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Ultrasensitive Detection of Nickel(II) Ion by Capillary Electrophoresis–Post Chemiluminescence with Field-amplified Sample Injection

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An online ultrasensitive method for detection of nickel ions by capillary electrophoresis–post chemiluminescence with field-amplified sample injection has been developed. Under the optimal conditions, the detection limit for Ni^{2+} was 1.0×10^{-14} mol L^{-1}, relative standard deviations of peak area and migration time using 1.0×10^{-12} mol L^{-1} Ni^{2+} ($n = 7$) were 6.23% and 2.86%, respectively. This is a lower detection limit for Ni^{2+} than previously reported. The proposed method was successfully applied to the separation of Hg^{2+}, Ni^{2+}, and Cu^{2+} in a mixture.

Ultrasensitive detection as one of the most focused topics in analytical chemistry has wide applications in chemical analysis, biodetection, and early disease diagnose.[1] Current methods for ultrasensitive detection are primarily based on laser-induced fluorescence (LIF) because of its high sensitivity.[2] The LIF suffers from significant drawbacks including relatively high instrumental costs and the fact that the majority of molecular species do not fluoresce or are not easily converted to fluorescent species, which prohibit its universal use. Chemiluminescence (CL) could be an ideal alternative to LIF in ultrasensitive detection owing to advantages such as simple cheap optical systems requiring no light sources, avoiding the effects of stray light and the instability of the light source and providing low background with high sensitivity. Thus, CL has been often used as an ideal detector coupled with HPLC, microfludic chips, and capillary electrophoresis (CE). Among these, CE–CL has received extensive attention because of its virtues of high separation efficiency, short analysis times, lower cost, and relatively simple instrument setup.[3] Moreover, field-amplified sample injection (FASI), which takes place when the conductivity of the sample is smaller than that of the running buffer, is an inherent phenomena in CE and particularly useful to enhance detection sensitivity.[4]

Recently, post chemiluminescence (PCL) as an interesting phenomena in CL reactions has been reported by Lu et al.[5] They further concluded that PCL was characterized by broad spectra. We found that metal ions, such as Ni^{2+}, also can generate the PCL reaction in a luminol–H_2O_2 system, it can greatly enhance the CL intensity after completion of the luminol–H_2O_2 CL reaction. Also, FASI was observed during detection of Ni^{2+}. These inspired us to develop a highly sensitive method for detection of Ni^{2+} by FASI by CE–PCL. In this letter, we indeed prove this concept, and the detection limit for N^{2+} reached 1.0×10^{-14} mol L^{-1}.

A schematic diagram of the apparatus is shown in Figure 1. A 75-µm i.d. × 375-µm o.d. separation capillary was inserted into a 530-µm i.d. reaction capillary. The post-column reagents (mixture of luminol and H_2O_2) were stored in a reservoir and were delivered by gravity. A steel needle, as grounding electrode, was connected with the outlet of the reaction capillary. A 1.0-cm detection window was formed on the reaction capillary and was situated just in front of the photon-counting photomultiplier tube (PMT).

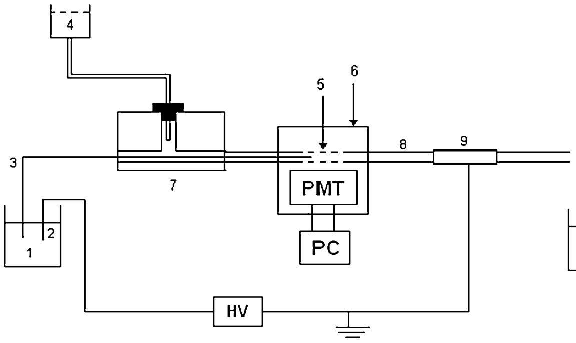

Figure 1. Schematic diagram of CE–CL setup in this work. (1) running buffer reservoir; (2) Pt electrode; (3) separation capillary; (4) post-column reagent reservoir; (5) detection window; (6) black box; (7) three-way joint; (8) reaction capillary; (9) grounding electrode (steel needle); (10) waste reservoir.

When luminol and H_2O_2 were mixed in a base aqueous solution, a strong CL signal was generated, reached maximum in a short time, and then declined quickly to a plateau at about 30 min, and CL intensity decreased slowly for 6–8 h. We found that injecting a trace of Ni^{2+} into the above mixture could greatly enhance the CL intensity and that a new CL peak emerged, namely, post-chemiluminescence (PCL). Compared with post-column online mixing in previous reports, PCL can provide more stable baseline, thus higher S/N ratio and detection sensitivity (Figure S1).[8]

On-capillary sample stacking is one of the simplest ways to improve the detection sensitivity in capillary electrophoresis.[4,6] Sample stacking is the process that occurs when a voltage is applied along a capillary tube containing a sample plug with a lower conductivity than that of the carrier electrolyte (field-amplified sample injection, FASI).[4b] Herein, the same amount of Ni^{2+} was prepared in water and in different concentrations of HAc–NaAc buffer solutions, the effect of concentration of HAc–NaAc on sensitivity is shown in Figure 2. The sensitivities in water or lower buffer concentration are markedly higher than those obtained in higher buffer concentrations. The results indicate that: (i) the sensitivity of Ni^{2+} can be enhanced remarkably by utilization of field-amplified injection; (ii) a large amount of cations (Na^+) and anions (Ac^-) has a great influence on the behavior of Ni^{2+}. The lower the ionic strength is, the smaller influence on Ni^{2+}, and the higher sample stacking efficiency.

The effects of concentration of running buffer on CL intensity and electrophoretic current are shown in Figure S2.[8]

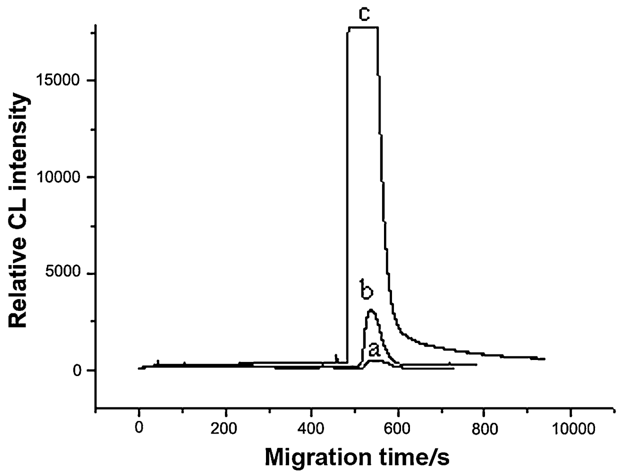

Figure 2. Effect of field-amplified sample injection on CL intensity. Identical amount of Ni^{2+} of $1.0 \times 10^{-6}\,mol\,L^{-1}$ in different buffer solutions of $25\,mmol\,L^{-1}$ HAc–NaAc (a), $5\,mmol\,L^{-1}$ HAc–NaAc (b), and pure water (c). Operation conditions: temperature, 25 °C; flow rate of post-column reagent, $44\,\mu L\,min^{-1}$; post-column reagent, $2\,mmol\,L^{-1}$ luminol + $10\,mmol\,L^{-1}$ H_2O_2 + $0.05\,mol\,L^{-1}$ $NaHCO_3$–NaOH (pH 12.0); running buffer solution, $10\,mmol\,L^{-1}$ HIBA + $50\,mmol\,L^{-1}$ HAc–NaAc buffer (pH 4.70); sampling time, 10 s; injection voltage, 10 kV; applied high voltage, 15 kV.

The CL emission was found to increase with increasing concentration of running buffer. The increase of concentration of electrophoretic buffer results in a large difference between the conductivity of the sample solution and that of the carrier electrolyte; therefore, higher sample stacking efficiency and signal intensity are produced. However, considerable Joule heating from the larger electrophoretic current will be also produced.[4a] The larger Joule heating makes the baseline more unstable (Figure S3).[8] In a compromise, 50 mM was chosen as running buffer concentration for further testing.

We measured the linear range and detection limit for Ni^{2+} using CE–PCL under optimized conditions (Figure S4).[8] The linear range is from 1.0×10^{-13} to $2.0 \times 10^{-12}\,mol\,L^{-1}$, and the detection limit ($S/N = 3$) is $1.0 \times 10^{-14}\,mol\,L^{-1}$. The relative standard deviations ($n = 7$) of migration time and peak area were 2.86% and 6.23% at $1.0 \times 10^{-12}\,mol\,L^{-1}$ Ni^{2+}, respectively. In contrast to earlier reported methods (Table 1 in Supporting Information[8]), the detection limit of the proposed CE–CL by utilization of the field-amplified injection is three orders of magnitude lower than that of the best result as reported.

The ultrasensitive analysis of metal ions is very important in environmental and biological analysis. The weak complexing agent, hydroxyisobutyric acid (HIBA), was used to enhance differences between the electrophoretic mobility of metal ions.[7] The separation of trace amounts of Hg^{2+}, Ni^{2+}, and Cu^{2+} was carried out. A mixed solution of $1.0 \times 10^{-6}\,mol\,L^{-1}$ Hg^{2+}, $1.0 \times 10^{-10}\,mol\,L^{-1}$ Ni^{2+}, and $1.0 \times 10^{-7}\,mol\,L^{-1}$ Cu^{2+} was injected, and the electropherogram is shown in Figure 3. It can be seen that the Hg^{2+}, Ni^{2+}, and Cu^{2+} are separated successfully from the mixture.

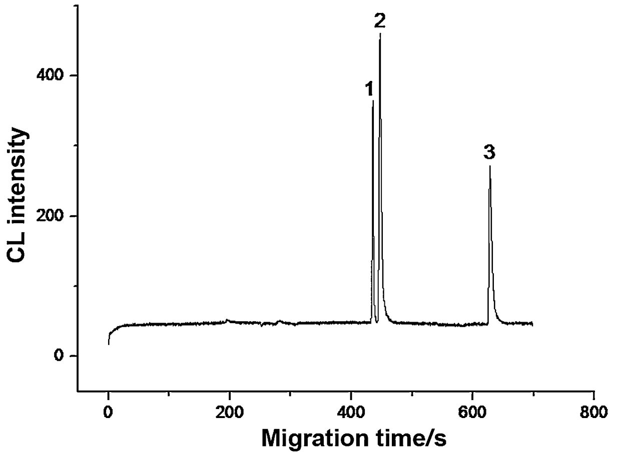

Figure 3. CE–CL spectrums of $1.0 \times 10^{-6}\,mol\,L^{-1}$ Hg^{2+} (1), $1.0 \times 10^{-11}\,mol\,L^{-1}$ Ni^{2+} (2), and $1.0 \times 10^{-7}\,mol\,L^{-1}$ Cu^{2+} (3) in pure water mixture. Conditions: temperature, 25 °C; flow rate of post-column reagent, $44\,\mu L\,min^{-1}$; post-column reagent, $2\,mmol\,L^{-1}$ luminol + $10\,mmol\,L^{-1}$ H_2O_2 + $0.05\,mol\,L^{-1}$ $NaHCO_3$–NaOH (pH 12.0); running buffer solution, $10\,mmol\,L^{-1}$ HIBA + 50 $mmol\,L^{-1}$ HAc–NaAc buffer (pH 4.70); sampling time, 10 s; injection voltage, 10 kV; applied high voltage, 15 kV.

In this paper, an ultrasensitive detection of Ni^{2+} with CE–PCL by field-amplified sample injection has been developed. Under the optimal conditions, the detection limit for Ni^{2+} can be reached $1.0 \times 10^{-14}\,mol\,L^{-1}$ ($S/N = 3$). To the best of our knowledge, this result is the highest sensitivity ever reported for nickel ion detection. The significant improvement in sensitivity is attributed to: (1) PCL provides a better S/N ratio and stable baseline, (2) utilization of FASI for enhancing sensitivity, (3) Ni^{2+} has excellent catalytic behavior for the CE–CL reaction of luminol and H_2O_2, the mechanism is still under investigation.

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8 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.