PROGRESS REPORT FOR AINGRA07152

**PROJECT TITLE**
Investigation of conditioning methods on the gold electrode surface employed in electroanalyses of arsenic

**INVESTIGATOR(S)**

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<th>Chief Investigator</th>
<th>Institution and Department</th>
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<tr>
<td>Dr Magdalena Wajrak</td>
<td>Natural Sciences, Edith Cowan University</td>
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**Other Investigators**
Assoc Prof Roland De Marco, Curtin University of Technology.

**Students**
Kathryn Prince

**ANSTO Investigators**
Kathryn Prince

**Specialist Committee**
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**SCIENTIFIC OBJECTIVES**

The main objective of this project was to obtain profile of the surface of a gold electrode after subjecting it to electrochemical process, which detects arsenic in water. The sensitivity of the gold electrode for arsenic ions seems to be significantly dependant on the surface of the gold electrode and so the aim of this project was to try to correlated the various conditioning methods applied to the electrode to its affinity for deposition of arsenic.

**PROGRESS REPORT, RESEARCH OUTCOMES and DATA**

Anodic stripping voltammetry (ASV) offers an alternative method for the detection of heavy metals, and in particular arsenic in groundwater, however, the sensitivity of this method is greatly dependant on the surface of the working electrode. Arsenic has affinity for gold and therefore gold working electrode is chosen for arsenic detection.

However, although the ASV method can be very sensitive for arsenic analysis (down to 2.5 ppb), the ability of the instrument to detect to such low levels is greatly dependant on the surface of the electrode being used. Extensive laboratory work carried out by the investigator has shown that different conditioning techniques can activate or deactivate the surface of the electrode towards arsenic. In order to fully understand the relationship between the various conditioning methods and what they 'do' to the surface of the electrode it is necessary to obtain atomic image of the surface of the electrode. Such investigation would provide valuable information with regard to what conditioning treatment is necessary to improve the sensitivity of the electrode. At the moment it is all guess work and we don't actually understand why for example conditioning the electrode by doing a high arsenic concentration pre-run is necessary to activate the electrode.

The aim of this project was to examine the composition of the surface of the gold electrode after depositing arsenic on the electrode under different conditions (various electrolyte solutions – HCl and CH₃COOH, deposition potentials and electrode polishing techniques).

The first stage of the investigation involved obtaining a profile of the ‘bare’ gold electrode prior to arsenic deposition. This was necessary in order to establish the type of source beam to use (Cs +ve or –ve ions), raster size and voltage. Surprisingly, this preliminary analysis revealed that the gold electrode already contained significant arsenic within its surface (see Figure 1). A number of runs were performed to confirm that. This was unexpected because the electrode was 99.99% pure gold and previous SEM analysis did not detect any arsenic. Unfortunately, the supplier of the gold electrodes did not provide composition analysis and therefore it was not possible to have known the % of impurities in the electrode.

In addition a number of different gold electrodes were examined and it was found that the distribution of arsenic within the surface of the gold electrode varied with the electrode. This created a problem, because after arsenic
was deposited on the surface of the gold electrode using electrochemical process, it was not possible to confirm that the arsenic profile was due to the film of deposited arsenic and not the arsenic already present within the bulk of the gold electrode. If the same electrode was used for each deposition run then a profile difference would have allowed us to observe the deposited arsenic film, but because of the electrode size, once electrochemical run was done, the tip of the electrode had to be cut off in order for it to fit into the SIMS compartment (see Figure 2) and therefore each time a new electrode had to be used. This introduced variation in the arsenic composition within the gold electrode.

Due to the above mentioned issue and additional concern as to the possibility of interferences from, for example F and Si contributing to the arsenic count, it was decided to trial depositing a gold film on top of the gold electrode in order to eliminate the arsenic contamination from the gold electrode. A new gold electrode was placed in a solution of 100ppm Au standard in 1M HCl and gold was deposited for 1200sec at -500mV. The profile of this electrode is shown in Figure 3. As expected there is no arsenic detected and both silicon and chlorine drop off as the beam goes deeper into the bulk of the gold electrode. Viewing the electrode under a light microscope and SEM* clearly shows (see Figures 4c and 4d) the gold film being deposited on the gold electrode as compared to bare gold electrode (see Figures 4a and 4b).

* Please note that the SEM work was performed at Curtin University in Perth three days after the SIMS work was done.
Gold (100ppm) film deposited for 1200sec in 1M HCl

Figure 3.
a) bare gold electrode (light microscope, x90),
b) bare gold electrode (SEM – secondary electrons, x2000),
c) gold film, 100ppm Au, deposited for 1200sec in 1M HCl (light microscope, x 90),
d) film deposited.

The next step was to try to deposit arsenic film on top of that gold film and detect it. Arsenic film was deposited on top of the gold film by placing the electrode in 1ppm solution of arsenic standard in 1 M HCl and depositing for 960sec at -700mV. To confirm that arsenic film was deposited, a strip run was performed into a fresh 1 M HCl solution, the arsenic peak is shown in Figure 6. SIMS profile of this electrode (see Figure 5) shows that we were able to finally detect arsenic on top of the gold film (compare with Figure 3 above), but it does appear to be very thin, because the arsenic count drops off quickly. Further analysis needs to be done to confirm the presence of arsenic film, but once that is done, investigation of the deposition time and electrolyte solution can be performed.

Figure 4. Chemical profile of the electrode with gold film deposited. As can be seen there is no arsenic detected.
Arsenic (1 ppm) deposited for 960 sec on top of gold (100 ppm) film deposited for 1200 sec in 1M HCl

Figure 5. Chemical profile of the electrode with gold film and arsenic film on top of the gold film. Initial arsenic count is high and then it drops off as the beam reaches the gold film.

Figure 6. Electrochemical scan, showing arsenic peak after arsenic was deposited on top of the gold film and then stripped into a fresh 1M HCl solution.

Unfortunately, I was not able to complete any further investigations as my beam time ran out. Therefore, I was not able to examine the relationship between the chemical profile of the electrode and the deposition of arsenic. I do hope to be able to obtain more beam time next year and continue this investigation.

Further investigations would involve:

1. Confirming presence of the arsenic film on top of the gold film.
2. Determination of the quality and quantity (thickness, using SIMS) of arsenic film on top of the gold electrode using different electrolyte solutions and deposition periods.
3. Detecting arsenic on top of the bare gold electrode, but this time using the same electrode for each electrochemical run and knowing the amount of arsenic in the gold electrode prior to SIMS analysis.
4. Investigating factors such as electrolyte type, deposition time, polishing of the electrode and other conditioning methods on the quality and quantity (thickness, using SIMS) of the arsenic film being deposited on the bare gold electrode.

There are a number of additional issues I would like to examine, such as the role of chlorine and silicon in arsenic deposition.

Although, I was not able to complete all of the aims of the original application, I did obtain significant information with regard to what information I can obtain from the SIMS instrument, the SIMS set-up
needed for the type of data I want to collect and most importantly what type of design that is required for the gold electrode in order to do this analysis successfully.

The information that will be hopefully obtained from this research project will help to understand the link between chemical profile of the electrode and arsenic deposition and thus provide valuable information how to obtain reliable and accurate results from using ASV to detect arsenic, in particular for infield measurements. This is become a rather important issue, due to the fact that the disturbance of acid sulphate soils found in large sections of Australia can cause arsenic and other heavy metals to leach into groundwater. Not to mention the desperate need for an accurate and reliable infield arsenic detection method for countries such as Bangladesh and India, where millions of people are being poisoned by drinking arsenic contaminated groundwater.

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PUBLICATIONS / REPORTS arising as a result of your work.

Because the work was only completed in July 2007, no publications have yet been submitted. However, I have presented the results from this research work at a departmental seminar at Curtin University, Perth.

PhD STUDENTS

N/A