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Trace detection of Ce³⁺ by adsorption strip voltammetry at a carbon paste electrode modified with ion imprinted polymers^{*}

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9 Abstract

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To develop a convenient method for sensitive and selective determination of Ce^{3+} in aqueous 10 11 phase with complicated matrices, a carbon paste electrode (CPE) modified with ion imprinted polymers 12 (IIPs) were fabricated. The polymers were prepared by precipitation polymerization using Ce^{3+} as 13 template, allyl phenoxyacetate (APA) as monomer, ethylene glycol dimethacrylate (EGDMA) as 14 crosslinker and azobisisobutyronitrile (AIBN) as initiator under the molar ratio of Ce³⁺, APA and 15 EGDMA as 1:4:40, respectively. Ce^{3+} was detected directly by differential pulse adsorptive stripping 16 voltammetry (DPASV) and its oxidation peak appears at about 0.93 V. All parameters affecting the 17 sensor's response are optimized and a calibration curve is plotted at a linear range of $1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ mol/L and $1.0 \times 10^{-5} - 2.0 \times 10^{-4}$ with the detection limit of 1.5×10^{-7} mol/L. All other rare earth ions have 18 19 no interference with the determination of Ce³⁺ even at a concentration 500 times higher than that of 20 Ce³⁺. This sensor was successfully applied to determination of Ce³⁺ in two catalyst sample solutions 21 with RSD \leq 3.3% (*n*=5) and recoveries in the range of 99.2%-106.5% at our optimal conditions.

Key words: Cerium; Electrochemical sensor; Ion-imprinted polymers; Carbon paste electrode; Rare
earths

24 1 Introduction

25 The rare earth elements (REEs) are widely distributed in the earth's crust in low concentration and have slight toxicity^[1]. Cerium as the most abundant rare earth element has been used in many advanced 26 materials science fields such as catalysis, chemical engineering, nuclear energy, metallurgy 27 28 microelectronics, magnetism, agriculture and therapeutic application^[2-5] because of its unique quality 29 compared with other lanthanide elements. Moderate cerium can improve the crop's production^[6,7] at 30 some degree which has attracted more and more attention in recent years. However, rare-earth elements 31 including cerium usually have accumulation toxicity; they can accumulate in human body and lead to a 32 series of disease such as acute myocardial infarction, abnormal blood biochemical indices, leukemia 33 and skin lesions^[8,9]. Therefore, a method for selective and fast determination of cerium is in crying 34 needs.

35 Many instrumental techniques have been used to detect cerium, such as neutron activation analysis (NAA)^[10,11], X-ray fluorescence^[12,13], inductively coupled plasma-atomic emission 36 37 spectrometry (ICP-AES)^[14], spectrophotometry^[15], etc. All of them can detect the cerium effectively but lack of selectivity. Electrochemical methods, include spectrophotometry^[16,17], potentiometry^[18,19] 38 39 and voltammetry^[20-23], are better choices when determination of trace element due to their ease of 40 handling, great sensitivity and selectivity as well as cost effectiveness. Generally, voltammetry analysis of cerium and other lanthanide ions are conducted via their complexes wave^[24] because of their poor 41 42 electrochemical response. But the selectivity of indirect method is often not satisfactory for the 43 chelating agent can react with different metal ions at the same time. So studying a modified material to 44 construct an electrochemical sensor for determination of cerium with perfect selectivity and high 45 sensitivity is of great significance.

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