TRACE LEVEL DETERMINATION OF
HEAVY METALS IN DRINKING WATER
BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

Objectives:

(1) To determine the impact of selected empirical parameters on the sensitivity and precision of analysis of heavy metals by differential pulse anodic stripping voltammetry (DPASV)

(2) To analyze the heavy metal content of tapwater and distilled water by DPASV

(3) To verify that the levels of heavy metal contamination in the drinking water available in the Boggs Building are in compliance with the acceptable levels recommended by the State of Georgia and the EPA

Text References


Introduction

The term stripping analysis refers to a group of related techniques. All of these techniques involve a two-step process. The analyte is concentrated in (or onto) an electrode and then removed from the electrode by either oxidation or reduction. For the analysis of metals, the most common concentration process is to electroreduce metal ions from solution to their zero-valence state by plating the metal onto the surface of a solid electrode or as an amalgam into a hanging mercury drop electrode (HMDE). Subsequent oxidation of the metal from the surface of the solid electrode or the mercury drop serves as both the stripping and detection step.

The concentration step is a heterogeneous reaction and thus depends on the rate of mass transport (the rate-limiting step). Since in most cases only a small fraction of the total analyte present in solution is concentrated on the surface, the amount concentrated is highly dependent upon such factors as area of the electrode, electrode potential, time of deposition and efficiency of stirring. For reproducible results, rigorous control of these experimental variables is essential. The final part of the concentration step is often a carefully timed rest period with no stirring. This rest period allows the solution to become stationary and homogeneous and is especially important with mercury amalgam electrodes. The rest period allows the amalgam to become homogeneous as well.

In this experiments a static mercury drop electrode (SMDE) produced commercially be EG&G Princetong Applied Research will be used. In this unit, a solenoid valve opens to allow mercury to flow from a reservoir into the capillary. The valve then closes and the drop remains suspended from the capillary tip. This unit is capable of producing new drops with excellent reproducibility.
The stripping technique will be differential pulse voltammetry. This technique provides symmetrically shaped peaks on the current-voltage plots for adequate resolution of closely spaced redox processes along the potential axis. In addition, the peak currents are proportional to the concentration of the analyte in the amalgam. Since this technique provides efficient discrimination of capacitance current relative to the current of interest, excellent sensitivities to heavy metal ions are routinely obtained.

**Experimental:**

**Preparation of Standards**

Clean all glassware thoroughly before using to prepare your solutions. Remember, this is a trace metal analysis. Clean with soap and water, rinse 2-3 times with tap water, rinse 2 times with Nanopure water. *Never clean volumetric glassware with a brush that may scratch the inside!*

1. Prepare 1.0 L of a 4.00% acetic acid solution using Nanopure water.

2. Pipette 4.00 mL of glacial acetic acid into an appropriately labeled 100-mL volumetric flasks. Dilute to the mark with tapwater.

3. Prepare the standard addition solutions for each of the metals by a 1:100 dilution of each of the stock solutions using 1.0-mL pipettes and 100-mL volumetric flasks. Dilute each of these solutions to the mark with the acetic acid solution prepared in step 1.

**Preparation of the Instrumentation**

*NOTE. Mercury is highly toxic! Use care when performing the procedures described below. Notify the TA immediately in case of a mercury spill.*

Also, note that the capillary is a precision-bore device designed specifically for the SMDE. The replacement cost for the capillary is $135.

4. Carefully remove the sample cell from the sample area on the Model 303 SMDE. Wash all electrodes with Nanopure water. Pipette 15.00 mL of the acetic acid solution into the cell. Add the magnetic stirring bar to the cell and carefully place it in position on the Model 303. Energize the stirrer, carefully recording the setting on the magnetic stirrer dial.
5. Set the controls on the EG&G PARC Model 174 Polarographic Analyzer to the following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Potential</td>
<td>-1.20 V</td>
</tr>
<tr>
<td>Mode</td>
<td>Differential Pulse</td>
</tr>
<tr>
<td>Scan Direction</td>
<td>+</td>
</tr>
<tr>
<td>Drop Time</td>
<td>0.5 s</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>10 mV / s</td>
</tr>
<tr>
<td>Current Range</td>
<td>100 µA</td>
</tr>
<tr>
<td>Modulation Amplitude</td>
<td>25 mV</td>
</tr>
<tr>
<td>Scan Range</td>
<td>1.5</td>
</tr>
</tbody>
</table>

6. Make sure the Selector Toggle is in the OFF position. Turn the Main Power switch to the ON position.

7. Set the controls on the Model 303 to the following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>HMDE</td>
</tr>
<tr>
<td>Size</td>
<td>S</td>
</tr>
<tr>
<td>Purge Time</td>
<td>4 min</td>
</tr>
</tbody>
</table>

8. Activate the nitrogen purge and allow the solution to be deoxygenated for at least 4 min.

Analyzing the Solvent (4% Acetic Acid)

9. After the solution has purged for 4 minutes, perform a DPASV measurement via the following:

- Alternately press the DISPENSE and DISLODGE buttons several times to ensure that a fresh mercury drop is available.

- Begin to plate the metals into the drop by first activating “HOLD” (This holds the set voltage). Next, simultaneously begin timing and flip the Selector Toggle on the Model 174 to “EXT CELL”.

- Plate for 2.0 min and then turn off the stirrer. Begin recording data.

- After exactly 30 s, depressing the “SCAN” button on the Model 174 and record the voltammogram.

At the completion of the scan, flip the Selector Toggle to “OFF.” Activate the “INITIAL” button. Now, carefully remove the cell from the holder and decant the solution (which contains mercury drops) into the labeled waste beaker provided. Carefully rinse the cell and the electrodes with several portions of Nanopure water.

Basic Steps for Measurement: stir, purge, new electrode, plating, equilibrate, scan
**Determining the Empirical Parameters**

10. Pipette 15.00 mL of the tapwater/acetic acid solution into the cell. Activate the magnetic stirrer. **DO NOT PURGE THE SOLUTION AT THIS TIME!!** Perform a DPASV measurement using the conditions listed in step 9 (plating time 2.0 min, rest time 30 s), adjusting the current range as necessary to keep all peaks on scale.

11. Repeat step 10 after purging the same solution for at least 4 min with nitrogen gas.

12. Determine the effect of mercury drop size by carrying out three successive DPASV experiments at the following settings: S, M and L. Purge for 0.5 min, plating time of 2.0 min and a rest time of 30 s.

13. Determine the effect of plating time by carrying out successive DPASV experiments at the following settings: Plating time: 1.0 and 3.0 min (using a small mercury drop, purge 0.5 min and a rest time of 30 s). [Compare these results with those obtained for 2.0 min from step 11]

14. Determine the effect of modulation amplitude by carrying out successive DPASV experiments at the following settings: Modulation Amplitude: 10, 50 and 100 mV (using a small mercury drop, purge 0.5 min, plating time of 2.0 min and a rest time of 30 s). Note: you will probably make adjustments to the current range to keep all peaks on scale.

**Determining Heavy Metal Concentrations**

15. Discard the contents of the cell (decanting into the waste beaker) and take a fresh sample of the tapwater/acetic acid solution (15.00 mL). After deoxygenating this sample (4.0 min), record the voltammograms from duplicate DPASV experiments at the following settings: Plating time: 2.0 min; rest time: 30 s; modulation amplitude: 25 mV and Electrode size: S.

16. The concentration of each metal in this solution will be determined by the method of standard addition. Pipette a 100 uL aliquot of the diluted copper stock solution into the cell and purge for 0.5 min. Then perform the DPASV experiment at the settings given in step 15. Identify which peak in the voltammogram increased in amplitude. Add 2 successive 100 uL volumes to the same solution in order to have 3 data points. Quantify the amount of zinc, lead and cadmium in solution in a similar fashion in the same solution. The in-lab construction of the standard addition curve is strongly encouraged. This will provide ample opportunity to repeat any experiments which yield suspect data.

17. At the completion of the experiment, wash the electrodes with copious amounts of Nanopure water. Replace the beakers containing Nanopure water and mercury in the respective positions. Decant the contents of the cell into the waste container. Turn off the instruments. Turn off the nitrogen gas. Clean all glassware.
**Results:**

Carefully label each of the voltammograms you have obtained. Measure the peak heights for each redox process. Construct a table containing the corrected peak heights and concentrations for each metal ion. Prepare standard addition plots for each metal analyzed using these quantities (i.e. a plot of corrected height versus concentration). Determine the concentration of each metal ion (in ppm) for both water samples and report these results in tabular form.

**Questions:**

1. What is the effect of varying the mercury electrode area, the plating time, and the modulation on the sensitivity and precision of the your measurements? What is the theoretical relationship between each of these factors and the peak current?

2. Compare the levels of zinc, cadmium, copper and lead in your sample of tapwater with the recommended safe levels as reported by the state and federal agencies (you must find this information). What are the health risks associated with drinking water contaminated with each of the metals quantified in this experiment?

3. Compare and contrast the method of standard addition versus the standard series (also known as the calibration curve) for quantitating the analyte. Under what conditions is the method of standard addition preferable? Under what condition is the standard series method more appropriate?

4. Why is a mercury electrode good to use with aqueous solutions? Explain. Draw a labeled diagram of a hanging mercury drop and explain the processes that occur during electrodeposition and stripping. Why did the respective heavy metals get reduced in a particular order?
Differential Pulse Anodic Stripping Voltammetry

Grading Scheme

Clint Jones TA

CHEM 3211, Spring 2000

• Title Page

  *Experiment title, name, partner’s name(s), class section, date performed, date submitted*

• Introduction 20 points

  *Must at least include: Theory, purpose, principles of experiment*

• Procedure (only deviations from)

• Sample Calculations, Tables, Charts 25 points

• Discussion 30 points

  *Must at least include: Empirical results versus theory (explain why empirical parameters changed the output), pertinent errors*

• Questions 25 points

• References

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  100 Total