg}} = 0.1$  down to 0.0005 ML (equivalent Hg monolayers) could be used. This contributes to the considerable reduction of the analysis time. The lower detection limit of Hg, LDO = 0.3 ppb has been achieved using slow scan stripping voltammetry and was further enhanced using differential pulse technique to 0.05 ppb. Moreover, the analysis can also be performed in acidic environment where other electrode modifiers become inactive. *Copyright © 2008 IFSA.*

**Keywords:** Glutathione SAM, Hg stripping voltammetry, Nanogravimetry, Adsorptive stripping voltammetry (AdSV), Differential pulse (DP) stripping voltammetry, Modified-Au EQCN

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### 1. Introduction

The determination of toxic heavy metals in environmental and biological samples is an important factor in preventing serious diseases and pathological disorders. Recent studies of environmental effects on human health indicate on an increased susceptibility to diabetes [1], autism [2, 3], and other diseases [3-8] due to diminished active glutathione (GSH) levels in cells and body fluids and the reduced antioxidation capacity [9,10] to protecting against radicals. The bonding of toxic heavy metals

(Hg, Cd, Pb) to GSH and disabling the GSH/GSSG redox regulation system in living organisms is one of the suspected mechanisms of the environmental effects, in addition to inducing biochemical pathways affecting cell differentiation, proliferation and apoptosis. The formation of reactive oxygen species has been treated as a biomarker of methylmercury and trimethyltin neurotoxicity [11]. In previous studies [9,10], we have examined the role of redox regulation in cell survival at an early point in the recognition of the role of oxidative stress in induction of cell death. Along with some fundamental discoveries related to antioxidants and cell survival, we have found that the efficacy of survival factors can be enhanced by applying them in combination with antioxidants. These studies have created the basis for the analysis of novel roles for redox modulation in cell development [12-17].

The electrochemical reactions of  $\text{Hg}^{2+}$  on polycrystalline Au [18-20] and on Au single crystal faces [21-23] have been extensively studied. Strong effects of the electrolyte anions on the surface structure of underpotentially deposited  $\text{Hg}^0$  monolayer (upd-Hg) have been found [24]. Thin mercury films have also been deposited on various substrates as the medium for analytical determinations of other species including those forming amalgams [20, 25]. The trace analysis of Hg(II) samples is usually carried out by anodic stripping voltammetry at glassy carbon or carbon paste electrodes [26], including adsorptive stripping voltammetry (AdSV).

In this work, we have investigated electrochemical processes of Hg(II) on a GSH-modified Au film electrode deposited on a quartz crystal piezoresonator for the purpose of developing a new type of sensors for determination of Hg(II) in environmental samples in a wide concentration range. GSH is a tripeptide with sulfhydryl group and forms readily a self-assembled monolayer (SAM) on gold substrates owing to the strong Au-S bonding and lateral interactions between the peptide chains. Au is convenient for studying SAM of thiols since their oxidation is strongly inhibited on Au (for thiourea it is shifted anodically by ca. 600 mV with respect to Pt substrate to  $E_{p,\text{an}} = 1.27$  RHE [27] and for GSH to  $E_{p,\text{an}} = 1.3$  RHE [28]). Thus, sensors based on GSH-modified electrodes have been investigated. Gooding et al. [29] studied GSH bonded to mercaptopropionic acid as the sensor for  $\text{Cd}^{2+}$ . In our earlier studies, we have found that metal cations such as  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ , can penetrate the Au-SG films through ion-channels induced by conformational transitions of adsorbed GSH. The interactions of adsorbed GSH with  $\text{Cu}^{2+}$  have also been studied [30, 31]. We have shown earlier that GSH-modified Au piezoelectrodes can act as chemically controlled ion gates [31,32] and as templates for metal depositions [32]. Here, we report on the development of GSH-modified Au piezoelectrode sensor for mercury(II).

## 2. Experimental

**Chemicals.** All chemicals used for investigations were of analytical grade purity. L-Glutathione (GS) was purchased from Aldrich Chemical Company and used as received. Solutions were prepared using Milli-Pore Milli-Q deionized water (conductivity  $\sigma = 55$  nS/cm). They were deoxygenated by bubbling with purified nitrogen. The experiments were performed at room temperature, 22°C.

**Apparatus.** A standard electrochemical setup was employed for voltammetric measurements. It consisted of a Potentiostat/Galvanostat, Model PS-205B (Elchema, Potsdam, NY), an Electrochemical Quartz Crystal Nanobalance, Model EQCN-930, and a Data Logger and Control System, Model DAQ-716v, operating under Voltscan 5.0 data acquisition and processing software. In voltammetric measurements, a high purity (99.999%) Au wire with 1 mm diameter and 6 mm in length ( $A = 0.196$  cm<sup>2</sup>) was used as the working electrode. In combined nanogravimetric and voltammetric measurements, mirror polished quartz crystal piezoresonators (QC-10Au-PB) with 5 mm diameter Au disk working electrodes, vacuum-sputtered over a 10 nm Ti underlayer, were used. The resonant frequency  $f_0$  of these Au-piezoelectrodes was 9.975 MHz and their geometrical surface area was 0.1963 cm<sup>2</sup>, with the roughness factor  $R = 1.3$ . A standard EQCN cell with 30 mL capacity, having a

side opening for sealing a quartz crystal resonator wafer (with siloxane adhesive), was used in experiments. The working electrode was polarized using a Pt wire counter electrode and its potential measured vs. a double-junction saturated (KCl) Ag/AgCl reference electrode. The interfacial mass changes were determined from the changes in oscillation frequency of the EQCN according to the Sauerbrey relationship [33-35]:

$$\Delta f = -\frac{2\Delta m n f_0^2}{A\sqrt{\mu_q d_q}} \quad (1a)$$

fulfilled for thin rigid films. The latter condition was confirmed using quartz crystal immitance spectroscopy. In the above formula, the change in the resonant oscillation frequency ( $\Delta f$ ) is related to the change in the interfacial mass ( $\Delta m$ ), the piezoelectrically active area ( $A$ ), the fundamental frequency ( $f_0$ ), which depends on the quartz properties and resonator thickness (here: 0.166 mm), the overtone number ( $n$ ), and to the physical properties of quartz: its density ( $d_q = 2.648 \text{ g cm}^{-3}$ ) and shear modulus ( $\mu_q = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$ ). Hence, the film mass changes  $\Delta m$  are directly related to the observed fundamental frequency shift:

$$\Delta m = -0.8673 \Delta f \quad (1b)$$

provided that the solution density and viscosity remain constant during the experiment (54). For the sake of simplicity, we will use symbol  $m$  to denote apparent mass changes derived from equations (1ab).

**Procedures.** The gold working electrodes deposited on quartz crystal wafer piezoresonators were cleaned with acetone, ethanol, and Milli-Q water, then etched in piranha solution (conc.  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 4:1$ ) for 120 s, rinsed with distilled water and immediately immersed in 0.1 M  $\text{HClO}_4$  solution. The Au and Pt wire electrodes were etched in 10 M  $\text{H}_2\text{SO}_4$  and flame annealed with quenching in water. The Au-SG modified electrodes were prepared by immersion of freshly prepared metal electrodes in 10 mM GSH + 0.1 M  $\text{HClO}_4$  solution for 20 minutes which resulted in reproducible films. The electrodes were emersed from the analyte solutions under a protecting potential ( $E_{\text{cond}} = +0.9 \text{ V vs. Ag/AgCl}$ ) to avoid any uncontrolled mercury deposition and/or amalgam formation.

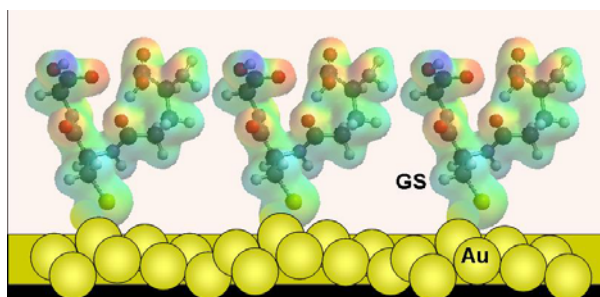
### 3. Results and Discussion

#### 3.1. Reactivity of Hg(II) on Au-SG Modified Piezoelectrodes

The electrochemical processes and interactions of  $\text{Hg}^{2+}$  cations with GSH SAM modified Au electrode are complex and depend strongly on different factors including the conformation and degree of GSH film ordering, interaction time scale, concentration level of Hg(II), kinds of anions present in the electrolyte, and others. In this section, the reactivity of Hg(II) on a Au-SG electrode investigated in a wide range of Hg(II) concentrations from 1.5 mM to 15 nM, is discussed.

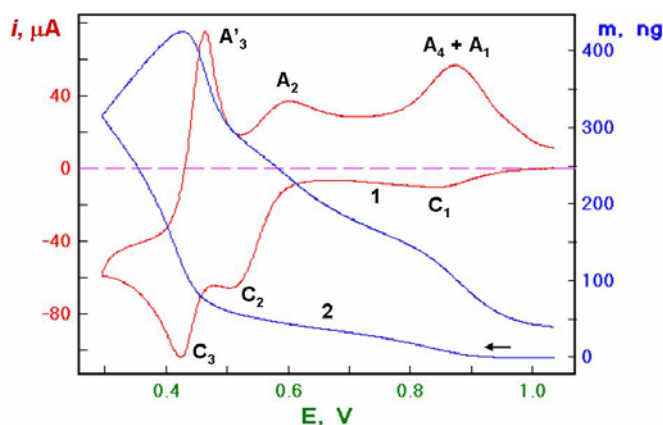
The schematic view of a GSH-modified Au piezoelectrode surface is depicted in Fig. 1. The GSH tripeptide molecules are anchored on a Au surface by a strong Au-S chemisorption bond and the glutamate and glycine branches are directed toward the solution phase.

Typical linear potential scan voltammetric characteristics of a Au-SG modified electrode in 0.1 M  $\text{NaClO}_4 + 0.001 \text{ M HClO}_4$  solution containing different concentrations of Hg(II) are presented in Figs. 2-4.



**Fig. 1.** Schematic view of the GSH-modified Au|QC piezoelectrode.

At a relatively high, 1.5 mM, Hg(II) concentration (Fig. 2), the ion-channels in Au-SG films are sufficiently wide opened to provide ionic pathways between the solution phase and Au surface for efficient  $\text{Hg}^{2+}$  transport and electrochemical discharge at the bottom of ion channels in Au-SG film.



**Fig. 2.** Current  $i$  (1) and mass  $m$  (2) vs. potential  $E$  characteristics for a Au-SG piezoelectrode in 1.5 mM Hg(II) + 0.1 M  $\text{NaClO}_4$  + 0.001 M  $\text{HClO}_4$  solution recorded at a scan rate  $\nu = 50$  mV/s.

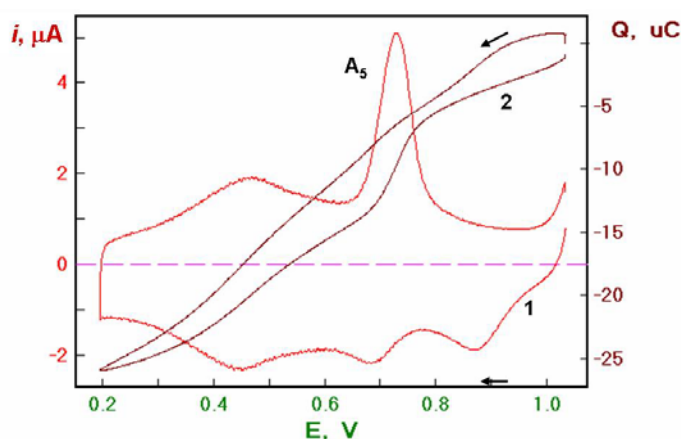
The voltammetric and nanogravimetric curves (curves 1 and 2, respectively) were recorded at a potential scan rate  $\nu = 50$  mV/s in the potential range from +1.05 to +0.3 V vs. Ag/AgCl reference. The very first process encountered at the beginning of the cathodic going potential scan ( $C_1$ ) is due to the upd-Hg formed at the bottom of Au-SG channels. A small mass increase of 36.6 ng corresponding to this process is observed on the nanogravimetric curve 2 (measured from  $E = +0.9$  V to the current valley at  $E = +0.668$  V). The surface coverage  $\theta_{\text{Hg}}$  estimated from this mass change and the equivalent full Hg monolayer mass,  $m_{\text{Hg,mono}} = 424.55$  ng/cm<sup>2</sup> (or: 108.3 ng per QC), based on a hypothetical 2D hexagonal close packing with  $2r_{\text{Hg}} = 0.301$  nm), is less than 0.33 ML. This includes  $\text{Hg}^{2+}$  ions reduced to  $\text{Hg}^0$  atoms forming upd-Hg as well as the  $\text{Hg}^{2+}$  ions inserted in the film in the capacitive charging process. Next process begins at potentials below  $E = +0.6$  V. Its maximum rate is observed at the cathodic current peak  $C_2$  at  $E_{p,C2} = +0.52$  V. This process is the reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}_2^{2+}$  and it is controlled by solution diffusion. No mercury deposition is taking place in this process as evidenced on the mass curve 2. In the potential range  $E < +0.46$  V, the deposition of bulk  $\text{Hg}^0$  is observed (voltammetric peak  $C_3$ ). A sharp mass increase associated with  $\text{Hg}^0$  deposition is clearly seen on curve 2. The maximum mass change of  $m = 415$  ng (1600 ng/cm<sup>2</sup>) corresponds to ca. 16 equivalent  $\text{Hg}^0$  monolayer (ML). It is believed that once a monolayer of  $\text{Hg}^0$  is completed, further Hg(II) ion discharge leads to the incorporation of Hg atoms into the Au substrate and the formation of a Au(Hg) amalgam.



During the anodic backward potential scan, we observe  $\text{Hg}^0$  dissolution (Fig. 2, peak  $A_3'$ ) and a concomitant electrode mass decrease. We have shown earlier that this process is a single electron  $\text{Hg}^0$  electrooxidation with the formation of  $\text{Hg}_2^{2+}$  ions (i.e.  $\text{Hg}^0 - e^- = \frac{1}{2}\text{Hg}_2^{2+}$ ), in contrast to the counterpart deposition process  $C_3$  which is a two-electron process (i.e.  $\text{Hg}^{2+} + 2e^- = \text{Hg}^0$ ). Further oxidation of  $\text{Hg}_2^{2+}$  to  $\text{Hg}^{2+}$  proceeds in the process  $A_2$ . In the final stage of mercury electrodisolution, the amalgam releases  $\text{Hg}^{2+}$  in the process  $A_4$  and the upd-Hg is also desorbed ( $A_1$ ). The latter peak is well resolved when the amalgam formation is diminished, e.g. by increasing the cathodic reversal potential to  $E = +0.6$  V.

The EQCN characteristics presented in Fig. 2 and similar characteristics obtained for different potential windows and scan rates (not shown) provide an important survey of Hg(II) reactivities at a Au-SG electrode and form the basis for comparisons with the system behavior at lower Hg(II) concentrations revealing new phenomena. From the analysis presented above, we can say that whereas the Hg determination based on bulk  $\text{Hg}^0$  formation is not useful for analytical purposes (mainly because of the effects of conproportionation reaction of Hg(II) with  $\text{Hg}^0$  deposit), the 2D process of upd-Hg formation at the bottom of GSH ion-channels and the redox reaction (Hg(II)/Hg(I)) can be utilized in analysis.

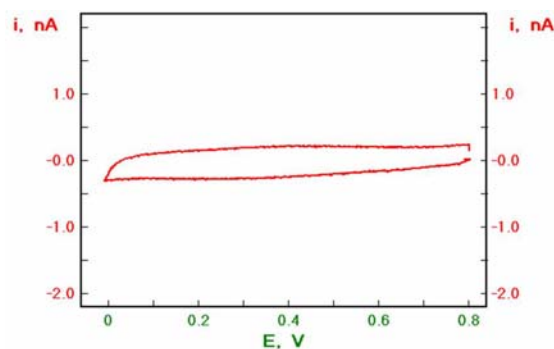
The amount of deposited mercury is considerably decreased when the Hg(II) concentration is lowered to  $4.5 \mu\text{M}$  (Fig. 3). We have found that the upd-Hg stripping peak  $A_1$  is no longer present on the voltammogram and it is replaced by a desorptive stripping peak  $A_5$  at  $E = +0.73$  V. All other peaks are lower in value due to slow mass transport of Hg(II) from the bulk solution to the film surface.



**Fig. 3.** Current  $i$  (1) and charge  $Q$  (2) vs. potential  $E$  characteristics for a Au-SG piezoelectrode in  $4.5 \mu\text{M}$  Hg(II) +  $0.1 \text{ M NaClO}_4$  +  $0.001 \text{ M HClO}_4$  solution recorded at a scan rate  $\nu = 50 \text{ mV/s}$ .

Similar voltammetric experiments performed for lower yet Hg(II) concentration, in the nanomolar range, show a complete blockage of the electrode surface, as illustrated in Fig. 4.

The cyclic voltammogram in Fig. 4 was obtained for a Au-SG electrode in  $75 \text{ nM Hg(II)} + 0.1 \text{ M NaClO}_4 + 0.001 \text{ M HClO}_4$  solution. Only capacitive currents are observed. However, as will be shown in the next sections, the electrode can still be activated and with appropriate mercury accumulation procedure, it can be used for very low Hg level determinations.



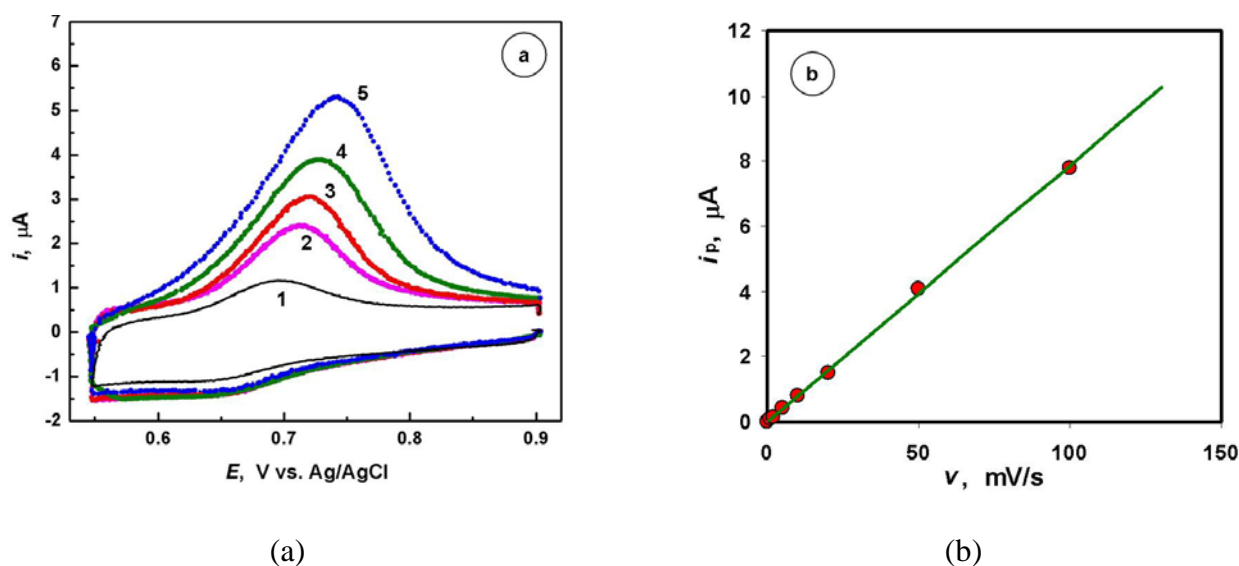
**Fig. 4.** CV for a Au-SG piezoelectrode in 75 nM Hg(II) solution;  $\nu = 50$  mV/s.

In summary, we can see that the relatively weak electrode surface blocking observed in more concentrated Hg(II) solutions is replaced with full blocking at low concentrations. This is due to the interactions of Hg(II) ions with GSH functional groups leading to the opening of ion channels in Au-SG film at higher Hg(II) concentrations ( $[\text{Hg(II)}] > 1$  mM) followed by fast solution diffusion and efficient discharge on a Au substrate surface at the bottom of ion channels. At lower Hg(II) concentrations, the mass transport rate is diminished not only due to the slower solution diffusion but also due to the increased steric hindrance for the active species diffusion through the blocking film.

In the following sections, we will analyze the behavior of a Au-SG modified electrode in solutions of low mercury concentrations where a considerable blocking leads to new adsorptive stripping phenomena.

### 3.2. Adsorptive Stripping of Hg

A family of stripping voltammograms for varying deposition times  $t_{\text{dep}}$  from 0 to 80 s, in quiescent solution, is presented in Fig. 5. The curves were obtained for a Au-SG modified electrode in 0.1 M  $\text{HClO}_4 + 4.5 \mu\text{M Hg(II)} + 0.1$  mM La(III) solution, at  $\nu = 50$  mV/s.

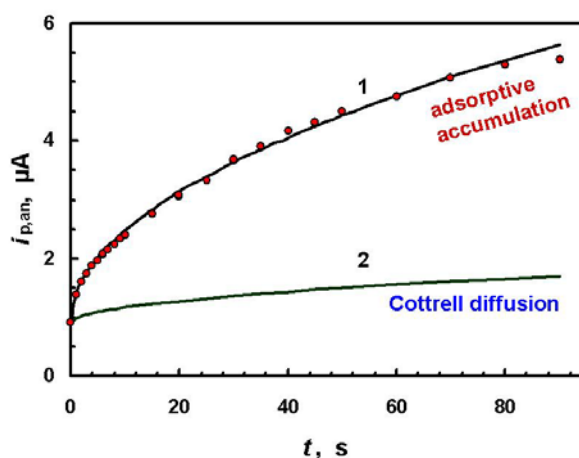


**Fig. 5.** (a) Stripping voltammometric characteristics of a Au-SG piezoelectrode in  $4.5 \mu\text{M Hg(II)} + 0.1$  M  $\text{NaClO}_4 + 0.001$  M  $\text{HClO}_4$  solution recorded at a scan rate  $\nu = 50$  mV/s; accumulation potential:  $E = +0.55$  V, accumulation time  $t_{\text{dep}}$  [s]: (1) 0, (2) 10, (3) 20, (4) 40, (5) 80. (b) Dependence of  $i_p$  on scan rate  $\nu$ , for  $t_{\text{dep}} = 60$  s.

The curves are nearly symmetrical, with the half peak width increasing with  $t_{dep}$ . The peak potential shifts toward higher potentials with increasing  $t_{dep}$ . The stripping peak current increases linearly with  $v$  (Fig 5b). However, the dependence of  $i_p$  on  $t_{dep}$  is not linear. A non-linear dependence of  $i_p$  on  $t_{dep}$  is, for instance, expected for Cottrell solution diffusion conditions (up to 60-90 s), which may apply for these experiments. The relationship of  $i_p$  vs.  $t_{dep}$  (where  $i_p$  is the rough peak current, i.e. it is not background-corrected) for a larger set of stripping experiments is presented in Fig. 6. The fitting line in the form:

$$i_p = i_b + a\sqrt{t_{dep}} \quad (2)$$

is obtained, where  $i_b$  and  $a$  are constants:  $i_b = 0.898 \mu\text{A}$  and  $a = 0.503 \mu\text{C s}^{-3/2}$ . The constant  $i_b$  corresponds to the generalized background correction and represents the peak current at  $t_{dep} = 0$ .



**Fig. 6.** Dependence of anodic peak current  $i_p$  on  $t_{dep}$  for a Au-SG piezoelectrode in  $4.5 \mu\text{M Hg(II)} + 0.1 \text{ M NaClO}_4 + 0.001 \text{ M HClO}_4$  solution recorded at a scan rate  $v = 50 \text{ mV/s}$ : (1) experimental data (circles) and fitting line according to eq. (2); (2) theoretical curve for semi-infinite solution diffusion control of accumulation.

The dependence of  $i_p$  on  $t_{dep}$  seems to reflect the semi-infinite diffusion of analyte from solution in the accumulation stage. However, simple calculations indicate that a solution diffusional wave can not support the accumulation process at this rate because of low concentration level. The maximum Hg stripping peak height which would be observed for a semi-infinite diffusion can be calculated for the Cottrell limiting current:

$$i_{dep} = \frac{nFAC_0D^{1/2}}{(\pi t_{dep})^{1/2}} \quad (3)$$

leading to the accumulated charge:

$$Q_{dep} = 2\pi^{-1/2}nFAC_0D^{1/2}t_{dep}^{1/2} \quad (4)$$

Assuming a fast reversible stripping process, one obtains:

$$i_p = \frac{Q_{dep}v}{w}, \quad (5)$$

where  $w$  is the half-peak width (e.g.,  $w = 90$  mV). The deposition time dependence of  $i_p$  is then obtained by combining the last two equations:

$$i_p = \frac{2nFACD^{1/2}\nu}{\pi^{1/2}w} t_{dep}^{1/2} = bt_{dep}^{1/2} \quad (6)$$

This dependence is plotted in Fig. 6, curve 2, for  $b = 0.0844 \mu\text{A s}^{-1/2}$  (obtained for  $F = 96,485$  C/equiv,  $A = 0.255$  cm<sup>2</sup>,  $C = 4.5 \times 10^{-9}$  mol cm<sup>-3</sup>,  $D = 1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>,  $\nu = 50$  mV s<sup>-1</sup>,  $w = 90$  mV), after adding the background contribution of  $i_b = 0.898 \mu\text{A}$  (i.e., the same as obtained for the experimental curve 1). The large difference between the maximum solution transport controlled process (curve 2) and the experimental dependence (curve 1) indicates that the primary source of Hg<sup>2+</sup> ions is the outer film|solution interface populated by the carboxylate-bound Hg<sup>2+</sup>.

For longer deposition times, deviations from the square-root dependence become apparent beginning from  $t_{dep} = 90$  s (last point on the graph in Fig. 6) and continue for times up to 180 s (not shown). The observed downward deviations may be associated with gradual depletion of the Hg<sup>2+</sup> source on the outer film boundary. Note that upward deviations should be expected if a solution diffusion transport would be the rate controlling step and was disturbed for times longer than 60-90 s by the thermal convection, which is normally expected.

The amount of carboxylate-complexed Hg<sup>2+</sup> cations at the outer film boundary can be estimated. The charge integrated over the stripping peak for  $t_{dep} = 80$  s (Fig. 5, curve 5) is  $Q_p = 10 \mu\text{C}$  and corresponds to surface coverage of less than  $\theta_{\text{Hg}} = 0.1$  ML. The limiting Cottrell process can supply only a maximum of  $\theta_{\text{Hg}} = 0.013$  ML ( $t_{dep} = 80$  s). The complexed-Hg<sup>2+</sup> source should then contain *ca.* 0.1 ML of Hg<sup>2+</sup>. The source depletion begins at longer deposition times ( $t_{dep} > 80$  s) and leads to the saturation of the  $i_p$  vs.  $t_{dep}$  dependence. The square root dependence of  $i_p$  vs.  $t_{dep}$  at shorter deposition times is then rather fortuitous since the mass transport within the thin GSH film must be influenced by many factors including also local electric fields, charge centers, close distance interactions with atoms of the tripeptide chains, etc., in addition to kinetic hindrance of the interfacial charge transfer.

The dependence of  $E_p$  on  $t_{dep}$  is presented in Fig. 5c. The experimental points are fitted using the logarithmic function:

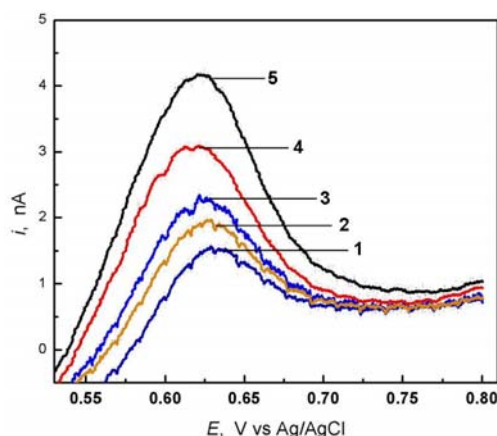
$$E_p = E^* + S \log\left(\frac{t_{dep}}{\tau_u}\right), \quad (7)$$

where  $E^*$  and  $S$  are constants and  $\tau_u = 1$  s is the unit normalization constant. The slope  $S = \partial E_p / \partial \log(t_{dep} / \tau_u) = 31.34$  mV and  $E^* = 680.5$  mV.

### 3.3. Accumulation of Hg on Au-SG Film from Nanomolar Hg(II) Solutions

At very low Hg(II) concentrations, in the nanomolar range, the enhanced accumulation procedures utilizing RDE, flow-cells, stirring, or other means of mass transport acceleration are usually used. Also, when very small coverages of accumulated species (here  $\theta_{\text{Hg}}$ ) are obtained then a special attention has to be paid to the stripping technique used, as the discrimination against capacitive background currents becomes of primary importance. The pulse relaxation techniques can be applied (see next section). Here, to discriminate against capacitive background, we have applied a slow scan stripping voltammetry with  $\nu = 1$  mV/s. Since capacitive currents  $i_c$  are proportional to  $\nu$  (i.e.:  $i_c = k\nu$ , where  $k$  is the constant) while the Faradaic currents  $i_F$  depend on square root of  $\nu$  (i.e.:  $i_F = k'\sqrt{\nu}$ ), the

capacitive currents decrease faster than Faradaic currents with decreasing  $\nu$ . Thus, in a simple arrangement of using relatively short deposition times (up to 80 s) followed by a slow stripping scan, we have been able to obtain and analyze small coverages  $\theta_{\text{Hg}}$ . The results obtained for a Au-SG electrode in 15 nM Hg(II) + 0.1 M HClO<sub>4</sub> are presented in Fig. 7. The values of  $\theta_{\text{Hg}}$  typically obtained are in the range: 0.0001 to 0.004 which is sufficient to perform analysis. For instance, the integrated charge under the stripping peak of curve 5 is  $Q_p = 400$  nC. This charge corresponds to the apparent surface coverage  $\theta_{\text{Hg}} = 0.0038$  ML. Again, the solution mass transport can only supply a maximum of  $\theta_{\text{Hg}} = 0.000044$  ML ( $Q_{\text{diff}} = 18.1$  nC) in 80 s. Hence, the Hg determination can be done exclusively owing to the pre-accumulation of Hg<sup>2+</sup> cations at the outer film|solution interface by a convenient current-less equilibration. The equilibration time is considerably shortened by stirring but maintaining precise control of steady hydrodynamic conditions is not necessary, since the same final equilibrium state is always obtained.



**Fig. 7.** Current-potential characteristics for a Au-SG piezoelectrode in 15 nM Hg(II) + 0.1 M NaClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> solution recorded at a scan rate  $\nu = 1$  mV/s, with  $t_{\text{dep}}$  [s]: (1) 0 s, (2) 10, (3) 20, (4) 40, (5) 80.

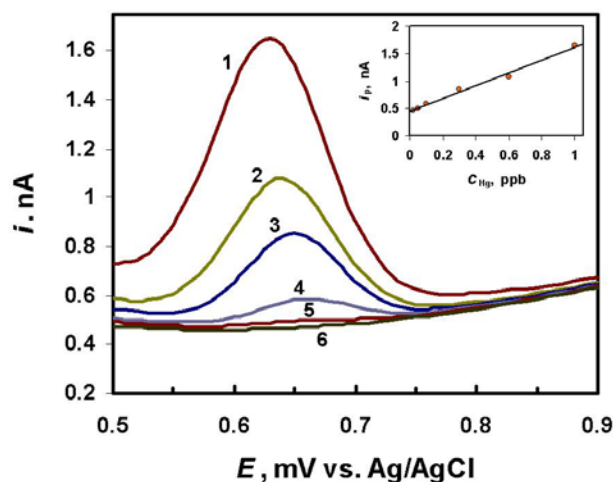
Since the level of Hg in the solution is 3 ppb, it follows from the data of Fig. 7 that the analytes with ca. 0.3 ppb Hg content can be analyzed in this way on a Au-SG modified electrode. Note that the FDA allowed Hg level in drinking water is 2 ppb.

### 3.4. Sub-ppb Hg Determination Using Differential Pulse Stripping Voltammetry

The analysis of trace Hg content in environmental samples has been performed using Au-SG SAM modified gold sensors using enhanced hydrodynamic conditions (stirring) in the accumulation stage and voltammetric analysis employing a differential pulse technique (DP). The measurements using DP stripping voltammetry were carried out using the following waveform parameters: pulse height  $h = 50$  mV, step height  $dE = 2$  mV, pulse duration  $\tau_p = 40$  ms, sample time  $\tau_s = 35$  ms. Typical DP voltammograms are presented in Fig. 8, for Hg(II) concentrations from 0.02 ppb to 1 ppb.

The dependence of  $i_p$  on mercury concentration is presented on the inset in Fig. 8. The relative standard deviation is 3.9% and the lower detection limit is 0.05 ppb. Further enhancements are possible by using rotating disk electrodes and longer accumulation times.





**Fig. 8.** Differential pulse stripping voltammetric characteristics for Hg(II) determination in 0.1 M NaClO<sub>4</sub> + 0.001 M HClO<sub>4</sub> + x Hg(II) solutions, using a Au-SG thiol modified sensor; x [ppb]: (1) 1.0, (2) 0.6, (3) 0.3, (4) 0.1, (5) 0.05, (6) 0.02;  $E_{\text{dep}} = 0.5$  V,  $t_{\text{dep}} = 600$  s,  $\nu = 2$  mV/s. Inset: calibration plot of  $i_p$  vs.  $c_{\text{Hg}}$ .

In the analysis of mercury using Au-SG and other thiolate SAM modified Au sensors, it is important to realize that the amount of accumulated analyte must be a small fraction of a monolayer and the accumulation should be performed with a low overvoltage. At high overvoltage and large accumulations, the deposited mercury is driven into the formation of an amalgam which leads to the effective dilution of the collected material and diminished analytical signal.

The analysis of accumulated analyte can be performed by employing either a slow scan chronovoltamperometry or a differential pulse voltammetry. However the latter technique offers in principle a better discrimination against capacitive currents since the double-layer capacitance is charged before each measurement is carried out. Some gains of this technique are offset in the slow scan voltammetry because a much lower bandpass filters can be applied to recover the analyte signal from the noise floor. The analysis time in both techniques is similar.

#### 4. Conclusions

The nanogravimetric measurements performed using a GSH-SAM modified Au piezoelectrode confirm a mercury uptake during the 2D and 3D phase formation. At high Hg(II) concentrations, the Hg<sup>2+</sup> cations play a dual role to control the Au-SG gate opening and to provide rich electrochemical reactivity at the open channel bottoms which enables monitoring of these processes by voltammetric and nanogravimetric methods. The 2D adsorptive processes offer ample opportunities for utilizing them in sensors for mercury(II). The upd-Hg, forming at the bottom of Au-SG channels, can be utilized at high Hg(II) concentrations ( $C > 100$   $\mu\text{M}$ ), whereas at lower Hg(II) concentrations, the pre-accumulated Hg<sup>2+</sup> cations bonded to carboxylate moieties at the outer Au-SG film boundary, which are at equilibrium with the bulk solution, can serve as a convenient source of analyte. Utilizing the latter mechanism and the stable background provided by the GSH SAM, we have been able to base our analyses on very small mercury accumulations, down to 0.0004 equivalent Hg monolayers, thereby reducing the analysis time which is especially important for trace Hg analysis. In slow scan adsorptive stripping measurements that enable sufficient discrimination against capacitive currents, the lower Hg detection limit of 0.3 ppb has been achieved. Further enhancement has been attained by applying voltammetric relaxation techniques and intensifying the accumulation processes. Using differential pulse technique, the detection limit of 0.05 ppb was achieved. We have found that the control of the

Au-SG film density and permeability is of primary importance. This is attributed to the involvement of mercury species transport through the film. Whereas the dense films are usually obtained after 12 or more hours of film self-ordering and conformational adjustments, they may not be suitable for analytical purposes. We propose to prepare the GSH SAM films *in situ* in 15-20 minutes. This procedure results in adequate films while considerably reducing the sensor preparation time. The film permeability can be adjusted to the concentration level of Hg(II) to yield sensors that can be used in a wide analyte concentration range. Further studies are necessary to develop films insensitive to modifying organic compounds which might be present in analyzed samples, such as other thiol molecules, neurotransmitters, etc. Trace heavy metal ions, having lower standard electrode potentials than mercury, do not interfere appreciably in mercury determinations but their effect on background current should be evaluated before analysis.

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## Guide for Contributors

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### Aims and Scope

*Sensors & Transducers Journal* (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In addition, some special sponsored and conference issues published annually.

### Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

### Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail [editor@sensorsportal.com](mailto:editor@sensorsportal.com) 6-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: <http://www.sensorsportal.com/HTML/DIGEST/Submission.htm> Authors must follow the instructions strictly when submitting their manuscripts.

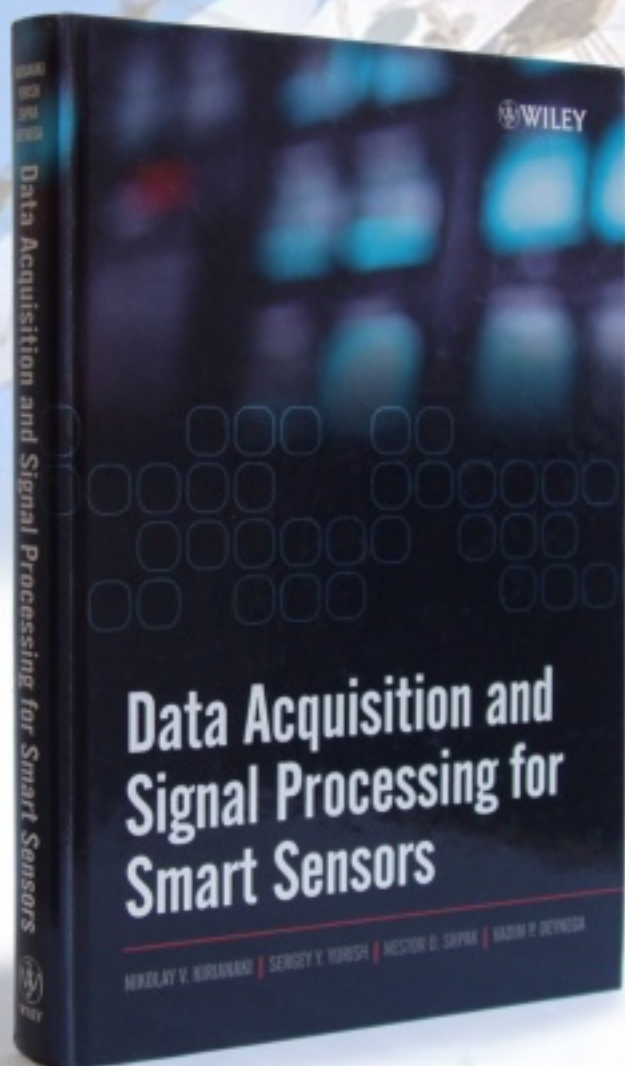
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