

# Detection of Cerium(III) by Optimized Adsorption Stripping Voltammetry Using a New Electrochemical Sensor

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## Summary:

A simple and rapid method for determining cerium was developed using an electrochemical sensor based on a mixture of multi-walled carbon nanotubes (MWCNTs), spherical glassy carbon powder (SGC), and epoxy resin. The adsorptive stripping voltammetric procedure was optimized by analyzing factors affecting the cerium signal. Experimental parameters, such as the composition and concentration of the supporting electrolyte, the concentration of the complexing agent (Alizarin S), as well as the accumulation potential and time, were carefully selected based on conducted experiments.

**Keywords:** cerium, adsorptive stripping voltammetry, electrochemical sensor, carbon nanomaterials

## Introduction

Cerium is a rare earth element of significant industrial and environmental importance, what makes developing of effective methods for its determination crucial [1]. A modern approach to trace metal analysis is adsorptive stripping voltammetry (AdSV), which combines the process of analyte adsorption on the surface of a working electrode with its electrochemical oxidation or reduction what effectively improves the sensitivity of the determination [2]. To increase the efficiency of this method, modern electrodes are being introduced, the surface area of which has a key influence on the adsorption capacity of metal ions. In the present study, an electrode based on a mixture of multi-walled carbon nanotubes (MWCNTs) and spherical glassy carbon powder (SGC) was used to improve conductivity and increase the active surface area [3]. Alizarin S was used to complex Ce(III) ions, allowing their selective accumulation on the electrode surface [4]. The developed method, carried out in acetate buffer, showed high sensitivity and repeatability of measurements, confirming its potential for the precise determination of cerium.

## Measurement Procedure

The analyzed solution was placed in a classic three-electrode quartz cell. Measurements were conducted in a 0.1 mol L<sup>-1</sup> acetate buffer solution (pH = 5.3) containing 5 × 10<sup>-5</sup> mol L<sup>-1</sup> Alizarin S, which acted as a complexing agent. The experiments were performed in deaerated solutions at room temperature. The voltammetric procedure consisted of the following steps:

1. Adsorption of Ce(III)-Alizarin S complexes onto the MWCNTs/SGC electrode at a constant potential of -0.6 V for 65 s.
2. Voltammetric scan – the potential of the MWCNTs/SGC electrode was swept from 0.55 V to 1.2 V, recording the voltammogram and obtaining the analytical signal in the form of a oxidation peak of the accumulated Ce(III)-Alizarin S complexes.

On the recorded voltammogram, the cerium peak appeared at a potential of 0.85 V. After each measurement cycle, the electrode was electrochemically cleaned by applying a potential of -1.3 V for 10 s, followed by 0.2 V for 10 s.

## Results and Discussion

*Optimization of the composition of the supporting electrolyte:* The effect of the composition of the supporting electrolyte on the peak current of cerium required precise selection, as the electrolyte ensures appropriate conductivity and conditions for effective oxidation of cerium ions. Acetate buffer with a concentration of 0.1 mol L<sup>-1</sup> was chosen as the electrolyte, and the effect of pH on the peak corresponding to the concentration of cerium ions in the solution was investigated, as pH can influence the dissociation degree and chemical activity of cerium ions. The experiments were conducted in the pH range from 3.5 to 5.5, using a solution containing a constant concentration of Alizarin S (1 μmol L<sup>-1</sup>) and Ce(III) ions. The best signal was obtained at pH 5.3, which was chosen for further measurements. The next parameter investigated

was the concentration of the acetate buffer. Its effect on the intensity of the cerium signal was examined by using a solution containing constant concentrations of Ce(III) and Alizarin S while varying the concentration of the acetate buffer at pH 5.3 in the range from 0.03 to 0.2 mol L<sup>-1</sup>. The peak current of Ce(III) increased with rising buffer concentration until the current stabilized at a concentration of 0.1 mol L<sup>-1</sup>. After analyzing the results, it was concluded that the optimal concentration of the acetate buffer is 0.1 mol L<sup>-1</sup>.

**Optimization of the concentration of the complexing agent:** To determine Ce(III) ions using the adsorptive stripping voltammetry method, a complexing agent is necessary to form electrochemically active complexes that effectively accumulate on the working electrode. In the proposed procedure, the complexing agent is Alizarin S, and the accumulation process occurs on the electrode surface through the adsorption of the Ce(III)-Alizarin S complex. The effect of the complexing agent concentration on the peak current visible on the voltammogram was investigated by conducting experiments at different concentrations of Alizarin S. The studies were carried out for a solution containing a constant concentration of Ce(III) ions, and the accumulation of the complexes was performed at a potential of -0.3 V for 40 s. The tested solution had a volume of 10 mL and contained, in addition to Ce(III) ions, a constant concentration of acetate buffer (pH 5.3) equal to 0.1 mol L<sup>-1</sup>, with varying concentrations of Alizarin S. Analysis of the results showed that the Ce(III) peak current increased with the concentration of Alizarin S, reaching the maximum current at a concentration of 1 μmol L<sup>-1</sup>. At higher concentrations, a decrease in peak current was observed.

**Effect of Accumulation Potential and Time:** The value of the accumulation potential has a significant impact on the sensitivity of the method, which directly influences the recorded current values. The accumulation potential was varied in the range from -1.0 V to -0.3 V, with steps of 0.1 V. For each potential, a voltammogram was recorded, and the peak current of cerium was measured. The peak current increased as the accumulation potential value rose in the range from -1.0 V to -0.6 V. After reaching an accumulation potential higher than -0.5 V, the peak current decreased. The optimal accumulation potential was found to be -0.6 V. Another important parameter in adsorptive stripping voltammetry is the accumulation time of the Ce(III)-Alizarin S complex on the working electrode. The effect of the accumulation time was studied in the presence of 0.1 mol L<sup>-1</sup>

acetate buffer at pH 5.3, a 1 μmol L<sup>-1</sup> concentration of Alizarin S as the complexing agent, and a constant concentration of Ce(III) ions. The accumulation potential was maintained at a constant value of -0.6 V, and the accumulation time was varied in the range from 0 to 80 s, with intervals of 5 s. The intensity of the cerium peak current increased with the accumulation time until it reached 65 s. After further extending the accumulation time, the peak current intensity started to decrease slightly.

Using a solution with an optimized composition, a low detection limit for cerium of 5 × 10<sup>-9</sup> mol L<sup>-1</sup> was achieved. Optimization of parameters such as buffer concentration, pH, accumulation time and potential significantly improved the sensitivity of the method. It was observed that, with appropriate parameter values, the method provides high precision and reproducibility of measurements. The results obtained demonstrate the great potential of the proposed method for the analysis of trace cerium concentrations in various samples.

## References

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