

Liquid-Liquid Extraction Combined With Capillary Electrophoresis for the Determination of Rare Earth Elements in a High Saline Matrix (LiCl-KCl Molten Salt)

Jihye Kim^{a*}, Kihwan Choi^b, and Tae-Hong Park^a

^a Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, Korea

^b Division of Metrology for Quality of Life, Korea Research Institute of Standards and Science, 267, Gajeong-ro, Yuseong-gu, Daejeon, Korea

*jihyekim21@kaeri.re.kr

1. Introduction

Rare earth elements (REEs) have been widely applied to many fields of geology, pharmacy, and agriculture. The determination of REEs has been reported using various analytical techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography (IC), capillary electrophoresis (CE). Generally, ICP-MS detection has been described as a powerful technique for the analysis of REEs in environmental samples because of low detection limits and high selectivity. However, the sensitive instrument is not widespread due to the running costs. No matter which analytical technique is adopted, sample pretreatment steps are required before analysis. Especially, the determination of REEs in highly saline sample matrix is difficult due to occurrence of matrix effects.

Liquid-liquid extraction (LLE) as the most common sample pretreatment technique has been used for sample cleanup and preconcentration of REEs. LLE is simple, robust, and compatible with many analytical techniques such as ICP-OES, ICP-MS, and CE. Recently, to analyze the REEs, CE has gained considerable interest owing to fast separation, high separation efficiency, and low sample requirement.

Here, we developed a new method of LLE coupling with CE for the determination of REEs from highly saline sample. The parameters influencing the LLE and CE separation of REEs were investigated. The proposed method was successfully applied to the analysis of REEs in high salts of LiCl-KCl solution.

2. Materials and methods

2.1 Liquid-Liquid extraction

REEs sample solution (donor phase) was prepared in the molten salt (44-56 wt% LiCl-KCl). A 4 mL of donor solution containing REEs was transferred into the vial. A 2 mL of organic phase (0.29 M 2-ethyl hexylphosphate as a carrier in heptane) was added on the top of the donor solution. Extraction was done by vortexing vigorously for 10 min. After extraction, the phases were separated by centrifugation at 3000 g for 5 min and the donor phase was discarded by a pipet. To decrease the complexation of the REEs and carriers, 2 mL of octanol was added into the organic phase (extract). Back extraction was achieved with 2 mL of 0.1 M HNO₃. In the process of back extraction, the sample was mixed for 10 min and then separated by centrifugation at 3000 g for 5 min. After centrifugation, two organic phases were discarded and the aqueous phase was removed using a pipet. After extraction, the aqueous phase was transferred into a 200 μ L vial and introduced into the capillary. The LLE procedure is shown in Fig. 1.

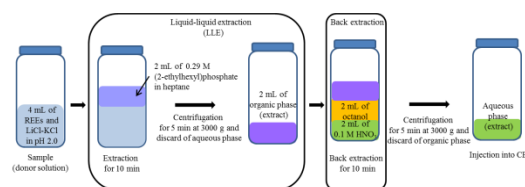


Fig. 1. LLE procedures for the determination of REEs from highly saline sample.

2.2 Electrophoretic conditions

CE was performed on a CESI 8000 system from Beckman (Fullerton, CA, USA) (Fig. 2) 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. 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 REEs.

2.3 Instrument



Fig. 2. CESI 8000 system from Beckman.

2.4 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. The electrophoretic mobility of analyte is dependent upon the charge of the molecule, the viscosity, and the atom's radius.

3. Results and discussion

3.1 Comparison of standard sample and REEs extract after LLE in capillary zone electrophoresis mode

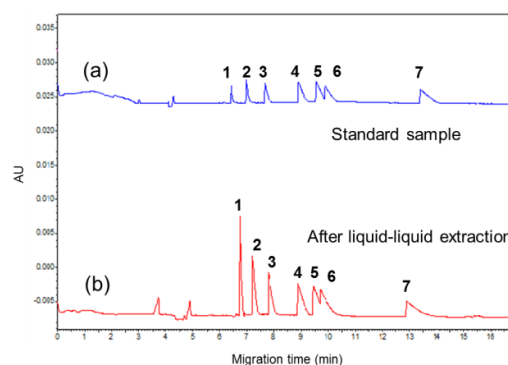


Fig. 3. Electropherogram of (a) the standard sample (b) sample extract by LLE. Sample solution was prepared in 44-56 wt% LiCl-KCl solution. Peak identification: (1) La, (2) Ce, (3) Nd, (4) Sm, (5) Eu, (6) Gd, (7) Er.

Fig. 3 described the sample cleanup was achieved by liquid-liquid extraction from highly saline sample. When the only LiCl-KCl solution was injected hydrodynamically at 0.5 psi for 5 s into the CE, Li^+ ion and K^+ ion were detected within 4 min with same CE conditions. However, after LLE, those ions were not detected in CE electropherogram. In fact, high amounts of Li^+ and K^+ ions removed from the sample matrix during LLE because they did not complex with a carrier (2-ethyl hexylphosphate).

4. Conclusions

LLE coupled to CE has been proposed for the determination of REEs in highly saline sample (44-56 wt% LiCl-KCl). The advantages of the proposed method are good extraction efficiency (70-98%) and efficient separation with relatively low running costs. Furthermore, the proposed method is applicable to determination of trace amounts of REEs in spent fuel cell containing molten LiCl-KCl salt.

5. References

- [1] C.W. Noack, D. A. Dzombak, and A.K. Karamalidis "Determination of rare earth elements in hypersaline solutions using low-volume, liquid-liquid extraction", *Environmental Science & Technology* 49, 9423-9430 (2015).
- [2] Z. Xu, K. Kawahito, X. Ye, A. R. Timerbaev, T. Hirokawa "Electrokinetic supercharging with a system-induced terminator and an optimized capillary versus electrode configuration for parts-per-trillion detection of rare-earth elements in CZE", *Electrophoresis*, 32, 1195-1200 (2011).