

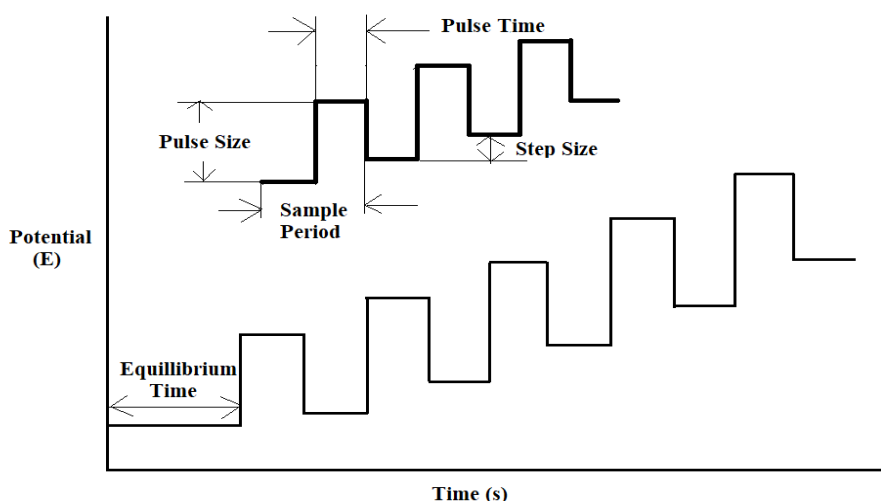
# Determination of Cd in water by Differential Pulse Anodic Stripping Voltammetry using Thin Film Mercury Electrode

*This article describes an experiment for an undergraduate chemistry laboratory to introduce Differential Pulse Anodic Stripping Voltammetry prior to studies of more complex systems. It also serves as a general introduction to computer-based instrumentation.*

## Introduction

Differential Pulse Stripping Voltammetry (DPASV) is a powerful electrochemical analytical technique that allows for the detection and quantification of a variety of metal ion species at very low concentrations in aqueous media. This technique consists of two main steps; Accumulation (preconcentration) and Stripping. The first step (Accumulation) is the electroplating of the analyte of interest on the electrode surface at a constant potential, followed by the second step (Stripping) which involves a potential sweep during which the preconcentrated analyte is stripped back to the solution, a process resulting in a current response proportional to the analyte concentration in the sample

The advantages of DPASV include sensitivity (extremely low detection in ppb), high accuracy, speed and modest cost.



*Figure 1: Potential wave form for differential pulse voltammetry.*

The potential wave form is composed of regular pulses that are consistently amplified and overlaid onto a staircase-like wave. Here, the current is sampled twice in each **Pulse Period** (once before the pulse, and at the end of the pulse), and the difference between these two current values is recorded and displayed

Differential pulse anodic stripping voltammetry (DPASV) is important for the detection of trace, heavy metal ions in very low concentrations in various sources like drinking water and soil, and in food industry for the determination of food contaminants such as toxic metal, pesticide, fertilizer, etc.

## Experimental Part

### Instrumentation

In this experiment a compact and portable potentiostat, **PhadkeSTAT™20** which runs on “EC-Prayog” a Windows supporting software was used.

### Requirements

A 3- electrode voltammetry cell, a **Glassy carbon working** electrode, a **silver/silver chloride reference** electrode, a **Platinum counter** electrode, a micropipette. (range from 100ul-1000ul)

The working electrode was cleaned by lightly polishing with alumina and then was rinsed with water. The connection between potentiostat and the cells are: Green= working; White= reference; Red= counter; Black= ground.



**Figure 2: From left to right (a) SVC-3 Voltammetry Cell (b) Reference electrode (Ag/AgCl) (c) Counter electrode (Pt Wire) (d) Working electrode (Glassy Carbon).**

## Reagent

All solutions should be prepared fresh and all the glassware should be soaked, preferably overnight in 3 M HNO<sub>3</sub> and rinsed several times with deionised water.

Acetic acid (CH<sub>3</sub>COOH), ammonia (NH<sub>3</sub>), Distilled Water, Hg standard stock solution (1000ppm), Hydrochloric acid (HCl) and Cadmium sulphate (3CdSO<sub>4</sub>·8H<sub>2</sub>O)

## Preparation of Standard solution

### (Cd Standard)

To prepare 1000ppm of Cd standard, weigh out 0.228g of 3CdSO<sub>4</sub>·8H<sub>2</sub>O and dissolve in by adding distilled water in a 100ml Standard flask then make it up to the volume and mix well. Then prepare a solution of concentration 10ppm by serial dilution method.

## Preparation of supporting electrolyte

### (Ammonium acetate buffer)

11.1 ml of acetic acid was taken in a 100ml volumetric flask, to this 20 ml of distilled water was added. 7.4ml of ammonia was slowly added to the volumetric flask. Ammonia has to be added slowly, because of the generation of heat while addition. After the addition of ammonia, the solution was diluted to 100ml with distilled water. The pH of the buffer is 4.6.

## Preparation of Hg plating solution

A 20ml solution of Hg<sup>2+</sup> is prepared. Take 0.4ml of Hg standard stock solution and put in the 20 ml volumetric flask. Add 0.2 ml of hydrochloric acid to it. Dilute the volumetric flask up to the mark with distilled water. This solution can be reused several times (20) and should be stable for a month.

## Nitrogen Gas

Used for purging to remove oxygen. Nitrogen is passed through a bottle containing the buffer solution for approx. 30 minutes to prevent evaporation of the sample solution.

## Procedure

### Preparation of Thin film mercury electrode

#### 1. Preparation of Glassy Carbon electrode for mercury film plating:

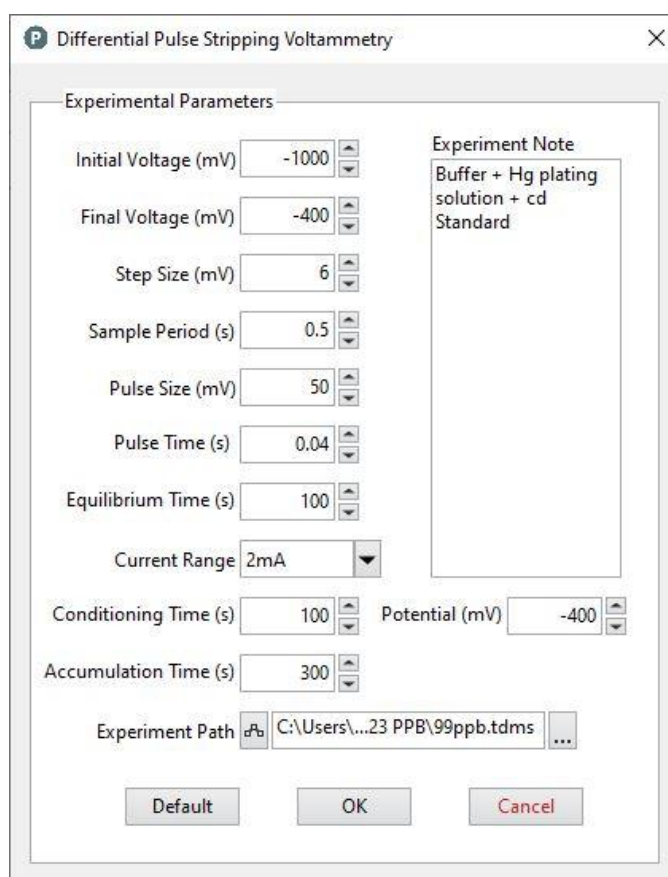
Clean the GC electrode with soft tissue, then the electrode is polished with electrode polishing kit; it is explained in detail in this [article](#). The electrode is then rinsed with acetone and afterwards thoroughly with distilled water.

#### 2. Plating of mercury film on GC electrode:

Here TFME is prepared in situ by adding the mercury plating solution directly into the supporting electrolyte at -0.4V for 300 seconds in the **DPSV** method. TFME can be prepared separately by plating mercury in a different solution then analyte and once the TFME is generated, it must be protected from oxygen to prevent oxidation of the film.

### Standardisation

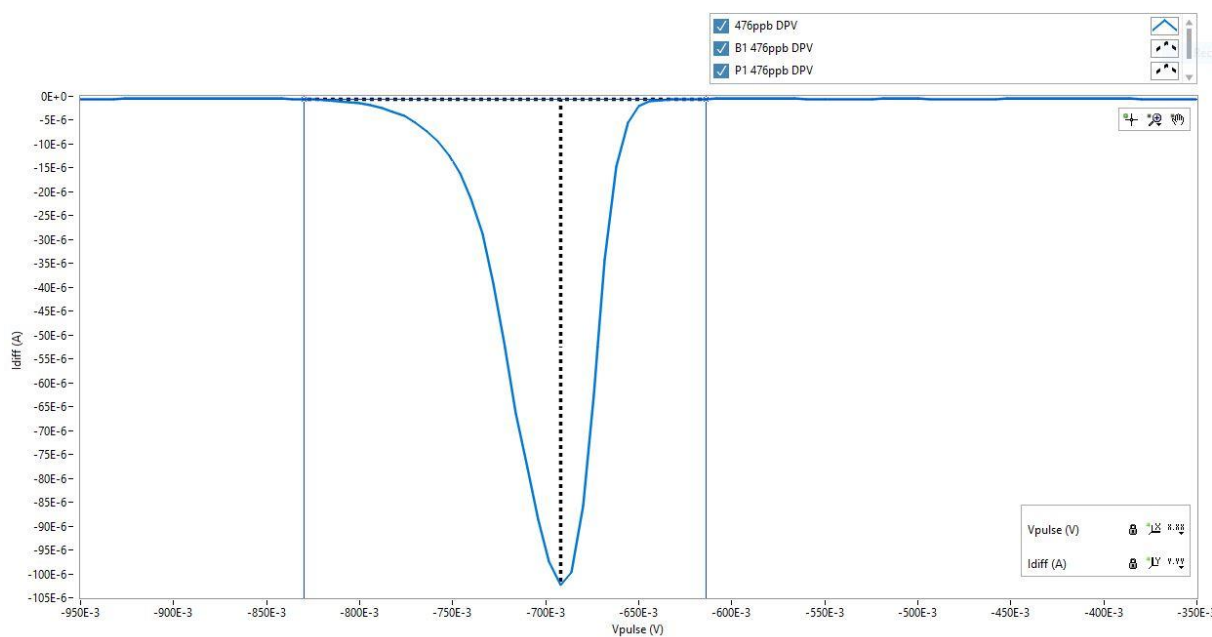
1. Take 100ml solution of Buffer and 20ml of mercury plating solution in the voltammetry cell add 1ml of Cd standard solution (10ppm), making the resultant concentration of the solution mixture of buffer, Hg plating solution and Cd standard 99ppb.
2. Go to **Experiment** menu to select Differential Pulse Stripping Voltammetry (DPSV) technique.
3. After selection of Differential Pulse Voltammetry, the **Experimental Parameters** box will open. Set the parameters as suggested below, you may change the parameters appropriately as per your requirement.



*Figure 3: Differential Pulse Stripping Voltammetry*

4. Once the parameters have been set, the experiment can be started by clicking **OK**, in the **Experiment** menu. The experiment is commenced; the voltammogram will appear on screen as it is generated and it will be rescaled automatically upon conclusion.

5. Keep on increasing the concentration of the solution by adding 1ml and repeat the experiment for different concentration.
6. After the experiment is concluded, go to the **Analysis** menu, a new tab will open showing the saved experiment files, select the file to be analysed another new tab will open; that is the Analysis window.
7. In the analysis window firstly select the file to be analysed, and then click on **Start Analysis**, then select both the cursor **Cursor 1** and **Cursor 2**, to find the peak on the graph manually. Move the cursor to the one end of the “peak” of the voltammogram and select a linear portion. Do the same thing at the other end of the “peak” of the voltammogram and then select **Draw Baseline & find Peak**.



**Figure 4: Analysis of voltammogram**

8. After getting the peak click on display result to find peak voltage and current from the baseline.

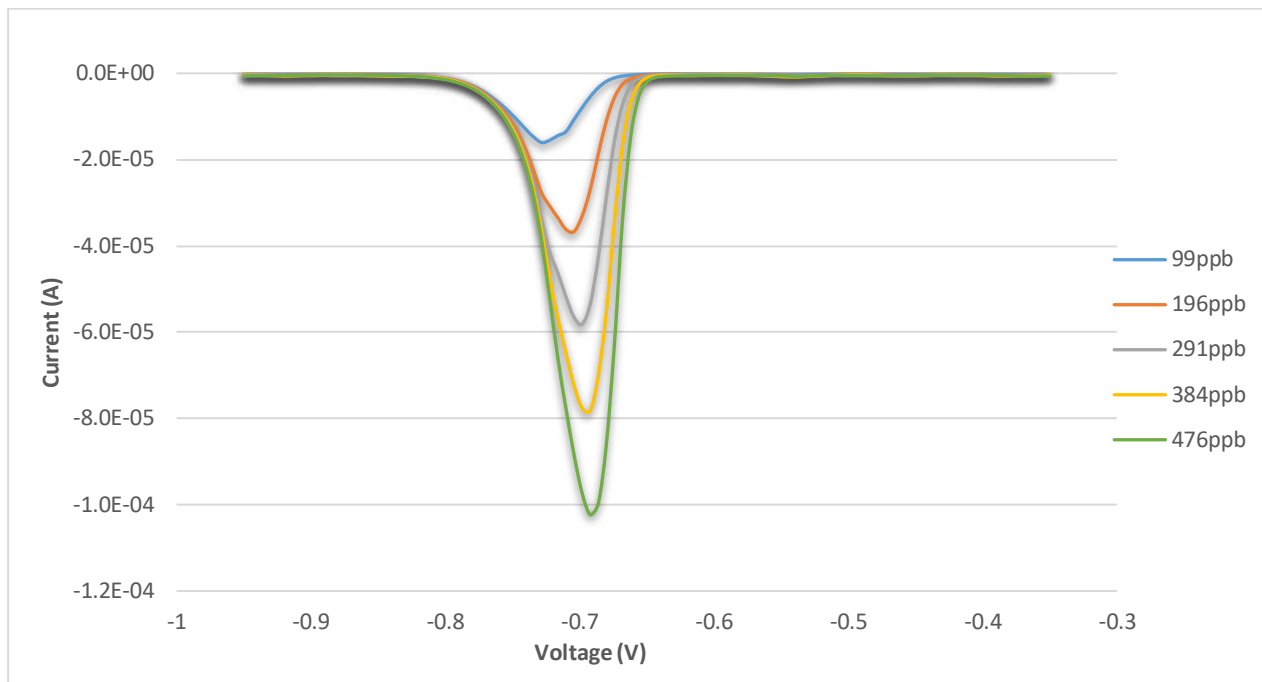
Result

Data Point	Vpeak (V)	Ipeak (A)
P1	-0.6920	-1.0178E-4

**Figure 5**

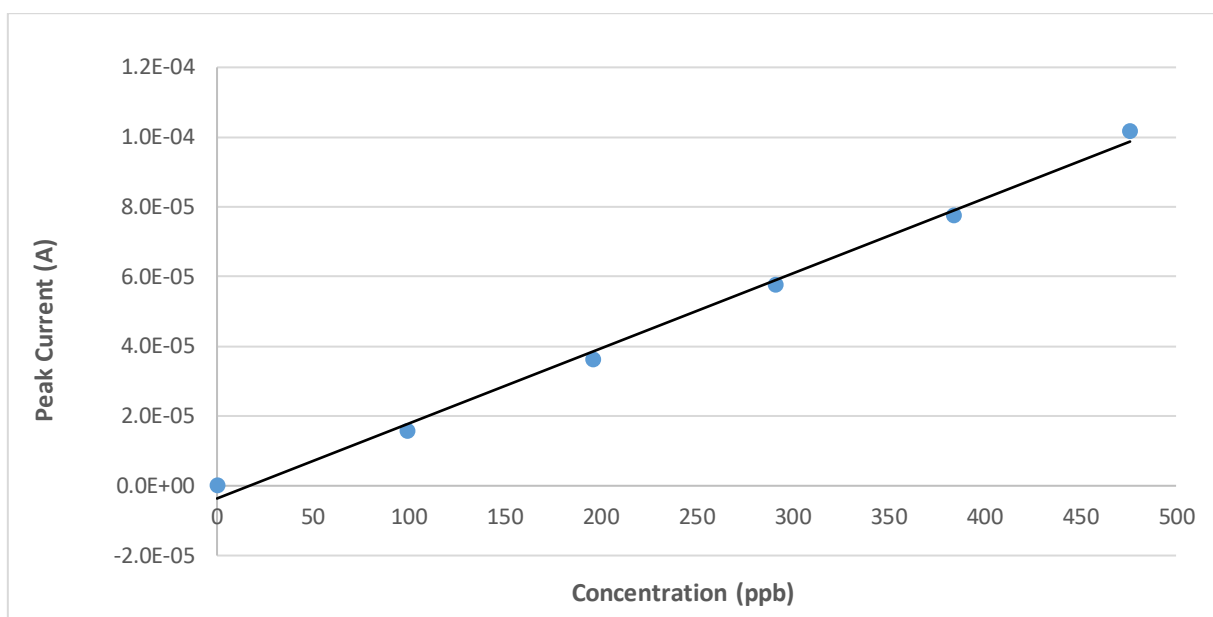
## Effect of concentration

1. The voltammogram overlay for each concentration is showcased below for your reference.



*Figure 6: Overlay of Differential pulse anodic stripping voltammograms of Cadmium standard in Ammonia Acetate Buffer by TFME are illustrated below. Concentrations = 99, 196, 291, 384 and 476 ppb*

2. The relationship between concentrations and peak currents can be depicted by plotting the peak current ( $i_p$ ) against different concentrations.



*Figure 7: The peak current increases linearly with the concentration of the analyte.*

## Conclusion

Differential pulse Anodic stripping voltammetry is inherently very sensitive voltammetric technique used in water and food analysis for detecting trace metal. Thin film mercury electrode TFME is used for very low levels (ppb) of trace metals analysis. The sensitivity of TFME depends on the electrode's surface area, lower limit of detection can be achieved by the electrode having larger surface area. Stripping voltammetry can be used for the detection of metals such as Zn, Pb and Cu etc.

## References

1. Modern Electrochemistry, Volume 2, Part 1 John O'M. Bockris, Amulya K.N. Reddy, Maria Gamboa-Aldeco (2000)
2. Electrochemical Methods: Fundamental and applications by Allen J. Bard, Larry R. Faulkner (2001)
3. Fundamentals of Analytical chemistry by Donald West, Douglas Skoog, F. Holer, Stanely Crouch (2013)
4. Fundamentals of electrochemical science by Keith R. Oldham and J C. Maryland (1993)
5. Electrochemistry for bioanalysis by B. Jill Venton, Dana J. DiScenza (2020)
6. Nanoscience and its Applications by F. R. Simões, M.G. Xavier (2017)
7. An evaluation and comparison of some techniques of Anodic stripping voltammetry by G.E Bately, T. M Florence (1974)
8. Anodic Stripping Voltammetry by W.D Ellis (1973)

**Phadke Instruments Pvt Ltd**

Email: [sales@phadkeinstruments.com](mailto:sales@phadkeinstruments.com)

Tel: 022 4970 9352

Ver: 13062023