# Anodic Stripping Voltammetric Determination of Mercury in Water by Using a New Electrochemical Flow Through Cell

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**Abstract**
A flow through electrochemical cell was designed for the implementation of a simple, efficient, rapid and sensitive method for determination of mercury in water samples by anodic stripping voltammetry. A solid gold or a gold film electrode can be used as working electrode in a wall-jet configuration of the cell. The analyte is electrolyzed on the electrode surface by pumping the liquid sample through a continuous flow manifold at a flow rate of 8 mL/min. Deposition efficiency increased by increasing the velocity at which the sample arrives to the cell. After deposition of the analyte, it was stripped from the electrode by using a linear anodic potential scan at 35 mV/s. Geometric and hydrodynamic variables of the system were studied in order to optimize the analytical response. A detection limit of 0.05 ng/mL was reached by using a preconcentration time of 540 s. The repeatability expressed as relative standard deviation was always less than 3%. The method shows a good selectively and was successfully applied to the determination of mercury in different water samples.

**Keywords:** Electrochemical flow through cell, Anodic stripping voltammetry, Mercury determination, Water

## 1. Introduction

Mercury is an element that has many uses, however it is well known as an environmental pollutant for several decades. Mercury can impair the human senses because it is a potent nerve toxin. Mercury evaporates readily and travels long distances in the atmosphere causing local and global pollution. When mercury is deposited in lakes or waterbays, bacteria convert it to methylmercury. Methylmercury accumulates in algae and is eaten by smaller fish, which in turn are eaten by larger fish. Fish at the top of the aquatic food chain, such as walleye, can have methylmercury concentrations as high as 130000 times that of the surrounding water. If contaminated fish are eaten on a regular basis, mercury can become high enough to become a serious health threat to humans. As a result, knowledge of the mercury content in various matrixes, together with the development of reliable analytical methods for determination at trace level are mandatory.

In this context, sample contamination and lack of method sensitivity have been the leading limitations for accurate determination of mercury at low concentration levels. Spectroscopy is so far the most used analytical technique for determination of mercury with the cold vapor atomic absorption spectrophotometry being the most popular at the present [1 – 10]. For ultra-trace analysis, it is possible to incorporate a preconcentration system based on gold amalgam, previous to the cold vapor atomic-absorption measurement [8 – 10].

Anodic stripping voltammetry has been proposed by US-EPA [11] as an alternative technique for determination of mercury in aqueous samples and soil extracts. A gold-plated electrode, using a glassy carbon surface as support, is used as working electrode. With respect to electrochemical deposition, plating and renewal of films are simple and can be done as frequently as needed. The film can be deposited either via external pre-electrolysis in a separate plating solution [12, 13] or in situ [14, 15]. Similar to mercury film electrodes, the electrochemical properties of gold films depends on the quality of support. The most common supports used for gold films are platinum disks, carbon and gold fibers, glassy carbon and carbon paste [16]. Alternatively to the plated electrodes, the solid gold electrode can be used for ASV of mercury [14 – 18].

The aim of this work was to develop an electrochemical flow injection cell and a manifold for ASV determination of mercury in a flow system. The flow cell contains a three electrode configuration of wall-jet type. Film electrode over a glassy carbon substrate and solid gold electrode were tested in this flow system. The solid gold electrode provides faster results and lower detection limits.

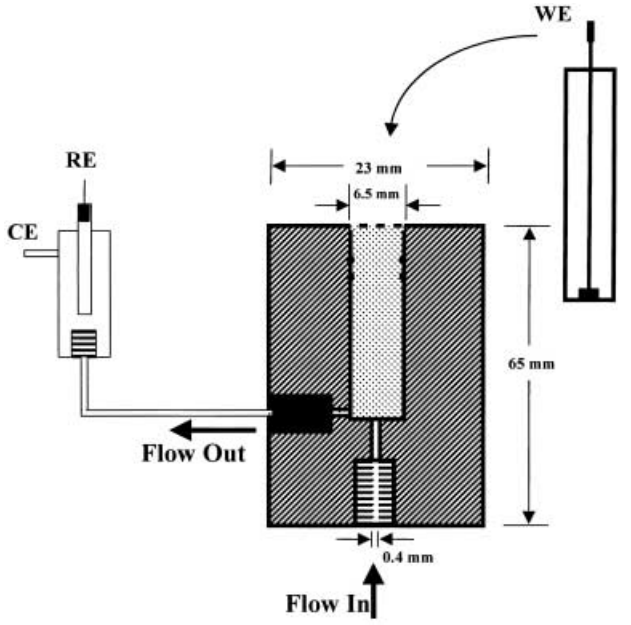


Fig. 1. Flow through electrochemical cell. WE, working electrode; RE, reference electrode; CE, counter electrode.

## 2. Experimental

### 2.1. Apparatus and Instruments

A CV 50 W instrument (Bioanalytical System, Lafayette, IN, USA) was used as potentiostat detector. The anodic stripping voltammetric signals were recorded and analyzed by using the CV-50 W software upgrade EF-1664.

Figure 1 illustrates the design of the flow-cell containing a three-electrode arrangement. The main body of the cell was made of Plexiglass, into which was fitted the working electrode (gold MF-1007, glassy carbon MF-1003 BAS). The correct location of the electrode corresponds when its surface reaches the bottom of the cell where the flow of sample enters. In this position the flow stream of the sample direct impacts the electrode surface. The reference (Ag/AgCl) and counter electrode (Pt) were located at the flow-out of the main cell.

The flow injection manifold (Figure 2) consisted of an Ismatec (MS-FIXO) four-channel persistaltic pump a selecting valve (Rheodyne 5041) and Teflon tubes of 0.5 mm (i. d.).

A 400 W mercury lamp, used in public illumination, without the external glass bulb was used for the UV treatment of the water samples before each analysis.

### 2.2. Reagents

All chemical used were of analytical grade. Deionized water (NANOpure ultrapure water system; Barnstead, Dubuque, IA, USA) was used throughout. Working solutions of different concentrations of mercury were prepared from a

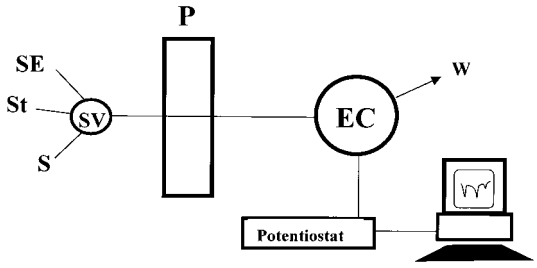


Fig. 2. Schematic diagram of the electrochemical flow system. SE, supporting electrolyte; St, standard solution of mercury; S, sample; P, peristaltic pump; EC, electrochemical flow through cell; W, waste.

Titrisol Merck 1000 mg/L standard solution. Diluted solutions were prepared freshly before use and stabilized by acidifying with nicric acid to pH $< 2$.

When the solid gold electrode was used the supporting electrolyte solution was prepared by dilution of 8.5 mL of concentrated perchloric acid (Merck) and 300 μL of hydrochloric acid (Merck) in water to reach 1000 mL. The same solution but containing additionally $2 \times 10^{-4}$ M gold(III) was used for when the gold film electrode was the selected. Previous to the analysis, the standards and samples were prepared in presence of the supporting electrolyte considering the same concentration of its ingredients.

### 2.3. General Procedure

Supporting electrolyte (blank), standard or water samples were pumped at a flow rate of 8 mL/min. When the sample reach the flow through cell the analyte starts to be accumulated on the electrode surface (solid gold electrode) by applying a potential of 0.0 V (vs. Ag/AgCl) for an accumulation time of 1 to 10 min, depending on the concentration of mercury on the sample. Subsequently, the pump was halted and after an equilibration time of 5 s, a linear anodic scan is carried out from 0.0 V to 0.950 V at a scan rate of 35 mV/s, while the anodic signal is obtained. After the processing of each sample or standard, the electrode surface is electrochemically cleaned by applying to the electrode a potential of 0.900 V for 15 s, while the supporting electrolyte remains flowing through the cell.

When the gold film electrode is used, previous to the above mentioned procedure, the film accumulation is carried out by using the suppoting electrolyte containing Au(III). The applied potential and time for accumulation of the gold film were $-1.1$ V and 250 s, respectively. After the sample has been measured the electrode is polished with polishing alumina on a felt wetted with water or ethanol and finally cleaned with acetone on a fluff-free tissue.

Before each analysis, 50 μL of $H_2O_2$ 30% were added to the acidified (pH 2) water samples and subsequently treated with UV lamp (400 W) according to the procedure proposed by Richter et al. [19].

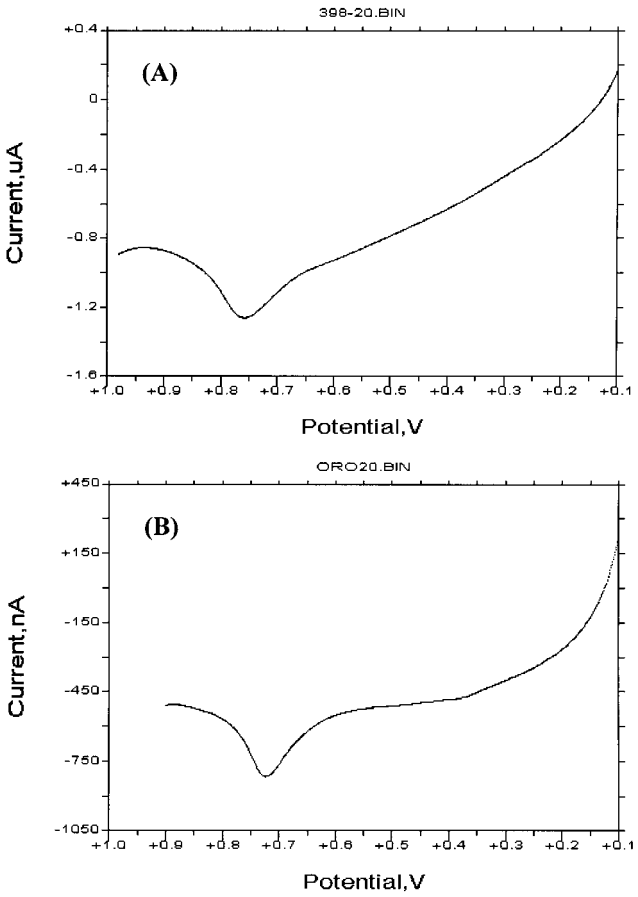


Fig. 3. Anodic stripping voltammograms for mercury, using A) solid gold electrode, and B) gold film electrode. Electrolysis time 60 s. Other conditions as in general procedure.

## 3. Results and Discussion

After continuous flow electrode deposition of the analyte in the presence of the supporting electrolyte used (0.1 M $HClO_4 + 3 \times 10^{-3}$ M HCl) mercury gives rise to a well-defined anodic stripping voltammetric signal, in both, solid and gold film electrode (Figure 3). When the film electrode is used the oxidation of mercury from the electrode is a little easier because the peak potential was shifted cathodically approximately 25 mV. Further the film electrode provides a smaller capacitive current when the anodic stripping voltammogram is recorded.

A survey of the literature indicates that the geometry of the electrochemical flow through cells normally involves tubular, thin layer or wall-jet configuration [20]. The last configuration was adopted in this work because the mass transfer in the electrochemical preconcentration can be improved considerably by driving the geometric and hydrodynamic variables involved on the electrochemical process.

Figure 1 shows the electrochemical flow through cell used. The first variable studied was the entrance speed of the sample to the cell, which was driven by varying the diameter of the flow enter hole of the cell. Cells with hole diameters of 0.4, 0.7, 1.0, 1.5 and 2.0 mm were constructed and tested,

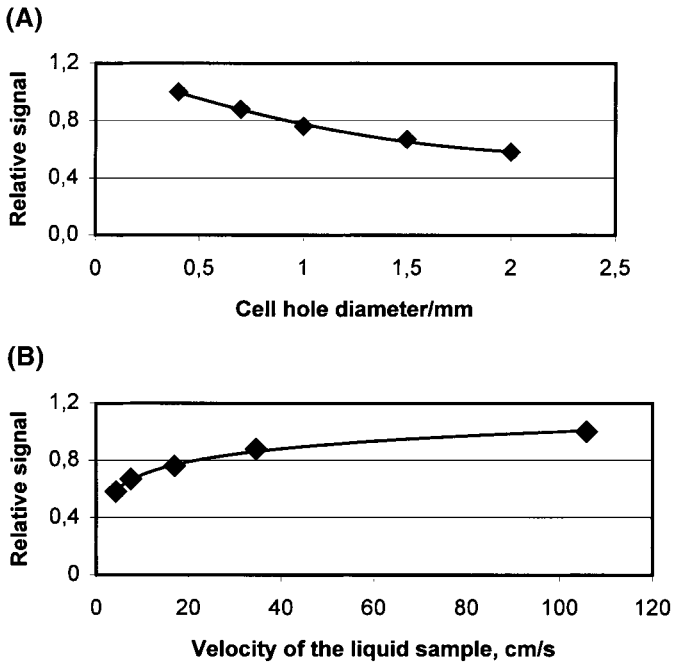


Fig. 4. A) Effect of the cell hole diameter on the analytical signal. B) Effect of the velocity of the liquid sample on the analytical signal. Signals were normalized to the highest response.

given rise to the following entrance speed (in cm/s), respectively: 105.8, 34.6, 17.0, 7.5, and 4.3. A constant flow rate of the sample of 8.0 mL/min and a preconcentration time of 1 min were used in all cases. Figure 4 shows that the ASV signal of mercury increases as the hole diameter decreases because the velocity of the fluid (sample) increases. This effect is equivalent to the increment of stirring speed in conventional batch ASV, because in this instance the Nernst diffusion layer becomes smaller when the speed of the fluid increases and consequently the efficiency on the deposition process is improved. Considering the sensitivity of the method, the cell of 0.4 mm was selected for further experiments. Under the same conditions of preconcentration time and working electrode the continuous system proposed is 11.2 times more sensitive than the batch ASV conventional alternative.

The other variable studied was the area of the electrode. The commercial electrode used have a diameter of 1.4 mm. We requested the BAS Company to construct a gold electrode with a larger diameter. BAS provide us an electrode with a gold surface of 3 mm diameter. By using this electrode the signal increases 3.05 times relative to the response obtained with the electrode of 1.4 mm, under the same conditions. The behavior described here is in accord with the theoretical-empirical aspects described previously [20]. The limiting current increases with both decreasing the Nernst diffusion layer and increasing the electrode area (increasing efficience of the preconcentration). The material of the electrode is particularly important for mercury analysis. Gold is very kindred as support for mercury. For example, if gold support is replaced by a glassy carbon

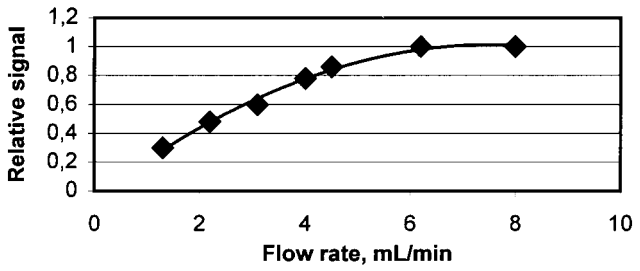


Fig. 5. Effect of the flow rate on the analytical signal. Signals were normalized to the highest response.

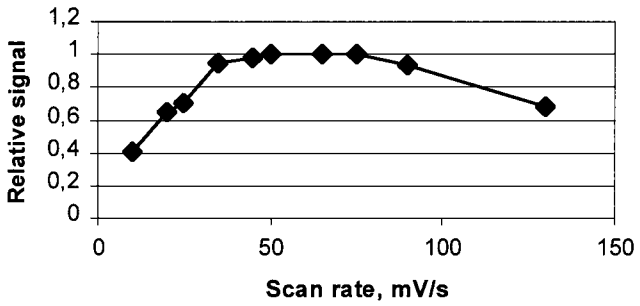


Fig. 6. Effect of the scan rate potential on the analytical signal. Signals were normalized to the highest response.

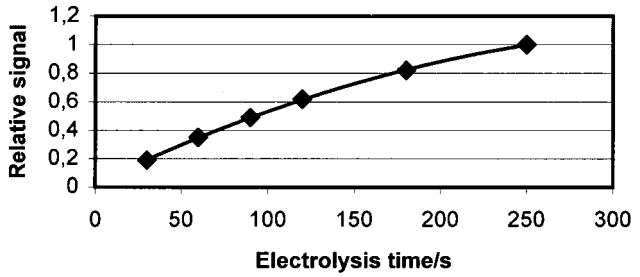


Fig. 7. Effect of the electrolysis time (preconcentration time) on the analytical signal. Signals were normalized to the highest response.

electrode of the same area, no signal was detected under the same experimental conditions. In this context, it is mandatory to form a gold film over the glassy carbon surface previous to the deposition of the analyte.

The effect of the flow rate was also tested because it is related to the amount of analyte potentially electrolizable. As can be seen in Figure 5, the amount of analyte that reaches the electrode in the preconcentration step increases with increasing flow rate and consequently the signal increases to reach a constant value at 6 – 8 mL/min.

The scan rate of the potential was also checked and its effect on the analytical signal is shown in Figure 6. A value of 35 mV/s was selected, since over this value a larger capacitive current is observed, increasing more than the faradaic signal. This effect is more evident over 80 mV/s. The electrolysis potential for deposition of the analyte was tested from $-1100$ to 400 mV. When potentials more positives than 300 mV are applied the signals become smaller. The selected potential for electrolysis was 0.0 mV. When more negative potentials are applied, the noise of the response increased slightly, decreasing consequently its repeatability.

The effect of electrolysis time can be observed in Figure 7. The relationship of the signal with this variable is not totally linear owing to some saturation effects of the electrode surface. However the preconcentration effect is evident.

### 3.1. Analytical Features

Under the optimum conditions stated in Table 1, calibration plots of the mercury ASV signal versus its concentration were established considering different concentration ranges and electrodes (Table 2). In the range 5 to 50 μg/L by using a preconcentration time of 1 min, the calibration was not totally linear, especially with the higher concentrations, owing to the same saturation effects of the surface. In any case in this range, the relationship between analyte signal and concentration is almost linear, as can be seen in the

Table 1. Study of variables.

| *Variable* | *Range studied* | *Selected value* |
|---|---|---|
| Cell hole diameter (mm) | 0.4 – 2.0 | 0.4 |
| Velocity of the sample (cm/s) | 4.25 – 105.8 | 105.8 |
| Flow rate (mL/min) | 1.3 – 8.0 | 8.0 |
| Potential scan rate (mV/s) | 10 – 130 | 35 |
| Electrolysis time (s) | 25 – 600 | Depends on concentration of the analyte |

Table 2. Calibration equations.

| *Gold Electrode* | *Concentration range/μg/L (prec. time/s)* | *Regression equation (n = 7)* | *R* |
|---|---|---|---|
| Solid | 5 – 50 (60 ) | $Ip\ (\mu A) = 0.0025 + \mathbf{0.0167}\ [Hg(\mu g/L)] - 0.0001[Hg(\mu g/L)]^2$ | 0.99999 |
| Solid | 0.5 – 5 (540) | $Ip\ (\mu A) = 0.0081 + \mathbf{0.0500}\ [Hg(\mu g/L)]$ | 0.99996 |
| Film | 5 – 20 (60) | $Ip\ (\mu A) = 0.0031 + \mathbf{0.0192}\ [Hg(\mu g/L)]$ | 0.99967 |
| Film | 0.3 – 5 (540) | $Ip\ (\mu A) = 0.0021 + \mathbf{0.0581}\ [Hg(\mu g/L)]$ | 0.99968 |

Table 3. Features of the method.

| *Electrode* | *Detection limit (μg/L) (Prec. time (s))* | *RSD[a] (%) (Concentration (μg/L))* |
|---|---|---|
| Solid | 0.05 (540) | 2.25 (2) |
| Solid | 0.14 (60) | 1.23 (30) |
| Film | 0.14 (540) | 2.55 (2) |
| Film | 0.40 (60) | 1.62 (30) |

[a] Repeatability of the method expressed as relative standard deviation ($n=11$).

Table 4. Interference study (Solid electrode). Mercury concentration 10 ng/mL.

| *Foreign species* | *Studied concentration range (μg/L)* | *Tolerance(μg/L) [a]* |
|---|---|---|
| Zn | 0–4000 | 4000 |
| Cd | 0–4000 | 4000 |
| Pb | 0–4000 | 4000 |
| Co | 0–4000 | 4000 |
| Cu | 0–1000 | 600 |
| Sb | 0–500 | 500 |
| Bi | 0–2000 | 2000 |
| Se | 0–200 | 150 |
| Ag | 0–1000 | 200 |

[a] Tolerance was determined considering an error of 5% of the signal.

small coefficient of the second order. The correlation was excellent in all instances, specially for solid electrode. In lower concentration ranges the regression equations were linear.

By using the same conditions, which were optimized for the solid electrode, the film electrode gave a little higher sensitivity (15%) as can be seen in Table 2 (bolt coefficients).

Detection limits depends on the preconcentration time. They were calculated by using the 3-$\sigma$ criterion for 60 and 540 s, by considering the sensitivity of the method and the blank signal (Table 3). The precision (repeatability) of the method was assessed at concentrations of 30 and 2 μg/L by using 60 s of preconcentration time (Table 3). As can be seen in Table 3, despite the higher sensitivity of the film electrode, the detection limit is lower for the solid electrode, because the standard deviation of the blank signal is lower. Repeatability was quite comparable for both electrodes at the concentrations assessed.

### 3.2. Interference Studies

Interference studies were carried out in order to check the selectivity of the proposed method. Different metal species were added to a sample of tap water which was also spiked with a known amount of mercury (10 ng/mL). Table 4 shows the tolerance for each species.

As can be seen in Table 4, the most severe interferences were from Se, and Ag. Fortunately, these species are not present in natural water at high concentrations. By applying the standard addition technique, the recovery ratio in tap water was essentially the same as that observed in deionized water, thus it can be concluded that normal compounds found in this kind of matrix do not interfere in the method. However, in sea- and river water an UV treatment of the samples was mandatory previous to perform the voltammetric determination. As was suggested previously [19], a period of 6 h of irradiation was adopted in order to liberate all the mercury in the spiked samples. By using different samples with spiked mercury, the mercury signal increases between 5 to 10% after 6 h irradiation.

Table 5. Determination of mercury in water samples.

| *Sample* | *Determined (ng/mL)* | *Added (ng/mL)* | *Recovery (%) (RSD)* |
|---|---|---|---|
| Tap water [a] | <DL | 10.0 | 97.7 (1.5) |
| Tap water [a] | <DL | 0.8 | 116.0 (3.0) |
| Sea water [b] | <DL | 10.0 | 105.3 (2.1) |
| Sea water [b] | <DL | 0.5 | 108.9 (2.1) |
| River water [c] | <DL | 0.5 | 112.8 (3.1) |

[a] from Santiago, Metropolitan Region, Chile.
[b] From Valparaíso, V Region, Chile.
[c] From San Gabriel (Maipo River), Metropolitan Región, Chile; value determined by cold vapor AAS 0.45 with a relative standard deviation of 2.2%

### 3.3. Applications

The present method requires a large amount of sample for the analysis (considering the application of standard addition method). In this context, standard reference samples could not be evaluated because the typical volume provided in the commercial product is not sufficient for the analysis. Just to exemplify, by using a preconcentration time of 540 s, and considering two standard additions, the total volume of sample needed is 216 mL.

In order to assess the real applicability of the method, different water samples were analyzed. Tap water samples were analyzed directly without pretreatment procedure. Sea-and river water were UV irradiated previously to the voltammetric determination. As can be seen in Table 5, the method provides good results, which agree well with those determined by cold vapor atomic absorption spectrometry.

## 4. Acknowledgement

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