TRACE ANALYSIS OF LEAD AND CADMIUM WITH GOLD AND SILVER MICROELECTRODES

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Abstract
In this study, microelectrodes made from gold (wire, 25 µm diameter, 4 cm length) and silver (band, 25µm diameter, 7mm length) were investigated for trace lead and cadmium analysis. The gold wires were electrochemically coated with mercury before use; the silver bands were used without coating. Preliminary studies of the behaviors of microelectrodes were examined. The microelectrodes exhibit specific characteristics such as high sensitivity, fast scan rate utility, and possibility to be employed in unstirred condition. In the optimized conditions, repeatability of mercury plated gold (using LSV) were 4% at Pb 70 ppb for 30 s deposition, 8% at 30 ppb for 60 s deposition, 11% at 10ppb for 60 s deposition; and those of silver (using DPV) were 3% at Pb 15 ppb for 30s deposition, 2.3% at Pb 10 ppb for 60 s. With silver electrodes and 60s deposition time, the detection limits were 0.64 ppb for Pb, and 1.06 ppb for Cd. Finally, silver micro bands were successfully applied to the determination of Pb and Cd in tape water.

Keywords: anodic stripping; gold and silver microelectrode; cadmium; lead.

Introduction
Microelectrodes have proved to be extremely advantageous in the field of analytical chemistry. Firstly, microelectrodes have low iR drop since very low current flows during analysis. Thus, faster scan rate can be employed and measurements can be made in low conductive media without adding supporting electrolyte. Moreover, the two-electrode system can be used that makes the instrumentation simple and portable. Secondly, microelectrodes attain enhancement in mass transport rate due to the radial diffusion of electro active species. The rate of mass transport increases as the electrode size decreases. The enhanced diffusion rate incorporated with the reduced charging current lead to greatly improved sensitivity. In addition, the convective contribution is unnecessary due to the high-speed voltammetric process. Microelectrodes can be constructed in many shapes: wire, disk, hemisphere, and band. The most popular materials for electrodes are mercury, carbon, gold, platinum, iridium, silver…Among the electrode materials; mercury was the most interest due to high over voltage of hydrogen evolution and the minimization of intermetallic formations. However, because of the high toxicity of mercury, mercury film and solid electrodes have been developed as the alternatives for mercury. The thin mercury film can be either pre-plated or in situ coated with the studied species [1,2].

In this study the main focus is on the characteristics of gold pre-plated with mercury as well as bare silver microelectrode; subsequently apply to determination of lead and cadmium by anodic stripping voltammetry (ASV). Electrode preparation was described, and the comparison in performances among electrodes was then made. Analytical parameters for determination of Pb and Cd were examined, and the interferences were considered to achieve the reliable analysis.

Materials and methods
Apparatus
The linear sweep (LSV) and differential pulse anodic stripping voltammetric (DP-ASV) experiments were carried out using homemade potentiostats. Available commercial Teflon stirrer (Radiometer TTA80 Titration Assembly) was used. For gold microelectrode, the reference electrode was saturated calomel electrode (SCE); the auxiliary electrode was a platinum (Pt) rod. The homemade working electrode was gold micro-wire (25 µm diameter, 99.99%, Goodfellow Company, UK) coated with a film of mercury. For bare silver microelectrode, two electrodes configuration was used including reference/auxiliary silver wire electrode (diameter 1.5 mm; area 1 cm²) and homemade working silver micro-band electrode (25 µm diameter, 99.99%, Goodfellow Company, UK)

Chemicals
All chemicals were of analytical grade. Lead, cadmium standard stock solution (1000 ppm); potassium nitrate, potassium chloride, anhydrous sodium acetate, mercury acetate, cadmium nitrate, copper nitrate, zinc nitrate,
iron nitrate were from Merck, p.a. Nitric acid, acetic acid were high purity reagents (Merck, p.a.). All solutions were prepared in MQ-water (18.2 MΩ resistivity). The electrochemical cell and glassware were cleaned prior to use by immersion in HNO₃ 10% solution for a few hours and then rinsed with MQ-water.

**Microelectrode preparation**

*Wire microelectrode*: a gold wire (25 µm diameter, approximately 4 cm length) was soldered with a shielded electrical conducting wire; then the electrode wire was protruded into a 1 ml polyethylene tip (about 1.5 cm long, 3 mm diameter); one end of the tip was heat-sealed and another was filled up with non-conductive epoxy glue. The electrode then stood for a few hours for the glue solidification. The proper electrode was obtained when the connection of gold and conducting wires was completely sealed with the glue. Finally, the electrode was put in the oven at about 130°C over night, rinsed with MQ-water to be ready for the following activation step. *Band microelectrode and disk macro-electrode*: A silver sheet (7 mm in length, 25 µm diameter), gold sheet (12 mm in length, 0.5µm thickness), and a gold rod (1 mm diameter) were utilized for making silver band, gold band, and gold disk microelectrode, respectively. The way of preparation was similar to that for wire microelectrode. However, the tip end where the sheet or rod protrudes was polished with sand paper, subsequently with diamond paste to mirror like surface. After the glue solidifies, the heating of the electrode was recommended to minimize organic interferences from the glue.

**Activation**
The electrodes were activated by using cyclic voltammetry; 10 cycles from 0 mV to -600 mV for gold microelectrode and 0 mV to -800 mV for silver microelectrode were performed in 10 mM HNO₃ at a rate of 50 mV/s. The stable background and stable responses were achieved after several cycles as the indication of the proper electrode behaviour. This activating step was needed before each experiment.

**Mercury plating on gold microelectrode**
Mercury film was deposited at the gold electrode before each series of experiments. Before the plating step, the gold electrode was rinsed with MQ-water and activated to obtain the stabilization. A solution of Hg(NO₃)₂ 500 ppm and 0.1M HNO₃ was used as the plating solution. The plating was then performed without stirring by holding the potential at -0.3V for 10-20 minutes. The performance of the mercury film electrode can be checked by linearly scanning the potential in the range of -1.4V-0V for several times.

**Experimental conditions**

<table>
<thead>
<tr>
<th>For gold electrodes:</th>
<th>Linear sweep anodic stripping voltammetry (LSASV) utilizing subtractive anodic stripping voltammetry (SASV) method.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte:</td>
<td>10⁻²⁻¹⁰⁻³ M nitric acid and 0.1M KNO₃</td>
</tr>
<tr>
<td>Deaeration time:</td>
<td>15 minutes, stirring with Teflon stirrer</td>
</tr>
<tr>
<td>Deposition time:</td>
<td>-0.9 -1 V</td>
</tr>
<tr>
<td>Scan rate:</td>
<td>0.1-1 Vs⁻¹</td>
</tr>
<tr>
<td>Cleaning time:</td>
<td>60s (at 0 mV)</td>
</tr>
<tr>
<td>Deposition time for Pb: 60-900s; 60-600s; 30-300s (levels 10ppb; 30ppb; 70ppb, respectively).</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>For silver electrodes:</th>
<th>Differential pulse anodic stripping voltammetry (DPASV) using SASV method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte:</td>
<td>0.01M HNO₃ and 0.01M KCl</td>
</tr>
<tr>
<td>Scan rate :</td>
<td>30 mV/s.</td>
</tr>
<tr>
<td>Deposition pulse:</td>
<td>-800 mV</td>
</tr>
<tr>
<td>Amplitude pulse:</td>
<td>50 mV.</td>
</tr>
<tr>
<td>Cleaning time:</td>
<td>60 s (at -100 mV)</td>
</tr>
<tr>
<td>Time deposition depends on concentrations of cadmium and lead:</td>
<td></td>
</tr>
<tr>
<td>Pb 10-100 ppb (15s), 5-80 ppb (30s), 3-60 ppb (60s), 2-40 ppb (90s).</td>
<td></td>
</tr>
<tr>
<td>Cd 15-80 ppb (30s), 10-65 ppb (60s), 5-45 ppb (90s).</td>
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</tbody>
</table>
Results and discussion

Gold microelectrode

Mercury plated and unplated electrode

The background current and SASV for lead at bare gold and gold plated with mercury electrodes in deaerated supporting electrolyte (0.1M HNO₃+0.1M KNO₃) were presented in Figure 1.

![Figure 1: Gold wire microelectrode (25 µm diameter, 4 cm length) before and after the plating of mercury; 1.A. Shape of background current; 1.B. SASV of lead, electrolyte 10⁻³HNO₃ and 0.1M KNO₃; (a) unplated, Pb 70 ppb, tₜₐₜₜ 120 s; (b) plated, Pb 70 ppb, tₜₐₜₜ 120 s; (c) unplated, Pb 140 s, tₜₐₜₜ 300 s. ASV conditions follow 2.5](image1)

The working potential window, for gold was -0.5 to 1.5V and for mercury film was -1.4 to 0.5V. The smoother background with the extended negative potential of mercury film electrode prove its applications in measuring lead and other metals with more negative redox potential. Moreover, the higher peak current results in greater sensitivity and selectivity.

Sensitivity versus dimensions of the electrode

The electrode geometry was also a considerable factor contributing to the sensitivity. As the size of electrode reduces, the greater sensitivity was achieved due to the reduced charging current incorporated with the enhanced diffusion rate.

![Figure 2: Sensitivity versus geometry of the electrodes, Pb 70 ppb, plated with mercury; (a) disk (1mm diameter); (b) band (12 mm length, 0.5 µm thickness); (c) wire (25 µm diameter, 4 cm length). ASV conditions follow 2.5](image2)

The performances of the mercury plated electrodes with various geometries and dimensions were compared in Figure 2. The peak current at wire microelectrode, at equal lead concentration and in the same analytical conditions, was much higher than those at band microelectrode and disk macro-electrode, respectively. In the case of band microelectrode, the peak current was, which was higher than that at the macro-electrode, still much
lower than at the micro-wire. This can be explained by the restricted spherical diffusion layer at the band microelectrode [3]. For the above demonstrations, wire microelectrode should be used for the improvement in sensitivity.

Effect of oxygen
In acidic solution, oxygen undergoes two-step reduction to $\text{H}_2\text{O}_2$, then to $\text{H}_2\text{O}$ that results in increased background current and hence the poorer sensitivity. As shown in figure 4, the background increases progressively in non-deaerated solution compared to that in deaerated solution (bubbled with nitrogen for 15 minutes). Since anodic stripping peak of lead was at about -0.4V, obviously it was affected by the present of oxygen. Figure 3 was a demonstration for the poor sensitivity in a non-deaerated lead solution.

![Figure 3: Effect of oxygen](image)

Figure 3: Effect of oxygen; 3.A. Background current; (a) deaerated; (b) non-deaerated; 3.B. SASV of Pb 70 ppb, $t_{\text{dep}}$ 60 s; (a) deaerated; (b) non-deaerated. ASV conditions follow 2.5

Effect of stirring
Microelectrode exhibits concentric diffusion, in theoretical aspect, which should minimize stirring effect [1, 2]. However, our experiments using micro-wire electrode in deaerated solution of Pb 70 ppb indicates that the response for lead was much higher by stirring during the deposition step (Figure 4).

![Figure 4: Effect of stirring](image)

Figure 4: Effect of stirring on SASV of Pb 70 ppb, $t_{\text{dep}}$ 120 s; (a) without stirring; (b) stirring. ASV conditions follow 2.5

It seems that true microelectrode behaviour was not achieved for the wire electrode in our experiment. Another previous study also has reported similar finding [3-6]. More experiments on cyclic voltametry may be needed to verify the electrode behaviour.

Behaviour of wire microelectrode
In this section, the performance of the gold wire microelectrode was examined by using cyclic voltametric technique. The cyclic voltamograms of different electrodes (gold micro-wire 25 µm diameter, and gold disk-1mm diameter) in deaerated ferrocene ($\text{K}_3\text{Fe(CN)}_6$) solution were recorded with varying scan rates (0.01-10Vs$^{-1}$).
The results (Figure 5) show that at the same scan rate, electrodes with larger diameter have more significant hysteresis in forward and backward curves. The shape of the voltamogram changes with the scan rate. At low scan rate (0.02 V/s⁻¹), the forward and backward scans were rather similar with the sigmoidal shaped curve. This was accounted for the dominating edge diffusion at the electrode surface, which gives rise to the diffusion rate. On the contrary, there was a hysteresis in the two scans at higher scan rates, the result of extended planar diffusion. The voltamograms were in agreement with the theoretical aspect demonstrating that expected performance of gold wire microelectrode was achieved. It can be inferred that the used scan rate (0.1 V/s⁻¹) in the testing of stirring effect was insufficient to minimize the influence of stirring.

**Silver micro band electrode**

**Characterization of the lead and cadmium deposition at micro band silver electrode:**

One of the problems which should be considered when studying at solid electrodes is under-potential deposition (UPD) that relates to the sub-monolayer formation of trace metals in solid electrodes [6]. UPD is very sensitive to the electrode material. Hence, UPD phenomena show the sensitivity of the analytes to the working electrode and the efficiency of the stripping step. This is a simple guidelines used for selecting electrodes and conditions for ASV. The UPD peak of lead was sharper and considerably better defined than that of cadmium (Figure 6).

![Cyclic Voltammograms of Pb (a) and Cd (b) at silver band microelectrode.](image)

**Solution:** 10 mM Pb and 10 mM Cd in 10 mM HCl and 10 mM KCl. Scan rate 30 mV/s.

Based on this guideline, lead was very suitable for determination at silver electrode while cadmium was not expected to be sensitive to silver electrode. However, the simultaneous determination of lead and cadmium can be carried out without overlapping peaks.
Effect of oxygen
Oxygen can dissolve in water at $10^{-3}$M. In acid medium, oxygen is reduced at Ag electrode in 10 mM HNO$_3$ + 10 mM KCl including two steps:

$$\begin{align*}
O_2 + 2H^+ + 2e^- &\leftrightarrow H_2O_2 & E^{0/2} = -440 \text{ mV vs. Ag-QRE.}
H_2O_2 + 2H^+ + 2e^- &\leftrightarrow 2H_2O & E^{0/2} = -600 \text{ mV vs. Ag-QRE} \quad [7]
\end{align*}$$

At the deposition potential of Pb and Cd (-800mV vs. Ag-QRE), the reduction of oxygen at Ag electrode into H$_2$O is dominated [8]. Hence, oxygen is depleted at the electrode during deposition period. Moreover, the difference between current samples of DPV allows moderating this effect during the stripping step. Therefore, the signals of cadmium and lead in presence or in absence of oxygen were nearly identical (Figure 7). The different results obtained in the experiments with mercury plated gold electrode might be caused by the use of LSV.

Figure 7: Effect of oxygen on 30 ppb Cd, 10 ppb Pb. ASV conditions

Effect of stirring
In agreement with the experiment on gold microelectrode, stirring affects significantly on the peak currents. Hence, the peak height of lead and cadmium was ill defined and decreases without stirring in the same deposition time with stirring condition. However, its effect can be, in another way, eliminated by the longer deposition time (Figures 8, 9).

Figure 8: Effect of stirring on 30 ppb Cd, 10 ppb Pb. ASV conditions follow 2.5

Figure 9: SASV of 15,30,45,60,75 Cd and 5,10,15,20,25 ppbPb without stirring. ASV conditions
Because of the convergent diffusion of silver band microelectrode [9], the current decays more slowly than the macro one and the quasi-steady state can be achieved for a sufficient time.

**Interference considerations**

**Effect of copper**

Copper is not a prime interference up to 50 times excess compared to lead at mercury plated gold electrode. At the silver one, effect of copper was negligible up to 90 times excess compared to lead and 30 times excess compared to cadmium.

**Effect of cadmium on lead**

At mercury film plated gold electrode, no cadmium peak was seen and stripping lead signal does not change even in the present of very high excess of Cd (7 ppm). This phenomenon was in agreement with some previous investigations: Cd usually has much poorer sensitivity than Pb (40 times) on gold substrate [3-6]. Moreover, the high lead concentration in environmental samples allows the its analysis in the present of Cd (Figure 10).

However, at silver electrode, Cd doesn’t affect on Pb peak up to 200 times excess to lead. The higher background due to nitrate reduction with the large excess of Cd concentration causes slightly distorting and decreasing the Pb peak. The problem can be solved with deposition potential -650mV (Figure 11, 12).

![Figure 10](image1.png)

Figure 10: Effect of Cd on SASV of Pb in solution of Pb 70 ppb, t_depot 60 s; (a) Cd 0 ppb; Cd 1.4 ppm; (c) Cd 2.8 ppm; (d) Cd 5.6 ppm; (e) Cd 7 ppm; ASV conditions follow 2.6

![Figure 11](image2.png)

Figure 11: ASV of effect Cd concentrations on 10 ppb Pb. ASV conditions follow in 2.5

![Figure 12](image3.png)

Figure 12: Voltammograms of 3,4,5,6 ppb Pb at 650 mV. ASV conditions follow in 2.5.
Effect of lead on cadmium at silver microelectrode

![Graph showing the effect of lead on cadmium](image)

Figure 13: Effect of Pb concentrations on 30 ppb Cd.
ASV conditions follow in 2.5

Figure 13 has shown that over 15 ppb of Pb decreases the 30 ppb of Cd peak and 35 ppb of Pb declines 30% the Cd peak height. Hence, the analysis of Cd can be carried out when Pb concentration was at least 2 times smaller than Cd.

Repeatability and detection limits

In our experiments, the calibration curves of cadmium and lead standard mixtures in various concentrations (Figure 14) have shown that the sensitivity of lead was 10 times higher than that of cadmium.

![Graph showing calibration plots](image)

Figure 14: Calibration plots of 15, 30, 45, 60, 75 ppb Cd and 5, 10, 15, 20, 25 ppb Pb mixtures, ASV conditions follow in 2.5.

The reproducibility for determination of lead at mercury film (LSV), cadmium and lead at silver microelectrode (DPSV) was tested with 10 repeatedly consecutive experiments of various concentrations. It was found that both kinds of electrodes gave high repeatability.

For mercury film microelectrode, RSD% at Pb 70 ppb was 4% (30 s deposition), at 30 ppb was 8% (60 s deposition), and at 10 ppb was 11% (60 s deposition). The repeatability of silver microelectrode was summarized in Table 1.
Table 1: Repeatability of the DP-ASV method at silver microelectrode

<table>
<thead>
<tr>
<th>$t_{dep}$ (s)</th>
<th>15s</th>
<th>30s</th>
<th>60s</th>
<th>90s</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (ppb)</td>
<td>Pb</td>
<td>Pb</td>
<td>Cd</td>
<td>Pb</td>
</tr>
<tr>
<td>20</td>
<td>15</td>
<td>45</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>3.1%</td>
<td>3.0%</td>
<td>3.9%</td>
<td>2.3%</td>
</tr>
</tbody>
</table>

The detection limits, calculated as three times of the standard deviation of 11 blank samples at silver microelectrode were 1.06ppb for Cd and 0.64 ppb for Pb at 60s deposition time.

**Determination of Cd and Pb in tap cold water**

Tap water was sampled at Roskilde University Center (RUC) and was pretreated by wet digestion with mixture of nitric/sulfuric acid to release free lead and cadmium. The effect of surfactants on silver electrode was also eliminated after digestion. The standard addition method was used for three consecutive series of 10, 20, 30 ppb of cadmium and 2, 4, 6 ppb of lead (three duplicates for each). The concentrations of cadmium and lead in tap water, efficiency of wet digestion and results of cadmium and lead in tap cold water were shown in Table 2.

Table 2: Results of tap cold water at RUC

<table>
<thead>
<tr>
<th>Average recovery of wet digestion</th>
<th>$C$ (ppb) in sample</th>
<th>MPL(*) (ppb) WTO</th>
<th>MPL(*) (ppb) EU</th>
<th>$C$ (ppb) drinking water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>85.9% ± 4.8</td>
<td>&lt; 5.00</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pb</td>
<td>98.2% ± 6.7</td>
<td>3.69 ± 0.31</td>
<td>10</td>
<td>50</td>
</tr>
</tbody>
</table>

(*) Maximum permissible level

The result showed that the concentrations of lead and cadmium in tap cold water were in range of the natural level of drinking water and below the maximum permissible level of WTO or EU.

**Conclusion**

It is, demonstrated that higher sensitivity was achieved with the microelectrode compared to the macro one. The sensitivity for metal analysis was strongly depended on the material and the geometries of the electrodes. Mercury plated gold electrode was not sensitive to cadmium but silver micro band electrode was sensitive to lead and cadmium. Hence, simultaneous analysis of cadmium and lead can be carried out at silver one.

Stirring affects on the sensitivity of the measurement; however, it can be compensated by faster scan rate or longer deposition time. With the optimized conditions, the repeatability for consecutive ASV runs was good at both electrodes. At mercury film electrode, RSD % were 4%, 8%, 11% at 70vppb (30 s), 30 ppb (60 s), and 10 ppb (60 s) for Pb, respectively. For silver micro electrode, RSD% were 3.1%, 3.0%, 2.3%, 4.6% at 20 ppb (15 s), 15 ppb (30 s), 10 ppb (60s), 5ppb (90s) for Pb, respectively and 3.9%, 5.5%, 4.0% at 45 ppb (30 s), 30ppb (15 s), 15 ppb (90 s) for Cd, respectively.

Finally, the analysis of cadmium and lead at silver band microelectrode in cold tap water proved the applicability of the method on monitoring environmental samples at trace levels.

**Acknowledgement**

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References