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Comparison of sensitivity constants of an electrochemical quartz crystal microbalance determined by potentiostatic deposition of Tl, Pb, Ag and Cu films

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ABSTRACT

In this paper, the sensitivity constant (C_f) of an electrochemical quartz crystal microbalance (EQCM) is determined through a calibration procedure using potentiostatic electrodeposition of Tl, Pb, Ag and Cu films onto a gold electrode. In the literature some researchers have proposed the use for example of thallium or lead films on gold electrodes to obtain the sensitivity constant for calibration and to keep these electrodes reusable. However, it is not clear if with these metals the C_f values are reliable, given the fact that generally silver or Cu films are employed for this purpose. One of the most significant results reached in this work was that C_f values obtained with Tl and Pb films are dependent on both the imposed potential and the thickness of deposits. In addition, the C_f values obtained with these metals were found to be very close to the theoretical value as those obtained with silver films.

KEYWORDS: thallium, sensitivity constant, potentiostatic deposition, lead, EQCM

1. INTRODUCTION

The quartz crystal microbalance (QCM) is a tool that has been extensively used in different domains to measure mass variations (Δm) falling in the order of nanograms [1-4]. When the QCM is coupled with classical electrochemical techniques, such as voltammetry, chronoamperometry etc., to measure mass variations at the interface of an electronic conductor and an ionic conductor, electrochemical piezoelectric microgravimetry is obtained and the QCM becomes electrochemical quartz crystal microbalance (EQCM) [5-8].

This is possible thanks to the electrodes used in this type of experiments, which are supported on a thin quartz wafer. The principle of this technique has been explained extensively by different authors and we suggest seeing references 7 or 8 for more details.

Herein, we will only mention that when a wafer of an acentric material, such as quartz, covered by a thin metal layer on both sides, is placed in an electric field whose polarity changes periodically, an acoustic wave develops and displaces perpendicularly through the surface of this wafer (resonator) characterized by a resonance frequency (f_o). If for any reason, a material is deposited on one of the sides of this wafer, the resonance frequency will change to a new value giving rise to a variation of frequency ($\Delta f(m) = f - f_o$) proportional to the change of mass. In electrochemistry, one side of the resonator may be used as electrode, which allows the total frequency variation, Δf, to include, in addition to the mass variations, also other contributions such as frequency variation due to temperature, pressure

or roughness. However, these latter terms may be made irrelevant with respect to the value of $\Delta f(m)$, so that the total frequency variation is equal to frequency variations resulting from mass changes only produced on the resonator. It is just in this situation that *Sauerbrey* expression may be considered [9] (Equation 1) in order to obtain information from experiments made with EQCM.

$$\Delta f = -C_f \Delta m \qquad (1)$$

It is important to mention that this only holds if the ideal layer of foreign mass is strongly coupled to the resonator. Furthermore, to keep the thickness measurements within a reasonable accuracy, the maximum frequency shift allowed by this method is limited to only about 2% of f_o [10]. The mass sensitivity of an EQCM, for example using a quartz crystal of $f_o = 9$ MHz, is 0.1834 Hz cm^2 ng^{-1}, which is approximately 320 times higher than that of an electronic fine-balance with a sensitivity of 0.1 μg.

In the case of the film deposited onto the resonator that meets the requirements of *Sauerbrey's* equation, it is possible to obtain quantitative data if the sensitivity constant C_f is known (Equation 2).

$$C_f = \left(\frac{2f_o^2}{A_{piezo} \sqrt{\mu_c \rho_c}} \right) \qquad (2)$$

This constant includes terms dependent on the nature and type of the quartz cut as for example the density of the quartz ($\rho_q = 2.648$ g cm^{-3}), the shear modulus ($\mu_q = 2.947 \times 10^{11}$ g cm^{-1} s^{-2}) and the piezoelectrical active area (A_{piezo}). Calibration of an EQCM is required to accurately convert measured frequency changes to mass changes. Due to this the sensitivity constant must be determined quickly and precisely.

There are abundant publications [5, 11-17] reporting some procedures to determine the value of C_f by using a calibration process. According to these publications, the value of C_f can be determined by the formation of a metallic deposit onto the resonator obtained potentiostatically [5], galvanostatically [11, 12] or by using voltammetry [15]. Silver [5, 11, 12, 15], copper [16, 17] or more recently lead [18] are some of the most

commonly used metals for obtaining C_f, however, especially the preparation processes of the Ag and Cu deposits have innumerable inconveniences for example, the formation of surface alloys between the substrate and the silver or copper film, making them useless in further experiments, or the production of intermediary species during film preparation on the substrate. Hence, other metals and procedures have been proposed for this purpose, for example Pb [18]. Additionally, when the same metal is used to obtain C_f, the values obtained are dependent on the preparation method of film. For example, Donjuan-Medrano *et al.* [19, 20] have proposed the use of a thallium film to obtain C_f and to evade the inconveniences previously mentioned. It is important to mention that one of the advantages of using thallium deposits to obtain sensitivity constant C_f is that the electrodes employed can be later reused without significant modifications of their surface [21, 22], because thallium forms no surface alloys with gold or silver substrates, which is not the case when using Pb, Cu and Ag deposits, known to form alloys with the substrate [23-25] that modify chemical composition and roughness to such extent that these resonators cannot be reused.

In the present paper the C_f is obtained using potentiostatically prepared Ag, Cu, Pb and Tl films that are further compared with each other.

2. EXPERIMENTAL METHODOLOGY

2.1. Chemicals and solutions

All chemicals (Tl$_2$CO$_3$, NaClO$_4$, H$_2$SO$_4$ AgNO$_3$, Pb(NO$_3$)$_2$, CuSO$_4$, etc.) were analytical grade (Fermont) and used as received. Water used in solution preparation was purified in a Millipore system (> 18 MΩ cm).

Experimental condition solutions of thallium were selected using the Pourbaix's diagram in a medium without complex species. According to this, the metallic ion would only exist in the wide pH range (pH -2 to 6) as hydrated species. Thus, the reaction of thallium in this pH range is

$$Tl^+ + e \leftrightarrows Tl \qquad (3)$$

In agreement with this diagram, at pH values between -2 and 2 the reaction (4) is promoted thermodynamically

$$2H^+ + 2e \leftrightarrows H_2 \uparrow \qquad (4)$$

so the formation of H_2 can take place concomitantly with the reduction by the Tl^+ ion.

Therefore, the solution to be used in this work must meet two minimum conditions:

a) Not to have complex species in the bulk, and b) To have a pH value less acidic than 2 in order to eliminate the reaction 4 as much as possible.

For that purpose, a 1 M $NaClO_4$ solution was used as supporting electrolyte and the pH value 3 was selected using $HClO_4$. In this case the ion concentrations of different metals were 1 mM for thallium, copper and lead and 1.5 mM for silver.

Finally, prior to each experiment the solution was deaerated with high purity nitrogen and measurements were performed three to five times per each metal.

2.2. Electrodes

Planar AT-cut quartz crystals (Seiko) having a resonant frequency of ~9 MHz in air were used as working electrodes in all experiments. The Au working electrode used in the EQCM was scanned in 0.1 M H_2SO_4 or $HClO_4$ solutions until a characteristic cyclic voltammogram (CV) for Au polycrystalline electrode is obtained. The Au surface roughness factor, R, was determined through charge density associated with AuO monolayer subtracted by the double-layer charge resulting in 1.12.

A platinum sheet was used as the counter electrode, and an Ag│AgCl (3 M KCl) electrode as the reference electrode, against which all potentials were measured and reported.

2.3. Apparatus

Electrochemical experiments were carried out using an EG&G potentiostat-galvanostat model 273A coupled to a QCM EG&G-Seiko model 910.

2.4. Equations involved in the determination of C_f

The electrochemical reaction involved in the electrodeposition of each metal can be represented by

$$M^{n+} + ne \rightarrow M \qquad (5)$$

Using Faraday's second law:

$$\Delta Q = \left(\frac{nF}{M_W} \right) \Delta M \qquad (6)$$

where ΔQ (C/cm^2) is the charge density measured from the electrochemical response; ΔM (grams/cm^{-2}) corresponds to the mass change of thallium on the Au electrode during electrodeposition process; n is the number of electrons transferred in the electrodeposition reaction; M_W (g/mol) is the molar mass of M, and F (C/mol) is the Faraday constant.

By combining the *Sauerbrey's* equation (Eq. 1) with the above formula, we obtain the following relation that is used in the experimental determination of the calibration constant for the EQCM:

$$\Delta f = -\left(\frac{C_f M_W}{nF} \right) \Delta Q \qquad (7)$$

As a consequence, the determination of C_f values consists in preparing ΔQ curves as a function of Δf, where ΔQ is generated from the electrochemical responses obtained at constant potential.

3. RESULTS AND DISCUSSION

3.1. Selection of the potential range

The potential interval to prepare deposits of each metal was selected using its voltammetric response obtained in the solution of M^{n+}. Figure 1 shows the response obtained for the 1 mM Tl^+ in 1 M $NaClO_4$ (pH 3.5) solution at the scan rate of 10 mV s^{-1}.

According to Figure 1a, at the potential scanned from +400 mV to -700 mV, the current obtained is very low, but there are two current peaks at about -100 mV associated with underpotential deposition (UPD) of thallium on the gold substrate [26, 27]. It is noteworthy that during this process, thallium forms a monolayer on the gold substrate which tends to compact as the potential approaches the reversible potential, E_r. Additionally, as the potential is swept from -700 mV towards more negative values, the response obtained shows a cathodic peak of the current between
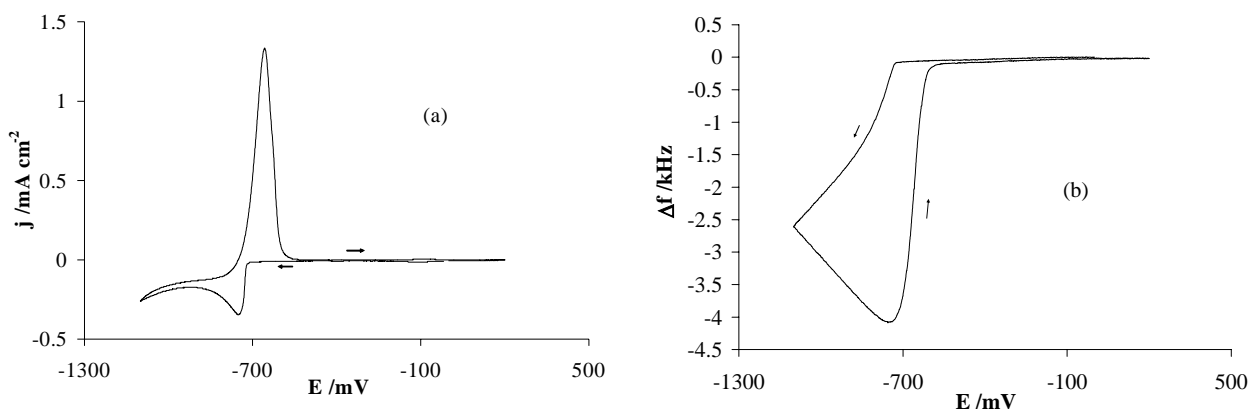
Figure 1. Simultaneously recorded at the Au/quartz electrode (a) voltammetric curves and (b) frequency change *vs.* potential curves for the 1 mM Tl^+, in 1 M $NaClO_4$ (pH 3.0) solution at the potential scan rate 10 mV s^{-1}.

-729 mV and -745 mV. This peak is associated with the process of bulk deposit formation of Tl on the Tl UPD and the magnitude of these current peaks is more negative as the scan rate increases. In this same potential region, there is an anodic peak between -729 mV and -700 mV associated with the process of dissolution of bulk thallium deposition, which is also dependant upon the scan rate.

On the other hand, the analysis of frequency variation (Δf) curve as a function of the potential explored (Figure 1b) offers more information on the formation process of thallium films. For example, the frequency changes observed during the scan towards negative potentials are very small ranging between +400 mV and -700 mV. These changes of frequency reach values close to 80 Hz and are associated with thallium UPD process on the electrode [27]. It is proper to mention that as the potential is swept towards values more negative than -700 mV, Δf decreases (the mass increases), but this decrease is not performed linearly, which seems to indicate that during bulk thallium deposition there are mechanical tensions resulting from the differences in atomic sizes (a_{Tl} = 1.48 Å, a_{Au} = 1.50 Å) that remain until the film thickness reaches values close to 1.5 kHz.

If the potential is scanned up to -1 V the frequency response reaches a minimum (Δf_{min}, film thickness) that depends upon the scan rate. Thus, if the scan rate is 10 mV s^{-1}, the Δf_{min} is almost -4 kHz. Finally, if the scan is returned to

**Table 1.** Potential range of each metal used to obtain C_f and their reversible potential, E_r.

Metal	E/mV	E_r/mV
Thallium	-720 a -900	-739
Lead	-470 a -675	-411
Copper	-18 a -250	+53
Silver	300 a 400	+433

initial potential, then the frequency returns to its initial value as well.

In accordance with this information it is possible to prepare the thallium deposit potentiostatically using a potential between -720 mV and -900 mV. On the basis of similar results obtained with different metal ion solutions, it was possible to select potential regions in which metallic deposits were prepared. Table 1 shows the potential range for the other metals and their reversible potential, E_r, obtained using the Nernst´s equation.

3.2. Obtaining the sensitivity constant C_f

The use of potentiostatic method to obtain sensitivity constant C_f implies imposing a potential step for some time and simultaneously recording two responses: a transient current-time and a change of frequency in terms of a time curve. Since this procedure is the same for all metals it will only be shown for thallium deposition onto gold substrate.
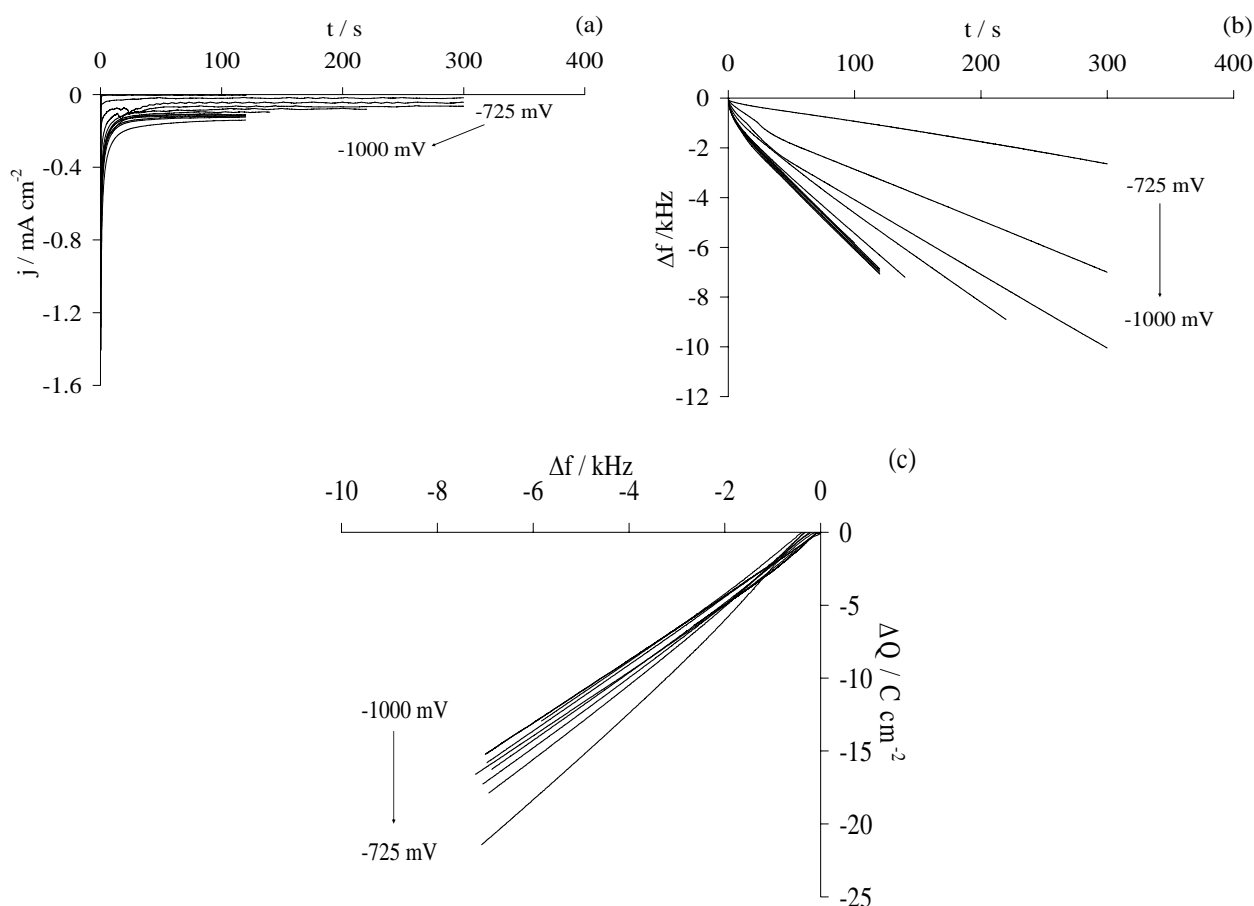
Figure 2. (a) Transients current-time responses (j *vs* t), (b) concurrent responses of change of frequency (Δf) in terms of the time and (c) charge density *vs.* Δf curves for the 1 mM Tl$^+$ in 1 M NaClO$_4$ (pH 3.5) solution obtained at the potential constant between -725 mV and -1000 mV.

Figure 2 shows a family of different transients (Figure 2a) and the corresponding frequency responses, Δf (Figure 2b) for thallium deposition on the Au electrode. Importantly, the time for each experiment was selected so that the obtained films had the same thickness for all the potentials imposed. In addition, Figure 2c shows the Δf-ΔQ curves used to obtain the sensitivity constant (see expression 7).

In Figure 2a the cathodic transients can be divided into two time intervals: In the first time interval, at the beginning of experiences, the potential step initiates an instantaneous current (j) and immediately decays exponentially as a result of the double-layer charging and the reduction of Tl$^+$ to Tl. In fact, the current decays smoothly from an expected value of ∞ at t ~ 0 and approaches zero

with increasing time as described by the Cottrell equation for a planar electrode. In accordance with this equation, the current is inversely proportional to the square root of time.

In the second time interval the current is approximately constant. This behavior can be due to the growth of independent nuclei and the process of formation of a massive deposit. If the time step is extended then the current maintains its value and the deposit thickness increases due to the charge (j×t = Q) increases.

As far as change of frequency-time responses are concerned (Figure 2b) their behaviors are observed to be linear, but a more careful analysis reveals that they have two slopes dependent upon time intervals. For example, there is one slope appearing at times shorter than 20 s and another at

times above 20 s. The first slope appears at values inferior to 1 kHz in which the first stages of thallium film growth onto the gold substrate take place. It is important to remember that the underpotential deposition of thallium onto the substrate occurs in these stages and as has been mentioned, the monolayer presents strong mechanical tension resulting from the differences in atomic sizes (a_{Tl} = 1.48 Å, a_{Au} = 1.50 Å) that remain until the film thickness reaches values close to 1.5 kHz or 2 kHz.

The second slope seems to be associated to the processes of bulk thallium deposition showing that the thallium deposit thickness is time dependent.

These characteristics of the responses obtained during the formation of thallium films have an effect on the sensitivity constant values. As can be seen in Figure 2c, the charge-density curves as a function of change of frequency (ΔQ *vs* Δf) show two slopes too. As has been mentioned, the first slope is associated with the initial stages of film formation, for which reason this section of curves was not taken into account for obtaining C_f.

According to Donjuan-Medrano *et al.* [20] and Vetankhah *et al.* [15] the sensitivity constant may present different behaviours depending on the thickness of a film deposited onto the electrode.

Consequently C_f was obtained as a function of thickness (l_f) at different potential steps considering the expression

$$l_f = -\frac{C_f}{\rho_f} \times \Delta f \qquad (8)$$

where ρ_f corresponds to density of the film deposited onto the resonator.

In agreement with this expression, the thickness l_f is proportional to $-\Delta f$ if C_f is known; however, in this case the curves C_f can be prepared as a function of $-\Delta f$ or $|\Delta f|$, instead of C_f *vs* l_f, Figure 3.

According to this figure, the C_f depends on both the potential imposed and the thickness of thallium films.

If all plots of C_f as a function of potential are considered to analyze only the effect of film thickness, it was found that for thicker films the values of C_f are farther from the theoretical value (1.81 x 10^8 g^{-1} Hz cm^2). This behavior of C_f values is associated with the morphology of thallium films obtained by using this methodology. Something similar has already been proposed by Lin *et al.* [28]. This explanation implies that when the deposit thickness is superior to 4 kHz, its roughness is superior too and the real active area (electrochemically active area) must be taken into
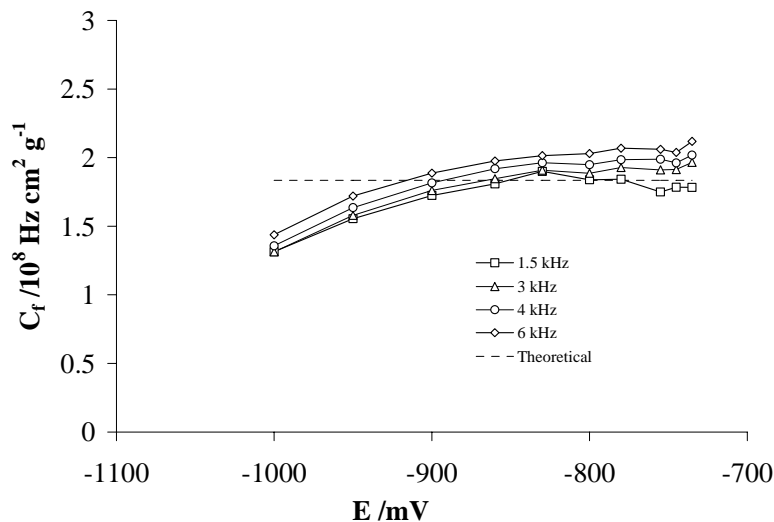
Figure 3. Sensitivity constant values C_f as a function of the thicknesses ($-\Delta f$) for Tl deposition on Au electrode in 1 M aqueous $NaClO_4$ + 1 mM Tl^+ (pH 3.5) at various constant potentials.

account to obtain C_f, because the charge is consumed over the entire area of the working electrode.

As far as the potential is concerned, for example, in the curve at 3 kHz, the C_f constant tends to remain almost the same with a value of 1.7844×10^8 g^{-1} Hz cm^2, when the potential step is between -725 mV and -875 mV, which implies that this value differ from the theoretical value by +3% (Relative Error% = 100 [C_f(experimental) - C_f(theoretical)]/C_f(theoretical)). Additionally, if the potential step is more negative than -875 mV then the value of C_f is smaller than the theoretical value (1.899×10^8 g^{-1} Hz cm^2) with a relative error of -4%, which implies high sensitivity of the resonator.

We assume that this behavior of C_f as a function of potential is related to morphologic proprieties of the films because the potential imposed is localized in the region of a mixed control [29, 30], that is to say, the deposit is produced by controlling the transport of thallium ions towards the substrate. In these experimental conditions the roughness of films obtained is very important and these deposits do not satisfy the requirements of the Sauerbrey´s expression. Furthermore, the current flowing at potentials more negative than -840 mV is a result of two processes: reduction of

Tl^+ ion and of H^+ ion. This can be seen if the faradic efficiency (fe) is calculated with the expression

$$fe = \frac{Q_a}{|Q_c|} \qquad (9)$$

where Q_a and Q_c are the anodic and cathodic charges respectively determined from voltammograms (see Figure 1a).

This parameter is 1.6 when the scan rate (v) is 10 mV s^{-1} using Q_a = 0.0045 C cm^{-2} and $|Q_c|$ = 0.00721 C cm^{-2}.

In this case, it is possible to observe that Qa is inferior to Qc due to another process taking place at the same time of the process of thallium deposit formation. Said process is undoubtedly the consequence of the generation of hydrogen [15]. In order to better distinguish this effect the curves j-E were prepared from Δf response and compared to directly obtained j-E curve, Figure 4.

As can be seen, both curves are superposed in approximately all ranges of potential except in the zone where the potential is more negative (more negative than -875 mV). It is precisely in this region where the hydrogen is produced and the anodic charge increases. This effect is explained if it is considered that the reaction 4 is produced at
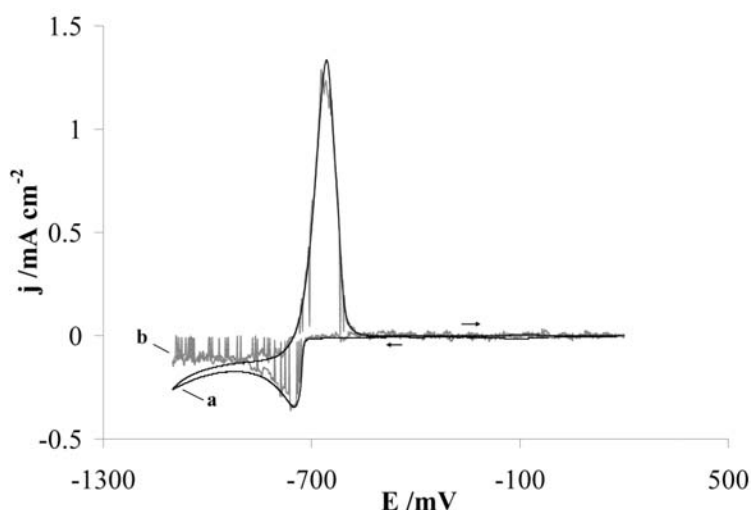
Figure 4. Responses j-E obtained directly in the experiment (a) and those obtained from corresponding quartz-crystal frequency changes (b) at for Tl deposition on and stripping from Au electrode in 1 M $HClO_4$ + 1 mM Tl^+ (pH 3.5) solution at a scan rate of 10 mV s^{-1}. See Figure 1.

overpotential onto the thallium film deposited on the gold substrate due to the fact that the exchange density current j_o associated with this reaction is inferior to 10^{-10} A cm^{-2} [20].

It is important to mention that the relative errors of C_f in this potential region can be between +2.89 and -28.46%.

3.3. Comparison of C_f values obtained in different metals

Figure 5 and Table 2 show the C_f values obtained using the four metals. It is important to mention that in the case of Tl, C_f values obtained at 1.5 kHz were plotted, whereas in the case of the other three metals, the effect of deposit thickness was not studied, and the values were rather calculated following the procedures proposed by different authors [5, 12-17].

In the first place, the C_f values obtained with Tl, Pb and Ag films shown in Figure 5 have almost the same behaviour; i.e., at the potentials close to E_r the relative error of sensitivity constant is low. On the contrary, when the potential is much farther than E_r, the relative errors of C_f values are very high.

In addition, these curves also show that C_f values obtained with a copper film are dispersed with respect to the theoretical value and their relative

errors are very high. It is curious that the potential interval in which the values C_f are closer to the theoretical value is larger with Tl (125 mV) than with silver (100 mV) or Pb films (75 mV). On the other hand, the C_f values shown in table 2 allow establishing that the behaviour of relative errors of C_f obtained with Tl and Ag films are very similar because these values fall between -0.2 and +4.6, and -0.03 and +3.2, respectively.

All these characteristics result from the very similar nature of the Tl and Ag films; i.e., they are uniformly distributed throughout the entire electrode surface as well as rigidly linked to it [17, 31].

Additionally, the C_f values having lower dispersion are those obtained with silver (1.884 x 10^{-8} g^{-1} Hz cm^{-2} at 1.775 x 10^{-8} g^{-1} Hz cm^{-2}) and lead (1.8094 x 10^{-8} g^{-1} Hz cm^{-2} at 1.7370 x 10^{-8} g^{-1} Hz cm^{-2}) with relative errors ranging between -2.7% and +3.2%, and +1.33% and +5.28% respectively. On the contrary, those having greater dispersion are obtained with copper (2.125 x 10^{-8} g^{-1} Hz cm^{-2} at 1.667 x 10^{-8} g^{-1} Hz cm^{-2}) with the errors from -15.9% to +9.1%. It is proper to mention that the values of sensitivity constants obtained with thallium and lead, are between those of silver and copper. In particular, constants obtained with thallium present a similar dispersion to that of
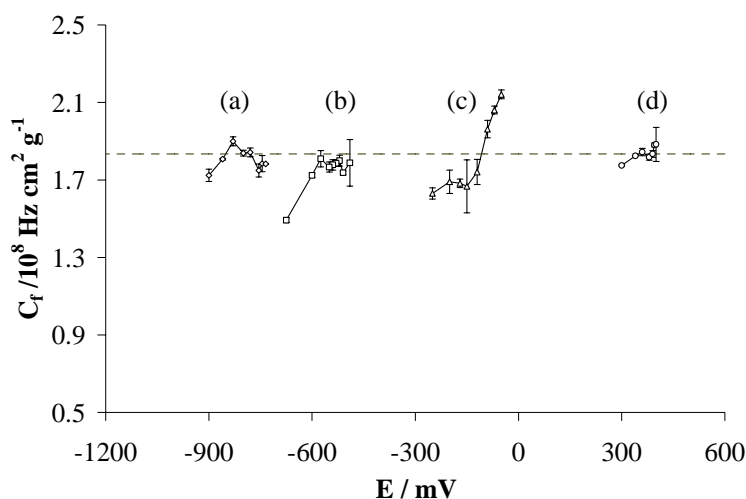
Figure 5. Curves of sensitivity constant (C_f) as a function of the potential for the different metals. (a) Thallium, (b) lead, (c) copper and (d) silver. Discontinuous line indicates the theoretical value of C_f obtained using equation 2.

Table 2. C_f values obtained for the four metals used. $^a C_f/10^8$ g^{-1} Hz cm^2.

| | Tl | | | Pb | | | Cu | | | Ag | |
E /mV	C_f^a	% Error	E /mV	C_f^a	% Error	E /mV	C_f^a	% Error	E /mV	C_f^a	% Error
-860	1.8078	1.4122	-490	1.7886	2.4659	-50	2.1251	-15.8802	300	1.7752	3.2008
-830	1.8994	-3.5730	-510	1.7370	5.2826	-90	2.0609	-12.3828	340	1.8246	0.5072
-800	1.8382	-0.2370	-520	1.7998	1.8584	-120	1.9627	-7.0230	360	1.8445	-0.5792
-780	1.8421	-0.4512	-530	1.7865	2.5846	-150	1.7408	5.0745	380	1.8178	0.8756
-755	1.7488	4.6363	-540	1.7777	3.0609	-170	1.6672	9.0897	390	1.8346	-0.0397
-745	1.7844	2.6976	-550	1.7669	3.6490	-200	1.6830	8.2241	395	1.8805	-2.5426
-735	1.7827	2.7911	-575	1.8094	1.3335	-250	1.6906	7.8098	400	1.8835	-2.7080

silver (1.899×10^{-8} g^{-1} Hz cm^{-2} at 1.747×10^{-8} g^{-1} Hz cm^{-2}) with errors ranging from -3.6% to +4.6%; whereas the dispersion in those obtained using lead, is greater than that achieved with thallium (1.809×10^{-8} g^{-1} Hz cm^{-2} at 1.737×10^{-8} g^{-1} Hz cm^{-2}) with errors from +1.33% to +5.3%.

CONCLUSIONS

In this work, the sensitivity constant (C_f) of an electrochemical quartz crystal microbalance is obtained by potentiostatic deposition using Tl, Pb, Ag and Cu films and gold electrodes.

One of the most significant results is that the C_f values obtained with Tl or Pb deposits show a similar dispersion, which is however lower than that of the values obtained with copper. In particular, the constants obtained with thallium deposits have relative errors similar to those obtained with silver ranging between 0% and 4%. Additionally, the potential interval in which a reliable value of C_f could be obtained by voltammetry is broader when using deposits of thallium than of other metals.

In agreement with these results, the thallium and lead films may be used to obtain C_f of an EQCM at experimental conditions well defined in this work.

Finally, it is important to mention that even though the thallium and lead are dangerous metals, as many other materials used in laboratory analysis, we believe that the user should choose one of these metals to obtain the sensitivity constant C_f very similar to actual C_f in order to be able to reuse the resonators without significant modifications of their surface or continuing to use Ag or Cu films for this purpose.

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