

## Electrogeneration of Ferrate(VI) in Low-concentration NaOH Solution for Capillary Electrophoresis–Chemiluminescence Detection

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A novel, eco-friendly, and stable homogeneous luminescent system for capillary zone electrophoresis (CE) detection was established, based on the chemiluminescence (CL) flash caused by mixing ferrate(VI) with luminol solution. It was found that the stable ferrate(VI) could be freshly electrogenerated in low-concentration NaOH solution for direct analytical application. To test this CL system, 8-hydroxyquinoline (HQ) was chosen as a model sample by CE detection.

Capillary electrophoresis (CE) is one of the most powerful and simple separation techniques, with high resolution, relatively short analysis time, and extremely small sample volume. Because of the advantages of chemiluminescence (CL) such as high sensitivity, wide linear range, simple instrumentation, versatility of use, and easy automation, it has been uniquely suited to on-line detection for CE. However, the existing CL systems and their applications are limited because most compounds have no native CL characteristics or catalytic effects.<sup>1</sup> Therefore, the development of new CL systems for CE is highly desired.

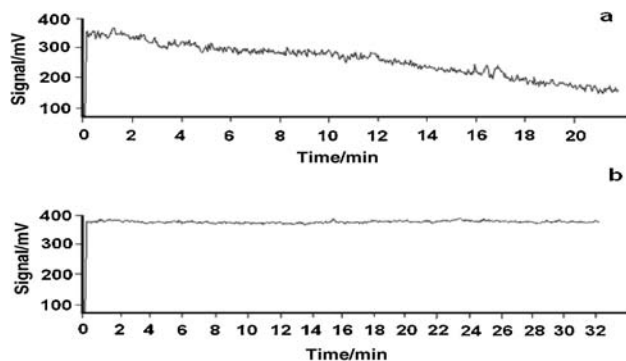
Ferrate(VI) is a high oxidation state compound of iron which possesses strong oxidizing power, relatively high redox potential and an environmentally benign reduction product. Recently, it has been focused on for the treatment of contaminants and toxins in water and wastewater,<sup>2</sup> clean technology for organic synthesis,<sup>3</sup> and high energy density rechargeable batteries,<sup>4</sup> but rarely has attention been paid to potential use in analytical chemistry. Stupin<sup>5</sup> and co-workers discovered that mixing solid sodium ferrate(VI) with luminol in alkaline solution gave rise to a CL flash for 20 min with approximately constant intensity; d-metal ions ( $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ , or  $\text{Co}^{2+}$ ) could enhance the CL intensity when mixed in the already luminescent heterogeneous system. Further research on this CL phenomenon and its application were hindered presumably by the rigorous synthesis conditions and instability of solid sodium ferrate(VI) exposed to ambient humidity even at room temperature.

We noticed that ferrate(VI) could be in situ electrogenerated in low-concentration NaOH solution at  $0 \pm 1^\circ\text{C}$ . Under the optimum conditions, the reproducibility of synthesis and the stability of ferrate(VI) solution were good enough to be directly used for analytical chemistry. Mixing the fresh ferrate(VI) with luminol solution could arouse a stable and reproducible CL signal, and this CL signal could be effectively increased by some analytes similar to that described in ref 5. Based on the phenomenon that the ferrate(VI)–luminol reaction could be catalyzed and enhanced by HQ, in this paper, we attempted the in situ electrochemical generation of ferrate(VI) in low-concentration NaOH

solution and chose HQ as a model sample to study the properties of homogeneous CL reaction for CE detection.

It was found that the internal cell temperature affects the efficiency of synthesis and the stability of ferrate(VI) solution. This is in agreement with that reported in the previous literature.<sup>6</sup> A stable, light purple ferrate(VI) solution was obtained when the cell temperature was carefully controlled at  $0 \pm 1^\circ\text{C}$  using an ice–water bath system. The spectra of analyte exhibited one broad band between 400 and 600 nm, with a maximum near 505 nm, characteristic of ferrate(VI) anion.<sup>7</sup> The stability of ferrate(VI) solution was not only affected by the internal cell temperature but also influenced by the storage temperature. As shown in Figure 1a, when the analyte stored at room temperature, the decay and instability of electrophoresis baseline and higher noise level were obtained. This problem could be avoided when the storage temperature was controlled at  $0 \pm 1^\circ\text{C}$  (Figure 1b). Thus, the ice–water bath system was used for the electrolysis process and CE–CL detection.

An anodic oxide layer, a firm film developed on the surface of the anode, prevents electron flow and then stops electrolysis.<sup>8</sup> During the experiment, we found that the removal of the oxide layer could improve both the ferrate(VI) synthesis efficiency and the reproducibility of electrolysis. Generally, the anode was activated by cathodic polarization for 30 min at high potential.<sup>9</sup> However, this method was complicated and time-consuming. Herein, we tested the possibility of anodic surface treatment with  $0.05 \text{ mol L}^{-1}$  oxalic acid solution for 5.0-min duration. The chemical compositions from XPS gave an overall characteriza-



**Figure 1.** Influence of storage temperature for CE–CL detection. (a) Ferrate(VI) solution stored at room temperature and (b) ferrate(VI) solution stored at  $0 \pm 1^\circ\text{C}$ . Conditions: electrolyte,  $0.3 \text{ mol L}^{-1}$  NaOH; electrolysis voltage, 4.0 V; electrolysis duration, 30.0 min; buffer,  $10.0 \text{ mmol L}^{-1}$   $\text{Na}_2\text{B}_4\text{O}_7$  +  $2.0 \text{ mmol L}^{-1}$  luminol (pH 9.3); separation voltage, 15.0 kV.

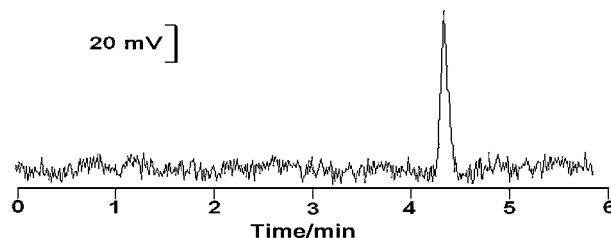
tion of the surface regions of the anode. The lower contents of  $\text{Fe}_2\text{O}_3$  of the anodic surface indicated that the proposed method was more beneficial to remove the oxide layer. The appearance of the anode surface was also observed by SEM. The surface of iron plate treated by the traditional method was compact; on the contrary, the surface treated by the presented method was more porous. This might be due to the high removal efficiency and the porous structure,<sup>10</sup> the ferrate(VI) synthesis efficiency was significantly enhanced by the developed method. The presented treatment method has many merits, such as short treatment time, simple operation, good reproducibility, and high ferrate(VI) synthesis efficiency.

The effect of NaOH concentration in electrolyte was examined from 0.1 to  $1.0 \text{ mol L}^{-1}$ , and the CL intensity reached a maximum at  $0.6 \text{ mol L}^{-1}$ . The effect of electrolysis voltage was studied in the range of 2.0–6.0 V; the best CL signal intensity was achieved at 4.0 V. It was found that the CL intensity increased with the increase of electrolysis duration within the range of 10.0–80.0 min, and the optimum duration was 60.0 min. Under the optimum conditions of electrolysis, the content of ferrate(VI) determined by a chromite method<sup>11</sup> was  $0.21 \text{ mmol L}^{-1}$ .

After the electrolysis conditions were optimized, the CE–CL conditions were considered. The effect of  $\text{Na}_2\text{B}_4\text{O}_7$  concentration on the CL signal intensity was studied, and  $10.0 \text{ mmol L}^{-1}$   $\text{Na}_2\text{B}_4\text{O}_7$  was adopted for the method. The influence of luminol concentration on the CL signal intensity in the range of  $0.5$ – $5.0 \text{ mmol L}^{-1}$  was investigated. We noticed that the best signal was acquired when the luminol concentration was  $2.0 \text{ mmol L}^{-1}$ . The pH of buffer had a significant impact on the surface characteristics of the fused-silica capillary and the relative migration time, and the best buffer pH was selected at 9.3. The applied voltage influenced the electroosmosis flow (EOF), and in the range of 7.0–23.0 kV, the best signal to noise ratio was gained at 15.0 kV. Finally, the injection time was examined, and the best injection time was 7.0 s.

Under the optimal conditions, the electropherogram of HQ is shown in Figure 2. The detection limit was  $5.0 \times 10^{-10} \text{ mol L}^{-1}$  ( $S/N = 3$ ). A calibration curve of the relative CL intensity versus the concentration of HQ was linear over a concentration range of  $5.0 \times 10^{-8}$ – $5.0 \times 10^{-10} \text{ mol L}^{-1}$  ( $R^2 = 0.997$ ). We examined the CL intensity of  $2.5 \times 10^{-9} \text{ mol L}^{-1}$  HQ in a repeated experiment, when the repeated injections were performed with the same run of electrolyzed ferrate(VI), the relative standard deviation (RSD) of peak height was 1.43% ( $n = 5$ ).

In the present work, the feasibility of in situ electrochemical synthesis of stable ferrate(VI) in low-concentration NaOH solution utilizing an iron electrode for CE–CL detection was first demonstrated. The new CL system (ferrate(VI)–luminol) for CE provided excellent reproducibility, good linearity, and low LOD and could be adopted as a useful tool for analytical chemists to analyze real environmental samples. Compared with the applications of ferrate(VI) reported previously, the analytical ap-



**Figure 2.** Electropherogram of HQ under the optimized conditions. Conditions: electrolyte,  $0.6 \text{ mol L}^{-1}$  NaOH; electrolysis voltage, 4.0 V; electrolysis duration, 60.0 min; buffer,  $10.0 \text{ mmol L}^{-1}$   $\text{Na}_2\text{B}_4\text{O}_7$  +  $2.0 \text{ mmol L}^{-1}$  luminol (pH 9.3); sample,  $1.0 \times 10^{-9} \text{ mol L}^{-1}$  HQ; separation voltage, 15.0 kV; injection, 7.0 s. The iron plate was washed with distilled water, treated in  $0.05 \text{ mol L}^{-1}$  oxalic acid solution for 5.0 min duration, ultrasonic cleaning in distilled water within 30.0-s duration and rinsed with distilled water.

plication of ferrate(VI) demonstrated here is not limited by problems of synthesis rate, difficulty of purification, transportation and storage, instability of ferrate(VI) solution, and rigorous reaction conditions. As electrophoresis is separation method, further research to study the possibility of this developed method for analyzing other compounds such as metal ions, organic compounds, and biomolecules is under way.

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