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Improvement on Simultaneous Determination of Cr(III) and Cr(VI) by Capillary Electrophoresis and Chemiluminescence Detection

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Abstract: A sensitive method for the simultaneous determination of Cr(III) and Cr(VI) using in-capillary reaction capillary electrophoresis separation and chemiluminescence detection was developed. The procedures were designed as follows: The sample, hydrochloric acid and sodium hydrogen sulfite solution segments were injected sequentially into the capillary. The reaction of Cr(VI) reduced to Cr(III) by HSO_3^- occurred inside the capillary after applying the running voltage. According to the migration time difference of both Cr(III) ions moving towards to the cathode (detection end), they could be separated and determined. The limits of detection for chromium(III) and chromium(VI) (S/N = 3) were 6.0×10^{-13} mol/L (12 zmol) and 1.9×10^{-11} mol/L (380 zmol), respectively.

Keywords: Chemiluminescence, in-capillary reaction, chromium, capillary electrophoresis.

Chromium exists in different oxidation states in groundwater, industrial wastewater, seawater, and soil of our environment [1,2]. Chromium (III) is an essential trace element for humans, required for the maintenance of normal glucose, cholesterol, and fatty acid metabolism. On the other hand, water soluble chromium(VI), in the form $Cr_2O_7^{2-}$ or CrO_4^{2-}, is highly irritating and toxic to humans and animals[3]. Its acute toxic effects include an immediate cardiovascular shock and later effects on kidney, liver, and blood-forming organs. Therefore, it is necessary for risk assessment, to determine not only the total chromium in the different environmental compartment but also its different oxidation states.

Capillary electrophoresis (CE)[4] has been used to determine Cr(VI) and Cr(III), which was chelated with ligands to form anionic complexes. But the sensitivity was not high enough. Our aim in this work was to introduce an on-line chemiluminescence(CL) simultaneous determination of Cr(III) and Cr(VI) following capillary electrophoresis (CE). A strategy for in-capillary transformation of Cr(VI) into Cr(III) was proposed. Samples, hydrochloric acid and $NaHSO_3$ were injected into the capillary prior to the application of the running voltage. In the electric field, Cr(III) migrated to the cathode (detection window), and Cr(VI) migrated to the anode and met with $NaHSO_3$, then reduced to Cr(III), which migrated to the cathode later and catalyzed luminol – hydrogen peroxide CL reaction in the detection window. According to their migration time

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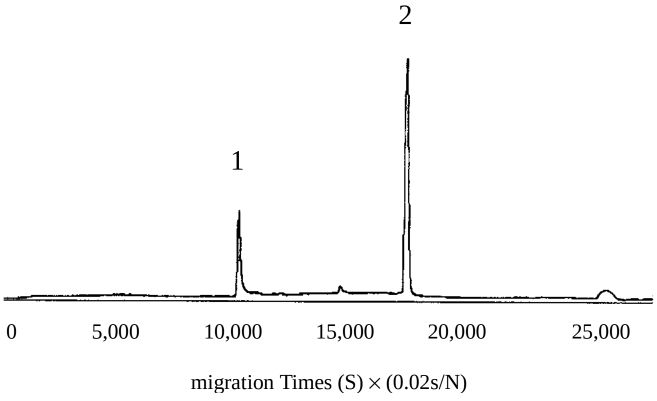
differences, Cr(III) and Cr(VI) could be separated and determined efficiently.

All the data were collected using a home-built CE – CL detection system. The capillary was rinsed with 0.1 mol/L sodium hydroxide for 2 min. and then with the separation buffer for 2 min. prior to each analysis by application of pressure (9-10 kPa). Samples were introduced to the capillary by electrokinetic injection by applying 10 kV for 9 s. The applied voltage was 15 kV.

Optimization of analytical conditions: A fused-silica capillary (60cm × 75μm I.D.) was used for separation; the chemiluminescence reagent consisted of 1×10^{-3} mol/L luminol, 1×10^{-2}mol/L hydrogen peroxide, 0.1mol/L KBr and 1×10^{-4}mol/L EDTA with 0.1 mol/L $NaHCO_3$-NaOH buffer to pH 11.5; reductant: 1 mol/L $NaHSO_3$ dissolved in 0.01 mol/L HCl solution; running buffer was composed of 0.02 mol /L HOAc-NaOAc (pH 4.7) with 1×10^{-3}mol /L EDTA.

Under selected conditions, the electropherogram of Cr(III) and Cr(VI) was shown in **Figure 1**. The peaks order was as follows: 1, 1×10^{-9}mol/L Cr(III); 2, 1×10^{-8}mol/L Cr(VI).

Figure 1 The electropherogram of Cr(III) and Cr(VI) separation



The linearity range extends from 3×10^{-12} to 8×10^{-10} mol/L for Cr(III) (R = 0.9985) and from 8×10^{-11} to 5×10^{-9} mol/L for Cr(VI) (R = 0.9991). A typical regression equation was Y= 361.10+4159.16X for Cr(III) and Y=338.23+1943.85X for Cr(VI). The limit of detection (LOD) of Cr(III) and Cr(VI) was 6×10^{-13} mol/L and 1.9×10^{-11} mol/L (S/N = 3), respectively. The mass LOD for Cr(III) and Cr(VI) was 1.2×10^{-20} mol (12 zmol) and 3.8×10^{-19} mol (380 zmol), respectively. The relative standard deviations (RSDs) of migration times and peak heights were less than 2.0% and 4.8%, respectively.

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