

Determination of Silver by Differential Pulse Anodic Stripping Voltammetry

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Experiment Overview

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 analysis². It is just as sensitive as ICP and AAS¹, 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.

Aims and Objectives

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 reasons¹. It is now well known that metals such as lead, mercury, cadmium and arsenic are toxic even at very small concentrations¹, 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 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.

Level of Experiment

Third year undergraduate

Keyword Descriptions of the Experiment

Domain

inorganic chemistry, analytical chemistry

Specific Descriptors

electrochemistry, differential pulse anodic stripping voltammetry, silver determination

Course Context

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 hanging mercury electrode a composite carbon electrode

is used. The metal ions in the solution are electro-reduced on to 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.

Prerequisite Knowledge and Skills

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'

Time Required to Complete

Prior to Lab: 1 h (reading)

In Laboratory: 2-3 h

After Laboratory: 2-3 h (report writing)

Experiment History

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 the *Journal of Chemical Education*³⁻⁶.

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.

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