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Parameters affecting the determination of mercury by anodic stripping voltammetry using a gold electrode

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Abstract

The electrochemical determination of aqueous Hg(II) by anodic stripping voltammetry (ASV) at a solid gold electrode is described. The aim of this work is to optimise all factors that can influence this determination. Potential wave forms (linear sweep, differential pulse, square wave), potential scan parameters, deposition time, deposition potential and surface cleaning procedures were examined for their effect on the mercury peak shape and intensity. Five supporting electrolytes were tested. The best responses were obtained with square wave potential wave form and diluted HCl as supporting electrolyte. Electrochemical and mechanical surface cleaning, aimed at removing the amount of mercury deposited onto the gold surface, were necessary for obtaining a good performance of the electrode. Response linearity, repeatability, accuracy and detection limit were also evaluated.

Keywords: Mercury; Anodic stripping voltammetry; Gold electrode; Supporting electrolyte; Wave form

1. Introduction

The determination of metals at trace and ultratrace levels is an important issue in environmental and clinical sciences, owing to their potential toxicity at concentrations above certain threshold limits. Much attention is devoted to mercury, which is particularly harmful even at low concentrations: strict legislation limits are imposed in many countries for its concentration in all environmental compartments, e.g. waters, soils and organisms [1].

The analytical techniques preferred for mercury quantification are cold vapour atomic absorption spectrometry (CV-AAS) [2], cold vapour atomic fluorescence spectrometry (CV-AFS) [3], inductively coupled plasma mass spectrometry (ICP-MS) [4] and, for relatively high concentrations, inductively coupled plasma atomic emission spectrometry (ICP-AES) [5]. Several chromatographic techniques coupled with spectrometric methods have also been used for mercury speciation [6, 7]. Among these, CV-AFS procedure is the preferred detection method due to its sensitivity. All these techniques require expensive and sophisticated instrumentation and/or the use of specific instruments (which cannot be applied to the determination of other analytes), in combination with complicated sample preparation processes [8]. Stripping electrochemical methods represent an interesting alternative for mercury determination owing to their sensitivity, versatility and low costs. The recommendation of the US Environmental Protection Agency (EPA) for the adoption of stripping analysis for the quantification of heavy metals as mercury [9] is a very representative example of this application. Electroanalytical techniques for the detection of aqueous mercury, either alone or in conjunction with such emerging technologies as piezoelectric sensors, were utilized for the development of sensors capable of remote quantification of mercury in the environment [10]. A number of papers were devoted to the determination of mercury by anodic stripping voltammetry (ASV) at different solid electrodes [e.g. 11

12]. Gold was found to be the best electrode material for the determination of mercury by ASV, with conventional [13], film- [14, 15] and micro-[16, 17] electrodes. Also stripping chronopotentiometry at a gold wire microelectrode was adopted for trace measurements of mercury [18]. One reason for the use of gold is its high affinity for mercury, which enhances the preconcentration effect.

The main disadvantage of gold electrodes is the well known phenomenon of structural changes of their surface, caused by amalgam formation, and the time-consuming cleaning treatments that are needed to achieve reproducibility [19].

Many parameters influence the analytical signal of mercury and we did not find in literature a paper reporting a complete study of their effect on the determination of mercury with gold electrodes. Moreover, the information about the optimal working conditions and the electrode performance is heterogeneous and sometimes discordant. For these reasons, in the present study, the use of a solid Au electrode for Hg(II) determination by ASV was investigated in terms of the parameters that normally can influence the analytical response. The shapes and intensities of the mercury peak in five supporting electrolytes were compared. The effects of different potential wave forms, namely linear scan (LS), differential pulse (DP) and square wave (SW), scan parameters (amplitude, frequency, step potential, interval time, modulation time, modulation amplitude) and of deposition time and potential were examined. The linearity, repeatability, detection limit and accuracy of the method were determined. The possible interference of As(V), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Mn(II), Ni(II), Pb(II) and Se(IV) was evaluated and compared with some data in literature [1, 14, 19].

The findings of this study can be useful for analysts in order to evaluate the real potentialities of the gold electrode and to choose the best conditions for the determination of mercury by ASV.

2. Experimental

2.1. Apparatus and Reagents

Voltammetric analyses were performed with a PGSTAT 10 potentiostat (Eco Chemie, Utrecht, The Netherlands) coupled to a 663 VA Metrohm (Herisau, Switzerland) stand, equipped with a rotating solid gold electrode as working electrode, a Ag/AgCl reference electrode and a glassy carbon counter electrode. The analyzer was interfaced to a personal computer. High purity water (HPW) obtained from a Milli-Q (Millipore, Bedford, MA, USA) apparatus was used throughout. Analytical grade reagents were used. In particular a 1000 mg/l standard solution of mercury was prepared from HgCl₂ in 0.012 M HCl. More diluted Hg(II) standard solutions were prepared from the concentrated standards in the desired supporting electrolytes. HNO₃ and HCl were obtained by sub-boiling distillation in a quartz still.

2.2. Procedures

10 ml test solutions of supporting electrolyte were delivered into the voltammetric cell. After 120 s of deposition a voltammetric scan was performed. Initially, the scan parameters were: i) for SWV: frequency 100 Hz, step potential 0.002 V, amplitude 0.02 V; ii) for DPV: modulation amplitude 0.05 V, modulation time 0.05 ms, interval time 0.3 ms, step potential 0.002 V; iii) for LSV: step potential 0.002 V, interval time 0.30 s. Initial and final potentials were 0 V and 0.80 V respectively.

For the value of the scan parameters after optimization, refer to section 3.3.

After recording the voltammogram of the blank, aliquots of Hg(II) were added and the corresponding signals were recorded.

A cell containing 50 µg/l of Hg(II) was utilized to investigate the effects of the different parameters on the signal of mercury.

The detection limit was estimated as three times the standard deviation of the blank signal.

All experiments were performed in triplicate.

3. Results and Discussion

The voltammetric behaviour of Hg(II) was investigated in different supporting electrolytes and in different conditions of analysis.

3.1. Preliminary considerations

A brand-new gold electrode displays an ill-defined anodic stripping voltammogram for mercury. In order to overcome this drawback the electrode was dipped into a solution composed by 10 mM HNO₃ and 10 mM NaCl and activated by applying a potential of 0.90 V for 60 s between the working electrode and the reference electrode. The activation procedure applied is identical to that used by Bonfil [19]. This simple one-minute electrochemical pre-treatment was found to be of utmost importance [20], as can be seen by comparing the anodic stripping voltammograms of 50 µg/l of mercury in HCl before and after activation (Fig. 1).

Fig. 1. Anodic stripping voltammograms of 50 µg/l of Hg(II) in HCl using SW a) before and b) after activation of the electrode.

The measurement of an analytical signal for Hg(II) on a gold surface is somewhat hindered by the baseline (background current) behaviour. This problem results from the nature of the deposit on the electrode, i.e. the amount of mercury deposited and/or the type of interaction between gold and mercury [16]. A possible origin of the high background, when working with HCl as supporting electrolyte, is the formation of calomel onto the electrode surface [16 21]. The definition of a proper baseline is

difficult. Good results in terms of accuracy and repeatability were obtained considering a horizontal baseline from the right base of the peak.

This determination does not require to purge the solutions with nitrogen. This finding is in agreement with the work of other researchers [22, 23], while others suggest a purge time of 300 sec before each measurement [24]. We found that the signal does not vary before and after purging.

3.2. Effect of supporting electrolyte and potential wave form

Five supporting electrolytes were tested, namely 70 mM HNO₃, 50 mM HClO₄, 60 mM HCl [22], 5 mM HNO₃/5 mM NaCl [19] and 40 mM HClO₄/0.6 mM NaCl/0.2 mM EDTA [24].

Each of the five considered electrolytes was tested working in LSV, DPV and SWV. After recording the voltammogram of the blank, the test solutions were spiked with two additions of Hg(II) standard solution (50 µg/l). Table 1 shows the heights and the potentials of the peaks obtained for 50 µg/l Hg (II) for each supporting electrolyte and scan mode. As an example, Fig. 2 reports the voltammograms obtained with the same electrolyte (HCl) using different potential wave forms, and Fig. 3 shows the effect of the supporting electrolyte composition using SW scan mode.

Table 1 Peak potentials (E_p) and intensities (i_p) obtained for a 50 µg/l Hg(II) solution with different supporting electrolytes and scan modes

Fig. 2. Voltammograms recorded using HCl as electrolyte and a) LSV, b) DPV and c) SWV: blank, 50 µg/l and 100 µg/l of Hg(II).

Fig. 3. Voltammograms recorded using SW as potential wave form and a) HCl, b) HNO₃, c) HClO₄, d) HClO₄/NaCl/EDTA, e) HNO₃/NaCl as electrolyte: blank, 50 µg/l and 100 µg/l of Hg(II).

With HCl the shape of the baseline was good, especially for SW and DP, and the peak was well-defined and regular. In the presence of HNO₃ and HClO₄ baseline and peak shape were somewhat irregular, and the peak did not increase after the second standard addition working in DPV. HClO₄ is used as supporting electrolyte in the determination of Hg(II) with other techniques: gold micro- [16] or film- [14] electrodes. Using HClO₄/NaCl/EDTA the baseline was almost regular with DP and SW scans and the peak shape was well defined. The mixture HNO₃/NaCl gave the worst results among the electrolytes tested, for all the investigated techniques: the baseline was very ill-shaped, and the peak height did not increase after the second addition of mercury.

Among the three utilized techniques, DPV and SWV are the most popular because they allow to enhance the analytical signal by removing the non-faradic current. Also in these experiments DP and SW wave forms permitted to obtain better signals than LSV. In particular, a peak for mercury with LS was observed only in HCl and HClO₄/NaCl/EDTA, and the sensitivities were very low. This behaviour is not in agreement with the studies of Jayaratna [22], who concluded that this scan mode was a good choice, but confirmed the findings of many other researchers that used DPV [e.g. 25] or SWV [e.g. 19].

The peak potentials vary in the order HCl < HNO₃/NaCl < HClO₄/NaCl/EDTA < HNO₃ = HClO₄ for both DP and SW modes. In particular, the stripping peak with HCl appears at a much more negative potential than those observed using the other electrolytes. This is in agreement with the results obtained by Okçu et al. with the gold film electrode: they used perchloric acid as supporting electrolyte, but they found that the addition of HCl was necessary to shift the stripping peak of mercury to less positive potentials, in order to reduce the background current, and to increase the sensitivity [14]. Probably the formation of mercury chlorocomplexes favours the oxidation of mercury, which

therefore occurs at less positive potentials. This shift is found at a lesser extent also in the case of the mixtures HNO_3/NaCl and $\text{HClO}_4/\text{NaCl}/\text{EDTA}$.

The peak heights increase in the order: $\text{HNO}_3/\text{NaCl} < \text{HClO}_4/\text{NaCl}/\text{EDTA} < \text{HCl} < \text{HNO}_3 < \text{HClO}_4$ with DPV, and in the order: $\text{HClO}_4 < \text{HNO}_3 < \text{HClO}_4/\text{NaCl}/\text{EDTA} < \text{HNO}_3/\text{NaCl} < \text{HCl}$ with SWV. The reasons of the different order of sensitivity is not clear. It is possible that the reversibility of the redox reaction of mercury, which enhances sensitivity in SW, increases in complexing electrolytes.

We decided to continue our work with HCl and with the mixture $\text{HClO}_4/\text{NaCl}/\text{EDTA}$ using both DP and SW, because the best results, in terms of peak shape and linearity, were obtained in these conditions.

3.3. Effect of wave form parameters

The effect of the different potential scan parameters on the mercury ($50 \mu\text{g/l}$) peak height and potential was investigated with the two supporting electrolytes selected. The results are shown in Fig. 4 and 5 for DP and SW respectively.

Fig. 4 The effect of a) step potential, b) interval time, c) modulation amplitude, d) modulation time on the mercury ($50 \mu\text{g/l}$) peak height. The corresponding peak potentials are reported in each plot. Wave form: DP. Supporting electrolyte: ● HCl and ○ $\text{HClO}_4/\text{NaCl}/\text{EDTA}$.

Fig. 5 The effect of a) step potential, b) frequency, c) amplitude on the mercury ($50 \mu\text{g/l}$) peak height. The corresponding peak potentials are reported in each plot. Wave form: SW. Supporting electrolyte: ● HCl and ○ $\text{HClO}_4/\text{NaCl}/\text{EDTA}$.

Working in DP mode, with the increase of the step potential, the signal slightly shifted to more positive potentials, and its height increased with scan rate. An increase of interval time had the opposite effect on the mercury peak owing to a decrease in scan rate. An increase of the modulation amplitude caused an increment of the signal intensities, probably due to the larger difference between the currents before and after

the application of the pulse, as measured in DP, and their shift to less positive potentials, whereas the variation of the modulation time had the opposite effect, likely because of the decrease of the faradic current for long pulses.

The results obtained using SW showed that when frequency and step potential were increased, the signal increased and shifted to slightly more positive potentials, in agreement with the increase in scan rate. The peak height increased with wave amplitude, as discussed above for modulation amplitude, and shifted to more negative potentials.

Therefore, the trends observed for the mercury peak following the variation of scan parameters are in agreement with theoretical predictions [26, 27].

Optimal values for the parameters were found to be: i) for DP, step potential 0.004 V, interval time 0.075 s, modulation amplitude 0.075 V, modulation time 0.0125 s with HCl, and 0.004 V, 0.075 s, 0.050 V, 0.0125 s respectively with HClO₄/NaCl/EDTA; ii) for SW, step potential 0.004 V, frequency 150 Hz, amplitude 0.03 V with HCl, and 0.004 V, 150 Hz, 0.04 V respectively with HClO₄/NaCl/EDTA.

The peak shape remained almost unchanged when the scan parameters were varied. The signals found in HCl were narrower and higher than the ones obtained using HClO₄/NaCl/EDTA for both scan modes. The highest peaks were obtained with SW, which is also the most rapid technique. As a consequence of the results obtained we continued our experiments using HCl as supporting electrolyte and SW with the optimized parameters as scanning mode.

3.4. Effect of deposition time and deposition potential

The effect of deposition potential (with 120 s of deposition) and deposition time (at 0 V) on the signal of 50 $\mu\text{g/l}$ of Hg(II) was evaluated and the results are reported in Fig. 6.

Fig. 6 The effect of a) deposition potential and b) deposition time on the mercury (50 $\mu\text{g/l}$) peak height ($E_p = 0.58$ V). Wave form: SW. Supporting electrolyte: HCl.

The highest signal with the best baseline shape was obtained with a deposition potential of 0 V. Other researchers worked with 0.1 [28], 0.2 [14], 0.3 [22] or 0.37 [24] V as deposition potentials, but using different supporting electrolytes. Using HCl, at deposition potentials more positive than 0 V the background is more relevant. Bonfil, working with 10 mM NaCl/10 mM HNO₃, observed that the repeatability and the magnitude of the analytical signal were independent of the deposition potential in the range +0.55 ÷ -0.4 V [19].

The amount of mercury deposited onto a gold surface should be carefully controlled to avoid saturation and to maintain linearity with increased loading. The greater solubility of mercury in gold compared to other metals could result in non-linear performance. Therefore we investigated the effect of the deposition time on the peak currents. As expected, the height of mercury peak increased with increasing deposition time (Fig. 6b). However, with deposition times longer than 120 s the electrochemical cleaning procedure was not sufficient to remove all deposited mercury, causing a worsening in the repeatability of the subsequent analyses.

Taking into account the results obtained, a deposition potential of 0 V and a deposition time of 120 s were adopted.

The effect of the optimisation of all parameters is well shown in Fig. 7.

Fig. 7. Comparison between the determination of Hg(II) with a) default and b) optimized parameters using HCl and SW.

3.5. Repeatability, Linearity, Detection Limit and Accuracy

The performance of the analytical method was evaluated using HCl as supporting electrolyte and the SW wave form, in the following conditions: frequency 150 Hz; step potential 0.004 V, amplitude 0.03 V, deposition potential 0 V, deposition time 120 s.

The repeatability was evaluated with ten replicates on 10 different cells containing 50 $\mu\text{g/l}$ of mercury. The relative standard deviation was 4.40 %. This value can be considered satisfactory, taking into account the relatively low concentration level involved.

The linearity of the analytical response was investigated. Initially, successive additions of 50 $\mu\text{g/l}$ of Hg(II) were made, but the peak height increased linearly with concentration only up 100 $\mu\text{g/l}$; therefore, we studied in more detail the increment of the signals in the range 0-100 $\mu\text{g/l}$ (with standard additions of 25 $\mu\text{g/l}$) and in lower ranges, namely 0 – 25 $\mu\text{g/l}$ and 0 – 5 $\mu\text{g/l}$ (with standard additions of 5 and 1 $\mu\text{g/l}$ respectively). Table 2 shows the equations of the calibration curves, R^2 values, and average sensitivities obtained.

Table 2 The equations of the calibration curves, R^2 values and the corresponding sensitivities obtained in different concentration ranges: a) 0 - 100 $\mu\text{g/l}$ (additions of 25 $\mu\text{g/l}$); b) 0 - 25 $\mu\text{g/l}$ (additions of 5 $\mu\text{g/l}$); c) 0 - 5 $\mu\text{g/l}$ (additions of 1 $\mu\text{g/l}$). R^2 values and sensitivities are also reported for sub-sets of the same data (a1; a2; b1; b2; c1; c2)

We examined both i) all data in the considered ranges (named a, b, c in the Table) and ii) sub-sets of the same data (named a1, a2, etc..).

The value of R^2 increases, within each range, as the number of considered data decreases (e.g. in the order $a < a1 < a2$): this trend is due to the more relevant increase of the peak height after the first additions, within each range, in comparison with the

last ones; in fact the data in Table 2 show that the average sensitivity decreases with the successive additions of mercury (e.g., in the order $a_2 > a_1 > a$). However, the intensities for 5 $\mu\text{g/l}$ were the same both after adding five 1- $\mu\text{g/l}$ spikes and one 5- $\mu\text{g/l}$ spike. According to previous studies [10], mercury is deposited onto the gold electrode and does not diffuse deeply into the gold, at least in the timescale of the experiment: therefore, at low concentrations the lower competition for electrode surface ensures a more efficient deposition and a higher sensitivity. Also the loss of linearity at concentrations higher than 100 $\mu\text{g/l}$ is presumably due to a partial saturation with mercury of the electrode surface. This change in sensitivity must be taken into account when analyzing real samples and indicates that it is convenient to perform the calibration with standard solutions having concentrations close to the ones present in the samples.

It can be presumed that at lower deposition times the dynamic linear range will be extended.

The limit of detection was estimated as $\text{LOD} = 3\sigma_B/\text{slope}$ of the calibration curve for the range 1- 5 $\mu\text{g/l}$ and was found to be 0.40 $\mu\text{g/l}$. Other papers in literature report lower detection limits than this, but the deposition times are generally very long; for example, Wu et al. found a detection limit of 22 ng/L using a deposition time of 40 min [23].

The accuracy of the procedure was tested by analysing a solution containing a known concentration (50 $\mu\text{g/l}$) of Hg(II). The concentration found was $49 \pm 2 \mu\text{g/l}$ and the relative error was -2 %. Therefore the accuracy of the method can be considered good.

3.6. Interferences

The interference of several metal ions (As(V), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Mn(II), Ni(II), Pb(II), and Se(IV)) on the mercury stripping signal was investigated. The voltammogram of a solution with 25 $\mu\text{g/l}$ of Hg(II) was recorded in

the presence of each element (added into the polarographic vessel in 1:1, 1:10, 1:100 concentration ratios with respect to Hg(II)). As other researchers [1, 14, 19] found, no interference was observed after the addition of 250 $\mu\text{g/l}$ of each element. Moreover, the linearity of the calibration curve of mercury was maintained also in the presence of 2.5 mg/l of the other ions in solution.

The only peak which appeared in the considered range of potential, at less positive potentials than the one of Hg(II), was caused by copper, but it did not interfere with the determination of mercury.

3.7. Cleaning procedure of the electrode surface

The importance of electrode cleaning in order to maintain linearity is well known, but the opinions found in literature about the frequency and the procedure of this step are not in good agreement. Some papers indicate a decrease in the signal of mercury in the absence of cleaning [22, 29], whereas other researchers found that the electrochemical characteristics of the electrode were not affected by repeated depositions and dissolutions of mercury, and stated that no pre-treatment of the gold surface between experiments was required in order to achieve good reproducibility [19, 30]. Watson et al. underline the importance of a cleaning step after each determination, defining this stripping determination as composed by a three-step cycle: preconcentration (deposition), measurement (stripping) and regeneration (cleaning) [10].

The results obtained in the present study showed that the determination of Hg(II) at a gold electrode was always hindered by the incomplete removal of previously deposited mercury. To eliminate this drawback, a good cleaning procedure was essential. Electrochemical and mechanical surface cleaning, as well as the control of the amount of mercury deposited onto the gold surface, were necessary for maintaining good reproducibility and linearity.

An electrochemical cleaning procedure was adopted: a positive potential (1.3 V) was applied for 30 s to remove the deposited mercury after each determination (consisting of the recording of three voltammograms: blank and two additions). During this step the polarographic vessel was filled with 20 ml of the mixture $\text{HClO}_4/\text{NaCl}/\text{EDTA}$ [24]: in fact, this electrolyte was more efficient to clean the electrode than the other four electrolytes used in this work. Probably the presence of EDTA favours the removal of mercury from the electrode.

Moreover, after about 100 determinations a mechanical polishing with alumina was necessary to obtain a good repeatability and a homogeneous background.

No difference in terms of cleaning requirement was observed among the use of the five supporting electrolytes tested in this study. This finding is in agreement with the results obtained by Jagner and Josefson [31], whereas Jayaratna chose to work with HClO_4 instead of HCl also because he noted that HCl required longer cleaning times than HNO_3 or HClO_4 [16].

Some problems of repeatability began after five months of intensive use. In order to check if this drawback was due to a damaged electrode surface, a SEM analysis was performed. The images obtained revealed that the surface of the gold electrode presented holes and scratches, caused by the repeated cleaning treatments with aluminum oxide: this was confirmed by a microanalysis of the holes, that showed only the presence of Al in these points.

In order to avoid, or at least reduce, this drawback, now another procedure for the mechanical cleaning is being adopted: alumina is suspended in water before being transferred onto the cloth. In this way, it forms a smoother layer and the electrode lifetime is extended.

4. Conclusions

The results obtained showed the efficiency of the gold electrode for the determination of low concentrations of Hg(II) by anodic stripping voltammetry. The reproducibility, sensitivity and accuracy are good, provided the proper instrumental parameters and supporting electrolyte are used.

We also demonstrated that the determination of Hg(II) at a gold electrode is negatively affected by the incomplete removal of previously deposited mercury. To eliminate this drawback, an electrochemical and a mechanical cleaning procedure are essential.

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Table 1
 Peak potentials (E_p) and intensities (i_p)
 obtained for a 50 $\mu\text{g/l}$ Hg(II) solution with
 different supporting electrolytes and scan
 modes

Electrolyte	Scan mode	i_p (μA)	E_p (V)
HCl	LS	0.13	0.54
	DP	0.80	0.51
	SW	19.0	0.58
HNO ₃	LS	n.d.	n.d.
	DP	1.45	0.66
	SW	6.63	0.73
HClO ₄	LS	n.d.	n.d.
	DP	1.48	0.66
	SW	5.14	0.73
HClO ₄ /NaCl/EDTA	LS	0.19	0.62
	DP	0.76	0.60
	SW	16.2	0.69
HNO ₃ /NaCl	LS	0.00	n.d.
	DP	0.78	0.55
	SW	16.3	0.67

n.d. = not detectable

Table 2

The equations of the calibration curves, R^2 values and the corresponding sensitivities obtained in different concentration ranges: a) 0 - 100 $\mu\text{g/l}$ (additions of 25 $\mu\text{g/l}$); b) 0 - 25 $\mu\text{g/l}$ (additions of 5 $\mu\text{g/l}$); c) 0 - 5 $\mu\text{g/l}$ (additions of 1 $\mu\text{g/l}$). R^2 values and sensitivities are also reported for sub-sets of the same data (a1; a2; b1; b2; c1; c2).

Data set	Concentration range ($\mu\text{g/l}$)	Equation of the calibration curve*	R^2	Average sensitivity ($\mu\text{A}/\mu\text{g l}^{-1}$)
a	0-100	$y = 9 \times 10^{-7}x + 3 \times 10^{-5}$	0.9868	1.03
a1	25 - 100		0.9981	0.90
a2	50 - 100		0.9987	0.85
b	0-25	$y = 1 \times 10^{-6}x + 2 \times 10^{-5}$	0.9999	1.45
b1	5 - 25		0.9999	1.44
b2	15 - 25		0.9999	1.43
c	0-5	$y = 3 \times 10^{-6}x + 1 \times 10^{-5}$	0.9978	2.96
c1	1 - 5		0.9991	2.78
c2	2 - 5		0.9999	2.67

* equations are referred to data sets a, b, c

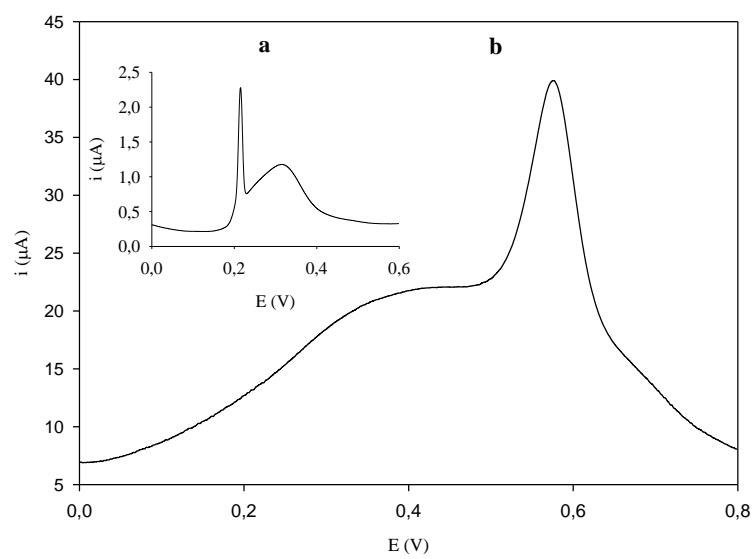


Fig. 1. Anodic stripping voltammograms of 50 µg/l of Hg(II) in HCl using SW a) before and b) after activation of the electrode.

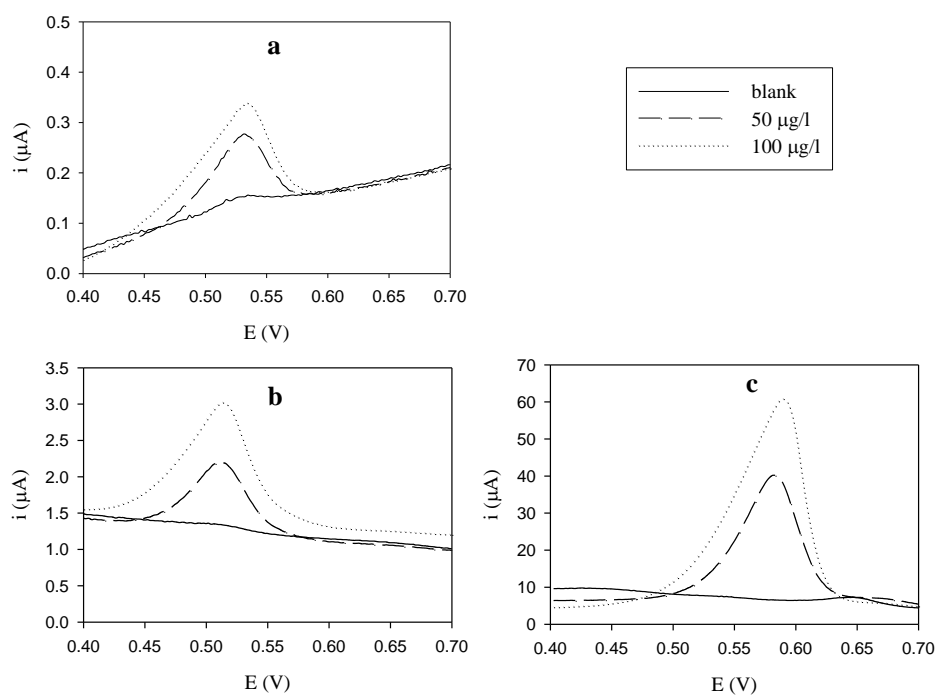


Fig. 2. Voltammograms recorded using using HCl as electrolyte and a) LSV, b) DPV and c) SWV: blank, 50 $\mu\text{g/l}$ and 100 $\mu\text{g/l}$ of Hg(II).

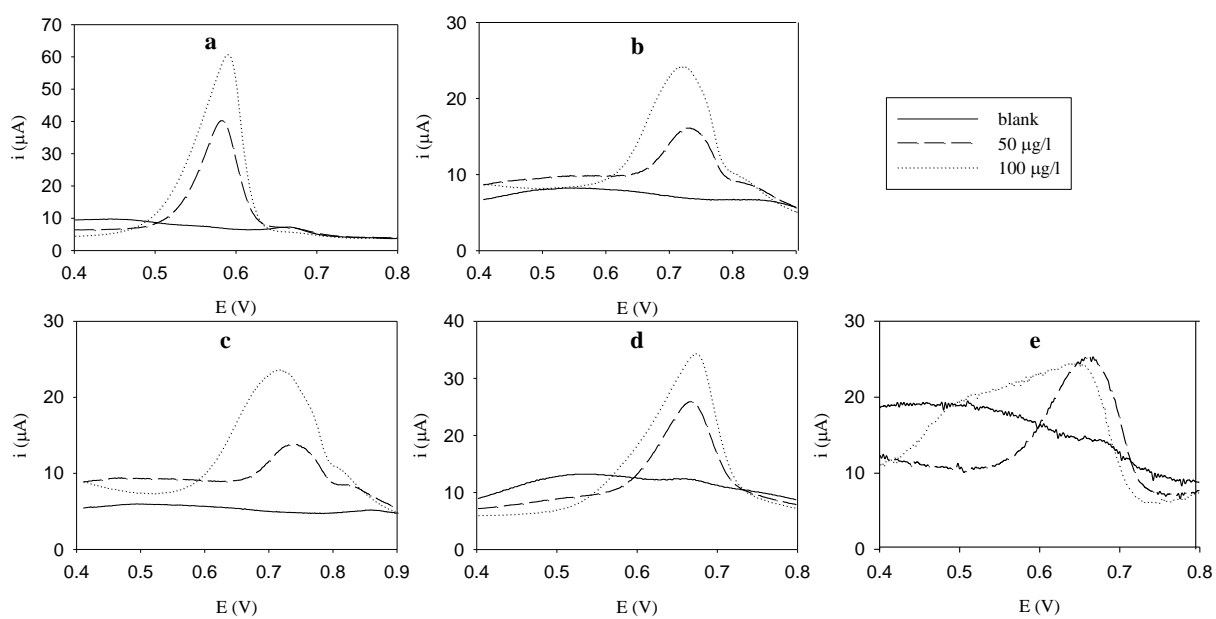


Fig. 3. Voltammograms recorded using SW as potential wave form and a) HCl, b) HNO_3 , c) HClO_4 , d) $\text{HClO}_4/\text{NaCl}/\text{EDTA}$, e) HNO_3/NaCl as electrolyte: blank; 50 $\mu\text{g/l}$ and 100 $\mu\text{g/l}$ of Hg(II) .

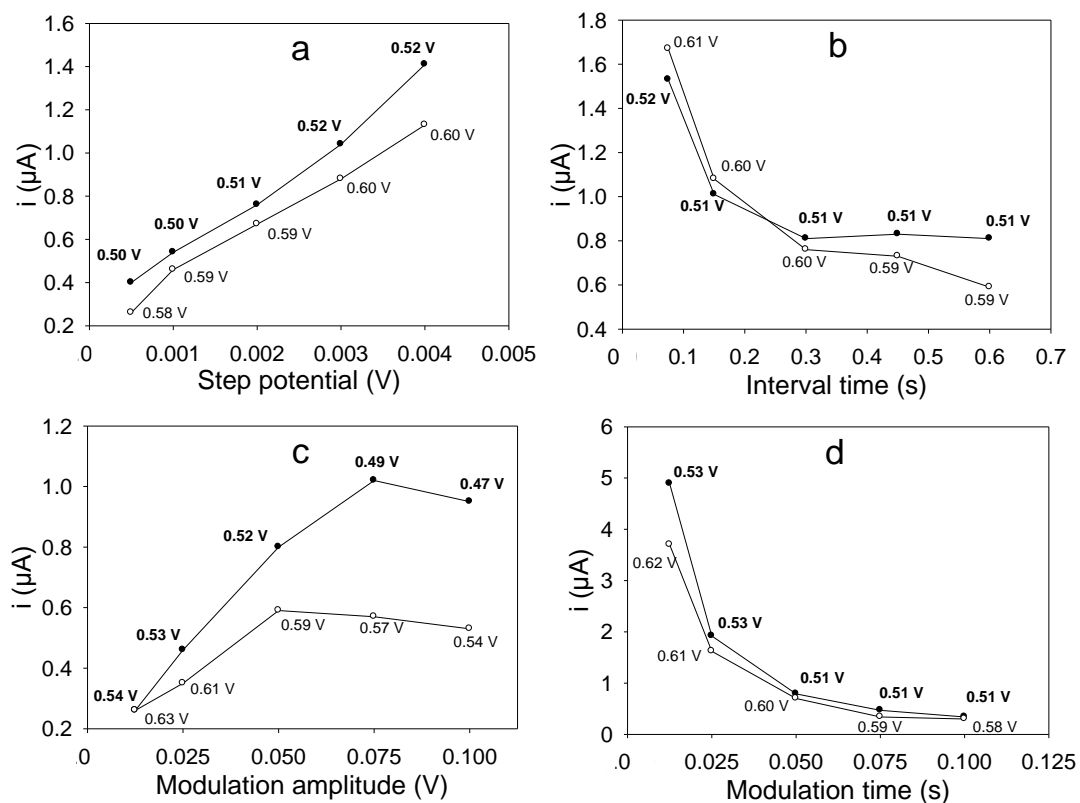


Fig. 4. The effect of a) step potential, b) interval time, c) modulation amplitude, d) modulation time on the mercury (50 $\mu\text{g/l}$) peak height. The corresponding peak potentials are reported in each plot. Wave form: DP. Supporting electrolyte: ● HCl and ○ HClO₄/NaCl/EDTA.

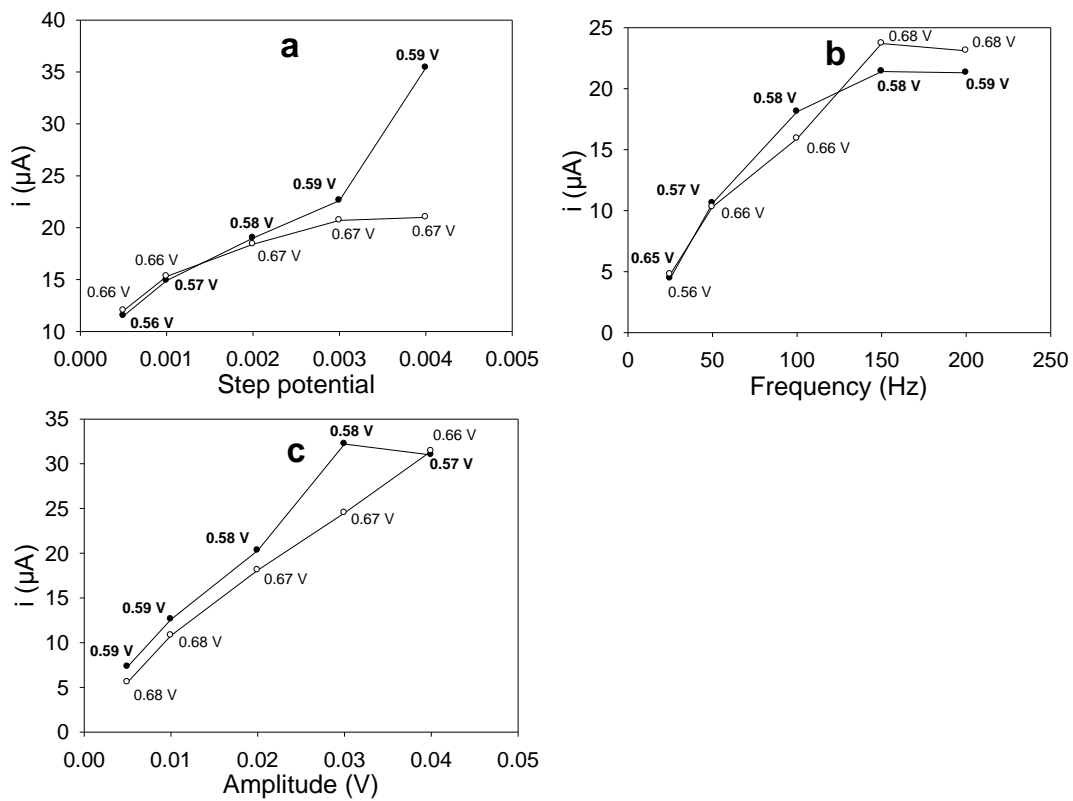


Fig. 5 The effect of a) step potential, b) frequency, c) amplitude on the mercury ($50 \mu\text{g/l}$) peak height. The corresponding peak potentials are reported in each plot. Wave form: SW. Supporting electrolyte: ● HCl and ○ HClO₄/NaCl/EDTA.

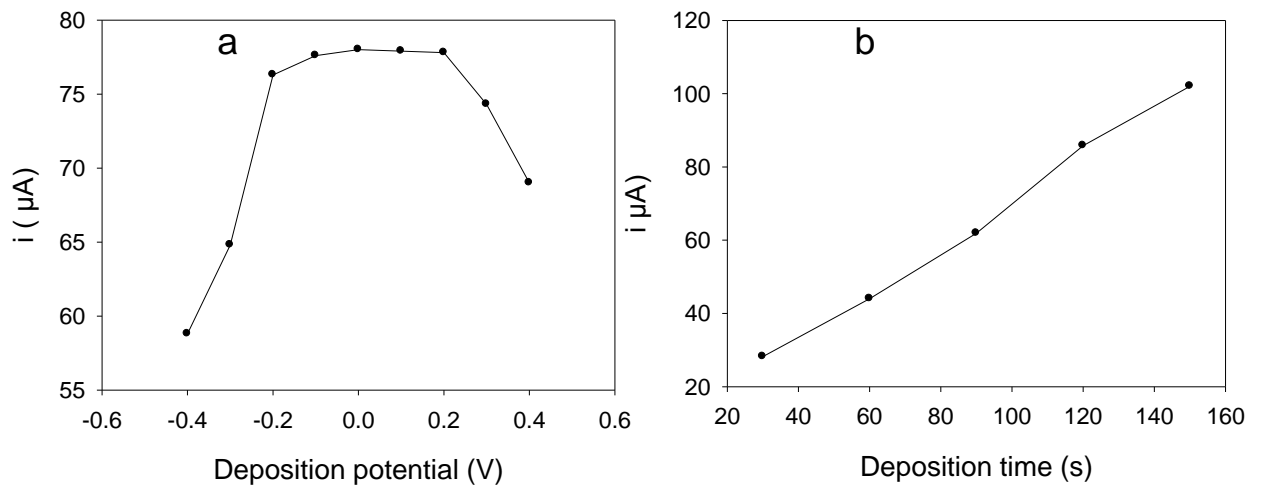


Fig. 6 The effect of a) deposition potential and b) deposition time on the mercury ($50 \mu\text{g/l}$) peak height ($E_p = 0.58 \text{ V}$). Wave form: SW. Supporting electrolyte: HCl.

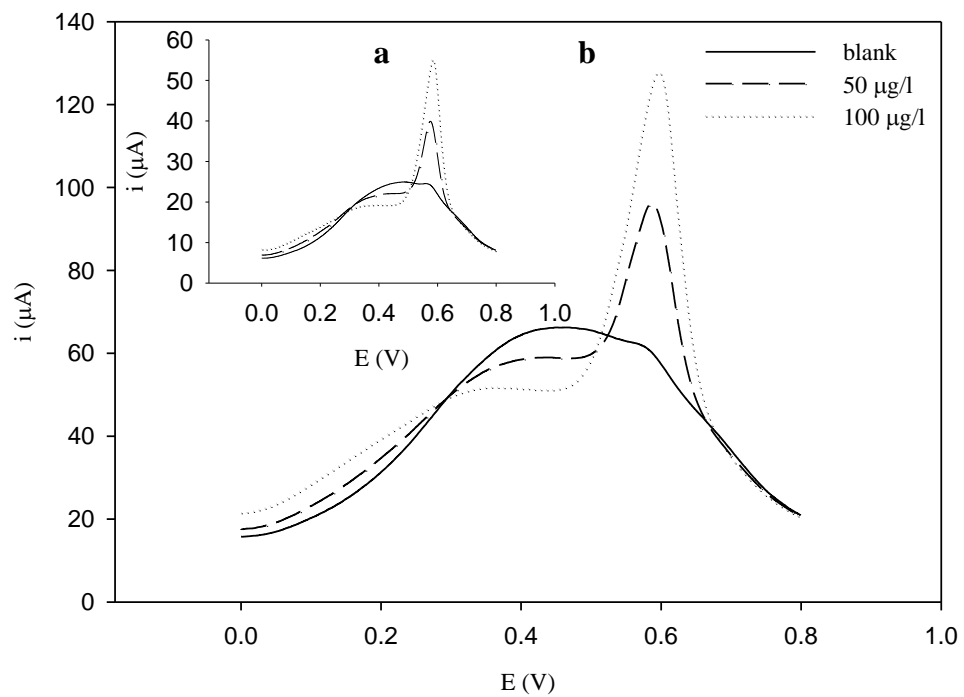


Fig. 74. Comparison between the determination of Hg(II) with a) default and b) optimized parameters using HCl and SW.