



Stripping voltammetric determination of cerium in food using an electropolymerized poly-catechol and ion-imprinted membrane modified electrode

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ABSTRACT

For the aim to detect Ce(III) in food with selectivity, sensitivity and speediness, an electrochemical sensor (Ce(III)-IIM/PC/GCE) was constructed by electropolymerization of a poly-catechol (PC) film on glassy carbon electrode (GCE) followed by modifying a Ce(III) ion-imprinted membrane (IIM) formed with electropolymerization using *o*-phenylenediamine as monomer. After that, a differential pulse adsorptive stripping voltammetry (DPASV) was developed for determination of Ce(III) by the obtained sensor. Under the optimal conditions, the sensor possesses good reproducibility and storage stability. Furthermore, it can be used directly for determination of Ce(III) in the concentration range of 3.0×10^{-12} – 1.0×10^{-4} mol L⁻¹ with the limit of detection of 1.0×10^{-12} mol L⁻¹. Since over 50-fold excess concentration of Fe³⁺, Cu²⁺ and Ni²⁺ will produce some interferences in the direct determination of Ce(III), an extraction method was adopted when it be used in food. After extraction of the samples with 1-phenyl-3-methyl-4-benzoyl-5-benzopyrazolone (PMBP), Ce(III) can be determined by Ce(III)-IIM/PC/GCE in the presence of > 500-fold excess concentration of Fe³⁺, Cu²⁺ and Ni²⁺ with the limit of detection of 4.7×10^{-9} mol L⁻¹. The sensor was successfully applied to determine cerium in food after extracted by PMBP with a relative standard deviation (RSD) of < 3.3% (n = 4) and recoveries in the range of 94.9–102.2%.

1. Introduction

Cerium is abundant in the earth's crust with the content of about 50–66 mg/kg [1], and has many industrial applications [2–5]. It is not only widely used in lightning and television, metallurgy, glass and ceramics, but also an important component of many products such as catalytic converters in vehicles, diesel fuel additive, and rare-earth fertilizers. However, rare-earth elements including cerium usually have accumulation toxicity, they can accumulate in human body and lead to a series of disease such as acute myocardial infarction, abnormal blood biochemical indices, leukemia and skin lesions [6,7]. Hence, control of the intake of cerium as well as search for a method to detect cerium in food with availability of simplicity, sensitivity and selectivity is in crying needs.

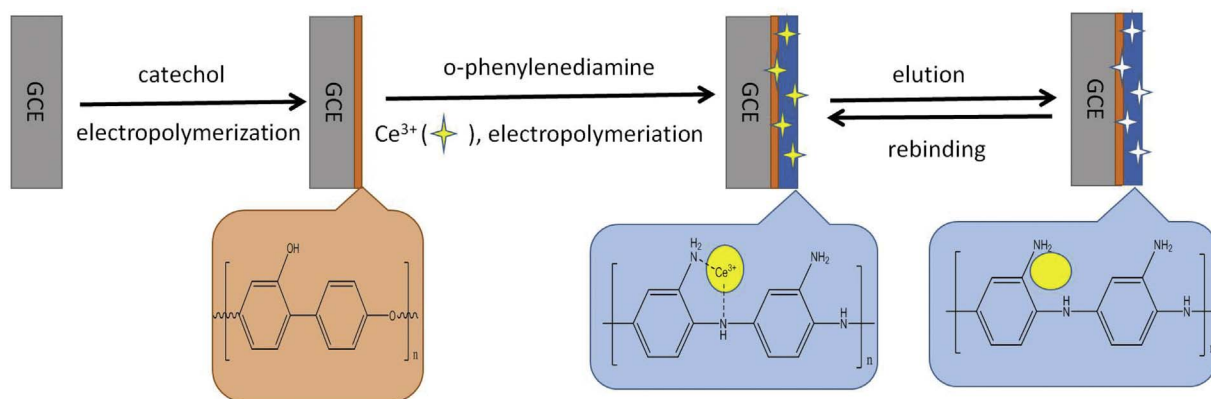
Many techniques have been reported for the determination of cerium, such as neutron activation analysis (NAA) [8–10], X-ray fluorescence spectrometry [11], inductively coupled plasma optical emission spectrometry (ICP-OES) [12], spectrophotometry [13,14],

potentiometry [15–18] and voltammetry [19–25], etc. Among these methods, voltammetry is regarded as a better choice for determination of trace components due to its high sensitivity, good selectivity, ease of handling and cost effectiveness [26,27]. Usually, cerium ion is detected via its complexes wave when refers to the voltammetry [19,21,22] because of its poor peak current of oxidation, but the selectivity of the indirect method is often not satisfactory for the chelating agent can react with different metal ions at the same time. So studying of a modified material to construct an electrochemical sensor for determination of cerium with perfect selectivity and high sensitivity is of great significance.

At present, an ion-imprinted material which can create specific sites for template, is considered to be the ideal recognition element for sensors since its high selective recognition, stability, reusability, simplicity and low cost in preparation. As a matter of fact, satisfactory analytical characteristics were obtained in most of the investigations published with respect to the ion-imprinted materials modified electrochemical sensors [28–32].

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Scheme 1. Detailed procedure diagram for fabrication of the Ce(III)-IIM/PC/GCE sensor.

There are also a few reports relate to the imprinted sensor for cerium, including a carbon paste electrode [23] and a screen printed carbon electrode [25] modified with cerium-imprinted polymer together with other nano-materials, but the selectivity or sensitivity of these electrodes for food samples remain to be further improved. To fabricate a sensor for simple, sensitive and selective determination of Ce(III) in this research, an electropolymerized Ce(III) ion-imprinted membrane was introduced as a recognition element to enhance the selectivity, and a poly-catechol film, which has been confirmed to possess notable signal amplification on glassy carbon electrode (GCE) for determination of Ce(III) [20] but not been used in the imprinted sensor, was selected as signal amplifying materials to increase the sensitivity. GCE was firstly modified with poly-catechol and then assembled with Ce(III) ion-imprinted membrane formed by electropolymerization using *o*-phenylenediamine as monomer (Scheme 1). The experimental parameters affecting the response sensitivity together with the analytical application and selectivity behavior of the sensor for Ce(III) were discussed. To our knowledge, Ce(III) ion-imprinted sensor prepared by electropolymerization as well as its application in food analysis has not been reported until now.

2. Experimental

2.1. Apparatus and instruments

All electrochemical data were carried out with a CHI760E electrochemical workstation (Shanghai CH Instruments Co., China). A three electrode cell (10 mL) was used with a bare or modified glassy carbon electrode as working electrode, a Ag/AgCl (with saturated KCl) electrode as reference electrode and a platinum wire electrode as counter electrode, respectively. All potentials were measured and reported versus Ag/AgCl electrode. Prior to modification, the glassy carbon electrode (GCE, 4 mm diameter) was polished with aqueous slurries of alumina powders (0.3 and 0.05 μm) on chamois leather until a mirror surface was obtained. Then rinsed thoroughly with absolute alcohol and water in ultrasonic bath successively, and finally dried under the infrared lamp in air.

2.2. Reagents and chemicals

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was obtained from Kunming Institute of Precious Metals (Yunnan, China). Catechol was purchased from Shanghai chemical reagent factory (Shanghai, China). *o*-Phenylenediamine was obtained from Tianjin Guangfu Fine Chemical Industry Research Institute (Tianjin, China). 1-Phenyl-3-methyl-4-benzoyl-5-benzopyrazolone (PMBP) was obtained from Aladdin Industrial Corporation (Shanghai, China). Sulfosalicylic acid and ammonium sulfocyanate were obtained from West Long Chemical Co. Ltd. (Guangzhou, China). The other reagents and solvents were purchased from Tianjin Kemiou Chemical

Reagent Co., Ltd. (Tianjin, China).

The standard solution of metal ions such as Ce(III), Pr(III), Gd(III), Tb(III), Ho(III), Yb(III), Dy(III), Er(III) and so on were prepared by dissolving appropriate amount of their nitrate or chloride with deionized water. The scrub solution was prepared by mixed 1 mL of 60% sulfosalicylic acid, 10 mL of 60% ammonium sulfocyanate, 12 mL of HAc-NaAc (pH 5.5) and 77 mL of deionized water.

The reagents and solvents used without special illustration were of analytical grade and used without further purification. Deionized water was produced by a Millipore water system composed of Milli-RO 60 and Milli-Q SP.

2.3. Preparation of the sample solution

Vegetable, rice and tea all were bought from supermarkets in Kunming (Yunnan, China). Firstly, the sample was washed with detergent, tap water and deionized water successively, and then dried at room temperature for 24 h followed by drying in an oven at 90 $^\circ\text{C}$ overnight. After that, about 5.0 g of the dried sample was accurately weighed and immersed with 10 mL of nitric acid for 12 h in a conical flask covered with a short neck funnel. Then, the mixture was heated at 140 $^\circ\text{C}$ until < 1 mL of liquid was left. After 5 mL of aqua regia was added, the solution was heated continuously at 160 $^\circ\text{C}$ until nearly dryness. The residue was dissolved with 5 mL of deionized water and boiled for 10 min. After cooling to room temperature, the solution was filtered and the filtrate was diluted to 25 mL with deionized water as stock solution.

To eliminate the interference of Fe(III), an extraction process was required prior to determination of the samples. According to reference [22], 20 mL of 0.01 mol L^{-1} PMBP was added to the mixture (pH 5.5, adjusted by NaOH solution) containing 10 mL of sample solution, 2 mL of 60% sulfosalicylic acid and 5 mL of 60% ammonium sulfocyanate in a 250 mL separating funnel. Shook the separating funnel for 2 min, and then discarded the aqueous phase. After that, the organic phase was firstly washed with 10 mL of scrub solution, and then re-extracted with 10 mL of 0.1 mol L^{-1} HCl twice. Finally, the re-extraction solution was combined and dried by evaporation. The residue was dissolved and diluted to 10 mL with 0.05 mol L^{-1} HAc-NaAc (pH 4.7).

2.4. Preparation of the poly-catechol modified glassy carbon electrode (PC/GCE)

The poly-catechol modified glassy carbon electrode (PC/GCE) was fabricated according to the reference [20] as follows: GCE was immersed in 0.1 mol L^{-1} NaOH solution containing 12 mmol L^{-1} catechol. The electropolymerization was performed without stirring by 7 consecutive cyclic scans in the potential range from -0.40 to $+1.00$ V at a scan rate of 20 mV s^{-1} . After that, the electrode was rinsed with water, and then scan several times by CV in 0.10 mol L^{-1} NaOH to

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