Thousand-fold Sensitivity Enhancement of Lanthanide by Capillary Electrophoresis

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1. Introduction

Capillary electrophoresis (CE) is a highly suitable tool to analyze inorganic ions with fast separation and high separation efficiency. Here, we applied stacking method called as electrokinetic supercharging (EKS) in CE for detection of lanthanide. Thousand-fold sensitivity enhancement was achieved without any modification of commercial capillary electrophoresis system.

2. Materials and methods

2.1 Electrophoretic conditions

CE was performed on a CESI 8000 system from Beckman (Fullerton, CA, USA) (Fig. 1) with preprogrammed Karat software. Analytes were monitored using a UV detector at 214 nm. The run buffer was 10 mM 4-methylbenzylamine (4-MB), 4 mM 2-hydroxyisobutyric acid (HIBA), 0.4 mM malonic acid, and 0.1% hydroxypropyl cellulose (HPC), adjusted to pH 4.8 with 2-ethylbutyric acid. Electrophoresis was carried out with a voltage of 25 kV. The capillary cartridge temperature was set to 25 °C (Fig. 2). A new fused silica capillary of 50 μm ID and 360 μm OD and effective/total length of 50/60 cm (Polymicro Technologies, Phoenix, AZ, USA) was washed with 0.1 M NaOH for 5 min, water for 5 min, and a run buffer for 5 min, each at 50 psi. Between runs, the capillary was treated by rinsing it with 0.1M NaOH for 2 min, water for 2 min, and the run buffer for 3 min at 50 psi.

4-MB was used as a UV absorbing probe for indirect UV detection. HPC was employed as EOF modifier. HIBA and malonic acid acted as a complexing agents for sufficient selectivity of lanthanide.

2.2 Instrument

Fig. 1. CESI 8000 system from Beckman.

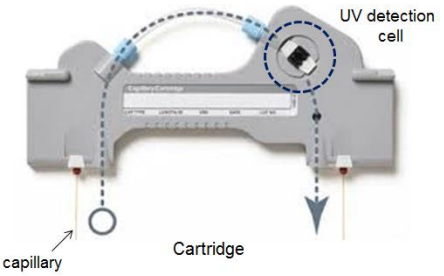

Fig. 2. Cartridge for CESI 8000 system.

2.3 Principle of capillary electrophoresis

Capillary electrophoresis is an analytical technique that separates ions based on their electrophoretic mobility with the use of an applied voltage in Fig. 3. The electrophoretic mobility of analyte is dependent upon the charge of the molecule, the viscosity, and the atom's radius.

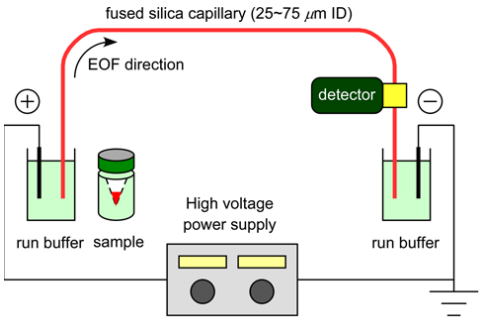

Fig. 3. Schematic diagram of capillary electrophoresis.

2.4 Advantages of capillary electrophoresis

- *Fast analysis time: 10 ~ 30 min*
- *High efficiency: N > 10^5 ~ 10^6*
- *Small sample volume required: 1 ~ 50 nL*
- *Numerous modes to vary selectivity and wide applications*
- *Simple and automated instrumentation*

2.5 Purpose of this study

The physical and chemical characteristics of lanthanide are so similar that for many years it was very difficult to separate them from each other. Here, we applied electrophoretic method using HIBA and malonic acid as complexing agents for enhancing high selectivity. Additionally, EKS method was used for thousand-fold enrichment of sensitivity.

3. Results and discussion

3.1 Comparison of EKS stacking and conventional method (capillary zone electrophoresis, CZE)

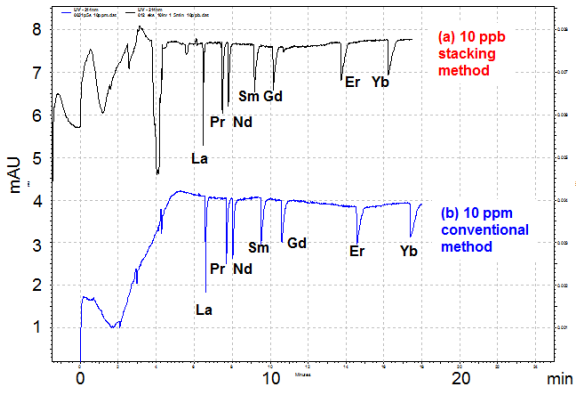

Fig. 4. Electropherogram of (a) a sample enriched by EKS using 10 ppb lanthanide and (b) 10 ppm lanthanide by CZE.

Fig. 4 described the EKS system was performed to concentrate and fully separate some lanthanides. In Fig. 4a, the electropherogram was obtained using CZE as a conventional method in CE. In this case, 10 ppm of some lanthanides was injected hydrodynamically at 0.5 psi for 5 s. However, for EKS method, the electropherogram in Fig. 4b showed same peak heights with the conventional method. In EKS method, 10 ppb of some lanthanides was injected electrokinetically for 90 s under a voltage of 10 kV.

Furthermore, seven lanthanides were sufficiently separated in CE using these conditions.

4. Conclusions

Thousand-fold sensitivity enhancements of lathanides were obtained by using EKS stacking method using indirect UV detection without any modification commercial CE system. This result is very compared to ICP-OES in terms of detection limit at the level of parts- per-billion (ppb).

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