

Determination of silver by differential pulse anodic stripping voltammetry: An APCELL experiment.¹

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Introduction

There are a number of sensitive and accurate analytical techniques that can be used to detect metal ions in water samples, for example, Inductively Coupled Plasma (ICP) [1] and Atomic Absorption Spectroscopy (AAS) [1]. However, those methods require the use of highly expensive instrumentation, can only be used in a laboratory with gas (eg. acetylene) access and be operated by a trained technician or chemist and most importantly they cannot speciate, ie. it is not possible to determine whether for example, As(III) or As(V) ions are present in the sample. Speciation of metal ions is required for understanding the role trace metals play in natural waters and the effect on human health. Voltammetry is another analytical method which is used in trace metal analysis [2]. It is just as sensitive as ICP and AAS [1], however, it is considerably less expensive in terms of instrument cost and set-up, can be used in field and most importantly has the advantage of species characterization, ie. possible to determine the exact chemical nature of the trace constituent. There are a number of different voltametric techniques; however the most widely used for trace metal analysis is Anodic Stripping Voltammetry (ASV). ASV is an electrochemical technique in which the current-potential behaviour is measured and it basically consists of two-steps; deposition and stripping. In the deposition step, metal ions from the solution are reduced at a negative potential and are deposited onto an electrode. Then the potential is gradually made more positive and the metal is oxidised or stripped back into solution generating a current which is proportional to the concentration of metal ions in solution for a given deposition time. The ASV instrument is very simple it consists of a cell where the sample is placed, a stirrer and three electrodes; working electrode, where at which the reaction of interest occurs, the reference electrode, which provides a known and steady potential and an auxiliary or counter electrode, which minimizes errors from cell resistance in controlling the potential of the working electrode. There are a number of different working electrodes which can be used, such as hanging mercury drop electrode (HMDE), thin film mercury electrode (TFME) and composite carbon electrode. The accuracy and reproducibility of ASV is highly dependent on the quality of the surface of the electrode, because of this HMDE has the advantage over the other two electrodes

since a new mercury drop is generated for each run. However, composite carbon electrodes provide an extended anodic potential range, which means they can be used for a wider range of metals. In addition, carbon electrodes are safer to use than HMDE and allow for the system to be used in field. Composite electrodes combine the advantages of micro-electrodes (e.g. analysis of small samples volumes, ability to work in highly resistive solutions) with much higher currents due to larger surface areas.

In this experiment students will investigate some aspects of ASV using carbon electrode to detect silver ion concentration in water samples. The exercise also encourages students to consider such issues as accuracy of different analytical techniques, relative costs, availability, etc.

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Educational Template

Section 1 - Summary of the Experiment

1.1 Experiment Title

Determination of Silver By Differential Pulse Anodic Stripping Voltammetry.

1.2 Description of the Experiment

Detection of trace amounts (down to ppb levels) of metal ions, especially heavy metal ions, in drinking water is of great importance due to health reasons [1]. It is now well known that metals such as lead, mercury, cadmium and arsenic are toxic even at very small concentrations [1], because they accumulate in vital organs in our bodies and can cause cancer and other health problems.

Anodic Stripping Voltammetry is the most sensitive electro-analytical technique currently available for the

¹ The complete documentation for this experiment is freely available on the APCELL web site [www.apcell.org]. It includes the educational template, a set of student notes, demonstrator notes and technical notes to allow ready implementation into a new laboratory.

detection of trace amounts of electro-active metal ions. Understanding the principles of voltammetry and acquiring skills in being able to use ASV to detect species of interest in a given water sample is the goal of this experiment.

In this exercise students will use ASV to determine concentration of silver ions in a given water sample. As part of the experiment students will gain better understanding of the ASV method by investigating the effect of accumulation or deposition time, performing chemical pre-treatment on the working electrode, analysing samples which contain two metal ions with similar stripping potentials, determining the difference in accuracy between two calibration methods and finally analysing a given water sample containing unknown quantity of silver ions.

1.3 Course Context and Students' Required Knowledge and Skills

This experiment forms part of a Bachelor of Technology (Applied and Analytical Chemistry) degree at Edith Cowan University. As part of their degree students enrol in Analytical Chemistry II unit, which is run in the first semester of the third year of that degree. The course focuses on the theory and application of analytical methods with an emphasis in the laboratory on experiments with a 'real world' component, a problem which they are likely to encounter in industry.

Most of the students enrolled in this unit are also concurrently completing a second unit which covers other analytical techniques, such as Atomic Absorption Spectrophotometry. This enables the students to consider how analytical techniques complement each other and the limitations and appropriateness of each technique in different sample analyses.

The students have already covered electrochemistry and polarography theory in previous year in a Physical Chemistry unit and they have completed one polarography experiment using hanging mercury electrode. Current experiment introduces students to a new technique called 'Anodic Stripping Voltammetry'. Instead of using a

hanging mercury electrode, a composite carbon electrode is used. The metal ions in the solution are electro-reduced onto the carbon electrode and then are stripped away by reversing the voltage. This experiment emphasises the application of this technique and investigation of some basic voltammetry concepts rather than getting students to perform another routine 'theory heavy' voltammetry laboratory.

The experiment assumes that students have the following skills and knowledge:

- Basic knowledge of polarography
- Basic understanding of the principles of voltammetry
- Ability to prepare standard solutions
- Skills in the use of automatic pipettes
- Understanding of the two types of calibration methods
- Ability to construct calibration curves and calculate standard deviations
- Completion of practicals; 'Atomic Absorption Spectroscopy' and 'Polarography'

1.4 Time Required to Complete

Prior to Lab	1 hour reading
In Laboratory	2-3 hours "wet" laboratory
After Laboratory	2-3 hour report writing

1.5 Providence

The original source of this experiment is unknown. It was adopted from a third year Analytical Chemistry 2 laboratory manual at ECU put together by Dr Jackie Rummey. There are however, many similar experiments which use ASV to determine various metal species in water samples, see for example those published in *J. Chem. Ed.* [3-6].

1.6 Other Comments

This exercise can be easily adopted for analysis of other metals such as zinc, cadmium, lead, mercury, arsenic etc., and is relatively cheap in terms of chemical cost. Portable voltammeters are now available for around \$5000.

Section 2 – Educational Analysis

Learning Outcomes	Process	Assessment
<i>What will students learn?</i>	<i>How will students learn it?</i>	<i>How will staff know students have learnt it?</i> <i>How will students know they have learnt it?</i>

Theoretical and Conceptual Knowledge

Students will gain a better understanding of some simple voltammetric concepts, such as deposition time.	For example, students will perform a number of runs on a silver standard of certain concentration and investigate the effect of changing deposition time.	Demonstrator will probe students for discussion during experiment and ask questions with regard to their results. Students are also expected to write and submit an 8-10 page scientific report where they will have to answer questions on their results, which the demonstrator will mark and return to students with comments.
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<p>Students will use theoretical aspects of analytical chemistry and voltammetry to analyse the given samples. For example, theoretically students know that a calibration curve is needed to determine concentration of an unknown solution, but how is this achieved practically?</p>	<p>The analysis is expected to be performed independently (or in pairs) with occasional guidance provided by a demonstrator. Students will perform “dummy runs” of the samples, and compare them against a known standard in order to determine the range of standards needed for calibration. They will then use the calibration data to determine concentration of the given unknown sample.</p>	<p>Interaction with a demonstrator will indicate that students are following the right path. If they do not select their standards appropriately then the unknown sample value will lie outside the calibration range. Students will submit a scientific report detailing the results of their data analyses. Demonstrator will mark the report commenting on the quality of student’s data with respect to the unknown sample. The unknown sample would have been previously analysed by the lab technician.</p>
<p>Students will use theory to explain the difference between standard addition and external standard calibration methods.</p>	<p>Students will determine concentration of the given unknown water sample using two types of calibration methods.</p>	<p>Demonstrator will probe students to comment on the accuracy of the two calibration methods prior to analysis and justify their answer with theoretical explanation. Students will report their results in the scientific write-up and discuss their findings in terms of whether their results reflect what they would have expected.</p>
<p>Students will be able to apply the concept of metal-chelate complexation to eliminate interfering metal ions in the ASV technique.</p>	<p>As part of further investigation students will be asked to add some copper standard to a silver standard solution and they will discover that the copper peak overlaps with the silver peak. They will then add EDTA to the solution to complex copper and then re-run the solution to see the effect of EDTA (ie. only single peak due to silver should be seen).</p>	<p>Students will be asked to answer questions explaining the effect of the EDTA and to comment on their results. All voltammograms will be submitted in the report for marking.</p>

Scientific and Practical Skills

<p>Experimentally students will learn how to use the GAT voltammeter. Specifically, they will learn how to correctly set-up all electrodes and how to set-up the GAT software with parameters such as; deposition, strip and clean potentials, accumulation, strip and clean time and chemical pre-condition.</p>	<p>The analysis is expected to be performed independently (or in pairs) with occasional guidance provided by a demonstrator. Student will successfully perform runs on standard samples and obtain peak heights which correctly reflect the concentration of silver ions in the standard solutions.</p>	<p>Demonstrator will monitor student’s progress during the laboratory session. If there are any problems with running the voltammeter demonstrator will probe student for possible explanation and guide the student to help him/her to come up with a solution. In addition students will be probed by the demonstrator to explain certain aspects of the voltammeter and how it works. Plus show that they know how to set up the GAT software for different types of runs, eg. if they wanted to analyse different metal ions.</p>
<p>Students will gain further practical skills in standard preparation and the correct use of automatic pipettes.</p>	<p>Students will be asked to prepare all standard solutions themselves and the quality of their results should reflect the accuracy of their analytical skills.</p>	<p>Demonstrator will monitor student’s use of automatic pipettes and standard solution preparation during the laboratory session. Students will be marked on the quality of their results.</p>

Students will learn how to use “dummy runs” to select and make up standards in the correct range for calibration.	Students will be given a sample with an unknown silver ion concentration and will need to determine the concentration of this sample using calibration curve. They will first need to work out the range of standards needed for the unknown sample by firstly performing some ‘dummy runs’. This will guide them in terms of what standards they will need to prepare so that the unknown sample is within the standard range.	The successful arrival at the correct concentration (as previously determined by lab technician) of silver in the unknown sample will indicate that students have been successful in the use of the ‘dummy runs’ in choosing the correct standard range.
Students will learn how to be proficient with a scientific data analysis/graphical package.	Students will use the GAT program to analyse their data and plot calibration curves using both the external standard method and standard addition method. Hence they will obtain result for their unknown silver solution.	Demonstrator will monitor student’s progress in the use of GAT software during the laboratory session. Students will be asked to submit all plots generated by the GAT software.

Generic Skills

Critical analysis of why one particular analytical technique is chosen over another.	Discussion with a demonstrator is vital to encourage the students to think about their results and what they mean. The guidelines for writing the report also pose some questions to encourage students to make comparisons between analytical techniques.	The demonstrator’s interaction with the students will allow their progress in the laboratory to be effectively gauged. The required written report will also provide evaluation.
Students will develop new and industry relevant computer skills.	Students will use a software driven voltammeter to set-up runs and to analyse their data.	Students will demonstrate familiarity with computer driven voltammeter and be able to use the software to different types of analyses.
Students will further practice written communication skills by having to submit an 8-10 page scientific report	Students will be asked to prepare a detailed, clear, well-structured formal scientific report.	The report will be marked according to criteria given in experimental notes and students will receive written feedback from the demonstrator commenting on the report.
If done in pairs, students will further develop cooperative skills in a team environment and learn how to coordinate activities.	When working in pairs students will need to divide the tasks between themselves ensuring equality in workload and access to instrument.	Demonstrator will observe that both students are engaged in most aspects of the experiment and that they both have had enough practice using the instrument by asking each student to demonstrate how to use the software.
Students will further develop their mathematical skills in working out standard concentrations and dilutions using ppb units for concentration.	Students will need to prepare all standard solutions themselves and use $c_1V_1 = c_2V_2$ to work out different concentrations of standard solutions in the electrochemical cell.	Students will be asked to show all calculations within their final report as marks will be given for all working out. Demonstrator will provide feedback for incorrect calculations.

Section 3 – Student Learning Experience

Explanatory notes to Student Learning Experience

The version of the experiment presented here and the associated documentation have all been revised incorporating suggestions from the APCELL workshop participants, APCELL referees and student responses.

3.1 Did this experiment help you to understand the theory and concepts of the topic? If so, how, or if not, why not?

S1: Yes, voltammetry was a bit of a puzzle. After the experiment, my understanding of the theory increased.

S2: Yes, it confirmed what I thought.

S3: Yes, the effect of accumulation time is investigated so we see that an increased time gives a larger peak. Also seeing the effect of EDTA and the difference between a calibration curve and standard additions.

3.2 How is this experiment relevant to you in terms of your interests and goals?

S1: N/A.

S2: It demonstrates how voltammetry is another analytical method which I may one day need to use in a job.

S3: It is relevant to the electrochemistry theory given to us in Analytical Chemistry 2 unit.

3.3 Did you find this experiment interesting? If so, what aspects of this experiment did you find of interesting? If not, why not?

S1: Yes. We got to know the advantages and disadvantages of using EDTA.

S2: Yes, the interesting parts of this experiment in the 'what ifs'. Getting errors and finding how to fix them is the good stuff. Running standards or even unknowns is easy but the investigation is very important.

S3: Yes, it is set-up in an investigative manner.

3.4 Can the experiment be completed comfortably in the allocated time? Is there time to reflect on the tasks while performing them?

S1: No. I suppose so.

S2: No, due to the fact that standards need to be repeated. It can be a pain.

S3: Time is an issue, maybe it should be two labs one as an introduction/investigation, ie. accumulation time/EDTA and a second as analysis of unknown and application of previous.

3.5 Does this experiment require teamwork and if so, in what way? Was this aspect of the experiment beneficial?

S1: Yes, students can do different tasks, ie. prepare sample, etc. and save time. Yes.

S2: Yes, conformation among others helps. Group thought processes are very important for this lab.

S3: Yes, as there are often several things to be done at once between scans so to get things done more efficiently.

3.6 Did you have the opportunity to take responsibility for your own learning, and to be active as learners?

S1: Yes, developing ideas.

S2: Yes, running our own theories and practicing our ideas. From thought out method and trial and error, our own results are well designed.

S3: Yes, as we explored the experiment we had opportunities to discuss what is happening and why.

3.7 Does this experiment provide for the possibility of a range of student abilities and interests? If so, how?

S1: Yes, if they are interested in voltammetry. Also it is fun.

S2: For some students electrochemistry and voltammetry maybe right up their alley. Exposure to this method is valuable.

S3: Yes, because there are different jobs which need to be done; ie. computer operator, making solutions, analysis.

3.8 Did the laboratory notes, demonstrators' guidance and any other resources help you in learning from this experiment? If so, how?

S1: Yes, having the voltammogram from the demonstrator helps in knowing what is expected.

S2: Yes, guidance was the most help. The notes were useful where applicable. Changes needed to be made on the day. Experiments are not expected to be perfect on the day.

S3: Yes, both the notes and the demonstrator. When we were unclear with the notes the demonstrator explained.

3.9 Are there any other features of this experiment that made it a particularly good or bad learning experience for you?

S1: Some of the solutions were old. The program used needs to be changed. It plays tricks!

S2: The errors are a good thing. Errors help in the understanding of the procedure. By correcting them, the theory becomes clearer.

S3: Being like an investigation makes it a powerful learning experience as it provides a proof for the theory.

3.10 What improvements could be made to this experiment?

S1: A new computer with another program would make the experiment more successful. Ways of getting reproducibility and limit of tasks to be done.

S2: Less work, that is, less standard additions or normal calibration. This is to save time.

S3: Need a section to show the reproducibility of scans and make the experiment into two parts.

3.11 Other Comments

S1:

S2: Mock examples are good, because we have little exposure to voltammetry so we don't know where to expect a peak. Questions 1 to 4 are very good, but by now 5 and 6 should be known.

S3: Having sample results is good because it gives some idea of what is expected.

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