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## Short Communication

# Hg(II) trace electrochemical detection on gold electrode: Evidence for chloride adsorption as the responsible for the broad baseline

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## A B S T R A C T

Investigations were performed in order to clarify the origin of the broad baseline observed during Hg(II) trace electrochemical detection on gold electrode in the presence of Cl<sup>-</sup> anions. The influence of Cl<sup>-</sup> concentration on the shape of the voltammograms was studied in the presence and in the absence of Bovine Serum Albumin (BSA) in order to bring out adsorption/desorption processes. On the basis of these experiments, and contrary to what has been proposed by several authors in the literature, it was proved that the broad baseline does not result from calomel (Hg<sub>2</sub>Cl<sub>2</sub>) formation but is rather related to an interaction between Cl<sup>-</sup> and polycrystalline Au electrode surface. The evolution of the shape of the baseline was also studied in the presence of other halide anions, namely F<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>. The latter two were found to induce a broad baseline similar to that recorded in the presence of Cl<sup>-</sup>. Finally, it was shown that BSA addition is not suitable for Hg(II) detection since it prevents Hg(0) deposition onto the electrode surface.

### Keywords:

Hg(II) trace electrochemical detection

Gold electrode reactivity

Calomel

Cl<sup>-</sup> adsorption

## 1. Introduction

Analysis of mercury (Hg) is of critical interest because this metal and its corresponding Hg(II) species, especially the methylmercury ones, are responsible for significant human health problems even at very low concentration [1]. This is mainly due to the successive chemical and biochemical transformations of Hg in natural media which lead to its bioaccumulation in living organisms [2]. Consequently, there is a dramatic need for highly sensitive, accurate and portable sensors to continuously monitor Hg in aquatic systems. In this context, electrochemistry provides an interesting alternative with respect to classical spectroscopic methods [3,4]. Because of the strong affinity of Hg for gold (Au), this latter is widely used as working electrode either as bulk [5,6], film [7,8], microdisk [9] or nanoparticle material [10,11], mainly for anodic stripping experiments. Many works have proved that operating in acidic medium in the presence of complexing anions such as Cl<sup>-</sup> enhanced the electrochemical response [6,12]. However, Hg(II) detection at low level on such electrodes is hampered by a broad, random baseline in the current–potential curves [10,12–14]. In several papers calomel formation has been proposed to be at the origin of this

broad baseline [10,12,14] on the basis of the works by the groups of van den Berg [13] and Compton [15]. However, this interpretation has to be considered with caution, since the group of Compton observed a well-defined anodic peak at 0.16 V vs. saturated calomel electrode (SCE) for Hg<sub>2</sub>Cl<sub>2</sub> oxidation and no significant evolution of the baseline on a Au microelectrode array [15] whereas the group of van den Berg only considered that calomel formation may have an influence on the background scan without providing further details [13]. The formation of calomel in chloride media containing Hg(II) has been also reported on Au film electrode by Okçu et al. [16]. Thus, the relationship between the broad baseline and calomel remains still unclear and gives rise to contradictory interpretations. Very recently, we reported an amperometric sensor for Hg(II) assay in chloride-containing media based on a Au nanoparticles-modified glassy carbon (AuNPs-GC) electrode, and also observed this broad baseline [17,18]. In order to improve the performances of our Hg(II) trace electrochemical sensor, we became interested in trying to better understand this phenomenon. In this work, we provide some basic voltammetric experiments which definitely clarify the origin of this broad baseline. Works have also been extended to other halide anions, i.e. F<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>.

## 2. Experimental

All the solutions were prepared using ultra-pure water (Milli-Q, Millipore, 18.2 MΩ cm). Stock solutions of 0.1 M NaNO<sub>3</sub> and 1 M

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NaCl, NaF, KBr and KI were prepared by dissolving the corresponding salts (Suprapur, Merck). A standard stock solution of  $4.99 \pm 0.01 \mu\text{M}$  Hg(II) was prepared by dilution of  $1001 \pm 2 \text{ mg L}^{-1}$   $\text{Hg}(\text{NO}_3)_2$  NIST standard solution (certiPUR, Merck), acidified to pH 2 with concentrated 65%  $\text{HNO}_3$  (Suprapur, Merck). 95%  $\text{H}_2\text{SO}_4$  (Normapur) and 30% HCl (Suprapur) were supplied by VWR Pro-labo and Merck respectively.  $1.2 \text{ g L}^{-1}$  Bovine Serum Albumin (BSA) solution was prepared by dissolving the corresponding amount of BSA (Sigma) in Milli-Q water (pH 6.8).

All the electrochemical experiments were performed at room temperature in a Teflon PFA three-electrode cell (Metrohm) using a Metrohm Autolab PGSTAT 128 N potentiostat interfaced to a laptop computer and controlled with NOVA 1.7 software package. A Metrohm Ag/AgCl/KCl 3 M electrode separated from the electrochemical cell by a Teflon PTFE capillary containing 0.1 M  $\text{NaNO}_3$  solution and terminated by a ceramic diaphragm (D type), and a Metrohm glassy carbon wire were used as reference and counter electrodes, respectively. All the potentials were referred to this reference. The working electrode was an Au rotating disk electrode from Radiometer (2 mm diameter,  $A = 3.14 \text{ mm}^2$ ). It was carefully polished successively by a 9  $\mu\text{m}$ , 5  $\mu\text{m}$ , 1  $\mu\text{m}$  and 0.3  $\mu\text{m}$  alumina slurry (Presi) on a cloth polishing pad for 5 min, 3 min, 2 min and 1 min, respectively. The electrode was then activated in 0.5 M  $\text{H}_2\text{SO}_4$  by running 20 scans between 0 and 1.6 V at a scan rate of  $100 \text{ mV s}^{-1}$ .

Prior to each measurement, solutions were deaerated by bubbling  $\text{N}_2$  for 10 min. Then a  $\text{N}_2$  atmosphere was maintained over the solution during the experiments.

Electrochemical measurements were performed using Square Wave Anodic Stripping Voltammetry (SWASV) in the same conditions as those previously reported [17,18]: preconcentration cathodic potential: 0 V for  $\text{Cl}^-$  and  $\text{F}^-$ ,  $-0.8 \text{ V}$  for  $\text{Br}^-$ , and  $-1.2 \text{ V}$  for  $\text{I}^-$ ; preconcentration time: 300 s; pulse amplitude: 25 mV; step amplitude: 5 mV; frequency: 200 Hz; anodic scan from 0 to 0.8 V for  $\text{Cl}^-$  and  $\text{F}^-$ , from  $-0.8 \text{ V}$  to 0.8 V for  $\text{Br}^-$  and from  $-1.2 \text{ V}$  to 0.8 V for  $\text{I}^-$ . For the experiments with varying halide concentration, the electrode was polished and activated between each new concentration.

### 3. Results and discussion

Fig. 1 reports the Square Wave Anodic Stripping Voltammograms (SWASVs) recorded on a polycrystalline Au disk electrode in 0.01 M HCl in the absence and in the presence of 10 nM Hg(II). The electrolytic conditions were adopted in accordance with both literature data [6,19] and our previous results dealing with Hg(II) trace electrochemical detection [17,18]. In the presence of Hg(II), a broad signal centered around 0.4 V was noticed together with a peak at 0.64 V, this latter being associated to Hg(0) reoxidation process [17,18]. In the absence of Hg(II), only the former anodic signal was observed, whose global current was slightly higher than that recorded in the presence of Hg(II). It should be noticed that this latter result was obtained using a freshly polished Au electrode which had never been in contact with Hg(II) solution. The shape of both curves is in accordance with our recent results recorded on AuNPs-GC electrode [17,18] and with previous works [10,12–14]. Many authors systematically invoked calomel formation to account for the broad baseline [10,12,14] on the basis of studies dealing with anodic characterization of Hg microelectrodes in the presence of  $\text{Cl}^-$  [20,21]. However, it is clear from the curves of Fig. 1 that the broad signal cannot be assigned to calomel since it was observed whatever Hg(II) was present or not in the solution. This is consistent with the works by Bonfil et al. who observed the same shape for the baseline recorded for Cu(II) and Hg(II) detection even in the absence of the subsequent metallic elements [22,23].

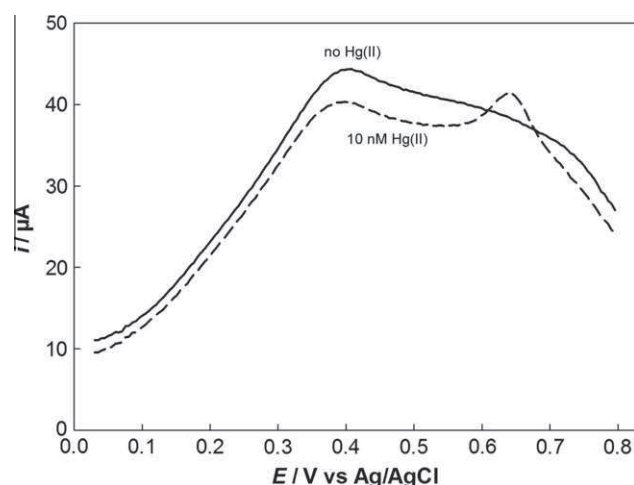
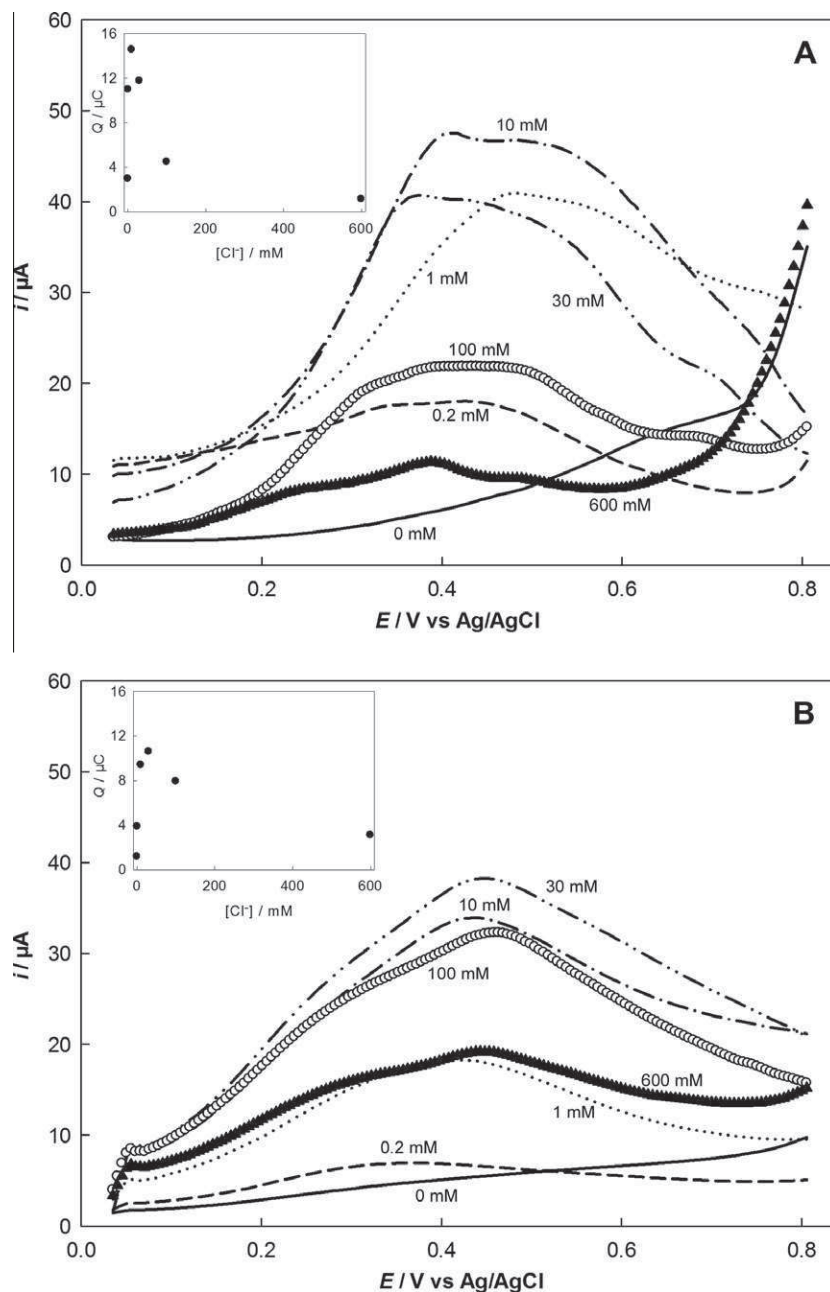


Fig. 1. SWASVs recorded on a Au disk electrode in 0.01 M HCl without (solid line) and with (dashed line) 10 nM Hg(II). Electrochemical parameters for SWASV are indicated in Section 2.

In order to get more information upon this phenomenon, several SWASVs were recorded on Au electrode in 0.1 M  $\text{NaNO}_3$  using various  $\text{Cl}^-$  concentrations (Fig. 2A). In the absence of  $\text{Cl}^-$  no signal was observed in the range from 0 to 0.5 V. Between 0.5 and 0.8 V, the current gradually increased, as the consequence of Au oxides formation which has been usually reported to occur in the potential range from 0.7 to 1.3 V [24,25]. On the contrary, in the presence of  $\text{Cl}^-$  a broad baseline was recorded between 0.1 and 0.8 V. This potential range is consistent with the one reported in several works for  $\text{Cl}^-$  adsorption on a Au electrode [26,27]. It was checked that a peak which corresponds to the formation of the  $\text{AuCl}_4^-$  complex ( $\log \beta_4 = 26$ ) was present at potentials higher than 0.8 V [28] (not shown). Thus, this latter may not be invoked to account for the broad baseline. When varying  $\text{Cl}^-$  from 0.2 to 600 mM, both peak current and charge associated to the broad baseline increased up to 10 mM  $\text{Cl}^-$  and then decreased for higher  $\text{Cl}^-$  concentrations (Fig. 2A). The plot of the charge consumed as a function of  $\text{Cl}^-$  concentration clearly shows two domains (Fig. 2A, inset). For  $\text{Cl}^-$  concentrations lower than 10 mM, the curve was almost linear, showing the strong interaction between  $\text{Cl}^-$  and Au, in agreement with literature data [29,30]. For  $\text{Cl}^-$  concentrations higher than 10 mM, the charge of the baseline gradually decreased. This trend may be attributed to the repulsive interactions between  $\text{Cl}^-$  ions which thwart the adsorption process. Replicates of measurements between 0 and 0.8 V at constant  $\text{Cl}^-$  concentration revealed decreasing and hardly repeatable peak currents with a relative standard deviation (RSD) around 11% ( $n = 3$ , not shown). This decrease suggests a progressive  $\text{Cl}^-$  adsorption process as reported by Salaun et al. [19], which induced a gradual change in the electronic structure of Au [27]. On the contrary, repeatable voltammograms were obtained when the Au electrode was activated in  $\text{H}_2\text{SO}_4$  between each curve, supporting the hypothesis of an adsorption process of  $\text{Cl}^-$  onto Au surface.

Similar experiments were performed using various concentrations from 0.2 to 100 mM of the other halide anions, namely  $\text{F}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ . In the case of  $\text{F}^-$ , no particular signal was observed on the SWASV whatever the halide concentration, in accordance with very weak adsorption process on Au, as previously reported by Magnussen [30].  $\text{Br}^-$  and  $\text{I}^-$  gave rise to a similar broad baseline to what was observed with  $\text{Cl}^-$ , although the corresponding potential shifted to more cathodic values in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  (not shown). The evolution of the broad baseline integration as a function of halide concentration for the three anions is shown in Fig. 3. The same trend upon concentration was observed in all three

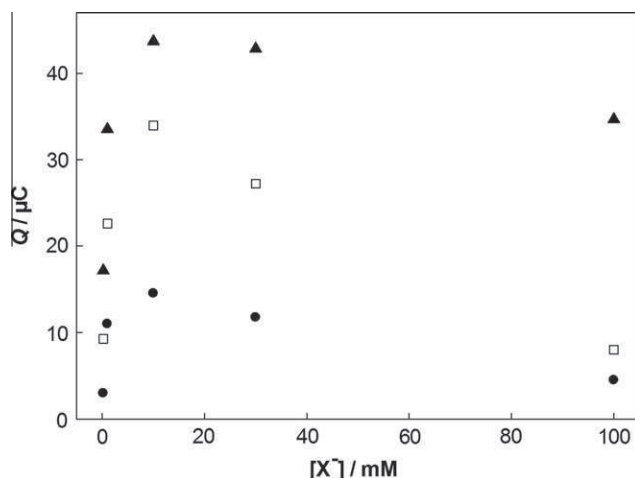


**Fig. 2.** SWASVs recorded on Au disk electrode in 0.1 M NaNO<sub>3</sub> containing various Cl<sup>-</sup> concentration: 0, 0.2, 1, 10, 30, 100 and 600 mM. Inset: charge consumed between 0.1 and 0.8 V as a function of Cl<sup>-</sup> concentration. (A) unmodified electrode; (B) electrode previously dipped in a 1.2 g L<sup>-1</sup> BSA solution for 30 min.

cases, and the global charge increased in the order  $Cl^- < Br^- < I^-$ . This is consistent with the evolution of the strength of ionic adsorption on Au reported by Lipkowski et al. [27].

Another set of experiments was performed using various Cl<sup>-</sup> concentrations on a freshly polished and activated Au electrode which was dipped for 30 min in a 1.2 g L<sup>-1</sup> BSA aqueous solution prior to electrochemical measurements. BSA is a high molecular weight protein known to adsorb onto surfaces and thus prevents further sorption process [31]. Fig. 2B shows the SWASVs obtained using the same Cl<sup>-</sup> concentrations range as in Fig. 2A. A broad signal around 0.35 V was also recorded, and the corresponding integration dependence upon Cl<sup>-</sup> concentration was found to follow roughly the same trend than while operating in the absence of BSA (Fig. 2B, inset). However, it has to be noticed that both peak current and charge values are significantly lower in this case for

Cl<sup>-</sup> concentrations lower than 100 mM. This is consistent with a Cl<sup>-</sup> adsorption process hindered by the presence of BSA onto the Au electrode surface. The contrary was observed for Cl<sup>-</sup> concentrations higher than 100 mM because BSA decreased the repulsive interactions between Cl<sup>-</sup> adatoms during the adsorption process. Finally, and contrary to what was observed while operating in the absence of BSA, successive voltammograms recorded for a same Cl<sup>-</sup> amount afforded repeatable peak currents (RSD = 1%,  $n = 3$ ) without further electrode treatment. Thus, the use of BSA allowed a control, to some extent, of Cl<sup>-</sup> adsorption, by preventing the formation of an adlayer of Cl<sup>-</sup> ions onto the Au electrode. This latter phenomenon was thus proved to be at the origin of the broad baseline. The difference observed between the two curves on Fig. 1 can thus be explained and the role of calomel rationalized. The broad signal is actually due to gradual Cl<sup>-</sup> adsorption onto the



**Fig. 3.** Comparison of the evolution of the charge consumed for the broad peak as a function of halide concentration for  $\text{Cl}^-$  (●),  $\text{Br}^-$  (□) and  $\text{I}^-$  (▲). The charge was integrated between 0.1 and 0.8 V for  $\text{Cl}^-$ , between  $-0.8$  and 0.4 V for  $\text{Br}^-$ , and between  $-1.2$  and 0 V for  $\text{I}^-$ .

Au electrode. When Hg(II) was present in solution, Hg(0) deposition occurred during the preconcentration step at 0 V, thus partially preventing  $\text{Cl}^-$  adsorption onto Au surface, and resulting in a slightly lower broad peak. Finally, it was checked that the use of BSA also prevented Hg(0) deposition (not shown), making this solution unsuitable for Hg(II) trace analysis. An alternative could be the use of a desorption step in the SWASV procedure, as suggested by Salaün et al. [19]. These authors noticed that progressive  $\text{Cl}^-$  adsorption underwent a gradual decrease in the height of Hg(0) reoxidation peak, but without relating this observation to the baseline.

#### 4. Conclusion

In this work, voltammetric experiments were used in order to identify the broad baseline observed during the anodic stripping step of Hg(II) trace electrochemical detection on Au electrode. In opposition with several previous papers, these experiments definitely proved that this broad baseline is not due to calomel formation, since this phenomenon was also observed in the absence of Hg(II) in the solution. It is actually due to the formation of an adlayer of  $\text{Cl}^-$  anions onto the electrode surface. Moreover, a similar broad baseline was observed while operating in the presence of other halide anions, namely  $\text{Br}^-$  and  $\text{I}^-$ , and in the absence of Hg(II). Coating the Au electrode with BSA allowed a better control of  $\text{Cl}^-$  interaction with Au surface, but also prevented Hg(0) deposition as well. Thus, the use of a desorption potential during the SWASV

sequence procedure may be a suitable strategy for optimizing Hg(II) trace detection.

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