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Pulsed Amperometric Detection of Metal Ions Complexing with EDTA in a Flow Injection System**

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A general and universal detection method, which can be used in high performance liquid chromatography (HPLC) and flow injection analysis (FIA) system for the determination of any metal ions complexing with ethylenediaminetetraacetic acid (EDTA), is demonstrated. Pulsed amperometric detection scheme is applied in a flow-through thin layer electrochemical cell at an Au working electrode. Fluctuation of peak current level at the same flow rate of carrier solution is minimized at this solid working electrode, whereas not at a dropping mercury electrode. Removal of dissolved oxygen can be omitted with this detection method, which is a required step for cathodic detection methods. Also, a group of metal ions can be determined selectively and indirectly with this detection scheme.

Introduction

Since the detection and quantitative measurement of metal ions require various analytical techniques, numerous research efforts have been focused to find a universal detection scheme which can be applied to metal ions as widely as possible. EDTA is one of the well known complexing agents and widely used in many fields such as commercial detergents, cleaning reagents, environment, and agriculture etc. Metal EDTA systems have been studied extensively using mercury electrodes. However, such systems can usually give us little information because oxidation potential of mercury itself is very close to those of metal EDTA complexes.[1]

Detections of rare earth metal ions with electrochemical techniques after separation by high performance liquid chromatography were reported by Boissonneau *et al.*,[2] where EDTA was mixed in the flow stream of rare earths at the exit of HPLC column. Concentration of the elements was then indirectly determined by measuring anodic diffusion current of EDTA at a dropping mercury electrode in a flow cell. A similar setup with different complexing agent, diethylenetriaminepentaacetic acid (DTPA), has been used for the determination of Tm, Ho, Yb rare earths because DTPA has a larger formation constant than EDTA and oxidation potential of DTPA is less interfered by oxidation of mercury electrode.[3] We have demonstrated here a general and universal method for the determination of any metal ions complexing with EDTA in flow injection analysis composed of a thin layer cell with a gold working electrode.

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**This article is dedicated to Prof. Woon-kie Paik (Sogang Univ.) in commemoration of his 60th birthday.

Experimental

Reagents. All chemicals including EDTA (Aldrich Chemical Co.) and ammonium acetate buffer prepared from acetic acid and ammonium acetate (Duksan Chemical Co.) were used as received without further purification. Water obtained through a Milli-Q purification system was used to prepare solutions and electrolytes.

Instrumentation. All electrochemical measurements were made by Amel potentiostat (Model No. 553) and function generator (Model No. 568). All data were recorded by IBM XT compatible computer with a data acquisiton card and home-made softwares. A thin layer type EG & G electrochemical cell (Model No.1303, *ca.* 13 μL), which composed of a dual Au electrode, was employed in these experiments. One of the two was used as a working electrode, the other was used as a counter electrode. A reference electrode (Ag/AgCl (3.0 M), EG&G Cat. No. 219054E) was inserted into the cell through holes in its top cover. All electrode potentials are reported with respect to the Ag/AgCl reference electrode.

A flow injection analysis system was assembled in our laboratory. The system consisted of a peristaltic pump (Gilson, Model No. Miniplus 2) for propelling the electrolytes, an injection unit attached to the pneumatic actuator (Rheodyne, Model No. 5701) for sample injection, and flow-through thin layer electrochemical cell (EG & G, Model No. 1303) connected to the potentiostat. The details of experimental setup were described in our previous paper.[4]

Results and Discussion

The use of a pulsed-potential waveform for detection of

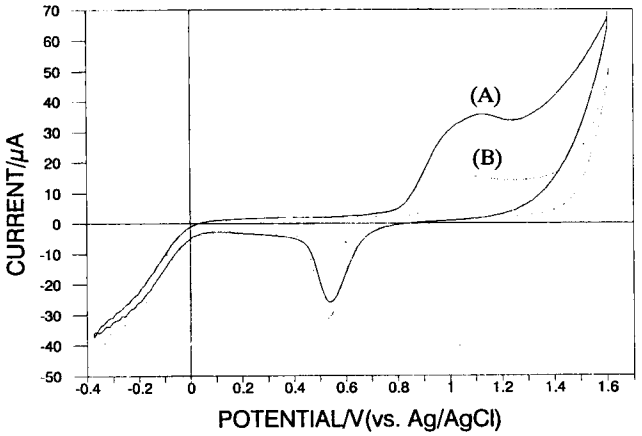

Figure 1. Current voltage curves; (A) an Au electrode containing 1×10^{-3} M EDTA in ammonium acetate buffer (pH=4.8); (B) an Au electrode in ammonium acetate buffer (pH=4.8), scan rate=50 mV/sec, reference electrode: Ag/AgCl (3.0 M).

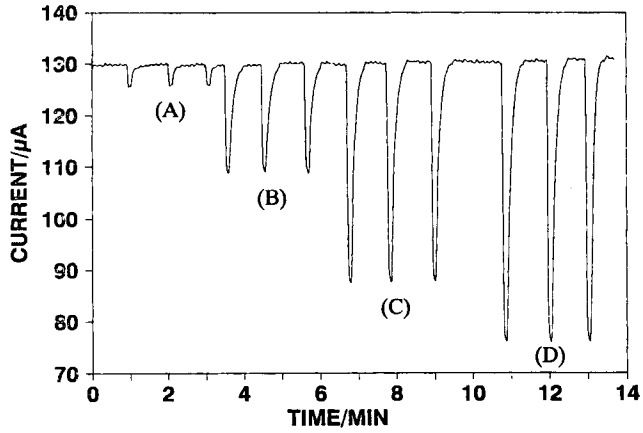

Figure 2. Representative peak currents for the injection of Ni^{2+} in 1.0 M ammonium acetate buffer containing 2×10^{-3} M EDTA at an Au electrode by pulsed amperometry; E_1: 1120 mV (500 msec), E^2: 1600 mV (50 msec), E^3: −800 mV (600 msec); flow rate: 1.5 mL/min, concentration of Ni^{2+}: (A) 1.0×10^{-4} M, (B) 5.0×10^{-4} M, (C) 1.0×10^{-3} M, (D) 1.5×10^{-3} M.

many organic compounds at an Au electrode has been demonstrated.[5-7] A three-step pulsed waveform,[8] which consists of a detection, an oxidation, and an reduction potential, was used for the detection of EDTA. The potentials were kept sequentially applying to the Au working electrode while the analytes was passing through the thin layer electrochemical cell. A detection potential was determined from voltammetric responses for an EDTA solution and for a blank electrolyte solution (see Figure 1). The anodic potential of 1120 mV where the difference in currents for the absence and presence of EDTA showed a maximum value was chosen as the detection potential. Faradaic current was sampled in the last 20 msec of the detection period at the detection potential, where the double layer charging current was substantially decayed away.

Ammonium acetate buffer as a carrier stream containing 2×10^{-3} M of EDTA was eluted at a constant flow rate of 1.5 mL/min. A series of metal ion concentrations was in-

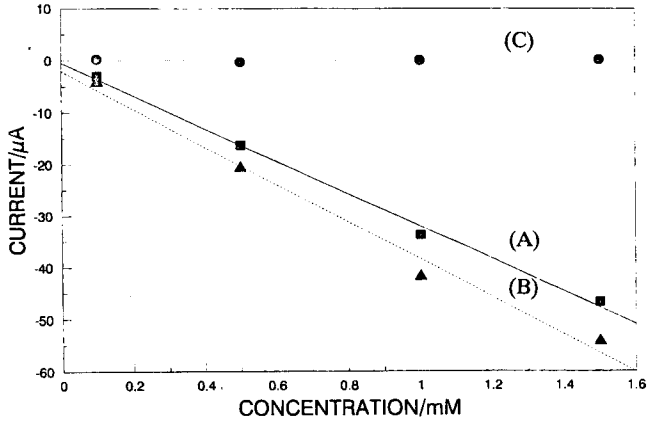

Figure 3. Plots of peak currents for oxidation of EDTA *vs.* concentration of metal ions in ammonium acetate buffer (pH=4.8). (A): Fe^{3+}, (B): Ni^{2+}, (C): Mg^{2+}.

jected into the carrier stream with a constant volume of sample loop, *i.e.*, 100 μL. It should be noted that the concentration of EDTA has to be always larger than that of the metal ions. Therefore, the uncomplexed EDTA always exist in the stream and can be then oxidized at the Au working electrode for the detection potential of 1120 mV. Successive injections of the Ni^{2+} ion with different concentrations are recorded and the results are shown in Figure 2. Without injection of Ni^{2+}, the current is responsible for oxidation of free EDTA in the carrier stream. The larger decrease in current was observed as the larger amount of Ni^{2+} was injected. This is because the smaller amount of free EDTA is left in the solution with the injection of larger amount of metal ions complexing with EDTA. A linear relationship between the magnitude of currents and the concentration of other metal ions is demonstrated in Figure 3. The detection limit is calculated to be 0.05 mM for the those metal ions, such as Ni^{2+}, Fe^{3+} with S/N ratio of 3. As can be seen in Figure 3, sensitivity (*i.e.*, slope of the plot) for each metal ion is different for the metal ions tested. This might be from the difference in complexing capability of metal ions with EDTA at the pH we used. The minimum permissible pH for a satisfactory end point in the titration of Fe^{3+}, Ni^{2+} and Mg^{2+} ions with EDTA is *ca.* 2, 4, and 10, respectively.[9] At the pH of 4.8, the Fe^{3+} and Ni^{2+} ions can make a complex with EDTA, whereas Mg^{2+} ions do not. Hence, there are no decreases in the currents for Mg^{2+} ions as the concentration of Mg^{2+} ions are varied because no EDTA is used to make the complexes. This shows that any metal ions can be selectively detectable by changing pH of the flow stream solution. Further investigation to enhace the selectivity of this detection scheme is in progress.

In summary, indirect detection of metal ions complexing with EDTA by pulsed amperometric method has been demonstrated. This detection scheme can be applied to any metal ions by selecting appropriate complexing ligands and the working electrode which is well suited for the detection of complexing ligands. Removal of dissolved oxygen is not necessary with this detection method, whereas the removal of the oxygen is required for anodic detection of EDTA at a dropping mercury electrode because reduction potential of oxygen is very close to the oxidation potential of EDTA at

the mercury electrode.

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A Novel Synthetic Route to Highly Cross-Linked Poly(vinyl ethers): III. Synthesis and Free Radical Polymerization of Aryloxyethyl Vinyl Ethers Having an Electron Acceptor in ortho- or meta-Position

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o-(2-Vinyloxyethoxy)benzylidenemalononitrile (**3a**) and methyl *o*-(2-vinyloxyethoxy)-benzylidenecyanoacetate (**3b**), *m*-(2-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl *m*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**) were prepared by the condensation of *o*-(2-vinyloxyethoxy)benzaldehyde (**1**) and *m*-(2-vinyloxyethoxy)benzaldehyde (**2**) with malononitrile or methyl cyanoacetate, respectively. Bifunctional vinyl ether monomers **3a** and **3b** polymerized quantitatively with radical initiators in γ-butyrolactone solution at 65 °C, while meta-isomers **4a** and **4b** gave lower yields of polymers under the same conditions. The polymers **5-6** obtained from the monomers **3-4** were insoluble in common solvents due to cross-linking. Under the same polymerization conditions ethyl vinyl ether polymerized well with model compounds *o*-methoxybenzylidenemalononitrile **7a**, methyl *o*-methoxybenzylidenecyanoacetate **7b**, *m*-methoxybenzylidenemalononitrile **8a**, and methyl *m*-methoxybenzylidenecyanoacetate **8b**, respectively, to give 1 : 1 alternating copolymers **9-10** in high yields. Cross-linked polymers **5-6** showed a thermal stability up to 300 °C, and showed a double phase degradation pattern in their TGA thermograms. Polymers **5-6** showed broad endothermic bands around 75-110 °C without any characteristic T_g peaks in DSC thermograms. Alternating copolymers **9-10**, except copolymer **9b** were soluble in common organic solvents. The inherent viscosities of polymer **9-10** were in the range of 0.35-0.62 dL/g. Polymer films cast from acetone solution were cloudy and tough and Tg values obtained from DSC thermograms were in the range of 118-165 °C.

Introduction

It is well known that electron-rich alkyl vinyl ethers do not radically homopolymerize, but copolymerize with vinyl monomers of electron deficient character such as vinylidene cyanide,[1] 2-vinylcyclopropane-1,1-dicarbonitrile,[2] alkyl α-cyanoacrylates,[3-5] alkyl vinyl ketones,[6] maleic anhydride,[7,8] and others by radical initiation. Cycloadditions frequently accompanied these polymerizations and most of the cyclic adducts are cyclobutane compounds. For example, alkyl vinyl ethers readily form cyclobutane adducts with a variety of electron-poor olefins such as tetracyanoethylene[9] and tricyanoethylene.[10] 3,4-Dihydro-2H-pyrans are formed in the reactions of alkyl vinyl ethers with alkyl α-cyanoacrylates, dimethyl dicyanofumarate,[11] and alkyl vinyl ketones.[6] These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.[12] It has also been reported that trisubstituted electron-poor olefins such as benzylidenemalononitrile and ethyl benzylidenecyanoacetate do not homopolymerize, but copolymerize with vinyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiat-