

Voltammetric determination of cadmium on mercury film electrode - MFE

Aim of the exercise:

Determination of trace amounts of cadmium in water using differential pulse anodic stripping voltammetry (DP-ASV)

Apparatus and measuring equipment:

- a) PalmSens electrochemical analyzer (potentiostat/galvanostat);
- b) three-electrode system consisting of: graphite working electrode, silver chloride reference electrode (Ag/AgCl/KCl_{sat}), the counter electrode (platinum wire)
- c) measuring vessels, measuring flasks, pipettes, wash bottle

Reagents

Cd²⁺ stock solution (100 µg/L), 1 M KNO₃, 5 • 10⁻³ M Hg²⁺ (in HNO₃), distilled water

Proceedings

1) Electrodeposition of a thin mercury film on the surface of graphite working electrode

- a) Before measurements polish the surface of the working electrode as instructed by the tutor
- b) Immerse the prepared three-electrode system into the electrolytic cell containing 10 ml of a solution of 0.1 M KNO₃ + 5 • 10⁻⁵ M Hg²⁺ and then pass nitrogen through the system for approx. 600 s. **Note: after 600 s shut off the nitrogen supply!** The recording of the voltammetric curve must be carried out under stable diffusion-convective conditions. Connect working, reference, and counter electrodes according to the apparatus diagram.
- c) Record the differential pulse voltammogram between -0.9 V and -0.4 V versus Ag/AgCl/KCl_{sat} without a flow of nitrogen. A well-developed anode peak should be expected on the voltammogram. **Note:** switch on the nitrogen supply immediately after the measurement!

Analytical data: preconcentration potential: -0.9 V, preconcentration time: 600 s (this is the time needed for the electrolytic deposition of the mercury film on the electrode), scan rate: 50 mV • s⁻¹

2) Measurement of background voltammogram in a blank electrolyte

Replace the solution in the cell with the basic electrolyte (0.1 M KNO₃) and after flowing the solution with nitrogen, record the differential pulse voltammogram in the potential range from -0.9 V to -0.4 V vs. Ag/AgCl/KCl_{sat}. Preconcentration time: 300 s. Other measurement parameters are the same as in p. 1.

3) Determination of Cd²⁺ in the basic electrolyte

The first measurement should be conducted for a real sample with an unknown amount of Cd²⁺ (wastewaters) in the 0.1 M KNO₃. Then, record the voltammetric curves after each addition of a known amount of standard solution (standard addition method). Usually, 50 to 150% of the expected content of the component is determined.

Record DPV from -0.9V to -0.4V versus Ag/AgCl/KCl_{sat} for each addition. Preconcentration time 300 s.

Data analysis

1. On the basis of the results obtained, create, and plot all voltammograms.
2. Based on the voltammograms, draw the calibration curve by the multiple addition method and then graphically extrapolate the obtained curve to the intersection with X-axis. **Determine the Cd²⁺ content in µg/l in the analyzed wastewater sample).**
3. Characterize the reactions that occur on the surface of the working electrode.

Learning issues:

electrochemical cell, three-electrode system (types of electrodes), Faraday's law, Nernst equation, galvanic series, electrolytes, depolarizer, types of electrode polarization, voltammetric measurements, differential pulse voltammetry, $I = f(E)$ relationship in differential pulse voltammetry technique, standard addition method